BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1927.

General, Physical, and Inorganic Chemistry.

Spectral notation. W. M. HICKS (Phil. Mag., 1927, [vii], **3**, 614—618).—A plea for the adoption of a uniform scheme of spectral notation to avoid ambiguity and confusion. A. E. MITCHELL.

Specific oscillations characteristic of continuous spectra. IV. A. WINTNER (Ann. Physik, 1927, [iv], **82**, 346—354; cf. *ibid.*, 67; this vol., 81).—Mathematical.

Intensity distribution in the fine structure of the Balmer lines. G. E. HARRISON (Nature, 1927, **119**, 393).—The relative intensities of the two components λ' and λ'' ($\lambda' < \lambda''$) of H_a are dependent on the conditions of the discharge, and in particular on the diameter of the tube in which the discharge takes place. A. A. ELDRIDGE.

Series spectra of boron, carbon, nitrogen, oxygen, and fluorine. I. S. BOWEN (Physical Rev., 1927, [ii], **29**, 231—247).—Practically all of the unidentified strong lines of boron, carbon, nitrogen, oxygen, and fluorine occurring in the extreme ultra-violet spectra of the vacuum spark have been classified as due to jumps between levels in B I, C I, C II, N II, N III, O III, O IV, F I, F II, F III, and F IV. The levels thus found are correlated with those demanded by the Russell–Heisenberg–Pauli–Hund theory. A. A. ELDRIDGE.

Second green line of the auroral spectrum. L. VEGARD (Nature, 1927, **119**, 349—350).—Further observations (cf. this vol., 91) indicate that the second green line of the auroral spectrum consists of a group of lines. Within the limits of experimental error, the wave-lengths of one of the components of the N_2 line from solid nitrogen corresponds with the maximum of the second green auroral line. A. A. ELDRIDGE.

Meteorological researches on some rays of neon and helium. A. PÉRARD (Compt. rend., 1927, **184**, 447—449).—The Michelson interferometer has been used to determine for neon and helium the error between the observed fractional excess of the order of interference and that calculated using the red ray of cadmium as reference and the usually accepted approximate value of the wave-length of the ray studied. Intervals between 0 and 202 mm. have been used, and correction curves constructed for use in meteorology. With neon, when the lamp was observed on end the results confirmed those previously obtained; when it was observed across the axis there was a minimum of intensity in the central region. J. GRANT.

Flash arc spectrum of sodium. F. H. NEWMAN (Phil. Mag., 1927, [vii], **3**, 364—368).—The method of excitation of the flash arc spectrum of sodium is similar to that described previously for the potassium spectrum (this vol., 2). In addition to the ordinary arc lines, most of the ordinary spark lines appear. These latter do not approach the D-lines in intensity. The flash arc spectrum observed comprises 99 lines between 5228 and 2493·8 Å. The spectrum is analogous to the neon red spectrum. The spectral centre is approximately 3300 Å., which is lower than the corresponding spectral centre of the lines in the potassium flash arc. It is suggested that the spectrum observed is the first spark spectrum of sodium. A. E. MITCHELL.

Persistent lines of hafnium. M. PETERSEN (Nature, 1927, **119**, 352—353).—The three most persistent lines of hafnium, in decreasing order, are : 2773·40, 2866·35, and 2919·55 Å., which were observed in all the spectra examined. Less persistent lines are : 2516·85, 2887·15, 2898·25, 2904·40, 2904·80 (?), 2940·80, 2964·85, 3194·20 Å. (Hansen and Werner's wave-lengths, A., 1923, ii, 807). Regularities in the hafnium spectrum are at present conjectural. A. A. ELDRIDGE.

Polarisation of mercury lines emitted from a discharge tube in a magnetic field. H. W. B. SKINNER (Proc. Camb. Phil. Soc., 1927, **23**, 508—515).—Both the quantum theory and the classical theory require that the light emitted by atoms in a magnetic field shall be unpolarised, but experiments yielding results to the contrary have been described. The polarisation of the lines emitted by a mercury-vapour arc under the influence of a magnetic field has therefore been examined. Two distinct types of polarisation have been observed, but both are probably due to the excitation being anisotropic. R. CUTHILL.

Duration of after–glow in mercury vapour. (FRL.) M. ASTERBLUM (Z. Physik, 1927, **41**, 294—300).—The duration of the after-glow in a rapidly moving stream (75 metres/sec.) of mercury vapour, excited by a direct-current discharge between two electrodes inserted in the stream, has been measured for the lines 3132, 3650, 4047 (4344, 4347, 4358), 5461 Å. Linear relations are obtained between the logarithm of the intensity and the distance separating the point at which the intensity is measured from the exciting cathode. From these data, the mean time of duration (sec. $\times 10^{-4}$) of the after-glow has been determined for the above-mentioned lines as 0·77, 0·77, 1·1, 1·2, and 1·1, respectively. R. W. LUNT.

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Reversal of lines in the explosion spectrum of lead. B. ARAKATSU (Mem. Coll. Sci. Kyōto, 1927, **10**, 171—174; cf. this vol., 2).—The self-reversal of lines in the spectrum of exploded lead wires has been investigated at higher pressures. The lines 4057 $(2p_2-2s)$, 3740, 3684 $(2p_5-2s)$, 3640 $(2p_3-2s)$, and 3573, which were previously difficult of reversal, have now been obtained as clear absorption lines. The 4168 $(2p_1-3d_3)$ and 4020 $(2p_1-3d_1)$ lines show weak reversal. The 2802 $(2p_2-3d_1)$ and 2614 $(2p_3-3d_2)$ lines are broadened symmetrically on both sides, whilst the other reversed lines in the diffuse series are fairly sharp. It seems probable that the continuous spectrum has many centres of development.   R. A. MORTON.

Ultra-violet arc spectrum of freshly-prepared uranium oxide. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 533—535).—The method of purifying uranium is described. In the region 2300—3100 Å., some 1400 lines have been measured. It appears that metals of the rare-earth and platinum groups are responsible for about a third of the lines. Lines from bismuth, lead, thallium, and helium, impurities or possible disintegration products of uranium, were also found. No definite conclusions can yet be reached concerning the uranium spectrum.   R. A. MORTON.

Vacuum grating spectrograph for the extreme ultra-violet and for X-rays : a grating with tangential incidence. J. THIBAUD (J. Phys. Radium, 1927, [vi], **8**, 13—24).—The theory of a diffraction grating with tangential incidence and a description of a vacuum spectrograph employing the principle are given. A glass grating, with 200 lines per mm., was found superior to one of speculum metal for wave-lengths of less than 500 Å. The spectrum from 6000 to 140 Å. is obtained on one plate. The spark spectrum of copper in particular has been studied, the results confirming those of Millikan. Evidence of new lines in the extreme ultra-violet spectrum of copper is given.   W. E. DOWNEY.

Spectrography of X-rays of long wave-length, N- and O-series, and the junction with the extreme ultra-violet. A. DAUVILLIER (J. Phys. Radium, 1927, [vi], **8**, 1—12).—A method of spectrographing the region 20—136 Å. is given. Slow electrons bombard an anticathode covered with a film of the element under examination. The film is constantly re-formed by evaporation from the cathode. The Schumann plate is protected from the general light of the X-ray tube by a screen, transparent to X-rays. This screen consists of a film of celluloid covered with a thin deposit of magnesium.

Using this spectrograph, the K-series has been completed by the measurement of the $K\alpha$ lines of oxygen, carbon, and boron. The spontaneous appearance of the $K\alpha$ line of carbon has been confirmed and its appearance controlled. By means of a Wehnelt cathode, covered on its underside, a given spectrum of an element can be obtained, and the method was used to follow the appearance of the $L\alpha$ and $M\alpha$ lines. The unknown N- and O-series have been obtained for thorium. The observed lines have approximately the calculated wave-lengths.

The O-lines (the $O\beta$ line of thorium has wave-length 121 Å.) establish, for the first time, the link between the X-ray region and the extreme ultra-violet region of Millikan.   W. E. DOWNEY.

Intensities of L X-ray spectra. A. JÖNSSON (Z. Physik, 1927, **41**, 221—229).—Using stationary potentials (max. 20 kilovolts) and a filament tube with an oil-cooled anticathode, the relative intensities of the lines $L\beta_1$, $L\beta_2$, and $L\gamma_1$ have been determined for molybdenum, ruthenium, palladium, silver, cadmium, indium, tin, and antimony. The intensities of the β_2- and γ_1-lines increase linearly with the atomic number from 42 to 46, increase suddenly at element 47 (silver), and then at a diminishing rate in the range 48—51, and approach the values obtained previously by the author (ibid., 1926, **36**, 426) for 74 and 78 (tungsten and platinum). The results are in agreement with the theory of Main-Smith and Stoner concerning the electronic orbits in an atom.   R. W. LUNT.

Intensity of X-ray spectra as a function of the exciting current. D. NASLEDOV and P. SCHARAVSKI (Z. Physik, 1927, **41**, 155—163).—The intensity of the lines Cu $K\alpha$, Cu $K\beta$, measured by an ionisation method, has been found to increase linearly with the exciting current up to 4 milliamps. in a tube of the Coolidge type. For larger currents, the increase remains linear, but at a diminished rate. The critical value, 4 milliamps., is independent of the exciting potential, which was stationary, in the range examined, 30—45 kilovolts.   R. W. LUNT.

L X-Ray spectra of the lighter elements. J. H. VAN DER TUUK (Z. Physik, 1927, **41**, 326—331).—The anomalies presented by the L spectra of copper and cobalt are discussed with reference to Bohr's theory of the periodic system.   R. W. LUNT.

Exact X-ray absorption measurements, in the K region, of cobalt and its compounds. F. DE BOER (Arch. Néerland., 1927, III A, **5**, 101—130).—Using an improved form of Siegbahn's spectrograph, which is described in detail, the limits of X-ray absorption in the K region have been determined for the following substances : cobalt, cobaltous oxide, chloride, nitrate, carbonate, phosphate, acetate, sulphate, and chromate, and several cobaltammine derivatives. The limiting wave-lengths for cobalt and the above cobaltous compounds are, respectively : 1604·2, 1602·7, 1603·0, 1602·9, 1602·7, 1602·8, 1602·9, 1602·7, and 1603·2 X. The mean for the seven cobaltammine derivatives examined was 1602·2. The results are held to show that this limiting frequency is associated with valency and chemical constitution.   R. W. LUNT.

Exact determinations of the K-series of palladium and silver. G. KELLSTRÖM (Z. Physik, 1927, **41**, 516—523).—Using the technique of Larsson (cf. following abstract), the following wave-lengths have been assigned to the lines Pd $K\alpha_1$, $K\alpha_2$, $K\beta_1$, $K\beta_2$, $K\beta_3$, Ag $K\alpha_1$, $K\alpha_2$, $K\beta_1$, $K\beta_3$, and $K\beta_3$, respectively : 584·266, 588·632, 519·474, 509·181, 520·093, 558·277, 562·669, 496·009, 486·030, and 496·647 X.   R. W. LUNT.

Exact determinations of the L-series of tantalum. I. WENNERLÖF (Z. Physik, 1927, **41**, 524—

529).—Using the technique of Larsson, the following wave-lengths have been assigned to the tantalum lines $L\alpha_1$, α_2, β_1, β_2, β_3, β_4, γ_1, γ_2, and γ_3 : 1518·85, 1529·8, 1324·23, 1281·90, 1304·1, 1343·1, 1135·58, 1102·9, and 1097·1 X.   R. W. LUNT.

Selective displacement of 0·0153 Å. in X-ray spectral lines. F. H. LORING (Chem. News, 1927, 134, 65—67).—It is shown that by the addition of 0·0153 Å. to the wave-lengths of hitherto apparently unidentified X-ray lines, they may often be brought into position with normal known lines. The coincidence or phenomenon seems to be selective, in that the lines of a given element may be normal except for one or two displaced by the above amount towards the shorter wave-length side.   R. W. LUNT.

Selective displacement of X-ray spectral lines. F. H. LORING (Chem. News, 1927, 134, 97—99; cf. preceding abstract).—A unit of 0·01527 Å. or integral multiples of this unit when added to certain unidentified X-ray wave-lengths gives numbers in agreement with known lines. The relation of this quantity to Planck's constant h is discussed.   R. A. MORTON.

Electron affinity of hydrogen and the second ionisation potential of lithium. L. PAULING (Physical Rev., 1927, [ii], 29, 285—291).—With certain assumptions, the electron affinity of hydrogen atoms is computed as $E_H = -1.85$ kg.-cal./mol., and the second ionisation potential of lithium as 76·2 volts.   A. A. ELDRIDGE.

Influence of oxygen on the optical absorptive power and the photo-electric electron emission of potassium. R. FLEISCHER (Ann. Physik, 1927, [iv], 82, 243—253; cf. this vol., 180).—By removing gas from potassium, it was shown earlier that the wave-length of maximum absorption and of maximum electronic emission could be shifted to 313 $\mu\mu$. This shift has now been extended as far as 302 $\mu\mu$, and the exact location of the maximum is shown to depend on the nature of the gas contaminating the potassium. The photo-electric maximum at 313 $\mu\mu$ with potassium-oxygen mirrors cannot wholly be related to the optical absorption, although the latter is not essentially different from the absorption of the outgassed mirror.   R. A. MORTON.

Influence of the gas content on the velocity distribution of photo-electrons from platinum, aluminium, and palladium. J. KLUGE (Ann. Physik, 1927, [iv], 82, 432—448).—It is shown, for platinum and aluminium, that the connexion between emergence velocity and wave-length limit is independent of the gas content, in accordance with Einstein's equation. The velocity distribution alters with outgassing in such a manner that V alters in the same sense as V_{max}.   W. E. DOWNEY.

Photo-electric emission as a function of composition in sodium–potassium alloys. H. E. IVES and G. R. STILWELL (Physical Rev., 1927, [ii], 27, 252—261).—The curve showing the relation between the atomic composition and the ratio of emission with the electric vector in the plane of incidence to that with the electric vector perpendicular thereto exhibits maxima at 20, 50, and 90 at.-% of sodium.   A. A. ELDRIDGE.

Variable mass of the electron. L. T. JONES (Phil. Mag., 1927, [vii], 3, 622—624).—It is pointed out that the mass of the electron is not a function of the velocity alone, but that it must depend on the potential at which the electron is emitted. Since measurements of the mass of the electron are made always at the potential of the observer, and not at the higher relative potential of the emission, it then follows that variations in the mass of the electron can never be shown by ordinary methods of measurement.   A. E. MITCHELL.

Velocity distribution of electrons issuing from small holes. R. H. DALTON and W. P. BAXTER (Physical Rev., 1927, [ii], 29, 248—251).—When the sides of a perforation in a copper plate were coated with lampblack, the percentage of 50-volt electrons transmitted without appreciable energy loss rose from 70 to 95.   A. A. ELDRIDGE.

Application of method of magnetic spectrum to the study of secondary electronic emission. C. F. SHARMAN (Proc. Camb. Phil. Soc., 1927, 23, 523—530).—The velocity distribution in a secondary electron emission has been investigated by the magnetic spectrum method. From the results obtained it appears that two distinct types of electrons are emitted. One group, which is only a small fraction of the whole, consists of electrons with nearly the same energy as the primary beam, and are electrons which have collided closely only with atoms, probably in the surface layer. The other group includes electrons with energies from zero up to that of the primary beam, and into this group would fall any " characteristic " corpuscular radiation from the atoms of the target excited by the primary beam, and also the electrons resulting from collisions between primary electrons and " free " electrons in the target. The form of the energy distribution curve does not, however, agree with the results obtained by the retarding potential method (cf. Becker, A., 1925, ii, 8).   R. CUTHILL.

Electron " reflexion " in a vacuum. D. BROWN and R. WHIDDINGTON (Nature, 1927, 119, 427).—A fraction of the electrons emitted from a filament and accelerated towards a reflecting plate under potential V are " reflected " with energy corresponding with the full potential V, and energies immediately less than about 12 volts below V were not observed. This gap is probably real, and not instrumental (cf. Sharman, preceding abstract).   A. A. ELDRIDGE.

Conductivity of clouds dispersed from an arc. II. H. P. WALMSLEY (Phil. Mag., 1927, [vii], 3, 587—600).—It has been shown previously (A., 1926, 654) that the ionisation currents obtained from the cloud of particles produced from an arc between cadmium electrodes show an initial fall in current strength, followed by a subsequent rise. It is shown that the subsequent rise is due either to the production of new charges within the cloud as it ages or to an increase in the mobility of the existing ions.   A. E. MITCHELL.

Ionisation equilibrium in stellar atmospheres and in the earth's atmosphere. A. PANNEKOEK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1165—1171).—Although the Saha ionisation formula is not strictly applicable to stellar atmospheres, since these are not gases in thermodynamical equilibrium, true values for the ionisation are obtained by substitution of the effective temperature for the atmospheric temperature and the introduction of a constant correction factor. Using the modified formula, the ionisations of hydrogen, nitrogen, and oxygen in the upper layers of the earth's atmosphere, due to photo-electric ionisation by solar radiation, have been calculated. If the temperature be assumed to be −55°, it appears that on descending from great heights, the number of electrons increases regularly to a maximum value of 10^5—10^6 electrons/c.c., and then rapidly falls to zero because of increasing absorption of the radiation. For nitrogen and oxygen, the maximum values are at 145 and 128 kilometres, respectively, the minimum at 130 and 113 kilometres, respectively. The number of electrons agrees very well with that deduced from wireless experiments, although the lower limit lies at a greater height than that usually accepted. The presence of a considerable number of electrons at a height of 90 kilometres would indicate a much lower temperature of these upper layers than is generally assumed. For hydrogen, the region of ionisation begins at about 700 kilometres. Ionisation at such an altitude would extinguish all solar wavelengths below 766 Å., which are the frequencies necessary for the ionisation of nitrogen and oxygen. The existence of a hydrogen atmosphere above the nitrogen and oxygen atmosphere makes the existence of a Heaviside layer due to photo-electric ionisation impossible. Unless this layer may be explained by other causes (e.g., impacts by particles), hydrogen cannot occur in the atmosphere in the usually accepted quantities. J. S. CARTER.

Magnetic moment of the hydrogen atom. T. E. PHIPPS and J. B. TAYLOR (Physical Rev., 1927, [ii], **29**, 309—320).—Stern and Gerlach's atomic-ray method, applied to atomic hydrogen produced in a discharge tube by Wood's method, indicates that the magnetic moment of the hydrogen atom is one Bohr magneton. A quantitative result was not obtained from atomic hydrogen produced by Langmuir's hot filament method. Experiments with the product of the exposure of a mixture of mercury vapour and hydrogen to ultra-violet light were unsuccessful; possibly only small amounts of atomic hydrogen are formed, or the active substance may consist of excited hydrogen or mercury hydride molecules. A. A. ELDRIDGE.

Paramagnetism of the elements comprised between calcium and zinc. A. CARRELLI (Atti R. Accad. Lincei, 1926, [vi], **4**, 569—574).—Just as Cabrera (A., 1925, ii, 358) found with the rare-earth metals, so also with the elements lying between calcium and zinc, spectroscopic data indicate a double period of variation in the number of magnetons as a function of the atomic number. T. H. POPE.

Constant paramagnetism of quinquevalent vanadium. N. PERRAKIS (Compt. rend., 1927, **184**, 445—447).—Quinquevalent vanadium has a paramagnetism independent of temperature between 17° and 77° in vanadium pentoxide and in sodium vanadate, and between 17° and 45° in ammonium vanadate. The mean value (to within 10%) of the coefficient of atomic magnetisation of quinquevalent vanadium derived from these determinations is 44.0×10^{-6}. Vanadium pentoxide has the same paramagnetism in the solid state as in solution. Like the atomic moment, the paramagnetism may have many different values in the same atom (cf. A., 1924, ii, 586). J. GRANT.

Magnetic properties of manganese pyrophosphate at various temperatures; measurement of the moment of the manganous ion. G. FOËX and (MLLE.) A. BRUNET (Compt. rend., 1927, **184**, 443—445).—The coefficients of magnetisation of manganese pyrophosphate have been determined between the temperatures −80° and +485°, and the existence of the manganous ion with 30 magnetons has been established from the molecular Curie constant. The manganese pyrophosphate follows Weiss' law and remains unchanged in its magnetic properties between these temperatures. Since this is maintained for at least 6 months, the compound is suggested as a standard of magnetic susceptibility. The coefficient of magnetisation (103.1×10^{-6} at 16.1°) varies inversely as the quantity, temperature Abs.+23°, instead of following Curie's law. J. GRANT.

Atomic moment in the complexes of the iron family. P. WEISS (Compt. rend., 1927, **184**, 417—419).—The " effective atomic number " (N') of an ion is obtained by subtracting its valency (v) from the atomic number (N) of the corresponding atom. Thence a simple rule is obtained which enables the moments of complex ions of the iron family to be correlated with those of the normal ions. Thus $N-v+2i$ gives the number of electrons surrounding the central atom, where i is the co-ordination index; and $N'=N-v+2(i-p)$, where p is the number of pairs of electrons with zero moment formed as a result of chemical combination. A curve is given from which the ionic moment is obtainable from the value of N', and is used to show that the diamagnetic carbonyls of nickel and iron possess zero moments. J. GRANT.

Degenerated gases and paramagnetism. W. PAULI, jun. (Z. Physik, 1927, **41**, 81—102).—By identifying the electrons in metals from which electrical conductivity arises with the valency electrons, and by considering these electrons as a degenerated ideal gas to which the statistical restriction of Fermi is applied, it is shown that, in the solid state, paramagnetism should be weak and approximately independent of temperature. The values calculated for the susceptibility of sodium, potassium, rubidium, and cæsium are in qualitative agreement with those observed. R. W. LUNT.

Intrinsic fields in ferromagnetic substances. J. DORFMAN (Nature, 1927, **119**, 353).—Experiments on the deflexion of β-particles passing through nickel foil indicate that no magnetic field exceeding 10^5

gauss exists in a ferromagnetic substance. Hence Weiss' " molecular field " cannot be purely magnetic.
A. A. ELDRIDGE.

Hall effect in bismuth with small magnetic fields. C. W. HEAPS (Physical Rev., 1927, [ii], **29**, 332—336).

Atomic weight of silver. B. BRAUNER (Nature, 1927, **119**, 348).—Riley and Baker's value of $107·864 \pm 0·0013$ for the at. wt. of silver (A., 1926, 1190) is regarded as being too low, since it leads to the improbable values of 35·452—35·450 and 13·999 for chlorine and nitrogen, respectively. If, as appears to be the case, silver is appreciably volatile at 1000°, the low value would be explained, losses of 0·08—0·14 mg. occurring.
A. A. ELDRIDGE.

[**Atomic weight of silver.**] H. B. BAKER and H. L. RILEY (Nature, 1927, **119**, 348—349).—A reply to Brauner (preceding abstract). The experimental conditions preclude the loss of silver as vapour, neither is there any evidence of the deposition of silver on the cooled parts of the weighed tube. Further, in each determination the silver obtained, after being melted several times, attained constancy of weight to within 0·01—0·02 mg.
A. A. ELDRIDGE.

Radioactivity and the heat of the earth. J. W. EVANS (Nature, 1927, **119**, 424—425).—Polemical (cf. Lawson, this vol., 225).
A. A. ELDRIDGE.

Missing element 87. G. VON HEVESY (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**, No. 11, 1—11).—As only radioactive isotopes of the elements following number 86 (radon) are known, it is improbable that inactive isotopes of the missing element 87 can be discovered. Since this element has an odd atomic number, it is expected that it can be found only as a comparatively short-lived body. Attempts were made to discover by the scintillation method an α-particle from mesothorium-2; the emission of an α-particle by this element (89) would lead to the formation of element 87. It was found that, if such a disintegration occurs at all, fewer than 1 in 200,000 atoms of mesothorium-2 can disintegrate in this way. Trials to find 87 as a β-product of radon, by removing chemically all the known members of the active deposit of 100 millicuries, failed. It is suggested that it may be possible to find an inactive isotope of polonium, and the possible formation of the element 85 is discussed.
W. CLARK.

Computation of the distribution of range of α-particles. M. VON LAUE and (FRL.) L. MEITNER (Z. Physik, 1927, **41**, 397—406).—An expression has been derived for the distribution of the range of α-particles about the normal when measured by the Wilson cloud method by considering the change in range due to the alteration of pressure necessary to produce the cloud. The data of Schoch on the tracks of α-particles in argon, nitrogen, and oxygen saturated with water vapour have been analysed on this basis. The scattering coefficient of argon is thus found to be 0·013, in good agreement with Bohr's theoretical value 0·0119 and that of Meitner and Freitag, 0·0121 (A., 1926, 772). The values for nitrogen, and oxygen particularly, are higher than

those of Bohr or of Meitner and Freitag; the discrepancy is attributed to the effect of the water vapour present.
R. W. LUNT.

Effect of α-particles on paraffin. W. T. RICHARDS (Proc. Camb. Phil. Soc., 1927, **23**, 516—522).—The chemical effect of α-particles on paraffin, measured by the volume of hydrogen produced, is the same whether the paraffin be in the solid or in the liquid state. Where divergences from this behaviour occur with other substances, they are probably due to secondary action.
R. CUTHILL.

Behaviour of materials of different atomic numbers towards Hess' ultra-γ-rays ; natural radioactivity of the elements. G. HOFFMANN (Ann. Physik, 1927, [iv], **82**, 413—431).—On the assumption that Hess' rays are ultra-γ in character, the scattered radiation is discussed in terms of the Compton theory. Determination of the absorption coefficients of radiations in lead distinguishes clearly between Hess' rays and other radiation, and it is concluded that there are various reasons for supposing the existence of a very penetrating radiation. Measurements of absorption in lead, zinc, copper, iron, aluminium, and water show that there is a distinct scattering of this radiation of the kind to be expected if it is an ultra-γ radiation. The equality of the ionisation from the metals examined after allowance is made for the direct and scattered very penetrating radiation indicates that the natural radioactivity of these metals is less than 10^{-14} g. of radium per g. metal.

This conclusion is in agreement with the earlier experiments on the natural radioactivity of the elements (A., 1922, ii, 184).
W. E. DOWNEY.

Emission of short-wave radiation by poor conductors. E. BODIN (Ann. Physique, 1927, [x], **7**, 35—102 ; cf. Reboul, Compt. rend., 1920, **171**, 1502 ; 1921, **172**, 210, **173**, 1162 ; 1922, **174**, 1452 ; J. Phys. Radium, 1922, [vi], **3**, 341).—When a *P.D.* of a few hundred volts is applied between two points on a piece of paper, short-wave radiations capable of affecting a photographic plate are emitted from various centres; the same type of emission can be obtained from materials other than paper so long as they are heterogeneous in structure and are poor conductors of electricity. On account of their superior power to withstand moderate voltages, pastilles of agglomerated powders can be used for obtaining more intense emission. No relationship has been found between chemical constitution and the emission of these rays, although sulphates and some oxides give the best results. The radiation is complex in nature both for paper and powders, and its penetration varies directly as the time and the applied voltage. The intensity across the centres of emission falls off with time and does not conform with Ohm's law. The distribution of *P.D.* indicates a connexion between emission and a discontinuity produced at the point of contact of the metallic electrode with the surface under consideration. Those substances which are ineffective as sources of emission do not exhibit voltage discontinuities. In some cases (*e.g.*, copper carbonate), the emission occurs from one electrode only and the voltage discontinuities behave similarly.

Usually the emission appears mainly at the positive pole. The radiations appear to extend as far as 50 Å. R. A. MORTON.

Luminescence due to radioactivity. D. H. KABAKJIAN (Proc. Nat. Acad. Sci., 1927, **13**, 4—7). —The luminescence produced by α-, β-, and γ-rays is the result of changes in molecular energy. Three distinct types of luminescence due to radioactivity are recognised : (a) a reversible type in which the exciting rays supply the required energy and are capable of forming and destroying the molecular modification in the substance; (b) luminescence due to the action of rays on certain previously-heated substances, the configurations of higher quantum state formed as a result of molecular agitation at a higher temperature being destroyed by the rays with production of luminescence; (c) the so-called thermo-luminescence of crystals, the energy being furnished by the rays and liberated as a result of molecular agitation in the crystal. In this last case, the amount of energy which can be absorbed by the crystal increases with decreasing temperature, the molecular configurations of higher quantum state being more stable at low temperatures. When the temperature is raised, the large amount of energy absorbed at the lower temperature is released as luminescence. Luminescence is not always due to the presence of minute quantities of impurities in the various substances examined, since a number of pure compounds have been shown to luminesce under the action of α-, β-, and γ-rays. In most substances, all three types of luminescence co-exist with varying degrees of intensity. It is, however, possible to select compounds where one of the three possible types predominates. J. S. CARTER.

Chemical effects of penetrating radium radiation. Organic compounds containing nitrogen. A. KAILAN (Monatsh., 1927, **47**, 643—658).—The action of penetrating radiation from radium on aqueous solutions of uric acid in presence and absence of lithium carbonate has been investigated. In both cases, the number of molecules of uric acid which underwent chemical change (m) was of the same order as the number of ion pairs (n) formed : $m/n=0.2$. Pyridine in the undried and dried states and also an aqueous solution have been subjected to the action of the radiation for considerable periods. For the ratio m/n, the values obtained were 0·7 for the solution and 0·3 for the dried and undried pyridine. In each instance, irradiation brings about an increase in the density and electrical conductivity. For aniline, m/n is 0·4; the density is increased whilst the conductivity remains constant. After three or four months' irradiation, aniline and pyridine develop a reddish-brown coloration. The same result is observed with either wet or dry nitrobenzene. On the basis of the production of o- and p-nitrophenol in the latter reaction, the ratio m/n is 0·1. Although these are not the only products formed, it seems clear that m and n are always of the same order of magnitude. With o-nitrotoluene, the colour changed from yellowish-green to green after irradiation for 2000 hrs. A collateral change occurred in the conductivity and alkali titre. R. A. MORTON.

Transmutation of the elements. E. PATERNÒ (Atti R. Accad. Lincei, 1926, [vi], **4**, 541—544).— An extract from a paper read by the author at the VIth International Congress of Applied Chemistry, Rome, 1906. The transmutation of metals in the laboratory is considered unlikely. T. H. POPE.

Fulminating matter. Spontaneous and almost noiseless decomposition of certain ball-lightnings of great diameter. E. MATHIAS (Compt. rend., 1927, **184**, 312—314; cf. ibid., 1925, **181**, 1038).—Uncharged spherical ball-lightnings decompose spontaneously and almost without noise if they are thermally homogeneous. Otherwise explosions occur which are not dangerous. Charged ball-lightning may give rise to dangerous explosions by the ejection of charged matter. If the fulminating matter (an unknown compound of oxygen and nitrogen) is pure, spontaneous decomposition occurs without the production of vapour or sparks. If animal or vegetable corpuscles are absorbed, a state of thermal heterogeneity is produced which results in partial explosion and the expulsion of incandescent matter. The latter produces electrocution if it comes from a charged source. J. GRANT.

Effect of intense light on the energy levels of atoms. A. E. RUARK (Nature, 1927, **119**, 389).— The broadening or shift of the sodium D lines in absorption on illumination of the vapour, sought but not observed by Kuhn (A., 1926, 985), should admit of detection, if it exists, in the solar spectrum or in the spectra of very hot stars. Kuhn's assumption that the atoms are subjected to an electric force E obtained from the equation energy density $=E^2/4\pi$ is criticised. A. A. ELDRIDGE.

Energy of the crossed-orbit model of the hydrogen molecule. E. HUTCHISSON (Physical Rev., 1927, [ii], **29**, 270—284).—With the classical quantum theory, the energy of a model of the hydrogen molecule, similar to the crossed-orbit model of the helium atom, with the nucleus separated into two parts is computed as 45·2 volts, whereas the experimental value is 31·42 volts. Also the moment of inertia is computed as $4·91 \times 10^{41}$ g. cm.^{2} A. A. ELDRIDGE.

Calculation of atomic fields. L. H. THOMAS (Proc. Camb. Phil. Soc., 1927, **23**, 542—548).—A method of calculating from theoretical considerations the approximate fields of heavy atoms is described. R. CUTHILL.

Atomic model for the chemist. (MRS.) F. LANGWORTHY (Chem. News, 1927, **134**, 113—117). —A contention that atomic systems resemble the solar system. S. I. LEVY.

Quantum mechanics of multi-charged atoms and resonance. W. HEISENBERG (Z. Physik, 1927, **41**, 239—267).—The author's theory of the spectra of atomic systems associated with two electrons (this vol., 5) has been extended to the cases in which the number of electrons is greater than two. In particular, from a consideration of resonance phenomena explanations are advanced for the anomalous variations of intensity in rotation band spectra. R. W. LUNT.

Quantum theory of continuous spectra. J. R. OPPENHEIMER (Z. Physik, 1927, **41**, 268—293).— Schrödinger's mechanics have been employed to derive the characteristic function of systems exhibiting extended absorption. From this point of view, the hydrogen atom, the coefficients of continuous X-ray absorption, the polarisation and energy distribution in the continuous X-ray emission spectra, and the velocity and distribution in direction of photo-electrons have been discussed at length. This analysis also leads to derivations of the formula of Compton and of Kramers. R. W. LUNT.

Quantum mechanics of atoms. A. UNSÖLD (Ann. Physik, 1927, [iv], **82**, 355—393).—The meaning of " penetrating " and " outer " orbits in terms of Schrödinger's quantum mechanics is investigated. The older shell-model gives only qualitative results for penetrating orbits. The S terms for helium, Li$^+$, and stripped atoms are calculated. The behaviour of atoms in a heterogeneous electric field is the basis of the calculation of the outer orbits. The calculation to a first approximation proves and extends Pauli's quadripole summation proposition, whilst the second approximation leads to the problem of the dispersion theory. The " middle " terms for the outer orbits of the alkaline-earths are then calculated and the separations of the singlet–triplet systems for some alkaline-earth terms. Finally, the Stark effect of series spectra is determined. W. E. DOWNEY.

Wave mechanics and the rotation of homopolar molecules. D. M. DENNISON (Nature, 1927, **119**, 316—317).

Radiation and absorption on Schrödinger's theory. J. C. SLATER (Proc. Nat. Acad. Sci., 1927, **13**, 7—12).—Mathematical. The author has previously shown (A., 1925, ii, 478) that the radiation and absorption of light by atoms can be treated by replacing the atoms by a set of oscillators, the frequencies of which are the frequencies of quantum transitions. Use of the Schrödinger wave-mechanics enables the theory to be placed on a more satisfactory foundation. The essential features of the author's treatment of absorption have already been put forward by Dirac (A., 1926, 1078). J. S. CARTER.

Band spectrum of mercury from the excited vapour. (LORD) RAYLEIGH (Nature, 1927, **119**, 387; cf. this vol., 82).—The green, visual band, extinguished by heat, partly recovers as the excited vapour moves to a cold part of the tube. The " forbidden " line 2270 was observed, and a separate stretch of band spectrum reaches from this point to the band 2345 Å. Below 2270 Å., and from 2345 to 2537 Å., the background of the spectrum is dark. A. A. ELDRIDGE.

Band spectrum of mercury from the excited vapour. (LORD) RAYLEIGH (Nature, 1927, **119**, 423).—The " forbidden " line at 2655·73 Å. has been observed (cf. preceding abstract). A. A. ELDRIDGE.

Infra-red oscillation spectrum of water molecules and its variation with state. J. W. ELLIS (Phil. Mag., 1927, [vii], **3**, 618—621).—A collection of data for the infra-red spectrum of water showing that the spectra for the various states can be explained as being combinations of two primary bands, each pair being characteristic of the special state. A. E. MITCHELL.

Infra-red absorption by the N·H linking. I. Aniline and alkylaniline. J. W. ELLIS (J. Amer. Chem. Soc., 1927, **49**, 347—356).—Infra-red absorption spectra below 2·8 μ are recorded for aniline and some mono- and di-alkyl derivatives. The absorption bands at 1·47 μ and 1·04 μ are associated with the N·H linking; together with the band at 2·8 μ (Bell, A., 1925, ii, 928) these bands form members of a parabolic series : $\nu = 376n - 18\cdot3n^2$, where ν is the frequency in waves per mm. The bands near 2·0 μ and 1·2 μ may be produced by the combination of N·H frequencies and a fundamental C·H frequency. S. K. TWEEDY.

Absorption of ultra-violet light by copper sulphate solutions. L. KWIECIŃSKI and L. MARCHLEWSKI (Bull. Inter. Acad. Polonaise, 1926, A, 247—253).—Beer's law is obeyed for the ultra-violet absorption of $N/10$- and $N/20$-copper sulphate. R. A. MORTON.

Absorption spectra of " saturated " and " unsaturated " organic substances. J. E. PURVIS (Proc. Camb. Phil. Soc., 1927, **23**, 588—592).—The vapour of *cyclo*hexanone between 100° and 200° gives a large absorption band at about 2777 Å. Comparison of the absorption of geraniol with that of the pelargonic ester shows that weighting the geraniol molecule with the heavy pelargonic radical shifts the position beyond which absorption occurs towards the red. Pentabromophenol and tetrabromo-*o*-cresol show bands comparable with those of phenol. R. CUTHILL.

Spectrochemical studies of hydroxyazo-compounds. II. T. UEMURA, N. YOKOJIMA, and T. ENDO (Bull. Chem. Soc. Japan, 1927, **2**, 10—15; cf. this vol., 238).—The absorption spectra of neutral and alkaline solutions of benzeneazopyrocatechol, benzeneazoquinol, *p*-nitrobenzeneazopyrocatechol, *p*-nitrobenzeneazoquinol, *m*-nitrobenzeneazophenol, *o*-nitrobenzeneazophenol, *o*-nitrobenzeneazoresorcinol, *p*-nitrobenzeneazoguaiacol, and *p*-nitrobenzeneazoquinol monomethyl ether have been studied, and the results correlated with the colour and the structure of the compounds. L. L. BIRCUMSHAW.

Absorption of ultra-violet light by *d*-galactose. L. KWIECIŃSKI and L. MARCHLEWSKI (Bull. Int. Acad. Polonaise, 1926, A, 255—262).—Purification of galactose brings about the disappearance of selective absorption at 265 μμ. Aqueous solutions of pure galactose (m. p. 165—165·5°) exhibit feeble general absorption in the ultra-violet down to 228 μμ. The rotation $[\alpha]_D^{20}$ falls from $+107°$ to 81·23° in 9 hrs., but a concomitant change in absorption cannot be detected with certainty. If the carbonyl group causes selective absorption, then it seems that aqueous solutions of galactose must contain only two stereoisomerides in equilibrium, neither of which possesses an aldehyde group. R. A. MORTON.

Fluorescence spectra of the sulphur group. J. C. McLENNAN, I. WALERSTEIN, and H. GRAYSON SMITH (Phil. Mag., 1927, [vii], **3**, 390—395).—New fluorescence spectra have been found in the saturated

vapours, at comparatively low temperatures, of sulphur, selenium, and tellurium, excited by intense illumination from a quartz mercury arc. The fluorescence spectrum of sulphur consists of a large number of bands extending from 5670 to 4050 Å. The bands are mostly sharp, and there are certain sequences of approximately equally spaced bands. There is marked absorption of the diffused mercury spectrum below 4050 Å., indicating that this is probably the active region for the excitation of this sulphur spectrum. At 325°, selenium exhibits a fluorescence spectrum extending from 5079 to 2229 Å., which is apparently analogous to the ultra-violet fluorescence spectrum of iodine. Above 325°, this spectrum disappears and is replaced at 430° by a spectrum comprising nine faint broad bands between 4178 and 4829 Å. At 550°, tellurium vapour shows two groups of regularly-spaced bands covering the region 6580—4130 Å. These spectra are all different from the fluorescence spectra found for these elements by Diestelmeier and others, using superheated vapours. At 500°, bismuth vapour exhibits a fluorescence spectrum showing eighteen fairly sharp lines in the region 4890—4410 Å.　　　　A. E. MITCHELL.

Polarisation of the resonance fluorescence of sodium vapour. W. HANLE (Z. Physik, 1927, 41, 164—183).—The polarisation of the fluorescence of sodium vapour when excited by circular polarised light, using a silica discharge tube containing sodium vapour and a little argon as the light source, has been determined as a function of the pressure of the sodium vapour in the range 10^{-7} to 8×10^{-6} mm., and in fields from 60 to 600 gauss. At 600 gauss and 10^{-7} mm., a maximum value corresponding with 87% of the theoretical was observed, the difference being attributed to errors introduced by the apparatus. The depolarisation produced by the introduction of argon, nitrogen, hydrogen, and helium–neon mixtures has also been recorded as a function of the temperature.　　　　R. W. LUNT.

Line fluorescence of cadmium vapour. W. KAPUŚCIŃSKI (Z. Physik, 1927, 41, 214—220).—The fluorescence of cadmium vapour, carefully purified from mercury and occluded gases, has been examined in the temperature range 200—900°. In addition to the resonance lines 2289, 3261 Å., the following lines of the arc spectrum have also been observed, using the light from a condensed cadmium spark discharge to excite the fluorescence : 3614·6 ($2^3P_2-3^3D_1$), 3467·8 ($2^3P_1-3^3D_1$), 3403·7 ($2^3P_0-3^3D_1$), 3613·0 ($2^3P_2-3^3D_2$), 3466·3 ($2^3P_1-3^3D_2$), 3610·7 ($2^3P_2-3^3D_3$) (maximum intensity at 600°); above 450°, 5086·1 ($2^3P_2-2^3S$), 4800·1 ($2^3P_1-2^3S$), 4678·4 ($2^3P_0-2^3S$), and 3133·3 Å. ($2^3P_1-3^3S$). Using iron electrodes, the triplet 5086, 4800, 4678 Å. was observed, and also a weak emission of the triplets 3613, 3467, 3404 Å., in addition to the resonance line 3261 Å. The resonance lines 3261 and 5086, 4800, 4678 Å. were excited by the spark spectra of zinc, magnesium, and aluminium ; and 3261 by the light from copper and carbon electrodes, and from the mercury arc. The lines 2573 and 2749 Å. were also observed, using cadmium electrodes, and are thought to correspond with absorption by atoms in the 2^3P_1 state,

whereby they become in the 2^3S or 3^3D_j state, from which they return to the 2^3P_i state, emitting the corresponding radiation ($2^3P_i-3^3D_j$ and $2^3P_i-2^3S$). When excited with the light from zinc electrodes, cadmium vapour emits the zinc lines 2502 and 2558 Å.　　　　R. W. LUNT.

Line fluorescence of tellurium vapour. (MME.) H. RAKOWICZ-POGORZELSKA (Bull. Inter. Acad. Polonaise, 1926, A, 243—245).—Tellurium exhibits an intense bluish-green fluorescence when illuminated by an incandescent lamp. The emission shows a banded spectrum. Under the light of a mercury-vapour lamp, the fluorescence is much less intense. The spectrograms indicate a number of fine lines between 413 and 542 μμ which are regularly spaced. The wave-lengths of the more intense lines have been tabulated. The exciting rays are shown to belong to the visible region, with maximal activity in the bluish-violet region extending from 400 to 435 μμ.　　　　R. A. MORTON.

Fluorescence bands of mercury vapour. F. G. HOUTERMANS (Z. Physik, 1927, 41, 140—153).—Mercury vapour when excited by the mercury line 2537 Å. exhibits a short and a long afterglow. The former commences at 2537 and shows a maximum at 4850 Å. ; it is attributed to the 2^3P_1 state. The latter commences at 2560 and exhibits a maximum at 3300 Å. ; it is attributed to the 2^3P_0 state.　　　　R. W. LUNT.

Anticathodic luminescence of organic compounds. J. K. MARSH (J.C.S., 1927, 125—130).—Observations have been made of the light emitted by various organic substances when placed on an anticathode in a discharge tube. The conditions under which the discharge tube was operated are not described, except that the substance on the anticathode was kept at the temperature of liquid air. The light emitted was examined by a glass spectroscope, but for the following substances only was it sufficiently intense to photograph : toluene, p-cymene, m-xylene, mesitylene, naphthalene, tetrahydronaphthalene, octahydroanthracene, acenaphthene, triphenylmethane, diphenylmethane, α-methylnaphthalene, β-methylnaphthalene, α-naphthol, and β-naphthol. It is shown that between the short wave-length boundary of the absorption and fluorescence spectra and that of the anticathodic luminescence of these substances there is an approximately constant wave-number difference of 1500 ± 100.　　　　R. W. LUNT.

Polarisation of the glow from canal rays. E. RUPP (Physikal. Z., 1926, 27, 796—799 ; cf. A., 1926, 450, 875).—The glow from canal rays sometimes exhibits marked polarisation. The phenomenon has been studied by means of photographic photometry. Viewing the stream at an angle of 90°, the fraction of the light polarised in a direction parallel to the direction of the canal rays is greater than the fraction polarised in a direction perpendicular to the stream. The difference is great for hydrogen (velocity, $6·4 \times 10^7$ cm./sec. : lines, H_β, H_γ, ratio 0·65). The $2p-3d$ line of lithium shows a considerable effect, as also do the $2p-md$ and $2P-mD$ series of orthohelium and parhelium. For the $1·5s-mp$ and $2p-ms$ series of lithium, the $2p-4s$ series of orthohelium, and the

$2S—3P, 2P—4S$ series of parhelium the polarisation is very small. The results are discussed theoretically by the author and others. R. A. MORTON.

Influence of lighting the cathode with ultraviolet light on the self–dependent glow discharge. E. SALZWEDEL (Ann. Physik, 1927, [iv], **82**, 305—345).

Investigation of gas discharges by means of an exploring electrode. K. G. EMELÉUS (Proc. Camb. Phil. Soc., 1927, **23**, 531—541).—The distribution of potential in the glow discharge in air, oxygen, nitrogen, and hydrogen has been determined by Langmuir's method, using an exploring electrode. At pressures of about 0·1 mm., nearly the whole of the *P.D.* is across the cathode dark space, but at higher pressures there may be a considerable *P.D.* across the remainder of the discharge. With hydrogen at low pressure, the cathode edge of the negative glow is at a higher potential than the anode. In the negative glow, there are two groups of electrons, with one fast group at the anode boundary of the cathode dark space, and a slow group in the Faraday dark space. R. CUTHILL.

Activation of molecular hydrogen by electron impact. G. GLOCKLER (Science, 1926, **64**, 505—506).—Activated hydrogen, produced in a 4-electrode tube, reacted with copper oxide, the water produced being removed by freezing and the decrease of pressure being determined as a function of the accelerating voltage. A sharp decrease occurs with electrons of 11·4 volts energy. Hence hydrogen molecules react at the ordinary temperature with copper oxide after having been brought into their first higher quantum state by electron impact. A. A. ELDRIDGE.

Photo-electric activity of the silver halides and silver sulphide. F. C. TOY, H. A. EDGERTON, and J. O. C. VICK (Phil. Mag., 1927, [vii], **3**, 482—495).—An investigation of the photo-electric activity of the silver halides and of silver sulphide has been made with light of wave-length less than 2800 Å. With silver halides prepared either by exposure of metallic silver to the halogens or by fusion of the resulting halide, the order of photo-electric activity has been found to be iodide>bromide>chloride. This order is probably the same for the halides prepared by precipitation from aqueous solution. Silver sulphide prepared by exposing metallic silver to hydrogen sulphide was found to be from two to three times as active as the iodide, and about twenty-five times as active as the bromide prepared in an analogous manner. Traces of silver sulphide in either silver bromide or iodide have been shown to cause no abnormal increases of photoelectric sensitivity. Small amounts of silver iodide in silver bromide did not result in any appreciable shift of the critical photo-electric wave-length towards the visible spectrum comparable with the chromatic sensitisation observed photographically. The results indicate that there is no parallelism between the photo-electric properties of the pure silver halides and the photographic properties of silver halide emulsions. A. E. MITCHELL.

Thermionic theory of the electrical conductivity of dielectrics. H. SAEGUSA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 795—803; cf. *ibid.*, 1925, **14**, 319).—It is assumed that the conductivity of dielectrics is due to some of the loosely-bound electrons becoming freed from their atoms and that the number of these electrons is given by Richardson's formula for thermionic emission. Using the electron gas theory of conductivity, an expression is obtained for the conductivity of dielectrics which is in reasonable agreement with the author's previous results (*loc. cit.*) for quartz. W. HUME-ROTHERY.

Dielectric constants of liquid and solid nitrogen. L. EBERT and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1188—1192).—Preliminary measurements. Using the same apparatus as for oxygen (A., 1926, 661), the dielectric constant of liquid nitrogen has been examined over the temperature range 63·9—76·5° Abs. The values of ε at the lower and higher temperatures are 1·472 and 1·440, respectively. The mean value of the molecular polarisation is 4·39, that for gaseous nitrogen being 4·34. The Maxwell relation and the equation of Clausius and Mosotti are approximately valid for gaseous and liquid nitrogen. The dielectric constant of solid nitrogen at 60° Abs. is of the order 1·45—1·46. J. S. CARTER.

Dielectric constant of bromine. A. BRAMLEY (J. Franklin Inst., 1927, **203**, 251—260).—The variation of the dielectric constant ε of bromine vapour with pressure, temperature, and electric intensity has been studied. Curves have been obtained by plotting ε—1 against pressure for different temperatures and electric fields. In the curves obtained at 23·9°, the quantity ε—1 increases with pressure more rapidly than the first power. The curve at 28·5° is linear and is independent of the electric gradient. It corresponds with the classical theory, except that ε—1 is about twice as large as the value expected from the refractive index. The curves at 77—80° show a decreasing tangent with increasing pressure, the reverse of the effect found at 23·9°. When the field was changed from 58 to 285 volts, a considerable variation was observed at 80°, the effect depending on the pressure of the vapour.

If the band spectrum of a diatomic gas is due to the rotational and vibrational energies of the two ions composing the molecule, the molecular moment should depend on the distance separating the ions. It is shown theoretically that the temperature variation of the dielectric constant is related to a constant e_0 corresponding with a wave-length λ_0. For water $\lambda_0=3·0$ μ, which agrees with the maximum in the absorption band of water vapour; for bromine vapour $\lambda_0=0·9$ μ. As no data were available to test this result, the absorption spectrum of bromine vapour was studied in this region. A broad absorption band makes its appearance at 0·95 μ, and extends as far as 1·5 μ. The theory is thus vindicated in this respect. R. A. MORTON.

Determination of the dielectric constant of air by a discharge method. A. P. CARMAN and K. H. HUBBARD (Physical Rev., 1927, [ii], **29**, 299—308).—A mean value of 1·000594 is obtained for the dielectric constant of air at 0° and 760 mm. A. A. ELDRIDGE.

Temperature variation of the dielectric constants of gases. H. J. von Braunmühl (Physikal. Z., 1927, **28**, 141—149).—The dielectric constants of hydrogen, carbon monoxide, argon, carbon dioxide, nitrous oxide, hydrogen sulphide, and hydrogen chloride have been measured by a heterodyne method at the frequency 10^6 cycles per sec. in the temperature range 280—400° Abs., and are found to vary in accordance with the equation of Debye, $m(\varepsilon-1)T/4\pi\rho = aT + b$, where ε is the dielectric constant, m the molecular mass, ρ the density, T the temperature Abs., and a and b are characteristic constants. The following expressions are given for a and b : $a = \Sigma n_i e_i^2/f_i$ and $b = \mu^2/3k$, where n_i is the number of particles of charge e_i per molecule, f_i the restoring force, μ the electric moment of the dipole, and k the Boltzmann constant. Values of a and μ are obtained in this way from the experimental data. R. W. Lunt.

Dielectric properties of ionised gases. H. Gutton and J. Clément (Compt. rend., 1927, **184**, 441—443).—The dielectric properties of hydrogen have been observed at various pressures and degrees of ionisation by the resonance method, and curves obtained which show the relation between the resonance wave-length and the square of the resonance current for constant pressures and an increasing degree of ionisation. Two current maxima are obtained, corresponding with zero and complete ionisation, the former being the greater. At low pressures an apparent decrease in ε is indicated by a diminution in the wave-length; this increases with the ionisation. At high pressures, the curves indicate the existence of forces analogous to friction, and the curves are similar to those obtained for a solution of an electrolyte as the concentration increases. J. Grant.

Electric moments of disubstituted benzene derivatives. R. N. Kerr (Phil. Mag., 1927, [vii], **3**, 330—336).—The dielectric constants of a number of disubstituted benzene derivatives in the liquid state at 58° have been determined for a wave-length of 95 metres. All the isomeric compounds show a gradation of the dielectric constant from *ortho*- through *meta*- to *para*-. In some cases, there is an increase in the value in this order, whilst in others there is a decrease. The theory of Thomson (A., 1923, ii, 683) regarding the method in which the magnetic moments of such isomerides should vary is shown to hold when both substituents are the same, but to fail in several cases when the latter are different. A. E. Mitchell.

Molecular volumes of the halopentamminecobaltic and chromic halides. R. Klement (Z. anorg. Chem., 1927, **160**, 165—170).—Ephraim and Schütz's values (A., 1926, 785) for the molecular volumes of chloro- and bromo-pentamminecobaltic halides are criticised, since they do not accord with the atomic volumes of the halogens; bromopentamminecobaltic bromide is reported as having a smaller molecular volume than chloropentamminecobaltic bromide, although the atomic volume of bromine is greater than that of chlorine. The possible sources of error are discussed, and new determinations given which are in agreement with the order of atomic volume of the halogens. H. F. Gillbe.

Changes in volume in the formation of halides, oxides, and sulphides. C. del Fresno (Anal. Fís. Quím., 1926, **24**, 707—716).—The contraction in volume, expressed by the negative fraction $V_m/\Sigma V_a$ (where V_m is the molecular volume and ΣV_a the sum of the atomic volumes), increases with the atomic volumes of the metals for the halides of elements of the first two groups. For different halides of the same metal, excepting hydrogen, the opposite relationship obtains. The contraction is smaller in the oxides than in the sulphides. Whilst the formation of homopolar compounds appears to be accompanied by dilatation, contraction is observed with the hydrogen halides. This may be explained on the assumption that the hydrogen nucleus penetrates the electronic layer of the other atom, whilst the electron remains with the other electrons, the hydrogen atom thereby losing its identity. With the oxides of elements of groups III—VI, the curve connecting contraction with atomic volume passes through a minimum. G. W. Robinson.

Dependence of free space on temperature. W. Herz (Z. Elektrochem., 1927, **33**, 76—77).—The influence of temperature on the free space, V_f, of liquids (A., 1926, 670) can be represented by relations similar to those for the effect of temperature on molecular volume, viz. : $(V_{f_2} - V_{f_1})/V_{f_1} = \alpha(t_2 - t_1)$ and $(V_{f_1} - V_{f_0})/V_{f_0} = kt_1$, where V_{f_2}, V_{f_1}, and V_{f_0} denote the free space at t_2, t_1, and 0°, respectively, and α and k are constants. Data for pentane, hexane, heptane, and octane are quoted. H. J. T. Ellingham.

Measurement of index of refraction of gases at higher temperatures. E. W. Cheney (Physical Rev., 1927, [ii], **29**, 292—298).—For air, nitrogen, ammonia, carbon dioxide, and sulphur dioxide, values of $(n-1)10^7$ at 0° and 760 mm. for 5852, 6143, and 6678 Å., respectively, are : 2925, 2985, 3795, 4485, 6637 ; 2919, 2977, 3785, 4473, 6615 ; 2912, 2969, 3771, 4465, 6598. For visible light the thermal coefficients do not differ from those of density change between 0° and 300°. Between 25° and 300°, the coefficient of (linear) expansion of quartz has the constant value 0.946×10^{-6}. A. A. Eldridge.

Refractivity of some anisotropic molecules. T. H. Havelock (Phil. Mag., 1927, [vii], **3**, 433—448).—By treating the molecule as a structure of isotropic polarisable constituents in fixed relative positions, expressions are obtained, in terms of the constants of the constituents and of the structure, for the refractivity and the depolarisation ratio of a gas the molecules of which are of three types : (a) three equal atoms at the corners of an equilateral triangle with a fourth atom equidistant from them, but not necessarily in the same plane, (b) four equal atom at the corners of a regular tetrahedron with a fifth at the centroid, (c) four equal atoms at the corners of a square with a fifth equidistant from them, but not necessarily in the same plane. Numerical results are deduced for some suggested models for ammonia and methane, and are discussed in relation to other members of the series of compounds of the form XH_n. A. E. Mitchell.

Action of magnetic fields on the refractive index of gaseous carbon dioxide. E. T. S.

APPLEYARD (Nature, 1927, **119**, 353).—The observations of Ghosh and Mahanti (A., 1926, 1194) cannot be attributed to molecular orientation. Further, repetition of Ghosh and Mahanti's experiments gave a straight line when pressure was plotted against fringe-shift whether the field was on or off.
A. A. ELDRIDGE.

Diffraction of X-rays by liquids. F. ZERNIKE and J. A. PRINS (Z. Physik, 1927, **41**, 184—194).—From a consideration of the effect of the relative motion of the molecules in a liquid an expression is obtained for the variation of the intensity of the scattered radiation with the angle of scattering when a liquid is irradiated with monochromatic X-radiation. The general characteristics of the experimental curves are reproduced, particularly the rapid increase in intensity, rising to a sharp maximum, which is observed as the angle of scattered radiation is increased from zero to $\pi/4$. This analysis also leads to the conclusion that, for small angles of scattering, the ratio of the intensities for a liquid and its vapour is equal to the ratio of the compressibilities of the two states. R. W. LUNT.

Anomalous dispersion of a silicate solution for wave-lengths between 50 and 60 cm. E. FRANKENBERGER (Ann. Physik, 1927, [iv], **82**, 394—412).—Using a Lecher-wire system, the band of anomalous dispersion at about 56 cm. wave-length in the refraction of water, found by Weichmann (A., 1922, ii, **5**, 331), is shown not to appear with pure water. $1·5 \times 10^{-4}N$-Sodium hydrogen silicate in water shows anomalous dispersion between 50 and 60 cm. wave-length. If the solution is prepared in the same manner, it always gives the same dispersion, even after keeping for a week. The dispersion band can be split up into three parts, each of which corresponds with a mode of resonance. The results fit the ordinary optical dispersion formula. The measured values of absorption coefficient agree in order of magnitude with those calculated from the dispersion–wave-length curve. It is necessary to note that water itself shows a fairly considerable absorption for these short waves. W. E. DOWNEY.

Intensity of anomalous dispersion in non-luminous vapours of thallium and cadmium. W. KUHN (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**, No. 12, 1—87).—From an extension of the theory of dispersion, an expression is developed for longitudinal magnetic double refraction for certain anomalous Zeeman effects. Previous results of anomalous dispersion and absorption in the neighbourhood of spectral lines are recalculated to a common basis and extended by more recent data. Anomalous magnetic rotation dispersion in non-luminous vapours of thallium and cadmium were measured, and the f-values for a number of lines are given. The absolute and relative f-values are discussed from various theoretical points of view. W. CLARK.

Rotatory dispersion of asparagine in the ultra-violet. (MLLE.) J. LIQUIER and R. DESCAMPS (Bull. Soc. chim. Belg., 1926, **35**, 459—465).—The rotatory dispersion of aqueous solutions of asparagine containing hydrogen chloride, sodium hydroxide, sodium chloride, potassium chloride, potassium sulphate,

calcium chloride, and various mixtures of these substances has been studied in the ultra-violet, with results in accordance with previously expressed opinions (A., 1926, 906). L. F. GILBERT.

Magnetic rotary dispersion of water, alcohol, and water–alcohol mixtures. D. J. STEPHENS and E. J. EVANS (Phil. Mag., 1927, [vii], **3**, 546—565).—The magneto-optical rotation of water at temperatures between 13·2° and 20° has been examined over the region of wave-lengths 0·5997—0·2383 μ; the results show that in this spectral region the only absorption band which contributes materially to the magnetic rotation is at 0·1192 μ. Similar measurements at 12·2—13° have been made with 99·4% ethyl alcohol over the spectral range 0·4390—0·2600 μ; the results indicate that the absorption band making the major contribution to the rotation is at 0·1114 μ. Examination of the magneto-optical rotation at 12·2—13° of various ethyl alcohol–water mixtures in the region 0·2753—0·3363 μ shows that the value of Verdet's constant diminishes initially with an increase in the percentage of alcohol up to 30%; between 30 and 70% alcohol its value is constant, and above 70% it decreases. A. E. MITCHELL.

Influence of solvents on the rotation of optically active compounds. XXIV. Menthyl benzenesulphonate, menthyl naphthalene-α-sulphonate, and menthyl naphthalene-β-sulphonate in various solvents. T. S. PATTERSON and (MISS) I. M. MCALPINE (J.C.S., 1927, 353—355; cf. ibid., 1916, **109**, 1204).—The specific rotations of each of the above substances in six different solvents for three different colours of light have been determined. From the data so obtained, it is concluded that there is no region of anomalous rotation dispersion. The dispersion ratios for the series of substances are practically constant. W. E. DOWNEY.

Molecular scattering of light in a binary liquid mixture. K. C. KAR (Phil. Mag., 1927, [vii], **3**, 601—604).—It is shown that the attempted improvement by Raman and Ramanathan (ibid., 1923, [vi], **45**, 213) of Einstein's equation for molecular scattering of light in a binary liquid mixture introduces a vanishingly small correction term, and is therefore unjustified. A. E. MITCHELL.

Absolute measurement of the intensity of light diffused by benzene in the liquid state. J. CABANNES and P. DAURE (Compt. rend., 1927, **184**, 520—522).—The intensity of light diffused through thiophen-free, non-fluorescent benzene has been compared with that found for gaseous ethyl chloride (A., 1925, ii, 753). In this, and in 66 liquids, the ratios of the intensity of the light diffused through the liquid to that of the gas indicates that the former diffuses less light than would be expected when the result is calculated from Einstein's formula corrected for anisotropy. Avogadro's constant (N) is $6·5 \times 10^{23}$ for the gas and $7·8—8·0 \times 10^{23}$ for the liquids. The method therefore is not suitable for the determination of N in liquids. J. GRANT.

Magnetism and molecular structure. E. C. STONER (Phil. Mag., 1927, [vii], **3**, 336—356).—The magnetic properties of uninuclear and simple bi-

nuclear systems are discussed in relation to their spectroscopic and chemical properties. For inert gas atoms and ions of similar configuration, the magnetic susceptibilities are roughly of the same order as those to be expected from ionisation potential data. For helium, the magnetic data suggest a model with two parallel approximately circular orbits. The model with $k=\frac{1}{2}$ for each electron orbit leads to a value for the susceptibility one sixth of that observed by Will and Hector (A., 1924, ii, 293). The magnetic moments of the ions of the first transition series of elements are shown to be almost all in disagreement with values predicted from the work of Hund (A., 1925, ii, 912). Ions with fewer electrons behave magnetically, as though they were in S-states. The simpler binuclear diamagnetic systems behave analogously to ^1S atomic configurations. From numerical values of the susceptibilities it is shown that the anomalous increase in molecular susceptibility at low pressures observed by Glaser (ibid., 82) cannot be due to an orientation phenomenon, and it is suggested that Glaser's results are due to some unrecognised experimental factor inherent in his method. The significance of the high value of the susceptibility of hydrogen is discussed, and it is suggested that in the hydrogen molecule the two electronic orbits are parallel to each other and to the plane of nuclear rotation, that the electrons move in opposite directions in quantum orbits for which the total quantum number is greater than one, that the molecule as a whole behaves as a ^1S-system, and when strongly quantised assumes a single definite orientation in a magnetic field. This view is in agreement with Mulliken's interpretation (A., 1926, 8) of the spectroscopic data. The magnetic moments of the binuclear paramagnetic systems NO and O_2 suggest that these two molecules form a sequence with N_2, the three molecules behaving as atom-like configurations in ^1S-, ^2S-, and ^3S-states. The various lines of evidence suggest that in the simpler molecules the outer electrons distribute themselves about the binuclear centre similarly to the electrons of atoms. A. E. MITCHELL.

Co-ordination theory in organic and physiological chemistry. P. PFEIFFER (Ver. Ges. Deut. Naturforsch. Aerzte, 1926, **19**, 1100—1108).—An address in which the theory of co-ordination compounds and complex metallic salts is considered in relation to complex organic molecular compounds etc. of medical interest. The implications of adsorption are also discussed. R. A. MORTON.
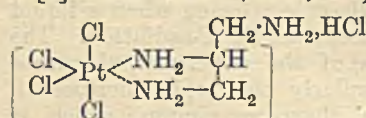
Isomerism of molybdenyl monochloride. W. WARDLAW and R. L. WORMELL (J.C.S., 1927, 130—139).—The authors report the existence of two forms of the co-ordination compound $MoOCl,4H_2O$. Assuming that tervalent molybdenum has a co-ordination number of six (from certain experimental evidence on ionisation values), and that the associating units are situated at the vertices of a regular hexagon, the authors show that two stereoisomerides of this compound are possible. From a consideration of the action of these compounds with sodium monosalicylate, using the salicylate group as an unsymmetrical chelate group, the authors assign a cis-configuration

to the brown compound and a trans-configuration to the green compound. R. W. LUNT.

Novel type of optically active complex metallic salt. F. G. MANN and (SIR) W. J. POPE (Nature, 1927, **119**, 351).—It is established that an auxiliary valency linking can render a carbon atom asymmetric. Tetrachloro-(triaminopropane monohydrochloride)-platinum (cf. A., 1926, 1234) has been resolved into optically active components by means of silver d- and l-camphorsulphonates, the hydrochlorides regenerated from the salts l-base-d-acid and d-base-l-acid having $M[\alpha]$ −502° and +501°, respectively. Hence the hydrochlorides must be represented by the annexed formula, where the enantiomorphism of configuration is associated with the asymmetry of the β-carbon atom of the triaminopropane molecule. A. A. ELDRIDGE.

Magnetic birefringence constant of benzene. C. V. RAMAN and K. S. KRISHNAN (Compt. rend., 1927, **134**, 449—451).—The Cotton–Mouton constant for benzene is calculated from the authors' formula (this vol., 92) on the assumption that the molecule has the hexagonal structure suggested by Pauling (A., 1926, 662). The values obtained for each method of linking of the electrons are calculated and a result is obtained which agrees with the observed value $(5\cdot90\times10^{-13})$ when it is assumed that all the carbon–carbon electronic orbits are in the plane of the hexagon and those of carbon–hydrogen are perpendicular to it. J. GRANT.

Diameter of molecules at the b. p. S. G. MOKROUSHIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 491—494).—By combining the author's earlier formula (A., 1924, ii, 820) $d=k\sqrt{T/\gamma}$, where T is the b. p., γ the surface tension, d the molecular diameter, and $k=1\cdot98\times10^{-8}$, with Kistiakowski's modification of the Ramsay and Shields expression (J. Russ. Phys. Chem. Soc., 1902, **34**, 74) $\gamma=(M/s)^{2/3}=1\cdot15T$, where s is the liquid density, a relation is obtained : $d=k/\sqrt[3]{M/s}$, the value of k_1 being $1\cdot79\times10^{-8}$. Molecular diameters given by this formula are compared with values obtained by other methods, including the kinetic theory of gases. The latter do not agree, since they are so-called " collision diameters." The views of Langmuir, Adam, and Marcelin as to the unimolecular nature of surface layers are adopted. M. ZVEGINTZOV.

Illinium. W. A. NOYES (Nature, 1927, **119**, 319).—Priority is claimed for Hopkins (cf. Rolla and others, this vol., 190) in the discovery of illinium. A. A. ELDRIDGE.

Element of atomic number 61 : florentium [illinium]. L. ROLLA and L. FERNANDES (Z. anorg. Chem., 1927, **160**, 190—192).—See this vol., 190.

Discovery and the K-absorption edge of the element of atomic number 61. R. BRUNETTI (Z. anorg. Chem., 1927, **160**, 237—241; cf. this vol., 190).—A claim for priority. H. F. GILLBE.

X-Ray analysis of single crystals. R. L. ASTON (Proc. Camb. Phil. Soc., 1927, **23**, 561—577).—Müller's method of determining the orientation

of a single crystal of metal by measuring the reflexion of characteristic X-rays from surface layers (Proc. Roy. Soc., 1924, **A**, **105**, 500) has been applied to iron crystals. Details of improvements in the technique are given. R. CUTHILL.

Crystal form of boron nitride. Eventual ambiguity in the analysis of powder-spectrograms. F. M. JAEGER and H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1218—1222).—Boron nitride was purified by a process of fractional sedimentation with water. The resulting substance, having d_4^{18} 1·99, was examined by the Debye–Hull powder-spectrogram method. The results of such measurements indicate that the underlying grating is simple cubic ($a_0=7\cdot44$ Å.) or simple tetragonal ($a_0=4\cdot295$, $c_0=5\cdot176$ Å., $a:c=1:1\cdot2052$). In the first case, the elementary cell would contain 20 mols. (an improbable figure), and in the case of tetragonal symmetry 4 or 5 mols. As all further necessary data are lacking, it is impossible to decide which structure is correct.

Conclusions as to crystal structure must not be drawn where only the results of powder-spectrograms can be used. Such data are valuable only when used in connexion with the results of other spectrographic methods, and of crystallographic measurements. J. S. CARTER.

Crystal structure of solid oxygen. J. C. MCLENNAN and J. O. WILHELM (Phil. Mag., 1927, [vii], **3**, 383—389).—X-Ray examination of solid oxygen at the temperature of liquid hydrogen (−252°) has shown that oxygen at −252° crystallises in the body-centred orthorhombic system with axial ratios $a:b:c=1\cdot44:1:0\cdot9$. The sides of the unit cell are $a=5\cdot50$, $b=3\cdot82$, and $c=3\cdot44$ Å., whence if two molecules be supposed to be associated in each cell, d is 1·46. The accepted value of the density of solid oxygen is 1·426. If it is assumed that this lower value is for the second modification existent at temperatures above that of the observations, then the present results afford confirmation of the observation of Wahl (A., 1913, ii, 208) that the low-temperature modification is the denser of the two forms of solid oxygen.

The existence of two modifications of oxygen is in agreement with the results that have been obtained for the other members of the same group of elements in the periodic table. A. E. MITCHELL.

Determination of the lattice spacing and of the rhombohedral angle of magnesium carbonate from a micro-crystalline powder. J. BRENTANO and W. E. DAWSON (Phil. Mag., 1927, [vii], **3**, 411—418).—X-Ray examination of a microcrystalline powder of magnesite has given a value for the rhombohedral angle of 103° 19', which is in close agreement with the value previously determined by Schröder (Ann. Physik, 1859, **106**, 226) by a goniometric method. The corresponding spacing d_{100} is $5\cdot477\pm0\cdot005$ Å. and the density 3·000. The corresponding values found by Levi and Ferrari (A., 1924, ii, 761) from X-ray measurement are 5·420 Å. and 3·08. The edge of the elementary cleavage rhomb is calculated to be 5·899 Å., corresponding with a unit cell of 4 molecules of magnesium carbonate. A. E. MITCHELL.

Crystal structure of magnesium platinocyanide heptahydrate. R. M. BOZORTH and F. E. HAWORTH (Physical Rev., 1927, [ii], **29**, 233—230).—The platinum atoms are located at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, and the magnesium atoms at 0, 0, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0, in a tetragonal unit $14\cdot6\times14\cdot6\times3\cdot13$ Å. The magnesium and platinum atoms alternate in rows with shortest distance of separation 10·3 Å., the distance between any two adjacent atom-centres being 1·57 Å. A. A. ELDRIDGE.

Space-groups of the rhombic and monoclinic heptahydrates of the sulphates of bivalent metals [and of rhombic magnesium chromate]. H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1223—1232).—The rhombic modifications of the heptahydrated forms of magnesium, zinc, and nickel sulphates and magnesium chromate have been examined by the X-ray spectrograph. The crystals have rhombic–bisphenoidal symmetry; the unit cell contains 4 molecules; V_4 is the only possible space-group. Similar measurements on the monoclinic–prismatic modifications of ferrous and cobalt sulphate heptahydrates lead to the conclusion that the unit cell contains 16 molecules and that the only possible space-group is C^6_{2h}.

		a_0	b_0	c_0
Rhombic	$MgSO_4,7H_2O$	11·89	12·01	6·86 Å.
	$MgCrO_4,7H_2O$	11·89	12·01	6·89 Å.
	$NiSO_4,7H_2O$	11·86	12·08	6·81 Å.
	$ZnSO_4,7H_2O$	11·85	12·09	6·83 Å.
Monoclinic	$FeSO_4,7H_2O$	15·34	12·98	20·02 Å.
	$CoSO_4,7H_2O$	15·45	13·08	20·04 Å.

J. S. CARTER.

Crystal structure of calcium silicide. J. BÖHM and O. HASSEL (Z. anorg. Chem., 1927, **160**, 152—164).—A study of the structure of the hexagonal crystals of calcium silicide, $CaSi_2$, and a discussion of the results with reference to Kautsky and Herzberg's views (A., 1924, ii, 852) on the structure of siloxen, $Si_6H_6O_3$. H. F. GILLBE.

X-Ray analysis of the system chromium–carbon. A. WESTGREN and G. PHRAGMÉN (Kungl. Svenska Vet. Handl., 1926, [iii], **2**, 3—11; cf. Ruff and Foehr, A., 1918, ii, 399).—X-Ray analysis shows the existence of three chromium carbides. The compound Cr_4C has a cubic, face-centred lattice; the elementary cube has an edge 10·638 Å. and contains 120 atoms. The carbide considered by Ruff and Foehr to be Cr_5C_2 is hexagonal, the height of the elementary prism being 4·523 and the edge of the basal surface 13·98 Å.; axial ratio 0·324. Since the elementary prism contains 80 atoms, the most probable formula is Cr_7C_3. The compound Cr_3C_2 is rhombic. The dimensions of the elementary parallelepiped are 2·821, 5·52, 11·46 Å.; axial ratios 0·246 : 0·480 : 1. The elementary cell contains 20 atoms. J. S. CARTER.

Crystal structure of gallium. F. M. JAEGER, P. TERPSTRA, and H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1193—1217).—Spectroscopically pure gallium has m. p. 30·2°, and is very susceptible to undercooling phenomena. Inoculation of the undercooled, molten metal yields crystals possessing ditetragonal–bipyramidal symmetry, $a:c=1:1\cdot6753$. If, however, crystals are

allowed to grow slowly from the only slightly super-cooled liquid, flat crystals much poorer in limiting forms are obtained. The ditetragonal–bipyramidal crystals have been examined by the X-ray spectrograph by different methods. The identity-distances of the fundamental grating in the direction of the a and c axes are 4·51 and 7·51 Å., respectively. The unit cell contains 8 atoms and D_{4h}^{10} is the only possible space-group. The parameters of the equivalent points are : $(u, u+\frac{1}{2}, v)$; $(u, \frac{1}{2}-u, v+\frac{1}{2})$; $(-u, \frac{1}{2}-u, v)$; $(u, u+\frac{1}{2}, v+\frac{1}{2})$; $(u+\frac{1}{2}, u, -v)$; $(u+\frac{1}{2}, -u, \frac{1}{2}-v)$; $(\frac{1}{2}-u, -u, -v)$; $(\frac{1}{2}-u, u, \frac{1}{2}-v)$, where u is about 0·2—0·225 and v about 0·15—0·175. A more precise determination of the parameters is at present impossible. Sufficient data are, however, available to indicate that the smallest distance of two gallium atoms is 2·56 Å., a result in agreement with W. L. Bragg's figure for the atomic radius of gallium, 1·3 Å. The proposed structure satisfactorily explains a number of the properties of solid gallium.

J. S. CARTER.

Structure of colloidal stannic oxide. R. FORSTER (Physikal. Z., 1927, **28**, 151—152).—Using the Debye–Scherrer interference method, the grating constants for the a- and the c-axis of colloidal stannic oxide, dried over phosphorus pentoxide, have been determined : $a=4·91$, $c=3·47$ Å. (for cassiterite $a=4·67$, $c=3·14$ Å.). It is concluded that the colloidal particles from both modifications of stannic acid have the same structure as cassiterite.

R. W. LUNT.

Allotropy of germanic oxide. J. H. MÜLLER (Proc. Amer. Phil. Soc., 1926, **65**, 193—199).—Pure germanium dioxide can exist in an insoluble (α-) modification, d 6·003 (the glassy oxide has d 3·3037). The X-ray powder spectra are different for the two forms. CHEMICAL ABSTRACTS.

Crystal lattices. I. Molecular space and atomic number. U. PANICHI (Atti R. Accad. Lincei, 1927, [vi], **5**, 123—128).—With the halides of the alkali metals the molecular space increases with the sum of the atomic numbers corresponding with the atoms of the molecule ; this sum is termed the molecular number. With analogous compounds of the same molecular number, the molecular space increases as the ratio between the atomic numbers of the metal and non-metal of the salt decreases. For non-analogous compounds, i.e., for those with non-isovalent metals, the molecular space diminishes as the valency increases, if the above ratio remains almost constant. T. H. POPE.

Refraction and dispersion of X-rays in calcite. A. LARSSON (Z. Physik, 1927, **41**, 507—515).—The author's investigation on the deviation from the Bragg equation $2d \sin \theta_n = n\lambda$ shown by calcite (ibid., 1926, **35**, 401) has been continued using the molybdenum and iron $K\alpha_1$ lines. The quantity δ in the equation $\mu=1-\delta$, where μ is the refractive index, has been evaluated from the equation $\delta=\sin \theta_1 \sin \theta_2 (n_2 \sin \theta_1 - n_1 \sin \theta_2)(n_2 \sin \theta_2 - n_1 \sin \theta_1)^{-1}$ in which θ_1 and θ_2 are the glancing angles, corrected for the effect of thermal expansion, corresponding with the two different orientations of the crystal to which n_1 and n_2 refer. The values of $\delta\lambda^{-2}$ so obtained for the line Mo $K\alpha_1$, 3·83 and $3·62 \times 10^{-6}$, and that for the line Fe $K\alpha_1$, $3·92 \times 10^{-6}$, agree well with that calculated from the dispersion formula $\delta\lambda^{-2}=Ne^2(2\pi mc^2)^{-1}=3·69 \times 10^{-6}$. The values of $\delta\lambda^{-2}$ have been employed to calculate the grating constant, d, using the corrected form of the Bragg equation, $n\lambda=2d \sin \theta_n(1-4\delta d^2 n^{-2}\lambda^{-2})$; the value found for d, 3·02945 Å., is in good agreement with the absolute value given by Compton, Beets, and DeFoe (Physical Rev., 1925, [ii], **25**, 625), 3·02904±0·001. Finally, from the alternative form of this equation $n\lambda=2d_n \sin \theta_n$, where $d_n=d(1-4\delta d^2 n^{-2}\lambda^{-2})$, λ has been calculated from experimental values of θ; λ for Mo $K\alpha$ is 707·830, and for Fe $K\alpha_1$, 1932·058 X. R. W. LUNT.

Scattering power of lithium and oxygen determined from the diffraction-intensities of powdered lithium oxide. J. M. BIJVOET, A. CLAASSEN, and A. KARSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1286—1292).—The scattering power of both lithium and oxygen has been determined by photographic intensity measurements on lithium oxide powder with Cu $K\alpha$-rays, using an apparatus previously described (Rec. trav. chim., 1924, **43**, 680). The blackening of the photographic plate was measured by a Moll photometer. The scattering power found for lithium is in agreement with that given by Debye and Scherrer from photometric data on lithium fluoride (A., 1919, ii, 20). The scattering power of oxygen in lithium oxide appears to be much less dependent on the diffraction angle than was found by Claassen for oxygen in Fe_3O_4 (ibid., 1926, 1072), and Hartree's calculated values for a free oxygen ion lie between the two. M. S. BURR.

Magnetisation of single crystals of iron. K. HONDA and S. KAYA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 721—754).—The magnetisation of single crystals of iron has been measured for both rectangular and ellipsoidal specimens, and the results are discussed theoretically. The hysteresis loss of a single crystal of pure iron is very small, but it increases, at first rapidly and then more slowly, with increase of grain number per unit volume ; this indicates that the hysteresis is chiefly caused by the irregular distribution of molecular magnets on the grain boundaries. The magnetisation curves in the direction of tetragonal, digonal, and trigonal axes are almost straight up to the intensities of magnetisation of 1400, 1000, and 900, respectively. The curves then show two sharp breaks or bends, and sometimes a third, which is not so well marked. The saturation of magnetisation is much more easily attained than with polycrystalline iron ; its value amounts to 1717, and is reached at 70, 650, and 450 gauss in the directions of the tetragonal, digonal, and trigonal axes, respectively. In plane (100), the direction of the tetragonal axis is more easily magnetisable than that of the digonal, whilst in plane (110) the directions of the tetragonal, digonal, and trigonal axes are in decreasing order of magnetisability. In planes (100), (110), and (111), the parallel and perpendicular components of magnetisation vary with periods of 90°, 180°, and 60°, respectively. The parallel component in the (100) plane shows a maximum in the direction of the tetragonal and a minimum in the

direction of the digonal axis, while the perpendicular component vanishes along these axes, and shows maxima or minima in between. Below 3 and above 500 gauss, the parallel component is almost independent of the direction of the field. In the (110) plane, the parallel component shows maxima in the directions of the tetragonal and digonal axes and minima in the directions of 55° and 125° from the tetragonal axis. The perpendicular component vanishes along the tetragonal, digonal, and trigonal axes. In the (111) plane, the parallel component with weak fields is a maximum in the directions of the equilateral triangles of the lattice, and a minimum in the directions of the bisectors of the vertical angles of these triangles; but above 300 gauss the reverse is the case. The perpendicular components vanish in these directions. The above facts are in general agreement with the theory of Honda and Okubo (Sci. Rep. Tôhoku Imp. Univ., 1916, **5**, 153), when the effects of thermal oscillations are considered.

W. HUME-ROTHERY.

Magnetostriction of single crystals of iron. K. HONDA and Y. MASHIYAMA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 755—776).—The magnetostriction of single crystals of iron has been measured in varying magnetic fields for both rectangular and ellipsoidal specimens. The magnetic expansion in the direction of the tetragonal axis is positive, and that in the direction of the trigonal axis is negative for all magnetic fields. The expansion curves in other directions are composed of the above two effects. The longitudinal effect in the direction of the magnetic field and the transverse effect at right angles to the field were both measured; the transverse effect is always the reverse of the longitudinal. In the (100) plane, the longitudinal effect is a maximum in the directions of the tetragonal axes and a minimum in between; the expansion orientation curves are sinusoidal, having a period of 90°, the amplitude increasing with the field strength. In the (110) planes, the longitudinal effect is a maximum in the directions of the tetragonal axes; a second slight maximum is shown in the direction of the digonal axes, and a minimum along the trigonal axes. The expansion–orientation curves have a period of 180°. In the (111) plane, the lattice consists of a series of equilateral triangles, and if the bisector of the vertical angle of these is taken as zero, the longitudinal effect is a maximum in the directions 30°, 90°, and 150°, and a minimum for 0°, 60°, and 120°, the expansion–orientation curves having a period of 60°. The magnetostriction effects are much larger for single crystals than for polycrystalline iron, the smallness of the effect for the latter being due to the opposing expansion and contraction of the differently oriented crystals. W. HUME-ROTHERY.

Magnetic properties of evaporated nickel and iron films. R. L. EDWARDS (Physical Rev., 1927, [ii], **29**, 321—331).—An abrupt change in coercive force takes place with iron films at a critical thickness of 50 mμ; nickel has no such critical thickness. Peculiar hysteresis loops were obtained. The effect is probably caused by the nature of the crystalline state, but may also depend on the aluminium base on which the films were deposited. A. A. ELDRIDGE.

Non-magnetic films of iron, nickel, and cobalt. L. C. JACKSON (Nature, 1927, **119**, 426—427).—" Non-magnetic " may indicate simply loss of ferromagnetism, or loss also of the magnetic moment of the metallic atom itself. Non-magnetic films may differ from metals in bulk in that (1) the metallic atoms are farther apart, (2) chemical combination, probably of a loose type, may have taken place, (3) there may have been an electronic rearrangement in the metallic atoms. A. A. ELDRIDGE.

Magnetic anisotropy of cubic crystals. J. FORREST (Phil. Mag., 1927, [vii], **3**, 464—476).—An application of previous work of the author (A., 1925, ii, 1133) to crystals belonging to the cubic system. It is indicated that the conception of doublets is sufficient to explain the known facts. The magnetic element is identified with the atom, and the agreement of the theoretical results with those of actual experiment, where such are available, appears to support the fundamental assumptions that the law of force between magnetic poles induced in a crystal is that of the inverse square, and that the ratio of the half length of a doublet to the distance apart of the nearest neighbours in an array of doublets is small.

A. E. MITCHELL.

Crystallographic and optical comparison of the chlorides of lead isotopes. D. KERR-LAWSON (Univ. Toronto Studies, Geol. Series, 1926, 37—43).—Values of p_0 (1·9959, 1·9953, 1·9954), q_0 (1·1875, 1·1871, 1·1869), and n_D^{20} (2·2602—2·2605) were essentially identical for lead chloride derived from a Katanga uraninite, a chemically " pure " sample, and that derived from thorite from Brevig, Norway.

CHEMICAL ABSTRACTS.

Polishing of surfaces. J. MUIR (Nature, 1927, **119**, 279).

[**Polishing of surfaces.**] N. K. ADAM (Nature, 1927, **119**, 279—280).

" Seizure " with sliding surfaces. J. M. MACAULAY (Nature, 1927, **119**, 425).—Actual fusion of the surfaces at the point of seizure is believed to occur (cf. also A., 1926, 998; Adam, this vol., 192).

A. A. ELDRIDGE.

Formation of twin metallic crystals. L. W. MCKEEHAN (Nature, 1927, **119**, 392—393; cf. this vol., 191; Carpenter and Tamura, *ibid.*, 191).

Tensile deformation of large aluminium crystals at crystal boundaries. R. L. ASTON (Proc. Camb. Phil. Soc., 1927, **23**, 549—560).—The deformation of an aluminium bar containing three large crystals when subjected to a tensile strain has been investigated by X-ray analysis of the orientation of the crystals. After deformation, the surface of the crystal showed effects similar to those observed by Carpenter and Elam (A., 1922, ii, 69). The deformation is less at the crystal boundaries than in the body of the crystals. R. CUTHILL.

Behaviour of aluminium crystals under tension. I. (FREIHERR) VON GÖLER and G. SACHS (Z. Physik, 1927, **41**, 103—115).—A mathematical analysis of the simple and double slipping of aluminium crystals when under tension. R. W. LUNT.

Behaviour of aluminium crystals under tension. II. R. KARNOP and G. SACHS (Z. Physik, 1927, **41**, 116—139).

Stresses involved in tests of hardness, and a table of the comparative hardness of certain metallic elements. A. MALLOCK (Nature, 1927, **119**, 276—277).

Surface tension of crystal surfaces. E. PERUCCA (Atti R. Accad. Sci. Torino, 1926, **61**, 318—334).—It is held that the energy of a crystal surface is determined by an amorphous unimolecular layer, as suggested by Beilby, and of which no account is taken in the theories of Gibbs, Curie, and Born. X-Ray data obtained by the Debye–Scherrer method indicate that the energy of a crystal surface does not vary with the plane of cleavage. Further experiments are projected in which the energy of a crystal surface is to be determined from the angle of contact of a globule of mercury on the crystal surface.
R. W. LUNT.

Pictet's rule and Born's grating theory. W. TARASOV (Z. Physik, 1927, **41**, 318—325).—For a crystal grating, such as sodium chloride, it is shown, on the basis of Born's theory, that $(R_s-R_0)/R_0 = \alpha T_s$, where R_s is the distance between the ion centres in the grating at the m. p., R_0 the distance at absolute zero, α the mean coefficient of linear expansion, and T_s the m. p. $(R_s-R_0)/R_0$ has been evaluated from quantities characteristic of the grating, 0·038, in good agreement with the values of αT_s for the chlorides, bromides, and iodides of sodium and potassium.
R. W. LUNT.

Glass as a fourth state of matter. G. S. PARKS and H. M. HUFFMAN (Science, 1926, **64**, 363—364).—The transition between the glassy and liquid states is not gradual and continuous; thus n-propyl alcohol glass softens sharply within the interval 90—102° Abs., with an abrupt 80% increase in heat capacity during the process. A glass, like a liquid, possesses a random arrangement of its units, and, like a crystalline substance, is held together by fixed, rigid linkings between these component particles; thus the glassy and crystalline states have nearly the same heat capacity. Glass may be regarded as a fourth state of matter.
A. A. ELDRIDGE.

Determinations of mol. wt. of sparingly soluble substances in camphor. H. CARLSOHN (Ber., 1927, **60**, [B], 473—476).—Rast's method (A., 1922, ii, 421) does not always yield reproducible results when applied to substances, m. p. above 180°, which are sparingly soluble in camphor. A modified method is given in which the f. p. instead of the m. p. is observed. Solidification usually occurs rapidly and within 1°. If the molten mass does not solidify within 2°, it is too concentrated, and unchanged substance initially separates. In this case, the experiment is utilised for the determination of the solubility of the substance in camphor by observation of the temperature at which the residual eutectic mixture rapidly and completely solidifies. This is deduced from the formula $40 \times a \times 1000/\Delta \times b = M$, in which a and b are the weights of substance and camphor, Δ is the depression, and M the supposed mol. wt. of the solute.
H. WREN.

Mol. wt. of sulphur trioxide from vapour density. G. ODDO and A. CASALINO (Gazzetta, 1927, **57**, 75—82).—Measurements of the vapour density at 25° of liquid and fibrous sulphur trioxide gave the following mean values for the mol. wt., respectively : 82·68 and 83·77.
R. W. LUNT.

Liquid, fibrous, and colloidal sulphur trioxide. G. ODDO (Gazzetta, 1927, **57**, 29—47).—Determinations of the lowering of the f. p. of phosphorus oxychloride produced by the addition of sulphur trioxide show that the liquid form corresponds with the formula SO_3, the ordinary fibrous form with $(SO_3)_2$, and a sample of fibrous form twelve years old with approximately $(SO_3)_5$, which is therefore termed " colloidal " sulphur trioxide. R. W. LUNT.

Weight of a normal litre and compressibility of ammonia. E. MOLES (Anal. Fís. Quím., 1926, **24**, 717—730).—The most probable value of the weight of a normal litre of ammonia, in the light of recent data, is 0·7715 g.
G. W. ROBINSON.

Precipitated magnetite, with particular reference to hysteresis. L. A. WELO and O. BAUDISCH (Phil. Mag., 1927, [vii], **3**, 396—410).—A comparison of the properties of precipitated magnetite is made by the methods of Lefort (Compt. rend., 1852, **34**, 488 ; 1869, **48**, 179) of Kaufmann (Z. Elektrochem., 1901, **7**, 733), and of the authors (A., 1925, ii, 1071). All three magnetites are shown by X-ray examination to have the same structure. There is evidence of closer packing in the magnetite made according to the method of Lefort, indicating that this product is of smaller crystal size than the others. Measurements of the magnetic permeabilities and hysteresis, both of the annealed and unannealed samples, support this observation. Magnetite has been prepared in a new way, by oxidising precipitated ferrous hydroxide with nitric oxide.
A. E. MITCHELL.

Magnetic susceptibilities of gases at low pressures. V. I. VAIDYANATHAN (Indian J. Physics, 1926, **1**, 183—198).—The magnetic susceptibility of carbon dioxide in the pressure range 0—700 mm. has been determined by an ingenious apparatus, described in detail, in which the motion of the gas is measured when placed in a heterogeneous magnetic field. The volume susceptibility is found to be proportional to the gas pressure $\kappa_{CO_2} = -0.00092 \times 10^{-6}$ ($\kappa_{air} = 0.0308 \times 10^{-6}$). The paramagnetic susceptibilities of oxygen and air in the same pressure range were determined in a slightly modified apparatus in which the motion acquired by the gas in the field was balanced by the motion acquired by a solution of known susceptibility. The values obtained were $\kappa_{O_2} = 0.142 \times 10^{-6}$, and $\kappa_{air} = 0.029 \times 10^{-6}$, and were proportional to the pressure. R. W. LUNT.

Magnetic susceptibilities of oxygen and nitrogen. F. J. VON WISNIEWSKI (Z. Physik, 1927, **41**, 385—394).—On the basis of the author's model of a diatomic molecule (A., 1926, 1194) the paramagnetic susceptibility of oxygen has been calculated from Langevin's equation relating this quantity to the magnetic moment and the temperature. The value obtained, 0.1399×10^{-6}, is in good agreement with that observed by Bauer and Piccard (J. Phys.

Radium, 1920, [vi], **1**, 97), 0.1407×10^{-6}. The diamagnetic susceptibilities of nitrogen, argon, and neon have been calculated by an extension of the author's theory, and are shown to vary as the fourth power of the circular quantum .number. The values obtained are within 8% of those observed by Hector (A., 1924, ii, 854). R. W. LUNT.

Critical survey of recent advances in the study of diamagnetism. E. S. BIELER (J. Franklin Inst., 1927, 203, 211—242).

Influence of temperature on gaseous films adsorbed on mercury and on the optical constants of mercury. J. ELLERBROEK (Arch. Néerland., 1927, III A, 5, 42—90).—The technique developed by Haak (*ibid.*, 1922, III A, 6, 198), and by Reeser (*ibid.*, 225) for the analysis of the elliptical polarisation produced in a beam of plane polarised light when reflected has been extended and improved. From measurements of the elliptical polarisation produced when the reflecting surface is mercury in contact with dry air or dry hydrogen, the thickness of the adsorbed film has been evaluated as 6 μμ and 2 μμ, respectively, on the basis of Drude's theory (Ann. Physik, 1889, **36**, 865; 1890, **39**, 481). These results are discussed at length, and in particular are thought to support the views of Iljin (A., 1925, ii, 958) and of Polányi (*ibid.*, 1916, ii, 474) rather than those of Langmuir.

The temperature variation of the eccentricity of the elliptic polarisation has also been determined for temperatures from 20° to 160°. At 160°, the thickness of the hydrogen or air film becomes less than 0.7 μμ (the limit of sensitivity of the method). The temperature variation of the principal azimuth of mercury has also been determined for 6700 and 5600 Å. It has been shown to be less than that characterising the metals of high resistivity, iron, and bismuth, in accordance with the author's theory.
R. W. LUNT.

Specific heats of gases at high temperatures and pressures. E. BURLOT (Mém. Poudres, 1926, 22, 69—106).—A previous investigation (A., 1925, ii, 1170) showed that the pressures obtained experimentally by the combustion of certain explosives in a closed vessel disagreed with those calculated from Abel's equation $p = f\Delta/(1 - \alpha\Delta)$, where α is the co-volume, Δ the density of charge, and f (the "force" of the explosive) $= P_0 V_0 T/273$, T being the absolute temperature of the gases at maximum pressure. This disagreement was attributed to the use of values for the specific heats of certain gases as determined by Mallard and Le Chatelier and also by Sarrau, which are appreciably too high. The values for the specific heats at high temperatures and pressures have therefore been reinvestigated, but the present communication is confined to the ratio between the specific heats at constant volume of nitrogen (c) and carbon dioxide (c'). The method employed is described in detail.

For carbon dioxide at 1890°, $V/P_1 = 449$ and at 2096° it is 279, the corresponding values for nitrogen being 610 and 400. It is then deduced that c'/c at 1890° is 1.36 and at 2096° 1.43. These values are considerably lower than those obtained by previous investigators. There are indications that the mean molecular heat of carbon dioxide at constant volume has been over-estimated more than that of nitrogen. The possible sources of error in this determination of the ratio c'/c are discussed and considered to be less than 6% of the value obtained. S. BINNING.

Specific heats of a highly-cooled non-condensed phase. N. DE KOLOSOVSKI (Compt. rend., 1927, 184, 322—323).—It is pointed out that the kinetic theory enables the conclusions of Perrakis (this vol., 101) to be obtained with fewer assumptions.
J. GRANT.

Velocity of sound in steam, nitrous oxide, and carbon dioxide, with special reference to the temperature coefficient of the molecular heats. W. G. SHILLING (Phil. Mag., 1927, [vii], 3, 273—301). —Determinations of the molecular heats of chemically pure carbon dioxide, nitrous oxide, and steam have been made over the temperature range 0—1000°. The method depends on the measurement of the velocity of sound in the gases at temperatures up to 1100°. The molecular heats at constant volume were found to be : for carbon dioxide, $6.688 + 0.00423t - 0.0_6712t^2$; for nitrous oxide, $6.629 + 0.00694t - 0.0_5241t^2$, and for steam, $7.266 - 0.00763t + 0.0_41261t^2 - 0.0_8401t^3$ g.-cal. at $t°$. The molecular heats at constant pressure were found to be : for carbon dioxide, $8.708 + 0.00415t - 0.0_6650t^2$; for nitrous oxide, $8.659 + 0.00677t - 0.0_5222t^2$, and for steam, $9.596 - 0.00925t + 0.0_4148t^2 - 0.0_8508t^3$ g.-cal. at $t°$. The equations apply for carbon dioxide and nitrous oxide only above 0° and for steam only above 100°. A. E. MITCHELL.

Maximum and minimum density and the heat of evaporation of helium. I. and II. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1303—1316, 1317—1334).—I. Theoretical.
II. From the available experimental data for the vapour pressure of helium at very low temperatures, vapour-pressure formulæ between the temperatures 0° and 4.2° Abs., and also between 3.5° and 5.2° Abs., have been deduced. With the help of these, the values of the molecular latent heat of evaporation, L, and the internal molecular heat of evaporation, $\lambda [= L - p(v_2 - v_1)]$, have been determined between 0° Abs. and the critical temperature, 5.19° Abs. L is thus found to have a maximum value at 3.5° Abs. and a point of inflexion at the temperature of maximum density 2.3° Abs., whilst λ has a minimum at 1.5° and a maximum at about 3.4°, the point of inflexion between being at 2.2° Abs. approximately. The values of L are of the same order of magnitude as those found experimentally by Onnes and Dana (this vol., 101). The appearance of a maximum can be explained naturally, and does not require the assumption of the "degeneration of energy" of the liquid at low temperatures. M. S. BURR.

Methods and apparatus used in the cryogenic laboratory. XIX. The methyl chloride and ethylene circulations. The hydrogen liquefier and circulation. The helium liquefier and circulation. H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1176—1183).

Melting curve of hydrogen. H. K. ONNES and W. VAN GULIK (Proc. K. Akad. Wetensch. Amster-

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dam, 1926, **29**, 1184—1187).—Using the same method as for helium (Keesom, A., 1926, 893), the above curve has been examined over the range of pressure 53·5—5·2 atm., corresponding with a temperature range 15·63—14·11° Abs. J. S. CARTER.

Thermal properties of gases. III. Critical constants and vapour pressure of sulphur dioxide. E. CARDOSO and U. FIORENTINO (J. Chim. phys., 1926, **23**, 841—847; cf. A., 1923, ii, 833).—The critical temperature and pressure of sulphur dioxide have been redetermined as 157·50±0·05° and 77·79±0·05 atm., respectively; vapour-pressure data are given from 0 to 157·50°. R. W. LUNT.

Physical constants of some alkyl carbonates. P. N. KOGERMAN and J. KRANIG (Acta Com. Univ. Tartuensis, *A*, **12**, 7).—The b. p., specific gravities, and refractivities of methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and *iso*amyl carbonates have been determined. iso*Propyl carbonate* was prepared for the first time, b. p. 147·2° (corr.), d_4^{20} 0·9162. The b. p. of *iso*amyl carbonate is 233°. The values found for d_4^{20} and for *n* for the compounds examined differ from those given in the literature. W. E. DOWNEY.

Dynamic method for measuring vapour pressures. J. N. PEARCE and R. D. SNOW (J. Physical Chem., 1927, **31**, 231—245).—A new modification of the dynamic method of measuring vapour pressure is described. The difficulty of measuring the large volume of air passing through the solution is eliminated by electrolytic generation of hydrogen and oxygen and the calculation of the volume of mixed gases from the weight of silver deposited in a voltameter. The number of molecules of water vapour, n_1, and the total volume of hydrogen and oxygen, n_2, are calculated from the respective weights of water absorbed and silver deposited. The vapour pressure is then given by the equation $p = n_1 P/(n_1 + n_2)$, where P is the corrected barometric pressure. The values for the vapour pressure of water at 25° found by this method vary from 23·745 to 23·756 mm. The mean value of eight determinations, 23·752 mm., is the same as that of Derby, Daniels, and Gutsche (A., 1914, ii, 533). Data for aqueous solutions of potassium chloride (0·2*M* to saturation) and mannitol (0·4—1*M*) at 25° are given, and the method is being extended to other aqueous solutions up to the limits of solubility. A *résumé* of the determinations made by other methods used in measuring vapour pressure is given. L. S. THEOBALD.

Vapour pressures of the alkali metals. H. ROWE (Phil. Mag., 1927, [vii], **3**, 534—546).—When experimental values of the vapour pressures of sodium, potassium, rubidium, and cæsium are compared with those deduced from various formulæ purporting to represent the variation of vapour pressure with temperature, many discrepancies are found. When the vapour pressures are extrapolated at various temperatures, many variations are shown in the pressures obtained from the different formulæ. It is concluded that no single formula can represent the variation of the vapour pressure of a metal with temperature, and that it is possible to arrive at an approximate value for the vapour pressure at any

temperature only from a comparison of all the available data. A. E. MITCHELL.

Influence of cold rolling on the rate of evaporation of metals. F. SAUERWALD, H. PATALONG, and H. RATKE (Z. Physik, 1927, **41**, 355—377).—The velocity of evaporation of cold-rolled zinc and silver sheet has been found to exceed that of the recrystallised metal by from 40 to 450%. The m. p. and transition points are but slightly changed. These phenomena are discussed at length. R. W. LUNT.

Expansion of liquids and heat of vaporisation. N. DE KOLOSOVSKI (J. Chim. phys., 1927, **24**, 56—61).—Combination of van der Waals' formula αT_c=constant, where α is the coefficient of expansion of a liquid at a given reduced temperature and T_c is the critical temperature, with Trouton's rule and the rule that the b. p.=$2T_c/3$, leads to the expression $M\rho\alpha$=constant, where $M\rho$ is the molecular heat of vaporisation. From the relation previously derived (A., 1925, ii, 646), connecting the expansion modulus of a liquid, k, and its critical temperature, the equation $M\rho = A + B/k$, where A and B are constants, may be deduced in a similar manner. If these formulæ are used to calculate $M\rho$ from expansion data, the values obtained for non-associated liquids agree satisfactorily with the experimental values. For liquefied gases, however, the calculated values are much too high. R. CUTHILL.

Mean free paths in a gas the molecules of which are attracting rigid elastic spheres. E. CONDON and E. V. VAN AMRINGE (Phil. Mag., 1927, [vii], **3**, 604—614).—Mathematical. An evaluation of the mean free path in a gas the molecules of which comprise attracting rigid elastic spheres, is made on the lines of classical theory. It is shown (*a*) that the Maxwell free path is represented accurately by a formula of the type suggested by Sutherland, in which the constant C is the ratio of the energy of two molecules in contact to the gas constant per molecule, and (*b*) that the mean free path appropriate to the transfer theory of viscosity is represented approximately by the same formula, in which the constant C is about three quarters of the above ratio. The results lead to a direct method of evaluating the energy of two molecules in contact from the experimental data on the temperature coefficient of viscosity. A. E. MITCHELL.

Diffusion of oxygen through silver. F. M. G. JOHNSON and P. LAROSE (J. Amer. Chem. Soc., 1927, **49**, 312—326).—The experiments previously described (A., 1924, ii, 750) have been continued with improved technique; in particular, an apparatus is described in which gases may be continuously and automatically mixed in any proportions and a constant flow of any definite mixture maintained. The results obtained with welded silver plates agree with those previously published. Richardson's equation (Phil. Mag., 1904, [vi], **7**, 266) is shown to represent the diffusion of gases through metals within experimental error. The mechanism of the diffusion is supposed to consist of an initial absorption in which the gaseous molecules become atoms which are transformed into ions in presence of the metal, and a dynamic equilibrium

between atoms and ions is set up, chain-like, through the metal. The atoms, on issuing from the partition, combine to molecules, or react with other substances.

S. K. TWEEDY.

Refractive indices of mixtures calculated by the formula of Dieterici and of Lichtenecker. E. VAN AUBEL (Bull. Acad. roy. Belg., 1926, [v], **12**, 476—480).—Lichtenecker's formula for the refractive index n of a binary mixture is $\log n = \theta_1 \log n_1 + \theta_2 \log n_2$, where n_1 and n_2 are the refractive indices of the respective constituents, and θ_1 and θ_2 their percentages by volume, a correction being necessary if any contraction takes place on mixing. For mixtures of acetone and water and of sulphuric acid and water, the maximum differences between observed and calculated values of n are found to be 6×10^{-4} and 34×10^{-4}, respectively. Dieterici's formula is slightly superior, the corresponding differences being 4×10^{-4} and 29×10^{-4}, respectively.

S. J. GREGG.

Cryoscopic determinations of the solubility of gases. F. GARELLI and E. MONATH (Atti R. Accad. Sci. Torino, 1926, **61**, 4—11, 12—20).—I. Cryoscopic and analytical data having shown approximately that acetylene is unassociated when dissolved in benzene, *cyclo*hexane, aniline, and dimethylaniline, it is suggested that the solubility of acetylene in these and other solvents may be determined cryoscopically.

II. The solubility at atmospheric pressure of nitric oxide and of carbon monoxide in benzene, bromoform, nitrobenzene, and *cyclo*hexane has been derived from cryoscopic data, on the assumption that the solute is unassociated in solution. The lowering of the f. p. by nitrogen and helium is so small that these gases can be used to free the solvents from gaseous impurities.

R. W. LUNT.

Solubility of gases in *cyclo*hexanol. (MLLE.) G. CAUQUIL (J. Chim. phys., 1927, **24**, 53—55).—The solubility in *cyclo*hexanol of hydrogen, neon, argon, oxygen, carbon monoxide, carbon dioxide, ammonia, phosphine, nitrous oxide, silicomethane, methane, ethane, propane, ethylene, acetylene, and methyl chloride has been determined at 26° and under approximately 76 cm. pressure. In every case, the solubility is greater than the solubility in water.

R. CUTHILL.

Solubility effects. V. Chloral–caffeine, urotropine [hexamethylenetetramine]–antipyrine, urotropine–chloral. VI. Chemical constitution and solubility. E. OLIVERI-MANDALÀ (Gazzetta, 1926, **56**, 889—896; 896—901; cf. this vol., 237, 238).—V. The existence of the crystalline compound of chloral hydrate and caffeine hydrate (Leulier, A., 1912, i, 644) has been confirmed. The solubility of caffeine is greatly increased by the presence of chloral; the solubility coefficient varies but little with the temperature. The f.-p. depressions obtained by dissolving antipyrine in hexamethylenetetramine solutions and hexamethylenetetramine in chloral solutions are normal. The compounds obtained by Mannich and Krösche (A., 1913, i, 101), and Leulier (*loc. cit.*) are therefore apparently non-existent in solution.

VI. [With A. NERI.]—The so-called solubility coefficients have been determined for various substances dissolved in solutions of other substances. The latter are shown in parentheses. No increase in solubility is found with thiocarbamide, thiocarbanilide, or benzanilide (in antipyrine). For other combinations, the solubility coefficients increase in the following order : phenacetin (antipyrine), benzamide (antipyrine), acetanilide (sodium benzoate), acetanilide (pyramidone), aspirin (pyramidone), acetanilide (antipyrine), caffeine (chloral hydrate), quinine hydrochloride (antipyrine), caffeine (sodium benzoate). No general relation between the chemical constitution and the solubility effect is apparent.

E. W. WIGNALL.

Analogy between conjugate pairs of liquids and systems consisting of a liquid phase with a vapour phase in equilibrium with it. A. BOUTARIC (J. Chim. phys., 1927, **24**, 50—52).—If from one of a pair of conjugate solutions one component is gradually removed by means of a semi-permeable piston impermeable to the other component, the curve representing the relation between the volume of the solution and its osmotic pressure will be similar to the isotherm of a gas. In particular, the curve for the critical solution temperature will be analogous to the critical isotherm. Just as in the case of a gas it is possible to pass continuously from the gaseous state to the liquid state, so with a pair of liquids it is possible to pass continuously from one conjugate to the other.

R. CUTHILL.

Properties of bromine as solvent. W. FINKELSTEIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 565—586).—The problem of electrolytic dissociation in feebly dissociating solvents is discussed. The conductivity and transport numbers of benzamide in liquid bromine were determined at 18° and 75°. Benzamide forms a solid *compound*, $Ph \cdot CO \cdot NH_2, Br_2$. The specific conductance rises sharply to a maximum of 2×10^{-2} at a concentration of 14·5% benzamide, and the molecular conductivity gives a similar maximum at $\nu = 0·5$, slowly sinking to $3·4 \times 10^{-3}$ at $\nu = 16$. The conductivity increases with time to a limit of almost double its original value in 3 days. Cryoscopic determinations show considerable association, the association factor being 5 at a concentration of 8% of $Ph \cdot CO \cdot NH_2, Br_2$. Transport number determinations suggest the presence of a bivalent cation $[Ph \cdot CO \cdot NH_2(Ph \cdot CO \cdot NH_2, Br_2)_6]^{++}$. The theoretical significance of the results is discussed in great detail. Liquid bromine is dissociated to a certain extent, $Br_2 \rightleftharpoons Br^+ + Br'$. The positive Br^+ ion removes two electrons from the tervalent nitrogen of the amide, and becomes a negative Br', leaving the nitrogen with a double positive charge. The ion $[Ph \cdot CO \cdot NH_2]^{++}$ combines with 6 molecules of benzamide dibromide to form the bivalent complex cation. In concentrated solutions, the dissociation of the bromine molecule is favoured, whilst dilute solutions favour dissociation of the bromine–benzamide complex.

M. ZVEGINTZOV.

Solubility of metals of the iron group and of copper in mercury. G. TAMMANN and K. KOLLMANN (Z. anorg. Chem., 1927, **160**, 242—248).—The solubilities of iron, cobalt, and nickel in mercury have

been determined by depositing the metal electrolytically in a known volume of mercury and measuring the potential of the amalgam against the calomel electrode. The potential falls, at first rapidly, and attains after a few hours a steady value corresponding with the $E.M.F.$ of the saturated amalgam. The solubilities in mols. per mol. of mercury are : iron, 4.1×10^{-19}; nickel, 2.0×10^{-5}, and cobalt, 5.7×10^{-3}, at 17°.

The same method is not applicable to the determination of the solubility of copper, owing to the slowness with which the saturated amalgam gives up its copper, but by measuring the $E.M.F.$ of a series of amalgams of varying copper content, the solubility is found to be $3.31 \times 10^{-3}\%$, in fair agreement with Richard's value of 2.4×10^{-3}. The lower value is ascribed to oxidation of the metallic copper in the latter case during filtration and to retention of the oxide in the filter. H. F. GILLBE.

Solubility of metals in mercury and the potentials of very dilute amalgams. G. TAMMANN and J. HINNUBER (Z. anorg. Chem., 1927, **160**, 249—270).—The following solubilities of metals in mercury have been determined potentiometrically : manganese, $2.5 \times 10^{-4}\%$; antimony, $2.9 \times 10^{-5}\%$; chromium, $3.1 \times 10^{-11}\%$; uranium, $1.4 \times 10^{-4}\%$; arsenic, vanadium, molybdenum, and tungsten, too small to be measured.

The solubility of metals in mercury is discussed from the point of view of the periodic classification. In general, the solubility increases as the mercury group is approached, except in the case of the alkali and alkaline-earth metals. The low-melting alkali metals are more soluble than the higher-melting alkaline-earth metals, which in turn are more soluble than the metals of the copper group. The solubility of the alkalis, zinc, and cadmium, and arsenic, antimony, and bismuth, decreases with rising m. p., the reverse being true of tin, lead, and the alkaline-earth metals. The statement that rise of m. p. is accompanied by a decrease of solubility is therefore untenable. An approximate rule is : metals having m. p. between 300° and 400° possess a solubility greater than 1%, which decreases with rising m. p.; those melting at above 1000° have a solubility not greater than 0.1%, which decreases still further with rising m. p.

Some experiments on the wetting of freshly-broken metallic surfaces by mercury are described.

The potentials of very dilute amalgams are discussed, and results are given for copper, cadmium, tin, and lead, agreeing very well with the calculated values. By plotting the $E.M.F.$ of various amalgams against the logarithm of the concentration of the dissolved metal, a series of straight lines is obtained which are parallel for metals of the same valency. H. F. GILLBE.

Solubility of lanthanum hydroxide. E. SADOLIN (Z. anorg. Chem., 1927, **160**, 133—151).— Addition of a strong base to a solution of lanthanum chloride gives a colloidal precipitate of $La(OH)_{3-x}Cl_x$, where x increases with increasing chloride-ion concentration and decreasing hydroxyl-ion concentration. The p_H of the solution shows a turning point at about three equivalents of added base, at which the precipit-

ation of the lanthanum is complete. The freshly-prepared precipitate gives no definite solubility product, on account of its chlorine content; the initial value is given by $\log L_{La(OH)_3} = 18.93$ at 18°. The solubility decreases with time for some weeks, owing to loss of chlorine. The stable end-product has a definite solubility product given by $-\log L_{La(OH)_3} = 20.98$ at 18°, a value similar to that of lanthanum oxide which has been heated at 950°. H. F. GILLBE.

Molecular association and mechanism of separation into two phases. G. N. ANTONOV (Phil. Mag., 1927, [vii], **3**, 571—580; cf. A., 1925, ii, 865; 1926, 786).—Further examination of the discontinuous variation of the physical properties of liquids with temperature and the anomalous results obtained in the regions close to the critical points lead to the conclusion that the change of state is intimately connected with the change of molecular aggregation. The association factor for liquids is not the same at different temperatures, but varies with the temperature, and may become very large at low temperatures. The presence or absence of the hydroxyl radical is not a criterion of the association of liquids. A. E. MITCHELL.

Partition of hydrogen chloride between water and benzene. R. W. KNIGHT and C. N. HINSHELWOOD (J.C.S., 1927, 466—472).—The solubility of hydrogen chloride in water and in benzene, and its distribution between the two solvents over a wide range of concentrations, have been determined at 20°. The results indicate the existence of an equilibrium between ionised and un-ionised molecules in the aqueous phase, such that the ionisation is half complete at a concentration of about 500 g./litre. Un-ionised molecules are present in appreciable amounts only at concentrations much greater than those indicated by osmotic and conductivity data to which the Debye–Hückel correction has not been applied. H. F. GILLBE.

Partition coefficients and solubility. W. K. PERSHKE (J. Russ. Phys. Chem. Soc., 1926, **58**, 495—510).—It is shown theoretically that the partition coefficient is the ratio of the solubilities of the dissolved substance in the two solvents. The partition of azobenzene between hexane and methyl alcohol, and of succinic acid between ether and water, and the changes in mutual solubility due to the third component, have been determined. The partition coefficient varies with the concentration, but is almost identical with the ratio of solubilities in a mixture of the two solvents, although it differs markedly from the ratio of the solubilities in the pure solvents. The case of the partition of a liquid between two solvents with each of which it is completely miscible is theoretically discussed, and shown to agree with the experimental results. M. ZVEGINTZOV.

Sorption of gas by charcoal as a dissolution phenomenon. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1927, **2**, 1—10).—Measurements of the velocity of sorption of carbon dioxide by granular and powdered cane-sugar charcoal under constant pressure show that although the same volume of gas is absorbed in each case (54.0 c.c. at $N.T.P.$), the velocity of

absorption is greater with powdered charcoal than with granular. The volume absorbed by different kinds of charcoal is roughly the same (40—50 c.c.). These facts support the view that the sorption is due to the dissolution of the gas in the mass of the charcoal. From measurements on bamboo charcoal, it is found that Henry's law is not applicable, and that the amount of gas absorbed decreases with rise of temperature.   L. L. BIRCUMSHAW.

Adsorption at solid surfaces. I. Adsorption of gases by activated and non-activated charcoals. O. RUFF and G. ROESNER (Ber., 1927, 60, [B], 411—425).—The adsorption of argon, carbon dioxide, ammonia, and sulphur dioxide by activated and non-activated alder and coconut charcoal, acetylene soot charcoal, supernorite, and technical activated carbon IV has been measured. The products were freed from tar and moisture by ignition at 900° and activated by carbon dioxide. The power of adsorbing gas appears to be less dependent on the activity than on the structure of the charcoal. For any particular variety of charcoal, ignition in a vacuum or indifferent gas at temperatures above 1100° produces a parallel diminution in activity (measured towards phenol) and in the power of adsorbing gases. For the adsorption of gases, the porosity of the material (atomic spaces in material) and its form are important factors, in addition to the extent of the surface, whereas activation, which is of prime importance for many dissolved substances, is of consequence only in so far as it leads to a certain expansion of the surface and to the opening of the pores of the adsorbent. The form of the adsorption curves at 0° is such as would be expected from any of the accepted theories of adsorption. At lower temperatures, irregularities are observed with sulphur dioxide, ammonia, and carbon dioxide which may be interpreted as indications of saturation with these gases. They are not, however, sufficiently definite to permit conclusions regarding the superposition of chemical on physical adsorption.   H. WREN.

Adsorption at solid surfaces. II. Specific and unspecific, particularly with regard to charcoal. O. RUFF (Ber., 1927, 60, [B], 426—432; cf. preceding abstract).—A theoretical consideration of the specific adsorption of molecular-disperse dissolved substances and unspecific adsorption of gaseous substances, particularly the rare gases.   H. WREN.

Adsorption. S. MOKRUSCHIN and O. ESSIN (Kolloid-Z., 1927, 41, 106—107).—The authors' equation for electrical adsorption (A., 1926, 573) has been applied to the adsorption of argon and carbon monoxide by coconut charcoal, and to the adsorption of bromine, acetic acid, propionic acid, and butyric acid by blood charcoal. The equation is thus found to be valid for purely chemical adsorption. The applicability of the equation confirms the dipolar character of the molecular forces.   E. S. HEDGES.

Adsorption of basic colouring matters by filter-paper. S. MOKRUSCHIN and O. ESSIN (Kolloid-Z., 1927, 41, 104—105).—The adsorption of the basic substances, malachite-green, diamond-green, rosaniline, safranine, and methylene-blue, was studied

at a surface of filter-paper. The authors' equation for electrical adsorption (A., 1926, 573) was found to be applicable.   E. S. HEDGES.

Adsorption equations. E. SWAN and A. R. URQUHART (J. Physical Chem., 1927, 31, 251—276).—A review of the literature in which the various adsorption equations are collected and considered with regard to their applicability to actual adsorption systems. The general adsorption equation, the isotherm, isobar, isostere, rate of adsorption, and the heat of adsorption are dealt with, and a bibliography is appended.   L. S. THEOBALD.

Adsorption and heat of adsorption of ammonia gas on metallic catalysts. W. A. DEW and H. S. TAYLOR (J. Physical Chem., 1927, 31, 277—290; cf. Taylor and Burns, A., 1921, ii, 630; Gauger and Taylor, ibid., 1923, ii, 398; Beebe and Taylor, ibid., 1924, ii, 159).—The adsorption of ammonia by copper, nickel, and iron catalysts, and of hydrogen by copper and iron catalysts has been studied. In the case of ammonia, the isotherms were obtained for copper at 218°, for nickel at 110° and 0°, for iron-molybdenum at 25°, and for iron at 0°. The integral heats of adsorption of ammonia by copper and nickel at 0°, and the differential heats of adsorption by copper, nickel, and iron are recorded. Adsorption of ammonia by sodium, supported on glass beads, was also measured at 0°.   L. S. THEOBALD.

Adsorption. XVII. Concentration of a sol and coagulation by electrolytes. S. GHOSH and N. R. DHAR (J. Physical Chem., 1927, 31, 187—206; cf. A., 1925, ii, 386, 511, 778; 1926, 673, 1004).—The influence of change in concentration on the coagulation of sols by electrolytes has been further studied. Sols of stannic hydroxide (positive), aluminium hydroxide, vanadium pentoxide, thorium hydroxide, sulphur (Weimarn), and gold follow the rule that the greater the concentration of the sol the greater is the amount of an electrolyte required for coagulation. Sols of antimony sulphide, Prussian-blue, gum dammar, and gamboge do not follow the law when coagulated by univalent and sometimes by bivalent ions. Antimony sulphide sol behaves normally, however, when coagulated by silver nitrate, strychnine hydrochloride, quinine hydrochloride, or methylene-blue. A negative sol of manganese dioxide behaved normally on dilution towards all electrolytes except potassium hydroxide, when the precipitating values remained practically constant, an effect attributed to the adsorption of hydroxyl ions by the sol. A positive manganese dioxide sol behaved normally towards the anions Cl′ and $NO_3′$ given by potassium chloride and potassium nitrate, respectively, but not towards those given by cupric chloride and silver nitrate, owing to the preferential adsorption of silver and copper ions by the sol. A sol of metallic silver was abnormal when coagulated by uni-univalent electrolytes on account of the highly adsorbed hydroxyl ions derived from the silver hydroxide usually present.

A uranium ferrocyanide sol has been prepared for the first time by the addition of uranium nitrate to a dilute solution of potassium ferrocyanide followed by dialysis. The Schulze–Hardy law applies to this sol,

but is only partly followed in the case of the gum dammar sol mentioned above.

The above results show that sols which do not adsorb an ion of the same charge follow the dilution rule, whilst the sols which do so are abnormal in this respect.   L. S. THEOBALD.

Adsorption of dyes on silver halides. S. E. SHEPPARD (Nature, 1927, **119**, 281).—A correction (cf. this vol., 107). At saturation, one dye molecule is associated with two ions of the surface lattice of silver bromide.   A. A. ELDRIDGE.

Dynamic surface tension and the structure of surfaces. O. K. RICE (J. Physical Chem., 1927, **31**, 207—215).—The theory of dynamic surface tension is developed from a new point of view. A simple thermodynamic proof is given that the dynamic surface tension is greater than the static when the surface is extended and less when the surface is contracted. The possibility that equilibrium may be established between all parts of the solvent, but not between portions of the solute near to and remote from the surface, is discussed, considering only the dynamic surface tension of extension. It is shown mathematically that the narrower the region to which adsorption is confined the larger will be this value, and if the laws for perfect solutions hold near the surface, the dynamic can never be greater than the static surface tension of the pure solvent when adsorption is positive, but when adsorption is negative, then an infinite value of the dynamic surface tension is theoretically possible.

Du Noüy's work on the surface tension of solutions of sodium oleate (A., 1925, ii, 109) is criticised.
                    L. S. THEOBALD.

Spreading of fatty acids, fats, and proteins. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1262—1274).—The spreading of fatty acids on water surfaces is highly dependent on the length of the fatty acid chain, the acidity of the water, and the temperature. With acids which have a chain of 14 or 16 carbon atoms, unimolecular spreading occurs at all temperatures, but the film may have either a condensed or an expanded form. With lower members of the series, unimolecular spreading is observed only at low temperatures and high acidities. Similar measurements with the corresponding triglycerides show the same influence of length of chain and temperature, the influence of acidity being, however, much less pronounced. Spreading occurs much more readily with fats than with the acids, a chain of six carbon atoms sufficing to render the molecule sufficiently stable to produce perfect spreading. It is believed that for certain lengths of carbon chains under appropriate conditions of temperature and acidity "colloidal spreading" occurs, i.e., associated molecules have their polar groups oriented towards an outer surface and the spreading of these aggregates is due to these superficially placed groups. This behaviour is also observed when the spreading of soaps is examined. Only by the use of strongly acid media (p_H 1—2) can the association which persists at the water surface be broken. With hæmoglobin, casein, and serum-protein it is possible to obtain unimolecular spreading on media which are sufficiently acid (p_H 1—2). Such spreading is not observed with gelatin, gliadin, or peptone. This is attributed to the presence of short-chained amino-acids in these molecules. The influence of acidity on the spreading of proteins is rather complex. The proteins were dissolved in sodium hydroxide solutions, and are hence comparable with the soaps, in that molecules are associated with their polar groups turned outwards. On pure water or faintly acid media, this association remains unaltered. On increasing the acidity, protein is gradually set free and at the isoelectric point spreads in a unimolecular layer. Further increase in the acidity results in the formation of associated protein hydrochloride molecules, which spread in a unimolecular layer only when the acidity is considerably increased.
                    J. S. CARTER.

Soap solutions. III. Effect of acids, bases, and salts on the surface tension of aqueous sodium oleate solutions. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1927, **30**, 75—80).—The changes in the surface tension (at 20°) of dilute aqueous solutions of sodium oleate produced by the addition of acids, sodium salts, and sodium hydroxide have been investigated stalagmometrically. The changes produced by the hydrogen and hydroxyl ions are greater than those due to other ions. The introduction of hydroxyl ion represses the hydrolysis, resulting in a loss of acid soap and a rise of the surface tension to its maximum. Further increase of the hydroxyl-ion concentration causes the surface tension to fall until the flocculating point is reached, when the surface tension again rises very slowly. The presence of hydrogen ion decomposes the soap and depresses the surface tension very rapidly by increasing the quantity of acid soap, but beyond the critical separation point the surface tension rises suddenly, owing to the separation of free acid. These effects depend on the strengths of the bases and acids. Salt solutions which are acidic (e.g., ammonium chloride) behave as acids, but acids weaker than oleic acid have but little action on the soap solution. Oleic acid also has a positive effect. The extremely low surface tension of soap solutions is mainly due to the presence of fatty acids produced by hydrolysis (perhaps acidic soaps in sol form) and concentrated in the surface layer. Slightly acidic substances, e.g., boric acid, increase the lathering and detergent action of soaps by lowering of the surface tension. Dilute alkali solutions seem to act as detergents in virtue of their peptising action.   K. KASHIMA.

Position of the absorption bands of potassium permanganate and uranyl nitrate in various colourless solvents. V. R. VON KURELEO (Biochem. Z., 1927, **180**, 65—84).—Five bands in the absorption spectrum of potassium permanganate and four in that of uranyl nitrate have been compared when these substances were dissolved in various solvents, many of which form homologous series. In most cases, the bands are displaced by the non-aqueous solvent towards the red with permanganate and towards the violet with uranyl nitrate. The opposite displacements are not conditioned by the fact that the bands for the two substances are at opposite ends of the

spectrum nor by a difference in charge. The extent of the displacement of the permanganate bands increases with the number of carbon atoms in the homologous series of solvents, but that of uranyl nitrate decreases. With uranyl nitrate, the position of the bands appears to depend on the specific gravity or refractive index of the medium, displacement being to the violet in media with specific gravity less than 1, but to the red if greater than 1.

P. W. CLUTTERBUCK.

Anomalous rotatory dispersion, in the ultra-violet, of aqueous solutions of tartaric acid containing boric acid. R. DESCAMPS (Compt. rend., 1927, **184**, 453—455).—The photographic spectro-polarimeter (A., 1926, 142) has been used to test the conclusions of Lowry and Austin (*ibid.*, 1922, ii, 414) in the ultra-violet region (5780—2537 Å.). For solutions containing different amounts of tartaric and boric acids, it is found that the rotatory dispersion curves belong to Lowry's anomalous complex type. Straight lines are obtained for Biot's law $\alpha = k/\lambda^2$ only between the wave-lengths 5780 and 4358 Å., and 5780 and 4047 Å. for solutions which contain equi-molecular mixtures and a slight excess of boric acid, respectively. The anomaly is explained by the presence of at least two types of optically active molecules which have different dispersions. J. GRANT.

Dielectric constants of solutions of electrolytes. III. Dielectric constants of solutions of salts in acetone, benzonitrile, o-nitrotoluene, and methyl cyanoacetate. P. WALDEN and O. WERNER (Z. physikal. Chem., 1926, **124**, 405—426; cf. A., 1925, ii, 773).—The dielectric constants of solutions of the alkylammonium halides and picrates in the above four solvents and also of solutions of barium perchlorate, ammonium iodide, mercuric chloride, and mercuric cyanide in acetone have been measured at 20°. For tetra-alkylammonium salts and barium perchlorate in acetone, the dielectric constant falls with increase in concentration, the concentration–dielectric constant curve being recti-linear, and having the same slope for all these salts. This is assumed to mean that in these solutions the solutes are completely ionised. With the other alkylammonium picrates, the rate of decrease of the dielectric constant with increase in concentration is less, and tends to fall still further with increasing concentration. The chlorides, as also mercuric cyanide, scarcely alter the dielectric constant at all, the curve frequently possessing very flat minima and maxima, and their solutions have extremely small conductivities. The present measurements therefore yield for the acetone solutions examined results closely analogous to those of conductivity determinations (A., 1926, 1104). Solutions in benzonitrile, o-nitrotoluene, and methyl cyanoacetate resemble the acetone solutions in behaviour, but for solutions of triethylammonium and diethylammonium chloride in benzonitrile the dielectric constant first falls very slightly with increase in concentration, then slowly rises again, and ultimately becomes greater than that of the pure solvent. R. CUTHILL.

Preparation of metallic colloids. E. FOUARD (Compt. rend., 1927, **184**, 328—329)—A method is described for the preparation of chemically pure colloidal solutions of arsenic, iodine, tellurium, mercury, lead, bismuth, copper, antimony, and the alkaloids. A solution of a salt of the metal containing a pure organic colloid (albumin, starch, or gelatin) is electrolysed with a current of a few milliampères. At the cathode the metal ions are neutralised by the repelled negatively-charged colloid micelles. A colloidal organo-metallic complex is thus formed. The anode is separated by immersion in a collodion cell rendered semi-permeable by precipitated copper ferrocyanide. The cathode should be a bad conductor (carbon, silicon, selenium, or arsenic), so as to reduce the frequency with which formation of the complex occurs on the cathode. The colloids are stable and present a characteristic dichroism to diffused light. They form heat-reversible gels spontaneously. J. GRANT.

Production of hydrosols. A. B. DUMANSKI, A. P. BUNTIN, and A. G. KNIGA (Kolloid-Z., 1927, **41**, 108—111).—A study was made of the formation of positively-charged hydrosols of ferric hydroxide by adding to a solution of ferric chloride a number of metallic carbonates and hydroxides in the dry state. The carbonates of the alkali metals, the alkaline-earth metals, and of magnesium, cadmium, and zinc readily gave hydrosols, whilst with carbonates of cobalt, lead, copper, and iron very slow reaction occurred, generally with formation of a gel, especially if excess of the carbonate was used. Similar results were obtained with the hydroxides of these metals. The production of sols of aluminium hydroxide from aluminium chloride was affected by the agents in a similar way, but chromic chloride gave in all these reactions unstable, easily coagulated sols. Stable, negatively-charged hydrosols of lead dioxide can be prepared in absence of a protective colloid by pouring into water a saturated solution of lead tetra-acetate in acetic acid, or of lead tetrapropionate in propionic acid. The brown sols lose their stability when freed from the organic acid by dialysis. Negatively-charged sols of the hydroxides of lead, iron, chromium, tin, and titanium were produced by dialysis of complex substances of the type $[Pb(CO_2)_2(CHO)_2,nPb(OH)_2]''2K$, formed when certain metallic hydroxides in alkaline solution act on tartaric acid. The properties of these sols and of the gels obtained therefrom are described. E. S. HEDGES.

Colloid syntheses with the aid of stannous chloride. I. and II. A. GUTBIER and B. OTTENSTEIN (Z. anorg. Chem., 1927, **160**, 27—47, 48—56).—I. Addition of stannous chloride solution to a solution of a palladium salt produces a series of colour changes resulting in the formation of a deep black precipitate. After the precipitation, which is always complete within 3 days, the solution is entirely free from palladium. It is shown that a stannous chloride solution cannot be neutralised without causing the partial formation of stannic compounds, and the conclusion is reached that an ordinary solution of stannous chloride contains a variety of substances, notably hydrated stannic oxide, SnO_2,xH_2O. The precipitate consists of colloidal palladium adsorbed on hydrated stannic oxide; no oxygen compound of the palladium

is present, and no stoicheiometric relationship exists between the constituents. It is easily peptised by ammonia, potassium hydroxide, or hydrochloric acid, giving a brown solution of fair stability, except when hydrochloric acid has been used, as this attacks the protective stannic oxide. Flocculation is brought about by much smaller quantities of electrolytes than are necessary in the case of the corresponding platinum solutions. The original precipitate is very readily acted on by the atmosphere, and after a few hours can no longer be peptised to a stable solution; it is thus similar to the platinum compound.

A very similar compound to that already described has been synthesised by mixing solutions of colloidal stannic oxide and colloidal palladium.

By mixing a strongly acid stannous chloride solution and a solution of palladium tetrachloride, a green liquid is obtained, in which the presence of colloidal palladium could not be detected by any method; a similar green solution could not be obtained by the use of any other reducing solution. The liquid rapidly turns brown and flocculates, the change being followed by conductivity measurements. The nature of this solution is discussed.

II. [With E. Kessler.]—Addition of an acid stannous chloride solution to a solution of selenious acid produces an opalescence; after a time, the mixture becomes yellow, and on keeping or dilution with water a red precipitate is obtained, which is an adsorption compound of selenium and hydrated stannic oxide in varying proportions. The initial opalescence is due to the formation of colloidal hydrated stannic oxide, which becomes yellow as it adsorbs the colloidal selenium. In concentrated solution, the initial reaction velocity is greater than in dilute solution, but the end velocity is greater in the latter case. The supernatant liquid is always free from selenium and tin at the end of the precipitation. The precipitate when freshly prepared can be peptised easily with ammonia or hydrochloric acid, giving a red solution of colloidal selenium of great stability. Analyses of a number of the preparations are given.

Tellurium forms a completely analogous series of compounds; the peptised solution is, however, more sensitive to electrolytes.   H. F. Gillbe.

Formation of colloids from complex ions. A. B. Dumanski, A. P. Buntin, S. J. Diatchkovski, and A. G. Kniga (J. Russ. Phys. Chem. Soc., 1926, **58**, 326—346).—An electrochemical method is described for testing the authors' theory that a colloidal particle is synthesised by the successive formation of more and more complex ions. The changes in conductivity and f.-p. depression are attributed to the formation of intermediate complexes inferred from the nature of the curves. The addition of acid to sodium tungstate and sodium molybdate gives ultimately colloidal solutions of tungstic and molybdic acid. The conductivity and f.-p. depression curves show several well-defined maxima and minima corresponding with intermediate complexes. Ultramicroscopical examination shows the presence of colloidal particles only towards the end of the reaction. The mechanism $Na_2MoO_4 + 2HCl \longrightarrow 2NaCl + H_2MoO_4$ and $H_2MoO_4 + MoO_4'' \longrightarrow H_2O + [MoO_4, MoO_3]''$ is suggested. Copper

ferrocyanide, Prussian blue, and silicic acid give similar curves. Characteristic curves are also obtained with ferric hydroxide, stannic acid, and zirconium hydroxide, which readily pass into the gel form with excess of reagent. The method is extended to several other colloids, and the application of it to the comparative study of the hydrosols and hydrogels of different elements is discussed.   M. Zvegintzov.

Sodium urate as a colloidal electrolyte. H. Freundlich and L. F. Loeb (Biochem. Z., 1927, **180**, 141—155).—Anomalous conductivity results obtained with sodium urate solutions which have been made alkaline and then neutralised or have been heated and then cooled lead to the conclusion that sodium urate is a colloidal electrolyte.
P. W. Clutterbuck.

Lyophilic colloids. M. Volmer (Z. physikal. Chem., 1927, **125**, 151—157).—Theoretical. A formula is derived which allows the numbers of particles of all sizes in a diluted colloidal solution to be determined, provided that their numerical distribution in the original solution is known.   L. F. Gilbert.

Centrifugal determination of the distribution of the size of particles of suspended material. J. B. Nichols and H. C. Liebe (Third Colloid Symposium Monograph, 1925, 268—284).—For lithopone, the approximate relation between the radius dividing the mass distribution curve into equal weights of material and the obscuring power depends on the amount of surface oxidation as well as on the size of the particles.   Chemical Abstracts.

Emulsification and distribution of size of particles. A. J. Stamm (Third Colloid Symposium Monograph, 1925, 251—267).—The method of preparation of the emulsion is the prime factor in determining dispersity. Different univalent soaps show the same mass maximum and total surface of dispersed particles. Excess of alkali increases dispersity in oil-in-water emulsions without affecting the mass maximum, but decreases dispersity in the reverse type for the smaller particles. The wedge theory of emulsification is insufficient, and an electrical effect is suggested. Palmitic acid gives a mass optimum corresponding with larger particles than do soaps. Increasing benzene concentration with constant soap content shifts the mass maximum exponentially. When the ratio of soap to dispersed material is small, calculations based on the total surface of dispersed particles indicate that the interfacial films are of unimolecular thickness.   Chemical Abstracts.

Calculation of thermodynamic properties of colloidal solutions from measurements with the ultracentrifuge. A. Tiselius (Z. physikal. Chem., 1926, **124**, 449—463; cf. Svedberg, A., 1926, 677).—A general theory of sedimentation equilibrium in colloidal systems containing electrolytes is derived thermodynamically, using the conception of activity.
R. Cuthill.

Particles causing scattering of light in the crystalline lens of the eye. G. I. Pokrowski (Kolloid-Z., 1927, **41**, 146—148).—It is suggested that the scattering of light in the crystalline lens of the eye, to which the halo observed in a sudden glance at a

bright light is attributed, is due to the presence of cylindrical particles in the eye. E. S. Hedges.

Viscosimetric investigation of cotton-yellow. Wo. Ostwald and R. Auerbach (Kolloid-Z., 1927, **41**, 112—122).—By means of the capillary viscosimeter and the overflow-viscosimeter, using varying rates of flow of liquid, the viscosities of sols of commercial cotton-yellow containing sodium sulphate were determined at different concentrations. The curve exhibits a series of maxima and minima, the highest viscosity being recorded with a 1·2% sol. The maxima and minima are less marked on heating or cooling the solution, or when the content of salt is diminished, but the effect is enhanced by increasing the amount of sodium sulphate. Similar experiments with a mixture of gelatin and sodium sulphate gave a curve showing two well-defined maxima. Mechanical treatment lowers the viscosity of sols of cotton-yellow. E. S. Hedges.

Ageing of gelatin. A. Nagorny (Kolloid-Z., 1927, **41**, 123—129).—Gelatin solutions were sterilised by boiling and kept at temperatures of 6° and 37°, respectively, the variation of viscosity with age being studied over periods of 1 or 2 months. Measurements at 20° showed the viscosity of the gelatin kept at 37° to decrease with age, whilst that kept at 6° underwent an increase in viscosity with age. On the other hand, measurements at 30° showed scarcely any change in the viscosity of either. At 20°, the specimen kept at 37° approximated to Poiseuille's rule, and both specimens did so at 30°. Little difference was found in the viscosity of gum-arabic solutions kept at 6° and 37°, respectively. A specimen of gelatin aged at 37° requires more ammonium sulphate solution to effect precipitation than does a specimen kept at 6°: the latter can be separated into two portions by fractional precipitation by means of ammonium sulphate, one of which gelatinises at the ordinary temperature. It is considered that the particles of the disperse phase are larger in the colder solution and that these remain intact when the measurement is carried out at 20°, but become more finely dispersed or dissolved at 30°. The question is discussed whether the difference between the small and large particles is merely one of size, or whether chemical differences are involved. The fractional precipitation by ammonium sulphate supports the latter view. E. S. Hedges.

X-Ray spectrum of the so-called Gladstone's alkali-cellulose compound (in relation to the change in X-ray spectrum of cellulose on swelling in concentrated solutions of alkali hydroxides). I. J. R. Katz (Z. physikal. Chem., 1926, **124**, 352—358).—When ramie fibres are swollen by treatment with a 14% solution of sodium hydroxide, the X-ray spectrogram of cellulose is replaced by a new spectrogram consisting of an "amorphous" ring, due to the alkali solution itself, within which are two equatorial bands, with the form of arcs of a circle. If the swollen fibres are dried, the amorphous ring disappears, but the bands remain. Washing out the free alkali with alcohol does not affect the bands, but there also appear new circles and segments of circles, corresponding with an orderly arrangement of the crystallites in the fibres. Fibres swollen with lithium hydroxide or potassium hydroxide give similar results. Since swelling with zinc chloride or calcium thiocyanate does not alter the spectrogram of the ramie, it seems that the effects observed using alkali hydroxides are due to the formation of compounds of the cellulose with alkali. R. Cuthill.

Behaviour of Prussian blue sol towards certain metallic hydroxides. E. Wedekind and Heinrich Fischer (Ber., 1927, **60**, [*B*], 544—545; cf. this vol., 328).—Titanic, tungstic, and tantalic acids and lead hydroxide do not adsorb Prussian blue from its colloidal solution. The hydroxides of aluminium, magnesium, lanthanum, thorium, cerium, neodymium, praseodymium, yttrium, gadolinum, and erbium adsorb the sol as readily as does ferric hydroxide, but in course of time the colour of the substrate disappears completely. Zirconium and dysprosium hydroxide and yellow mercury oxide cause slow decolorisation of the blue solution without showing visible adsorption; at 0°, the substrate becomes coloured, indicating that adsorption is the precursor of chemical change. H. Wren.

Existence of two zones of instability in the flocculation of ferric hydroxide sols by electrolytes with multivalent anions. A. Boutaric and [Mlle.] M. Dupin (Compt. rend., 1927, **184**, 326—327; cf. A., 1926, 905).—A ferric hydroxide sol containing 1·6 g. per litre showed two zones of flocculation when treated with increasing concentrations of a sodium phosphate solution: (1) between the concentrations $a = 207 \times 10^{-6} N$ and $b = 530 \times 10^{-6} N$; (2) above the concentration $c = 22 \times 10^{-3} N$. With more concentrated sols, a and b increase, and c decreases slightly. The limits are not affected by sulphuric acid and potassium hydroxide, but are increased by small amounts of ferric chloride, $(c-b)/b$ remaining almost constant, and $(b-a)/a$ decreasing. Stabilising colloids increase c and decrease b, whilst a varies according to the colloid used. The ratio $(b-a)/a$ decreases, but $(c-b)/b$ increases. At high colloid concentrations, the zone of flocculation between a and b disappears. J. Grant.

Dispersion and aggregation of silk in concentrated salt solutions. P. P. von Weimarn (Kolloid-Z., 1927, **41**, 148—152).—Silk dissolves at ordinary pressures to form a colloidal solution in hot concentrated solutions of many very soluble, strongly hydrated salts of the alkali and alkaline-earth metals. The order of influence of the anions is as follows: $F' < SO_4'' < $ citrate $<$ tartrate $<$ acetate $< Cl' < NO_3' < Br' < I' < SCN'$. Addition of strong solutions of the fluorides of ammonium or potassium, or the sulphates of sodium, potassium, ammonium, or lithium, to a solution of silk in hot, concentrated calcium chloride causes aggregation and reprecipitation of the silk. At the ordinary temperature, the silk is reprecipitated by addition of all easily soluble salts, except lithium iodide and lithium thiocyanate. The regenerated silk generally has a thread-like structure. Simple cooling does not cause gelatinisation, but only an increase in viscosity. The silk is also regenerated by the addition of alcohol, or an aqueous or alcoholic solution of tannin. The silk reprecipitated by alcohol may be obtained as a solid block. E. S. Hedges.

Influence of metals on thixotropic sols and gels. H. FREUNDLICH and W. RAWITZER (Kolloid-Z., 1927, **41**, 102—104).—Sols of ferric hydroxide exhibit the phenomenon of thixotropy, *i.e.*, on addition of electrolytes they set to a gel, which forms a sol once more on shaking. When the colloid is left in contact with certain metals for periods of a few days, the time of setting to the thixotropic gel is shortened, whether the contact with the metal is effected before or after addition of the electrolyte. It is definitely shown that the phenomenon is not due to cations of the metal, to adsorbed hydroxyl ions, or to the formation of hydrogen peroxide. Since a similar effect is produced by application of a direct or an alternating current, the phenomenon is supposed to be due to local currents in the metal. In confirmation of this, the effect increases with the electropositive nature of the metal.   E. S. HEDGES.

Colloidal and molecular solubility and a peptisation rule. WO. OSTWALD (Kolloid-Z., 1927, **41**, 163—169).—Contrary to the behaviour of molecularly-dispersed substances, the amount of a colloidal gel dissolved (or peptised) by a medium is not independent of the amount of gel present, but generally increases with the amount of gel used. It is supposed that the gel is heterogeneous in that it exhibits " state-isomerism," the " isomerides " varying in their susceptibility to peptisation. It is admitted that this explanation cannot account for von Buzágh's results (cf. following abstract), where a maximum of peptisation was observed.   E. S. HEDGES.

Theory of peptisation. I. Dependence of solubility on the amount of colloid. A. VON BUZÁGH (Kolloid-Z., 1927, **41**, 169—183).—In the peptisation of colloidal barium carbonate, casein, Congo-red acid, Congo-ruby acid, Congo-blue, and ferric hydroxide, the quantity of colloid which passes into solution is not independent of the amount of colloid taken (cf. preceding abstract). As a rule, the curve connecting these quantities exhibits a marked maximum, showing that for a given peptising agent and a given volume there is an optimum condition for sol formation when a medium amount of colloid is present. It is believed that the gels are composite, containing fractions with structural differences which are soluble in certain concentrations of the peptisation medium and insoluble at other concentrations.
                E. S. HEDGES.

String-formation of emulsoid particles in an alternating electric field. E. MUTH (Kolloid-Z., 1927, **41**, 97—102).—Under the influence of an alternating electric field, the particles of emulsions of milk, cream, butter, or petroleum with water arrange themselves into chains the long axes of which lie in the direction of the applied field. This resembles the effects observed by Thomson and by Whytlaw-Gray and Speakman (Nature, 1921, **107**, 520, 619) in clouds of metallic oxides dispersed from an arc. On removal of the field, the chains break up into the original primary spherical particles. An explanation is given, based on the electrical double layer existing at the colloid particle-dispersion medium interface. It is considered that an alternating polarity is here set up in rhythm with the frequency of the field. The string-formation is independent of the frequency of alternation of the field.   E. S. HEDGES.

Liesegang system of "rhythmic" precipitates. R. FRICKE and O. SUWELACK (Z. physikal. Chem., 1926, **124**, 359—393).—The occurrence of periodic precipitation when a solution of ammonia is allowed to diffuse into an agar-agar jelly containing magnesium chloride has been investigated by analysing successive sections of the jelly. It is found that the product of the activities of the ions of the magnesium hydroxide increases for some distance beyond the last precipitate and then falls again. The phenomenon is due to the ordinary processes of diffusion and precipitation and is not peculiar to solutions containing substances in the colloidal state (cf. A., 1924, ii, 26).   R. CUTHILL.

Cataphoresis technique. G. ETTISCH and D. DEUTSCH (Physikal. Z., 1927, **28**, 153—154).—The use of materials the resistivity of which is of the order of 10^5 ohms/cm.^{3}, such as parchment paper and unglazed porcelain, for the study of cataphoresis phenomena is described. With these materials, observations can be made in 1—5 min.   R. W. LUNT.

Use of Donnan's membrane equilibrium theory for the determination of the charge of colloid particles. N. BJERRUM (Phil. Mag., 1927, [vii], **3**, 22—26).—A reply to the criticism by Rinde (A., 1926, 347) of the author's paper (*ibid.*, 1925, ii, 111).
                A. E. MITCHELL.

Graphical method for the calculation of the energy yield of homogeneous reactions. P. JOLIBOIS and P. MONTAGNE (Compt. rend., 1927, **184**, 323—325).—Comparison is made of the yields obtained by experiment and those calculated on the hypothesis that the effect of an electric spark on a chemical reaction is purely thermal. At constant temperature, the yield decreases when the gas pressure increases. At constant pressure, the yield attains a maximum which, with increasing pressures, is displaced towards those obtained at higher temperatures. The yield tends to become independent of pressure at temperatures above 3500° Abs.   J. GRANT.

Organic acids and bases in non-aqueous solutions. II. Aliphatic acids. F. HÖLZL (Monatsh., 1927, **47**, 559—600).—The conductivity method already applied to the investigation of compound formation between acetic acid and various bases in absolute alcoholic solution at 25° (A., 1926, 1206) has been extended to the investigation of each of the acids formic, butyric, and succinic with the bases ammonia, ethylamine, diethylamine, ethylenediamine, benzylamine, aniline, *p*-toluidine, mono- and di-methylaniline, α- and β-naphthylamine, *o*-, *m*-, and *p*-phenylenediamine, diphenylamine, and carbamide. As previously observed, normal salts are obtained with the stronger bases, but with the weaker bases compounds containing a larger proportion of acid are found, and detected either by maxima or inflexions in the conductivity curves. The strength and degree of association of the acid are also important factors, since, for example, phenylenediamine forms a normal salt A_2B (A=1 mol. of the acid; B=1 mol. of the base) with formic acid, but not with

butyric acid. The following is a summary of the compounds formed at the various dilutions : (1) with formic acid, ammonia, 0·42N, and ethylamine, 0·93N yield only equimolecular compounds of the type AB; ethylenediamine 0·053N, AB and A$_2$B; aniline 0·05N, AB, but at higher concentrations up to N the maxima occur at points corresponding with a larger proportion of acid ; p-toluidine, mono- and di-methyl-aniline show the same phenomenon to a less extent, the concentrations at which the maxima correspond with the salt AB being, respectively, 0·1N, 0·05N, and 0·05N ; α-naphthylamine 0·1N, AB; β-naphthylamine 0·1N, A$_2$B and AB; o-, m-, and p-phenylene-diamine 0·1N, AB; carbamide 0·1N, AB. With none of the acids was there any evidence of compound formation with diphenylamine ; (2) with butyric acid, ammonia, mono- and di-ethylamine, ethylenediamine, benzylamine, aniline, mono- and di-methylaniline, m- and p-phenylenediamine, and carbamide all form salts of the type AB, the weaker bases behaving in the same manner as they do with formic acid ; α-naphthylamine 0·1N, AB and AB$_2$; β-naphthylamine 0·1N, A$_2$B and AB; o-phenylenediamine 0·1N, A$_2$B and AB : (3) with succinic acid, ammonia 0·01N, ethylamine 0·233 and 0·117N, and benzylamine 0·127N, all give AB and AB$_2$; aniline 0·2, 0·1, and 0·05N, methylaniline 0·1 and 0·05N, dimethylaniline 0·25, 0·1, and 0·05N, all give AB only ; α- and β-naphthylamine 0·1N, A$_2$B and A$_2$B$_3$; o-phenylenediamine 0·1N, A$_2$B and AB ; m-phenylenediamine 0·1 and 0·05N, AB; p-phenylenediamine 0·125, 0·1, and 0·09N, AB and AB$_2$; carbamide 0·2N, AB$_2$. J. W. Baker.

Influence of organic substances on the rate of absorption of carbon dioxide by solutions of sodium carbonate. P. Riou and P. Cartier (Compt. rend., 1927, **184**, 325—326).—The rates of absorption of carbon dioxide by solutions of sodium carbonate containing various quantities of sucrose, dextrose, and glycerol at 20° rise to maxima and then fall as the viscosity of the solutions increases. J. Grant.

Neutral salt effect. L. E. Bowe (J. Physical Chem., 1927, **31**, 291—302).—The influence of sodium chloride, bromide, and iodide ($N-4N$) on the rate of hydrolysis of sucrose and of ethyl acetate has been determined. Potential measurements show that the apparent hydrogen-ion concentration increases tenfold in the case of the 4N-sodium iodide solution, and the influence of the neutral salts, contrary to Harned (A., 1916, ii, 8), but in agreement with Arkadiev (ibid., 1923, ii, 369), follows the order iodide>bromide>chloride. The percentage increase in the apparent hydrogen-ion concentration indicated by the sucrose hydrolysis agrees well with that found by the potential method. The influence of sodium chloride on the rate of hydrolysis of ethyl acetate by 0·1N-hydrochloric acid is less than in the inversion of sucrose, and sodium bromide produces a smaller effect than the chloride (cf. Åkerlöf, A., 1922, ii, 134; Poma, ibid., 1911, ii, 707). Alcohol and acetic acid had but small influence on the reaction velocity. L. S. Theobald.

Lyotropy. H. R. Kruyt and C. Robinson (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1244—

1250).—The observations of Linderstrøm-Lang (A., 1925, ii, 30) on the influence of neutral salts on the solubility of quinol and quinone in water have been extended to m- and p-nitroaniline, p-phenylene-diamine, and p-nitrophenol. The influence of salts on the solubility of quinol is dependent only on the cation. For quinone, m- and p-nitroaniline, and p-phenylenediamine the reverse is true. The solubility of p-nitrophenol is influenced by both ions. In presence of bromides, iodides, nitrates, and thiocyanates, the solubilities of the various organic substances in pure water are often exceeded. The theory of Debye (ibid., 171) does not offer a satisfactory explanation of this increased solubility, nor does it suggest a specific influence of the ions. A more plausible explanation is to be found in the orientation of water dipoles in the immediate neighbourhood of the ions, i.e., orientation of the water of hydration. Various physico-chemical phenomena lead to the conclusion that hydration decreases in the order : cations : $Li^{\cdot}>Na^{\cdot}>K^{\cdot}>Rb^{\cdot}>Cs^{\cdot}$; anions : $SO_4''>Cl'>Br'>NO_3'>I'>CNS'$. In general, this will be the sequence of the salting-out effect, $Li^{\cdot}$ and SO_4'' having a strong, and $Cs^{\cdot}$ and CNS' a weak effect. Since dissolution implies an electrical, attractive force between solvent and solute molecules, the water molecules, in consequence of their dipolar character, will be oriented round solute molecules. Two kinds of orientation are possible, since either the positive or the negative end of the water molecule may be turned towards the solute molecule. Postulating a polar character for the dissolved substance, one type of orientation must predominate. With anionphilic molecules (e.g., quinone etc.), the orientation of dipoles round the anion favours the orientation round the organic molecules and increases their solubility. Cations will tend to decrease the solubility, but their influence is small, since they are kept far from the molecule. Hence, in addition to the usual salting-out effect, there is an actual solubility increase brought about by the anion. The feebly-hydrated thiocyanate ion lowers the solubility but little and hence the increase in solubility predominates. The sulphate ion, however, has such a powerful lowering effect that a considerable decrease in solubility results. For cationphilic substances (quinol etc.), a corresponding argument holds. J. S. Carter.

Nessler's reagent. S. M. Naudé (Z. physikal. Chem., 1927, **125**, 98—110).—The existence of the compounds KHgI$_3$ and KHgI$_3$,1·5H$_2$O is claimed from the results of an investigation of the system HgI$_2$–KI–H$_2$O. These results agree approximately with those of Dunningham (J.C.S., 1914, **105**, 368, 724). This author, however, reported KHgI$_3$,H$_2$O in the place of KHgI$_3$,1·5H$_2$O. Nessler's solution probably contains KHgI$_3$, not K$_2$HgI$_4$. L. F. Gilbert.

Equilibrium in binary systems containing guaiacol as a component. N. A. Puschin and B. Vaić (Monatsh., 1927, **47**, 529—535).—The f.-p. curves for mixtures of guaiacol with aniline, o- and p-toluidine, pyridine, β-naphthylamine, diphenylamine, ethylurethane, and naphthalene have been determined, and the duration of the eutectic crystall-

isation has been observed. The curves indicate the existence of equimolecular *compounds* with aniline, m. p. 17°, *o*-toluidine, m. p. 24°, *p*-toluidine, m. p. 24·3°, and pyridine, m. p. 5·6°; no compounds are formed in the other cases. The eutectic temperatures for the various systems in the order given above are, respectively, 10·3° and 12°; 15° (traced only to 80 mol.% of *o*-toluidine); 14° and 20°; —5° and —47·8°; 12°; 10°; 5°; and 18°. The eutectic mixtures contain 22 and 92; 20; 22 and 66; 31 and 92; 26; 24; 40; and 18 mol.% of the second component, respectively. J. W. BAKER.

Freezing of solutions. II. Crystallisation of maleic, fumaric, and succinic compounds. G. VISEUR (Bull. Soc. chim. Belg., 1926, 35, 426—450).— The f. p. of binary mixtures of the dimethyl and diethyl esters of fumaric, maleic, and succinic acids have been determined. Ethyl maleate and ethyl fumarate form an equimolecular compound which forms mixed crystals with each of the constituents. Methyl fumarate and methyl maleate, methyl succinate and methyl maleate, methyl succinate and methyl fumarate, ethyl succinate and ethyl maleate, and ethyl succinate and ethyl fumarate form mixed crystals. The f.-p. method is inapplicable to the acids and amides, as they decompose slowly at high temperatures. The m. p. of mixtures of maleic and fumaric, maleic and succinic, and fumaric and succinic acids, and of the corresponding diamides, were determined therefore by enclosing them in capillary tubes and immersing these in a series of baths at different temperatures, the temperature of " instantaneous fusion " being taken as the m. p. Mixed crystals were observed with the amides, but the results for the mixed acids had to be correlated with the results of solubility determinations in acetone before definite conclusions could be reached. It was then found that mixed crystal formation occurs only in the system succinic acid–fumaric acid.

The m. p. of the amides and acids, and the m. p., b. p., and densities of the esters are recorded. The following are to be noted : maleic acid, m. p. 241·7— 241·9°; methyl maleate, m. p. 7·6°, d 1·4513; ethyl maleate, m. p. —17°. L. F. GILBERT.

Mol. wt. of sulphur trioxide in various solvents. G. ODDO and A. CASALINO (Gazzetta, 1927, 57, 60—75).—Using sulphuryl chloride and ethyl chloroacetate as solvents, the molecular depression of the f. p. of the compound $SO_3,2POCl_3$ is found to be 106°. The irregular values obtained when liquid sulphur trioxide is used as solute show that solid solutions are formed; fibrous sulphur trioxide gives values corresponding with the theoretical mol. wt., 160. In sulphuric acid, the lowering produced by liquid sulphur trioxide corresponds with mol. wt. 79·8; and that produced by fibrous sulphur trioxide with mol. wt. 88, or approximately 55% $(SO_3)_2$. R. W. LUNT.

Behaviour of sulphur trioxide with phosphorus oxychloride. G. ODDO and A. CASALINO (Gazzetta, 1927, 57, 47—59).—The system phosphorus oxychloride and either liquid (SO_3) or fibrous ($[SO_3]_2$) sulphur trioxide shows two eutectics corresponding with $SO_3,POCl_3$ and $SO_3,3POCl_3$. The substances are completely miscible and give a

mixture of constant b. p. (111·5—111·9°/735 mm., m. p. —16·62°) corresponding in composition with $SO_3,2POCl_3$. R. W. LUNT.

Dissociation pressures of monopotassium and monosodium orthophosphates and of dipotassium and disodium dihydrogen pyrophosphates. Phosphate. IV. S. J. KIEHL and G. H. WALLACE (J. Amer. Chem. Soc., 1927, 49, 375—386).—The dissociation pressures of the following systems were measured by a static method, the apparatus being a modification of that described by Johnston (A., 1908, ii, 358): $nK_2H_2P_2O_7 \rightleftharpoons 2(KPO_3)_n + nH_2O$ (165— 260°); $nNa_2H_2P_2O_7 \rightleftharpoons 2(NaPO_3)_n + nH_2O$ (170— 280°); $nKH_2PO_4 \rightleftharpoons (KPO_3)_n + nH_2O$ (170—264°); $2NaH_2PO_4 \rightleftharpoons Na_2H_2P_2O_7 + H_2O$ (110—150°). The curves show that disodium dihydrogen pyrophosphate may be prepared by heating monosodium orthophosphate in an open vessel at 150°. The corresponding potassium salt, which forms a non-deliquescent, crystalline monohydrate, cannot be prepared in this way, since its dissociation pressure at lower temperatures is higher than that of the orthophosphate–metaphosphate system under the same conditions. For this reason, the systems : $2KH_2PO_4 \rightleftharpoons K_2H_2P_2O_7 + H_2O$ and $nNaH_2PO_4 \rightleftharpoons (NaPO_3)_n + nH_2O$ afford no equilibrium data. S. K. TWEEDY.

Pseudo-ternary systems containing sulphur. II. System sulphur–benzoic acid. D. L. HAMMICK and W. E. HOLT (J.C.S., 1927, 493—497).— Equilibria in the system sulphur–benzoic acid have been studied by the synthetic method. Discrepancies between the results and those of Kruyt are probably due to oxidation of the sulphur in the latter's experiments. On the sulphur side, the equilibrium is of Kruyt's type η, and on the benzoic acid side of the type ordinarily found for two partly miscible liquids. The clouding phenomenon noticed by Kruyt can be explained without the assumption that three liquid layers co-exist in the neighbourhood of 170°. H. F. GILLBE.

Dehydration and hydration of platinocyanides. P. GAUBERT (Compt. rend., 1927, 184, 383—385).— The changes undergone by small crystals of the hydrated platinocyanides of barium, lithium, yttrium, and magnesium mounted on a slide in an inert liquid (melted paraffin, vaseline, or monobromonaphthalene) have been observed under the polarising microscope, the crystals being gradually heated. The changes corresponding with the dehydration of the crystals occur at higher temperatures than in air, according to the nature of the compound. The phenomenon is reversible and is most marked in the case of the yttrium compound. The transformations of the magnesium compound are not polymorphic. The nature of the inert liquid has little influence on the results, the liberated water being absorbed by the dehydrated product rather than by the medium. J. GRANT.

Ionic equilibria. I. Equilibrium between calcium oxalate and dilute hydrochloric acid. M. AUMÉRAS (J. Chim. phys., 1927, 24, 24—49).— Desiccation of precipitated calcium oxalate at 25° indicates the existence of a hydrate, $CaC_2O_4,1·2H_2O$. If, however, the method of dehydration at increasing

temperature recommended by Guichard (A., 1925, ii, 559) is used, the formula for the hydrate is found to be CaC_2O_4,H_2O. For a solution of calcium oxalate in dilute hydrochloric acid in equilibrium with the solid salt, it is shown that if P is the solubility product of the oxalate and C and D are the first and second dissociation constants, respectively, of oxalic acid, then $PA=D$, and $AC=B$, where $A=[H^{\cdot}]/[HC_2O_4'][Ca^{\cdot\cdot}]$ and $B=[H^{\cdot}]^2/[H_2C_2O_4][Ca^{\cdot\cdot}]$. The value of B has been derived from determinations of the solubility of the oxalate in hydrochloric acid. Using published data for P and Chandler's value for C (A., 1908, ii, 467), the value of D is calculated from the above equations to be $5\cdot6\times10^{-5}$ at $13°$, in good agreement with Chandler's values of $4\cdot1\times10^{-5}$ and $4\cdot9\times10^{-5}$ at $25°$. If hydrobromic acid or nitric acid is used to dissolve the oxalate, instead of hydrochloric acid, similar results are obtained. The solubility at $20°$ of calcium oxalate precipitated from calcium chloride solutions is $0\cdot0066$ or $0\cdot0073$ g./litre of solution, according as the precipitant is oxalic acid or ammonium oxalate.   R. Cuthill.

Ternary system copper–zinc–manganese. O. Heusler (Z. anorg. Chem., 1926, **159**, 37—54).— An exhaustive investigation of the ternary system copper–zinc–manganese with diagrams and a short account of the magnetic properties of these alloys.
M. Carlton.

Equilibrium in the systems alkali chloride–cobalt chloride–water. H. W. Foote (Amer. J. Sci., 1927, **13**, 158—166).—The solubility curves at $25°$ have been determined for the systems sodium (potassium, rubidium, cæsium) chloride–cobaltous chloride–water. The saturated solutions for the five binary systems contain $26\cdot50$, $26\cdot46$, $48\cdot57$, $65\cdot61$, and $35\cdot67\%$ of salt, respectively. System $NaCl–CoCl_2–H_2O$. No double salts are formed. The solution saturated with respect to both salts contains $4\cdot70\%$ NaCl, $32\cdot91\%$ $CoCl_2$. System KCl–$CoCl_2$–H_2O. No double salts are formed. The univariant point is at $8\cdot24\%$ KCl, $34\cdot10\%$ $CoCl_2$. System RbCl–$CoCl_2$–H_2O. Two double *salts* are formed, $RbCl,CoCl_2,2H_2O$ (D_1) and $2RbCl,CoCl_2,2H_2O$ (D_2). Univariant points : $6\cdot09\%$ RbCl, $35\cdot02\%$ $CoCl_2$, solid phases, $CoCl_2,6H_2O$ and D_1 ; $7\cdot68\%$ RbCl, $34\cdot36\%$ $CoCl_2$, solid phases, D_1 and D_2 ; $38\cdot43\%$ RbCl, $11\cdot50\%$ $CoCl_2$, solid phases, D_2 and RbCl. System : CsCl–$CoCl_2$–H_2O. Three double salts exist, $CsCl,CoCl_2,2H_2O$ (d_1), $2CsCl,CoCl_2$ (d_2), $3CsCl,CoCl_2$ (d_3). Univariant points : $1\cdot86\%$ CsCl, $35\cdot67\%$ $CoCl_2$, solid phases, $CoCl_2,6H_2O$ and d_1 ; $5\cdot03\%$ CsCl, $31\cdot09\%$ $CoCl_2$, solid phases, d_1 and d_2 ; $40\cdot56\%$ CsCl, $8\cdot98\%$ $CoCl_2$, solid phases, d_2 and d_3 ; $65\cdot48\%$ CsCl, $0\cdot25\%$ $CoCl_2$, solid phases, d_3 and CsCl.   J. S. Carter.

System NH_4NO_3–$(NH_4)_2SO_4$–H_2O. E. Jänecke, W. Eissner, and R. Brill (Z. anorg. Chem., 1927, **160**, 171—184).—Solubility measurements of the system ammonium nitrate–ammonium sulphate–water show that no double salts other than $(NH_4)_2SO_4,2NH_4NO_3$ exist. The phase diagram for mixtures of ammonium nitrate and ammonium sulphate indicate that the double salt melts at $310°$. The presence of ammonium sulphate lowers the transition temperature and raises the m. p. of ammon-ium nitrate. Mixed crystals of ammonium nitrate with the double salt exist.

The crystallographic and optical constants of the double salt have been determined. X-Ray investig-ation shows that the crystal unit consists of not less than two molecules of the double salt.
H. F. Gillbe.

Univariant folds in salt-formation diagrams. Sodium nitrate. N. S. Kurnakov and W. T. Nikolaiev (J. Russ. Phys. Chem. Soc., 1926, **58**, 548—552).—The equilibrium in the system Na_2O–N_2O_5–H_2O has been examined at $25°$ and $65°$.
M. Zvegintzov.

Univariant systems, isothermal surfaces, and three-dimensional ridges. W. T. Nikolaiev (J. Russ. Phys. Chem. Soc., 1926, **58**, 553—556).—The influence of a fourth component on the univariant equilibrium states of a ternary system has been studied in reference to the quaternary combination Na_2O–N_2O_5–H_2O–EtOH. Solubilities and densities for $25°$ are recorded. The data refer to alcohol concentrations of 0, 5, 15, and 30%. The diminution in the solubility of the salt is almost proportional to the amount of alcohol.   M. Zvegintzov.

Cryohydric curves of the ternary system Na_2O–N_2O_5–H_2O. W. T. Nikolaiev (J. Russ. Phys. Chem. Soc., 1926, **58**, 557—564; cf. preceding abstracts).—The eutectic temperature of sodium nitrate–ice is $-18\cdot1°$, and the changes in temperature and composition caused by adding acid or alkali to the eutectic mixture ($38\cdot07\%$ by weight of sodium nitrate) have been determined. For small additions, the changes are proportional to the quantities added. The ternary eutectics are at $-46\cdot4°$ (acid) and $-39\cdot1°$ (alkaline), where crystals of $NaNO_3+ice+HNO_3,3H_2O$ and $NaNO_3+ice+NaOH,7H_2O$ separate out, re-spectively. By combining these results in a tri-angular space model with the isothermal diagrams at $25°$ and $65°$ (cf. preceding abstract), a univariant " isochoric " fold is obtained the ridge of which lies on an " isochoric " univariant plane through the central tie-line (H_2O)–$(NaNO_3)$, which divides it into an alkaline and an acid section. By joining the three binary eutectics ice+HNO_3 ($-43°$), ice+NaOH ($-28°$), ice+$NaNO_3$ ($-18\cdot1°$) and the two ternary eutectics, an " ice-field " is isolated which includes all those systems in which ice is present ; this is divided into an alkaline and an acid section by the f.-p. curve of neutral solutions of sodium nitrate.
M. Zvegintzov.

Distillation of heterogeneous ternary mix-tures. II. System ethyl alcohol–benzene–water. J. Barbaudy (J. Chim. phys., 1927, **24** 1—23; cf. A., 1926, 578).—The b. p. at 760 mm. of a large number of mixtures of alcohol and benzene, and of homogeneous and heterogeneous ternary mixtures of alcohol, benzene, and water have been determined, and the results represented graphically. The composition of the saturated vapour was deter-mined by the partial condensation method previously described (*loc. cit.*), and the distillates were also analysed.   R. Cuthill.

Reaction regions. XIII. Influence of size of particles of the reacting substances and of the

nature of the igniter. W. P. JORISSEN and C. GROENEVELD (Rec. trav. chim., 1927, **46**, 47—53; cf. A., 1926, 1206; this vol., 112).—Figures and curves are given showing the extension of the reaction regions of mixtures of aluminium and sulphur, iron and sulphur, and of iron, aluminium, and sulphur with increase in the power of the igniting mixture and decrease in the particle size of the constituents of the mixture.　　　　　　　　　H. F. GILLBE.

Reactions in the solid state. VII. D. BALAREV (Z. anorg. Chem., 1927, **160**, 92—100).—A large number of the reactions studied by Tammann, Hedvall, and the author are shown either to be complex or to be dependent on the presence of substances in the liquid or gaseous phase. The conclusion is that all such reactions which show a thermal effect on the heating curve and are simple in nature involve a straightforward distillation process.　　　　　　　　　　　　　H. F. GILLBE.

[Reactions in the solid state.] G. TAMMANN (Z. anorg. Chem., 1927, **160**, 101—106).—Polemical against Balarev (preceding abstract).
　　　　　　　　　　　　　　　H. F. GILLBE.

Specific inductive capacity of heterogeneous mixtures. J. ERRERA (Compt. rend., 1927, **184**, 455—458).—The variations of the ratio of the density of compressed powder to that of the substance in the solid homogeneous state have been studied in the case of lead chloride, lead nitrate, and potassium chloride and the changes plotted as a function of the specific inductive capacity. For densities greater than a lower limiting value, the variation is linear until the ratio=1. The value of the specific inductive capacity for potassium chloride (cubic system) when the ratio is unity is almost the same as for crystalline potassium chloride.　　　　　　　J. GRANT.

Applications of thermodynamics. E. DENINA (Gazzetta, 1927, **57**, 3—7).—A discussion of the method of application of general thermodynamical equations most appropriate to particular types of problems.　　　　　　　　　　R. W. LUNT.

Activity coefficients of electrolytes. I. Limiting law for a ter-tervalent salt. V. K. LaMER, C. V. KING, and C. F. MASON (J. Amer. Chem. Soc., 1927, **49**, 363—374).—The activity coefficients of the ions of the sparingly soluble hexammine cobalt ferricyanide were determined by measuring its solubility in aqueous magnesium sulphate, potassium nitrate, and sodium chloride solutions. In solutions of the first two salts, the limiting Debye–Hückel equation is obeyed up to an ionic strength of 0·007. A slight discrepancy in the case of sodium chloride suggests that Debye and Hückel's simple concept of ionic size cannot account for the deviations from the limiting law (see following abstract).
　　　　　　　　　　　　　　S. K. TWEEDY.

Activity coefficients of electrolytes. II. Unsymmetric valency-type effect in highly dilute solutions. V. K. LaMER and C. F. MASON (J. Amer. Chem. Soc., 1927, **49**, 410—426).—The "electric-type effect" (Brönsted and LaMer, A., 1924, ii, 306) is investigated for luteotetrammino-diamminocobaltiates and luteodinitrodiammino-oxalo-cobaltiates by measuring the solubilities of these salts

in salt solutions. When the salt solution involves a univalent anion, the Debye–Hückel theory and the Lewis and Randall principle of ionic strength are both satisfied; in other cases, abnormal results are obtained, even at the highest dilutions ($0·00008M$). These are attributed to the neglect of higher terms (z^3. . . .) in the Debye–Hückel expression for the density of electricity. A revision of the interionic attraction theory in this respect yields equations which are qualitatively in agreement with experiment and are in accord with Bjerrum's ideas on "ion association" (v. infra).　　　S. K. TWEEDY.

Ionic association. I. Influence of ionic association on the activity of ions at moderate degrees of association. N. BJERRUM (Kgl. Danske Videnskab. Selsk. math.-fys. Medd., 1926, **7**, [9], 1—48).—The formula developed by Debye and Hückel (A., 1923, ii, 459, 724; 1924, ii, 386; 1925, ii, 513) for calculating activity from the concentration and dimensions of the ions is shown not to be accurate for small ions and for ions of high valency. A method for obtaining more exact values is developed. New values are tabulated for the activity coefficients of univalent ions in water for various concentrations, and these are compared with the old values. By a simple transformation they can be applied to all solutions of electrolytes. From the experimental data, the following values for the sum of the ionic radii of a number of electrolytes were determined (values in Å.) : potassium nitrate, 1·57; potassium iodate, sodium iodate, 1·33; magnesium sulphate, copper sulphate, cadmium sulphate, 4·2; potassium sulphate, 3·8; barium chloride, 5·8; lanthanum nitrate, 6·4. In methyl alcohol, values of 4·1— 6·5 Å., and in ethyl alcohol, 2·4—7·8 Å., were calculated.　　　　　　　　　　　W. CLARK.

Activation of gases by adsorption. G. B. KISTIAKOWSKY (Proc. Nat. Acad. Sci., 1927, **13**, 1—4; cf. Fryling, A., 1926, 800).—On the assumption that the surfaces of metallic catalysts are composed of atoms in different states of lattice saturation (Taylor, A., 1925, ii, 562; 1926, 365), a study of the heat of adsorption in its dependence on the volume adsorbed for hydrogen and carbon monoxide on an active copper catalyst leads to the conclusion that only the unsaturated surface atoms are effective in bringing about activation of the adsorbed gas. Measurements of the heat of adsorption of hydrogen on a copper surface poisoned by a small amount of oxygen indicate that the rôle of oxygen is to oxidise preferentially the most unsaturated surface atoms.
　　　　　　　　　　　　　　J. S. CARTER.

Theory of the heat of adsorption of gases. H. CASSEL (Physikal. Z., 1927, **28**, 152—153).—An extension of the author's thermodynamic theory (A., 1926, 127), which is held to be more conformable with experiment. Iljin's work (ibid., 1104) is criticised.　　　　　　　　　　R. W. LUNT.

Change of entropy on melting. I. Variation of the entropy change of the elements with atomic number. E. KORDES (Z. anorg. Chem., 1927, **160**, 67—76).—The entropy change of the elements on melting is a periodic function of the atomic number, with maxima at the halogen elements,

subsidiary maxima at the metals of group VIII, and minima near the elements of group IV. Crompton's view that the entropy change of the metals is independent of the nature of the metal is thus untenable.

The periodicity is discussed in the light of the number of atoms composing the elementary molecule, and further investigations are in progress to correlate the periodicity with atomic structure.

H. F. Gillbe.

Ratio of the heats of combustion of benzoic acid and salicylic acid. E. Berner (J.C.S., 1927, 338—341).—The ratio of the heats of combustion of benzoic acid and salicylic acid has been redetermined and is found to be 1·2074 (vac.). This gives 5233·7 g.-cal.[15]/g. for the heat of combustion of salicylic acid when the value for benzoic acid is taken as 6319 g.-cal.[15]/g. Evidence is submitted that these values are more correct than those of Verkade and Coops (A., 1926, 785). H. F. Gillbe.

Heats of combustion of the different varieties of lustre carbon; existence of amorphous carbon. W. A. Roth and O. Doepke (Ber., 1927, 60, [B], 530—536; cf. A., 1926, 894).—Three different samples of lustre carbon with differing densities have been examined, from two of which Debye–Scherrer diagrams have been obtained. Increase in density is parallel to a strengthening of the graphite interferences and marked decrease in the heat of combustion. Attempts to base an explanation of the energy differences solely on surface change or surface tension involve the assumption either of extremely great surface tensions or particularly minute elementary units; the actual existence of amorphous carbon as a particular modification is therefore rendered more probable. A lustre carbon, d 2·07, had a heat of combustion greater by 195 g.-cal/g. than that of graphite, whereas a product d 1·86 had the value 8148 g.-cal/g., the highest value observed up to the present for pure carbon. H. Wren.

Investigations in the critical region. II. Specific heats at constant pressure of ethyl ether above and below the critical point. K. Bennewitz (Z. physikal. Chem., 1927, 111—134; cf. A., 1926, 1210).—An apparatus is described by means of which the specific volumes and the specific heats of ethyl ether were determined between about 33° and 215° at a constant pressure of 40 atm. The results show that the fall in the specific heat above the critical temperature is gradual and that the properties which are presumably characteristic of the substance in the state of vapour are not attained until the temperature is 10° or 15° above the critical temperature. L. F. Gilbert.

Physical chemistry of complex salts. I. Transport numbers of copper salicylate. W. E. Hamer and C. R. Bury (J.C.S., 1927, 333—338).—The solubility of copper salicylate in water at 25° is 10·19 g./litre, and the transport number of the cation 0·628, the latter being determined by a conductotitrimetric method. In neutral solution, the salt ionises as a simple cupric salt, which is not incompatible with its behaviour as a ψ-acid in alkaline solution. H. F. Gillbe.

Hydrate problem. V. Electrolytic transport of water in N-solutions. H. Remy (Z. physikal. Chem., 1926, 124, 394—404; cf. A., 1926, 1201).—Determinations by the diaphragm method (A., 1926, 128) of the transport of water in the electrolysis of N-potassium chloride solutions yield concordant results only if no correction for possible electro-endosmosis is applied. The value so obtained agrees satisfactorily with the one obtained by the method depending on the use of a reference substance. With sodium chloride, the electro-endosmotic effect may not be entirely negligible, but in general it is undesirable to attempt to apply any correction. Values for the water transport have been obtained by the diaphragm method for N-solutions of the chlorides of potassium, sodium, lithium, and ammonium, of the iodides of barium, strontium, calcium, and magnesium, and of hydroxylamine hydrochloride. R. Cuthill.

Variable resistance. O. Maass and J. H. Mennie (J. Amer. Chem. Soc., 1927, 49, 451—452).—The resistance of a mercury column of constant length is varied by the insertion of a glass rod which produces a change in the cross-section of a part of the column. The advantages claimed are ease and cheapness of construction, great sensitivity (about 0·0003 ohm), low temperature coefficient, and complete absence of contact resistance. S. K. Tweedy.

Electrical conductivity of mixtures of sulphuric and phosphoric acids. J. Meyer and A. Pawletta (Ber., 1927, 60 [B], 551—553).—A perfectly normal, mutual influence of the dissociation relationships is observed in mixtures of sulphuric and orthophosphoric acids. Contrary to Pessel (A., 1923, ii, 396), there is no evidence of chemical reaction between the acids. H. Wren.

Electrical conductivity of the system arsenious bromide–ethyl ether. M. Ussanowitsch (Z. physikal. Chem., 1926, 124, 427—435).—The specific conductance of solutions of arsenious bromide in ether at 18° rapidly increases with increase in the bromide concentration up to 95%, after which it quickly falls to the value for the pure bromide. For high concentrations, the temperature coefficient is positive, but decreases with falling concentration, and for concentrations below about 75% is negative. This effect does not appear, however, to be due to interaction between solvent and solute. If the molecular conductivity is calculated with reference to the bromide as the electrolyte, the conductivity-concentration curve has two maxima, but if the ether is taken as the electrolyte, a normal curve results. R. Cuthill.

Conduction process in glass. I. Replacement of the sodium by alkali metals and ammonium. C. B. Hurd, E. W. Engel, and A. A. Vernon (J. Amer. Chem. Soc., 1927, 49, 447—450).—Cells of the type (+) carbon|metallic salt (fused or in solution)|incandescent electric lamp (−) were investigated. The replacement of sodium by sodium in the glass of the lamp-bulb produced little or no effect; metallic sodium deposited within the lamp. Potassium penetrated readily, but fracture occurred with any considerable depth of penetration,

unless a potassium glass was used. Replacement of sodium by lithium ions was difficult. The ammonium radical readily penetrated sodium glass, sodium hydride and amide probably being formed; with sufficiently extensive replacement, however, fracture occurred. It is inferred that glass has a mesh-like structure, the mesh being more and more elastic as the temperature rises; the ease of replacement probably depends on the relative sizes of the sodium and replacing ions. S. K. TWEEDY.

Mixed electrical conduction in solid compounds. C. TUBANDT and H. REINHOLD (Z. anorg. Chem., 1927, **160**, 222—236).—The method of determining the mode of conduction through solid bodies (cf. A., 1920, ii, 279; 1921, ii 426) has been modified so that it can be employed at low temperatures. In the β-silver sulphide, previously characterised as a mixed conductor, there is a continuous exchange between ionic and electronic conduction. Increase in the current through the crystal favours electronic conduction, especially at low temperatures; as the temperature approaches the transition point (179°), the effect of change of current vanishes. Electronic conduction increases with rise of temperature, the rate of increase being the greater the smaller is the current; with greater currents, the temperature effect vanishes. An argument is developed in favour of the interchange between the two forms of conduction being bound up with the electron affinity of the ions composing the crystal. H. F. GILLBE.

Absolute values of electrode potentials. M. ANDAUER (Z. physikal. Chem., 1927, **125**, 135—143). —A method of measuring the *P.D.* between metals and solutions is described. A metal gauze of fine mesh (connected to earth) was placed above and parallel with the surface of the solution, and surmounted by a parallel metal plate connected to an electrometer. The air in the neighbourhood of the metal gauze was ionised by a constant radioactive source, consisting of a platinum wire coated electrolytically with polonium. The *P.D.* between the solution and the immersed electrode was determined from measurements of the changes produced in the leakage current from the charged electrometer, on connecting the electrode, plus a known variable potential placed in series with it, to earth. For calibration purposes, a second metal plate was substituted for the solution surface, and it was found that the potential at which the leakage current attained its maximum value varied with the nature of the metal. G. A. ELLIOTT.

Absolute electrolytic solution tension. II. Electrocapillary curve of mercury. K. BENNEWITZ and A. DELIJANNIS (Z. physikal. Chem., 1927, **125**, 144—150).—By plotting the surface tension of mercury in contact with mercurous nitrate against the potential of the electrode $Hg|xN\text{-}Hg_2(NO_3)_2$, the concentration of the mercurous nitrate being simultaneously varied, a parabolic curve is obtained passing through a maximum when the electrode potential has a value $\varepsilon_H = 0.475$ volt. This value corresponds with the absolute null point of the electrode potential determined by the scraping method (cf. A., 1926, 1212). H. TERREY.

General relation between *E.M.F.* and temperature. E. DENINA (Gazzetta, 1927, **57**, 8—15). —By considering the *E.M.F.* as due to contact potentials (Volta effect), a general thermodynamic expression is developed for the influence of temperature on the *E.M.F.* R. W. LUNT.

Electric potentials of ions in salt solutions. J. A. V. BUTLER (Phil. Mag., 1927, [vii], **3**, 213—215). —The electric potential at the surface of an ion due to its ion atmosphere is distinguished from the electric potential of the ion itself, and an equation is deduced which gives the *E.M.F.* of a simple concentration cell without transport and expresses the free energy of transfer of a binary electrolyte from one concentration to another. The results do not affect the general conditions of equilibrium previously obtained (A., 1926, 908). A. E. MITCHELL.

Potentials associated with adsorption and diffusion. O. BLUH (Physikal. Z., 1927, **28**, 16—22).—In a system comprising two blotting-paper electrodes partly immersed in a solution, and across which a potential of 500—600 volts *D.C.* is applied, thereby maintaining a current of 6 milliamp., determinations have been made, by electrostatic methods, of the potentials acquired by small platinum search-electrodes when placed in the solution adjacent to the blotting-paper electrodes. Solutions of simple acids, bases, and salts and of several acidic and basic dyes have been examined. The results are held to afford evidence of the diffusion of the solute due to the electric field. R. W. LUNT.

***P.D.* across a semi-permeable membrane.** N. KAMEYAMA (Phil. Mag., 1927, [vii], **3**, 235—240).— Measurements of the *E.M.F.* of the chain K-amalgam| $K_4Fe(CN)_6(m_1)||K_4Fe(CN)_6(m_2)|$K-amalgam, where || was a copper ferrocyanide membrane and m_1 was constant at $0.05M$, whilst m_2 was varied between 0.025 and $0.0005M$, gave only values the magnitude of which could be explained by the decomposition of the amalgam in the weaker solution. The membrane potential is thus just balanced by the concentration cell with respect to potassium ions at the ends of the chain, and the nullity of the total *E.M.F.* is taken as a verification of the relation $Em = (RT/F) \log_e [K]_1/[K]_2$, where Em is the *P.D.* across a copper ferrocyanide membrane in the system $K_4Fe(CN)_6(m_1)||K_4Fe(CN)_6(m_2)$ and K is the activity of potassium ion. The results confirm the theory of membrane potentials advanced by Donnan (A., 1911, ii, 848) in so far as the solutions examined are not so dilute as to produce disturbing effects due to interaction of the amalgam with water. A. E. MITCHELL.

Reduction potential of sugars. E. AUBEL, L. GENEVOIS, and R. WURMSER (Compt. rend., 1927, **184**, 407—409).—The oxidation–reduction potentials of a number of dyes have been determined, and also those of a number of sugars. Dyes reduced by lævulose have a reduction potential below —0.1 volt and those not reduced above —0.1 volt. Lævulose has a potential of —0.26 volt, dextrose —0.4, lactose —0.325, and galactose —0.235, all at p_H 8.2. L. F. HEWITT.

Overpotential at antimony cathodes and electrolytic stibine formation. H. J. S. SAND, J. GRANT, and W. V. LLOYD (J.C.S., 1927, 378—396).—Overvoltages at antimony cathodes in acid and alkaline solutions have been measured by the direct method and by a commutator method by which the polarisation could be determined during intervals of 1/5000 sec. at various periods after breaking the current. It is shown that at high current densities the direct method gives inaccurate results, on account of irreversible effects, although at low *C.D.* the two methods give sensibly the same results. Extrapolation to zero time from a few measurements at various time intervals is shown to be unsound, and it is suggested that polarisations should be stated together with their time interval. Such measurements correctly represent the average potential over the interval studied.

In acid solutions, small potentials remain practically constant for periods up to 1/140 sec.; at higher *C.D.* the polarisations fall off rapidly with time, but in every case the polarisation during a given period assumes a maximum independent of the *C.D.* The direct method gives an indefinite increase of polarisation with *C.D.* The overvoltage in acid solution increases with dilution to a less extent than is required by the formula applicable to Herasymenko's experiments, which are shown, therefore, to be of a different nature. Further, it is demonstrated that Heyrovsky's theory of the intermediate formation of negatively-charged hydrogen ions during the production of molecular hydrogen, based on Herasymenko's experiments, is untenable.

In alkaline solution, the overvoltage–*C.D.* curves obtained by the direct method show an inflexion corresponding with the maximum given by the commutator method. Similar results are found for solutions containing large amounts of alkali salts, but high *C.D.* are required to establish a constant overvoltage.

No simple relationship between overvoltage and stibine evolution could be established in either acid or alkaline solution. High *C.D.* are required, and the yield appears to depend on the solubility of the cathode in the electrolyte. The best yield in alkaline solution is obtained by blowing a rapid stream of hydrogen over the surface of the cathode, as otherwise the nascent stibine is decomposed by the electrolyte, with the formation of metallic antimony.

H. F. GILLBE.

Phenomena associated with cathode sputtering. T. BAUM (Z. Physik, 1927, **40**, 686—707).—From measurements of the magnetic deflexion of the stream of particles emitted from a silver cathode in an atmosphere at 10^{-2} mm. due to a current of 25 milliamp. at 2500 volts, it is shown that the particles are uncharged silver atoms. The disintegration of the cathode surface under such conditions is discussed at length. R. W. LUNT.

Valve action of silver in aqueous solutions of potassium silver cyanide. A. GÜNTHER-SCHULZE (Z. Physik, 1926, **40**, 879—882).—Silver in potassium silver cyanide does not act as a rectifier for alternating current, because it does not then form a non-conducting film, but it acts as an interrupter for direct current. E. B. LUDLAM.

Combustion of complex gaseous mixtures. III. Inflammation of mixtures of carbon monoxide and hydrogen with air in a closed vessel. G. B. MAXWELL, W. PAYMAN, and R. V. WHEELER (J.C.S., 1927, 297—310).—The application of the "law of speeds" (*ibid.*, 1922, **121**, 365) to the conditions of combustion of gaseous mixtures in closed vessels has been tested. Mixtures of air with hydrogen, carbon monoxide, and mixtures of these two gases in the proportions $3H_2+CO$, H_2+CO, H_2+3CO were exploded in a spherical bomb, with central ignition, the initial pressure being atmospheric. It is shown that the times for explosion for the full range of mixtures $3H_2+CO$ and H_2+CO with air can be calculated from the experimental values for the mixtures of air with hydrogen and the mixture H_2+3CO. The "effective" times of explosion of mixtures of carbon monoxide and air, calculated in the same way, are shown to correspond with the times of explosion when the mixtures are saturated with water vapour at 40°, the concentration of water vapour being then that which has the optimum effect on the speed of combustion of carbon monoxide. The law of speeds is shown to explain the results of Bone, Newitt, and Townend (*ibid.*, 1923, **123**, 2008), and of Fenning (Phil. Trans., 1926, **A, 225**, 331).

W. THOMAS.

Movement of flame in closed vessels : afterburning. O. C. DE C. ELLIS and R. V. WHEELER (J.C.S., 1927, 310—322).—The movement of a flame in a closed vessel consists of two phases : in (i) the proper motion of the flame and that of the unburnt mixture in front of the flame-front have the same direction ; in (ii) the direction of motion of the flame and of the mixture may be opposed, and combustion proceeds under an enhanced and increasing pressure. As (ii) begins, the explosion vessel is re-illuminated near the point of ignition, and this luminescence persists for a considerable time after the flame-front has reached the walls. These phenomena are illustrated by experiments with mixtures of carbon monoxide and air exploded within (*a*) a sphere and (*b*) a cylinder, ignition being central in each case. It is concluded that this luminescence is due to "afterburning," *i.e.*, the combination of molecules of carbon monoxide and oxygen that had escaped combustion while the flame was travelling. This is supported by the results of comparative experiments with mixtures $2CO+O_2+4Z$, in which Z is oxygen, carbon monoxide, carbon dioxide, argon, or helium, the mixtures in each case being saturated with water vapour at various temperatures. The extent to which the reactivity of carbon monoxide is dependent on the presence of water vapour is shown by the results. The duration of the after-burning is longest in the case of argon as a diluent, and its actinic effect is also greatest. W. THOMAS.

Effect of pressure on the limits for the propagation of flame in ether–air. A. G. WHITE (J.C.S., 1927, 498—499).—Limits for the horizontal propagation of flame in ether–air have been determined at pressures between 758 mm. and 90 mm. Reduction

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of pressure results in two separate ranges, of which the one containing more ether, the cool flame range, diminishes rapidly, to disappear entirely before the pressure has been reduced to 360 mm. The lower limit changes little until the pressure is 300 mm., but the upper limit of the " ordinary " range decreases fairly uniformly from 500 to 90 mm. pressure.

W. THOMAS.

Detonation of gaseous mixtures of acetylene and of pentane. A. EGERTON and S. F. GATES (Proc. Roy. Soc., 1927, **A, 114,** 137—151).—Mixtures of acetylene and of pentane vapour with the amount of oxygen required for complete combustion, and diluted with varying amounts of nitrogen, oxygen, argon, carbon dioxide, and excess of fuel, have been studied with the view of finding the position at which a detonation wave develops in a burning mixture of gases under fixed conditions, and the influence on this position of a change of concentration of the combustible gas mixture and of the nature of the diluent gas. The conditions for constancy of the position of detonation are thorough mixture of the gases, uniformity in the bore of the tube, and as little movement in the gas as possible. The degree of humidity of the gas, the method of ignition, and the presence of ions in the gas (from β-rays from radium) have no definite effect on the position. Weak mixtures give much less concordant results than stronger. Oxygen accelerates combustion, detonation occurring considerably earlier than with a similar quantity of nitrogen, and slightly earlier than with a similar quantity of argon (unless the mixture is weak). A large excess of combustible has a great delaying effect, but early detonation occurs with mixtures containing up to double the amount required for complete combustion. Carbon dioxide has a greater delaying effect than nitrogen. These results are discussed and explanations suggested. The velocity of the detonation wave is less in argon and in oxygen than in nitrogen, and greater in mixtures rich in combustible constituents. Dilution decreases the velocity. The conditions governing the establishment of a detonation wave are discussed, and it is supposed that detonation is initiated as a spontaneous explosion of a region of gas, and that, once initiated, the condition for combustion of the detonating type is more readily attained. Detonation appears to take place slightly ahead of the visible combustion front, Le Chatelier's view thus being confirmed. The addition of small quantities of the " antiknock " compounds, lead tetraethyl and diethyl selenide, does not affect the position of detonation at ordinary initial pressures and temperatures.

L. L. BIRCUMSHAW.

Detonation in gaseous mixtures at high initial pressures and temperatures. A. EGERTON and S. F. GATES (Proc. Roy. Soc., 1927, **A, 114,** 152—160; cf. preceding abstract).—The previous investigations on detonation in acetylene and pentane mixtures have been extended to embrace higher initial pressures (up to 10 atm.) and temperatures (up to 240°). A steel explosion tube is used having glass windows through which the explosion flame may be photographed. Explosion is thus effected under conditions somewhat similar to those which hold in an internal-combustion engine. The tendency to detonate increases considerably with increasing initial pressure up to 3 atm., after which further increase in pressure has very little effect (cf. Woodbury, Canby, and Lewis, J. Soc. Aut. Eng., 1921, **8,** 209). At a given initial pressure, rise of initial temperature appears to cause detonation to occur slightly later. Measurements of the velocity of the detonation wave from the slope of the start of the bands of light from the windows show that the velocity decreases with dilution, and is practically unaffected by increase in initial temperature or pressure. The phenomenon of " knocking " in internal-combustion engines is discussed. The " antiknock " lead tetraethyl is found to have no effect on the position of detonation of the mixtures investigated at high pressure, either at normal initial temperature or at 230—240°.

L. L. BIRCUMSHAW.

Gaseous reaction between hydrogen sulphide and sulphur dioxide. H. A. TAYLOR and W. A. WESLEY (J. Physical Chem., 1927, **31,** 216—230; cf. Lewis and Randall, A., 1918, ii, 159; Randall and Bichowsky, *ibid.,* 159).—The velocity of reaction of hydrogen sulphide and sulphur dioxide in pyrex tubes at temperatures ranging from 370° to 730° has been measured by a dynamic method. The velocity is proportional to the surface area of the reaction vessel, the glass acting as a contact catalyst for the reaction. The temperature coefficient decreases with a rise in temperature. At constant temperature, the velocity varies as the partial pressure of the sulphur dioxide and as the 1·5 power of the partial pressure of the hydrogen sulphide.

The mechanism of the reaction advanced is that the reactants are activated by adsorption on the glass surface, and reaction between activated molecules only then follows. Combination in the gaseous state, if any, is very slight. L. S. THEOBALD.

Mechanism of explosive reactions. C. Z. ROSENCRANS (Univ. Ill. Eng. Exp. Sta. Bull., 1926, No. 157, 1—64).—A study of the explosion of mixtures of ethyl ether and air in a cylindrical bomb of constant volume. Differences between the theoretical and experimental flame propagation curves are ascribed to the heat loss. Usually, but not always, the flame fills the bomb when maximum pressure is attained. At the time of the flame arrest, the pressure was in general 25% of its maximum. The flame arrest is believed to be due to the great decrease in density of the gases within and behind the flame front causing a momentary extinction of the flame. The existence of after-burning and the adjustment of chemical equilibrium behind the flame front were demonstrated. An equation expressing the reaction velocity as a function of the pressure is indicated.

CHEMICAL ABSTRACTS.

Chemical action in the electric spark discharge. Ignition of methane. H. F. COWARD and E. G. MEITER (J. Amer. Chem. Soc., 1927, **49,** 396—409).—The chemical changes attending the passage of a stream of regular sparks through air containing 6·8—11·2% of methane were investigated, each spark having just sufficient energy to ignite the mixture in

its path. For a given mixture, the extent of reaction appears to be nearly proportional to the square of the current. The reaction products contain a large quantity of carbon monoxide and some hydrogen, even when an excess of oxygen is present, from which it is concluded that a methane–air flame started by a spark discharge is propagated from the vicinity of the spark by means of the heats of the reactions $CH_4+O_2=CO+H_2+H_2O(gas)$; $2H_2+O_2=2H_2O$ (gas). The methane flame appears to have a small thickness, the first lamina including chiefly the formation of carbon monoxide and water vapour and the last chiefly carbon dioxide. Since the observed volumes of gas which have to be ignited in order to start general inflammation agree approximately with the known facts concerning the energy of the igniting spark and the thermal conductivity and ignition temperature of the mixture, it is concluded that the spark acts mainly, if not entirely, as a source of thermal energy in igniting a gas mixture.   S. K. TWEEDY.

Mechanism of the uniform movement in the propagation of flame. H. F. COWARD and G. W. JONES (J. Amer. Chem. Soc., 1927, **49**, 386—396).— The flame speeds in a series of mixtures of methane with " atmospheres " of air, 20·9% of oxygen and 79·1% of argon, and 20·9% of oxygen and 79·1% of helium were measured in tubes of various diameters and positions. The important factors determining flame speeds appear to be the heat developed in the flame, the heat capacities of the burnt and unburnt mixture, and the rate of chemical reaction. Very little change in flame speed is observed when helium (which has a high thermal conductivity and low absorption for radiant energy) is replaced by argon (which has a low thermal conductivity and a higher absorption for radiant energy; cf. Lind, J.C.S., 1924, **125**, 1867). This is because the energy is carried away so rapidly. It is suggested that the temperature coefficient of the rate of oxidation of methane is relatively small at flame temperatures.
                                    S. K. TWEEDY.

Kinetics of ozonisation by the action of α-particles. W. MUND and J. D'OLIESLAGER (Bull. Acad. roy. Belg., 1926, [v], **12**, 309—326).—The rate of production of ozone in a mixture of oxygen and radon was measured by a comparison method : two reaction vessels, one containing a small quantity of mercury, were connected to the two sides of a differential sulphuric acid manometer. In one vessel, the ozone was destroyed by the mercury as soon as formed, causing a pressure difference between the two vessels from which the rate of ozone production could be calculated. For a given intensity of irradiation, ozone is formed at constant velocity, and it is also destroyed with a velocity proportional to its concentration. The velocity of the two opposing reactions is proportional to the intensity of irradiation. The calculated velocity of the forward reaction corresponds with the formation of one molecule of ozone from each pair of ions formed. H. F. GILLBE.

Velocity of ionic reactions. J. N. BRÖNSTED and R. LIVINGSTON (J. Amer. Chem. Soc., 1927, **49**, 435—446).—The velocities of the reactions
$[CoBr(NH_3)_5]^{\cdot\cdot}+OH' \longrightarrow [Co(OH)(NH_3)_5]^{\cdot\cdot}+Br'$

and $2[CoBr(NH_3)_5]^{\cdot\cdot}+Hg^{\cdot\cdot}+2H_2O \longrightarrow$ $2[Co(H_2O)(NH_3)_5]^{\cdot\cdot\cdot}+HgBr_2$ were investigated in very dilute solution by colorimetric methods. The first reaction exhibits a negative, and the second reaction a positive, salt effect; both these effects are quantitatively accounted for by Brönsted's theory of ionic reaction (A., 1922, ii, 699).   S. K. TWEEDY.

Kinetics of the stages in the Landolt reaction· A. SKRABAL and A. ZAHORKA (Z. Elektrochem., 1927, **33**, 42—63).—A further study has been made (cf. A., 1922, ii, 488; 1924, ii, 543) of the kinetics of the reactions (1) $IO_3'+3SO_3''=I'+3SO_4''$; (2) $IO_3'+6H^{\cdot}+5I'=3I_2+3H_2O$ (Dushman reaction); (3) $3I_2+3SO_3''+3H_2O=6I'+6H^{\cdot}+3SO_4''$, which together constitute the Landolt reaction. Other recent work on the subject, especially that of Thiel (A., 1924, ii, 750) and of Eggert (A., 1925, ii, 407), is discussed and criticised. The validity of Dushman's equation, $-d[IO_3']/dt=K[IO_3'][I']^2[H^{\cdot}]^2$, for reaction (2) and the value of the constant, K, have again been confirmed by measuring the velocity of reaction between iodide and iodate in solutions buffered with acetic acid and acetate and containing arsenious acid to prevent the liberation of iodine. Measurements were also made in solutions buffered with potassium dihydrogen arsenate and disodium hydrogen arsenate, from which the second dissociation constant of arsenic acid is calculated to be $1·6 \times 10^{-7}$ at 25°. Reaction (1) has been investigated in solutions of acidity ranging from p_H 0 to p_H 13, but satisfactory results were obtained only over the range p_H 4—13. Over this wide range, the results can be represented by the equation $-d[IO_3']/dt=0·53 \times 10^6[H^{\cdot}][HSO_3'][IO_3']+0·67 \times 10^{17}[H^{\cdot}]^2[SO_3'']^2[IO_3']$ at 25°, when concentrations are measured in g.-mol./litre and time in minutes. Two terms appear on the right-hand side of this equation, since the sulphite in solution may exist partly as sulphite ion and partly as hydrogen sulphite ion, the proportion of each depending on the acidity of the solution. Over the range p_H 4—5 (solutions of iodate and hydrogen sulphite) the second term is negligible, whilst above p_H 9 (solutions of iodate and sulphite) the first can be neglected. Within the region p_H 5—9 (solutions of iodate, sulphite, and hydrogen sulphite) both terms must be taken into account. The above equation was established from data for the kinetics of the complete Landolt reaction, as well as from measurements on the isolated reaction (1). The derivation of the relationships employed in the interpretation of the experimental results is set out in detail, and the mechanism of reaction (3), which can be regarded as instantaneous in comparison with (1) and (2), is also discussed.   H. J. T. ELLINGHAM.

Kinetics of formate formation. G. BIRSTEIN and N. LOBANOV (Z. anorg. Chem., 1927, **160**, 377—386).—Measurements of the velocity constant of the reaction between formaldehyde and concentrated sodium hydroxide solutions ($6·3N$) in presence of methyl alcohol show that the reaction is probably termolecular, proceeding according to the equation $2H\cdot CHO+NaOH=H\cdot CO_2Na+MeOH$. The results, however, do not preclude the possibility that the reaction is really made up of two consecutive reac-

tions, such as $H \cdot CHO + NaOH = H \cdot CO_2Na + H_2$, and $H \cdot CHO + H_2 = MeOH$; in presence of cuprous or silver oxides, hydrogen is evolved, but no methyl alcohol is formed. The two reaction products, methyl alcohol and sodium formate, have a marked influence on the velocity, the latter accelerating and the former retarding the reaction. The action of the formate is probably secondary, in that it prevents the retarding action of part of the methyl alcohol.   A. R. POWELL.

Reduction of cupric oxide by dextrose and uric acid. E. LÁNYI (Biochem. Z., 1927, **180**, 85—96).—A study of the reduction by Bertrand's method of reduction of cupric oxide in alkaline solution in presence of sodium potassium tartrate by dextrose shows that if the amount of sugar used is plotted against the amount of oxide reduced for a particular time of heating, the curve gives low values for both small (20 mg.) and large (100 mg.) amounts of sugar, but shows a maximum with mean concentrations (50 mg.). The greater the time of heating the more pronounced is the maximum. As the amount of sugar increases, the relative amount of cupric oxide reduced decreases. The same general conclusion is reached when the reduction is carried out in presence of citric acid, glycerol, or dilute acetic acid in place of sodium potassium tartrate, and also when the reduction is effected by potassium urate.
P. W. CLUTTERBUCK.

Kinematographic study of the influence of gelatin on rates of crystal growth and dissolution of copper sulphate. W. G. FRANCE (Third Colloid Symposium Monograph, 1925, 317—323).—The rate of dissolution of copper sulphate crystals in water exceeds their rate of growth from saturated solutions. Gelatin in small quantities depresses growth far more than it does dissolution.
CHEMICAL ABSTRACTS.

Hydrogen electrode in the study of the rate of saponification of oils and fats by aqueous alkali. J. W. McBAIN, H. S. HOWES, and (MISS) M. THORBURN.—See B., 1927, 145.

Thermal decomposition of ozone in presence of chlorine. A. PINKUS and A. RADBILL (Bull. Soc. chim. Belg., 1926, **35**, 451—459).—Kinetic and colorimetric determinations show that a sufficiently small proportion of chlorine considerably retards the rate of decomposition of ozone (cf. Kistiakovski, A., 1926, 34), but that this effect diminishes rapidly with increase of chlorine or rise of temperature, positive catalysis eventually occurring. The same amount of chlorine may therefore act as a stabiliser at one temperature and as a decomposing catalyst at a higher temperature.   L. F. GILBERT.

Acid and salt effects in catalysed reactions. VI. The early stages of an auto-catalysed reaction. General form of the simple auto-catalytic catenary. H. M. DAWSON (J.C.S., 1927, 458—466).—The phenomena associated with the auto-catalytic reaction of acetone with iodine in aqueous solution are interpreted in terms of the joint catalytic activity of the hydrogen and hydroxyl ions. Equations have been derived which show that the reaction velocity falls to a minimum and then increases. The constant which in terms of the simple

hydrogen-ion theory appears to measure the initial hydrogen-ion concentration is found to represent the actual hydrogen-ion concentration at the point of minimum velocity, and this constant affords a means of determining the catalytic coefficient of the hydroxyl ion. The auto-catalytic catenary obtained by plotting v against p_H can be put in a general form by expressing the velocity and hydrogen-ion concentration in terms of those values which characterise the point of minimum velocity. The actual course of the auto-catalytic change is then given by $r = \cosh h$, where r is the reduced velocity and h is the natural logarithm of the reduced hydrogen-ion concentration.   W. THOMAS.

Catalytic properties of mineral waters. I. Behaviour of the water of Wiesbaden hot springs towards hydrogen peroxide solutions. L. FRESENIUS, A. EICHLER, and H. LEDERER (Z. anorg. Chem., 1927, **160**, 273—296).—Hydrogen peroxide solutions are decomposed fairly rapidly by fresh water from the Wiesbaden hot springs, but the rate of decomposition decreases slowly with the time that elapses after taking the water from the springs, owing to loss of carbon dioxide and a corresponding increase in the p_H value. Solutions of ferrous and manganous sulphate containing the same concentration of metal ion as the spring water have a similar catalytic action on hydrogen peroxide solutions, the activity of the manganous ion becoming greater as the p_H value of the solution is increased. In the presence of an alkali or alkaline-earth carbonate or hydrogen carbonate, the rate of decomposition is the same as in the spring water, hence it is probable that the activity of the water is due to its content of ferrous and manganous carbonates (7 parts and 1 part per million, respectively). The activity is destroyed by the addition of hydrocyanic acid, but not by ultrafiltration or by exposure to bright sunlight. The catalytic activity of the ultrafiltrate immediately after filtration is less than that of the unfiltered water, but increases rapidly in 3—4 hrs. to a maximum which is greater than that of the untreated water.
A. R. POWELL.

Catalysis of hydroxylamine. III. A. KURTENACKER and F. WERNER (Z. anorg. Chem., 1927, **160**, 333—346; cf. A., 1924, ii, 250).—Alkaline solutions of hydroxylamine are reduced quantitatively to ammonia by vanadyl salts, quinquevalent molybdenum salts, and ferrous sulphate. In dilute acid solutions, cuprous sulphate and molybdenum (V) sulphate have the same effect, ferrous sulphate and cuprous chloride are without action, and vanadyl sulphate causes a catalytic decomposition into ammonia, nitrogen, and nitrous oxide. In very strongly acid solutions, only the molybdenum salt has any action, causing a slow but eventually complete reduction to ammonia. Cuprous oxide induces a slow catalytic decomposition of alkaline hydroxylamine solutions, the velocity of the action increasing with the alkalinity.   A. R. POWELL.

Catalysis of hydroxylamine. IV. Decomposition of hydroxylamine in alkaline solution. A. KURTENACKER and F. WERNER (Z. anorg. Chem., 1927, **160**, 387—394; cf. preceding abstract).—The

course of the decomposition of hydroxylamine in alkaline solutions depends on the concentration of the alkali, on the temperature, and on the nature of any catalyst present. The higher is the alkali concentration in the absence of a catalyst or in the presence of pumice, platinised pumice, or platinum gauze, the smaller is the proportion of nitrous oxide and the greater the proportion of nitrogen formed. In presence of platinum-black, obtained from platinic chloride and formic acid, the proportion of nitrous oxide formed increases slightly with a rise in the concentration of alkali. Catalysts in general cause an increase in the yield of nitrous oxide for any given conditions, platinum-black being the most efficient catalyst in this respect, giving a yield up to 36% of the weight of hydroxylamine. The mechanism of the reaction is discussed at some length, together with theories that have been suggested by other investigators. The authors' results seem to show that the reaction proceeds through the formation of the labile condensation product, hydroxyhydrazine, which may react with a further molecule of hydroxylamine, giving ammonia and nitrogen, or may decompose into ammonia and nitroxyl, the latter being converted into hyponitrous acid, which decomposes into nitrous oxide and water (cf. Hofmann and Kroll, A., 1924, ii, 546). A. R. POWELL.

Catalytic minimum point. II. Iodine-acetone reaction in buffer solution. M. BERGSTEIN (J. Physical Chem., 1927, 31, 178—186; cf. this vol., 214).—The reactions between iodine and acetone have been studied at 25° near p_H 7 in standard sodium potassium phosphate buffer solutions and near the catalytic minimum point. The experimental curves show a break, the two portions being linear. The values of the velocity constant corresponding with the second portion show a linear relationship to the concentration of hydroxyl ion near p_H 7. These values also decrease with increasing concentration of added potassium iodide. The temperature coefficient, k_{35}/k_{25}, for the second stage of the reaction at p_H 6·813 in phosphate buffer solution is 3·61, a value which is not in conformity with the protion theory of catalysis (cf. Rice, A., 1924, ii, 98). In Walpole's standard acetate buffer solutions, the apparent catalytic minimum point is found to occur at p_H 3·85, a value which is unchanged from 25° to 40°. The reactions between iodine and acetone are complicated and the nature of the catalysis has not been fully established. L. S. THEOBALD.

Catalytic oxidation by complex iron salts. O. BAUDISCH and D. DAVIDSON (J. Biol. Chem., 1927, 71, 501—508).—The oxidation of sodium penta-cyanoammineferroate by molecular oxygen is inversely proportional to the p_H, whilst the reduction of the corresponding ferriate by an organic compound is directly proportional to the p_H. In accordance with this, it is found that, in the catalytic oxidation of hydantoin, isobarbituric acid, and 5-aminouracil, in presence of the complex ferroate, oxidation is more rapid at p_H 12 than at p_H 7, whilst at a given p_H the oxidation is catalysed to an equal extent by the ferroate or ferriate, but is dependent on the concentration of catalyst. C. R. HARINGTON.

Catalytic reduction of nitric oxide and oxidation of ammonia. IV. L. ANDRUSSOV (Ber., 1927, 60, [B], 536—540; cf. A., 1926, 582; B., 1926, 318; 1927, 217).—In comparison with the oxidation of ammonia at a platinum surface, the reduction of nitric oxide proceeds slowly, but by sufficiently prolonging the period of contact, ammonia may be obtained in 90% yield. At 600—650°, nitrogen is formed to an appreciable extent, which increases rapidly with rising temperature and is due mainly to thermal decomposition of the ammonia produced. It is assumed that the primary product of the change is nitroxyl, which is reduced successively to hydroxylamine and ammonia. In consequence of the relatively slow gas current, backward diffusion of the products occurs to a considerable extent. This is of less importance than in the oxidation of ammonia, since the di-imide formed from nitroxyl and ammonia is rapidly converted by the excess of hydrogen into ammonia. H. WREN.

Catalytic oxidation of ammonia. W. W. SCOTT and W. D. LEECH.—See B., 1927, 186.

Catalytic oxidation of cyanogen to nitric oxide, and the intermediate product. S. ABE and R. HARA (J. Soc. Chem. Ind. Japan, 1927, 30, 1—9).—Using platinum gauze as a catalyst, 90—96% of the cyanogen is oxidised by air to nitric oxide without difficulty. The effect of the reaction temperature (550—1000°), the gas velocity (20—802 c.c. per min.), and the concentration of cyanogen (1·5—15·2%) on the yield of nitric oxide is shown diagrammatically. The concentration of cyanogen is generally kept less than 4%. At 450—550°, nitric oxide is suddenly produced and a maximal yield is obtained at 700—800°. When the gaseous product is cooled in a freezing mixture, a small amount of a transparent, yellow, viscous liquid is obtained. In dry nitrogen or air, the liquid slowly polymerises into a solid of the same colour. The products are extremely reactive with moisture and have the empirical formula C_2N_2O. The catalytic oxidation of cyanogen is therefore assumed to proceed as follows, analogously to the oxidation of hydrogen cyanide (cf. Hara and Shinozaki, ibid., 28, 474): $2C_2N_2 + O_2 = 2C_2N_2O$ and $2C_2N_2O + 3O_2 = 4CO + 4NO$. K. KASHIMA.

Methane equilibrium. III. R. C. CANTELO (J. Physical Chem., 1927, 31, 246—250; cf. this vol., 204).—The catalytic decomposition of ethylene is most effectively accomplished by the nickel catalyst specially prepared from nickel oxide (cf. this vol., 20) At 300°, and above, methane is found in the decomposition products, the percentage of methane following one passage over the catalyst, increasing with rise of temperature. Repeated passage of the gaseous products over the catalyst showed that, contrary to Sabatier (A., 1900, i, 534), ethane was stable in presence of a nickel catalyst up to 360°. The constants for the methane equilibrium, obtained by repeated passage of the products of decomposition of ethylene over the catalyst, are in general agreement with those of Mayer and Altmayer (A., 1907, i, 457). L. S. THEOBALD.

Methane equilibrium. IV. R. C. CANTELO (J. Physical Chem., 1927, 31, 417—418; cf. preceding

abstract).—The free energy decrease accompanying the synthesis of methane from amorphous carbon and hydrogen is calculated to be 14,500 g.-cal.

L. S. THEOBALD.

Surface adsorption and velocity of chemical action at gas–solid interfaces. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1927, **23**, 593—606).—For small rates of flow of alcohol vapour over copper, the velocity of catalytic dehydrogenation increases with increase in the rate of flow. This is due to the circumstance that the products of reaction are present in amounts comparable with that of the alcohol, and by being adsorbed on the catalyst reduce its active surface. Increase of the velocity of passage of the vapour above a certain critical value produces no further increase in the rate of reaction. The relation previously deduced (A., 1926, 582) between the partial pressure of the reactant in a mixture and the fractional reaction velocity has been verified for mixtures of alcohol vapour with water, acetone, and benzene. An expression is derived for the effect of mixture of vapours on the temperature coefficient of reaction. The temperature coefficient is increased or reduced according as the heat of desorption of the reactant is less or greater than that of the diluent. Water present in alcohol proves to have little effect on the temperature coefficient of the reaction.

R. CUTHILL.

New method of measuring the absolute surface area of a metallic catalyst. F. H. CONSTABLE (Nature, 1927, **119**, 349).—If S is the surface area of the metal forming M g. of oxide spread over the china-clay support (cf. A., 1926, 1195), C is the electrical conductivity of the film, q the equivalent air thickness of the oxide film, μ the refractive index of the oxide, ρ the density of the oxide, k_c the initial value of the constant in the parabolic law for the fall in conductivity, and k_q the initial value for the equivalent air thickness, then $S/M=\mu\sqrt{k_c/k_q}/\rho C$. For an activated copper film (k_c and k_q being measured at 210°) : $k_c=1\cdot52\times10^{-2}$; $k_q=2\cdot50\times10^{-10}$; $\mu=2\cdot85$; $C=0\cdot64$; $\rho=6\cdot3$, whence $S/M=6900$ cm.² per g. of film, the corresponding area of the support being 3200 cm.² Reduced copper has a surface activity at least 8000 times as great as that of electrolytic copper.

A. A. ELDRIDGE.

Chemical yield in the decomposition of carbon dioxide at low pressure by the condensed spark. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1927, **184**, 522—525).—The decomposition of carbon dioxide at low pressures by the condensed spark increases with the voltage, and is influenced by the size and shape of the containing vessel and the position of the electrodes. The yield rises to a maximum and falls as the capacity of the discharge circuit decreases, and for a particular capacity the maximum yield falls off slightly as the pressure increases. These results agree with the authors' theoretical conclusions (this vol., 19), the yields indicating that the electrical energy is only partly used as chemical energy.

J. GRANT.

Electrolytic production of copper acetate. V. PAVLOV and B. BROUNSE (Ukraine Chem. J., 1926, **2**, 311—320).—Copper acetate is formed as an in-

tensely dark green powder, deposited on the anode, by the electrolysis of sodium acetate, which must be absolutely neutral. A larger concentration of the latter increases the yield. The best results are obtained when a current density of 16—20 amp. per dm.² is used. Addition of sodium chloride to the solution increases the yield of copper acetate at first, but if too much is added, a double salt, probably CuCl,NaCl, is deposited. By these methods, up to 95% of the copper dissolved during electrolysis is deposited as the salt $Cu(CH_3\cdot CO_2)_2,H_2O$.

E. ROTHSTEIN.

Electrolytic deposition of chromium from aqueous chromic acid solutions. E. LIEBREICH (Z. Elektrochem., 1927, **33**, 69—72).—Polemics arising out of a comparison of results obtained by Müller (A., 1926, 913) with previous work by the author (ibid., 1921, ii, 678; Z. Elektrochem., 1923, **29**, 208).

H. J. T. ELLINGHAM.

Electrolytic deposition of chromium from aqueous chromic acid solutions. E. MÜLLER (Z. Elektrochem., 1927, **33**, 72—76).—Reply to Liebreich (cf. preceding abstract).

H. J. T. ELLINGHAM.

Separation of bismuth by rapid electrolysis in acid solution. A. JÍLEK and J. LUKAS (Chem. Listy, 1927, **21**, 49—55).—Electrolysis may be carried out at 1·6—2·4 volts and with a current of 0·1 amp. in a platinum crucible with a rotating anode, if the solution contains specified quantities of fluoboric acid and sucrose. Directions are given for preparing solutions from the chloride, sulphate, and nitrate; the nitrate gives the best results. The bismuth is deposited as a coherent, lustrous layer, which may be dried and weighed in the usual manner.

S. I. LEVY.

Action of electrolysis. R. SAXON (Chem. News, 1927, **134**, 118).—Pyrites immersed in a solution of ammonium chloride and sulphate subjected to electrolysis, the pyrites being in contact with the carbon cathode, loses weight, iron passing into the solution and copper sulphide being deposited. S. I. LEVY.

Chemical method for the standardisation of ultra-violet light. J. E. MOSS and A. W. KNAPP (Brit. J. Actinotherapy, 1927, reprint).—The authors' "uroxameter" is described. The photolysis of oxalic acid sensitised by uranium acetate serves as a measure of the intensity of ultra-violet radiation below 320 $\mu\mu$, and quantitative determinations can be carried out with permanganate (cf. B., 1925, 906; J. Amer. Chem. Soc., 1925, **47**, 718). Recent alternative methods are discussed (Lancet, 1924, 745; 1925, 1205). The evidence concerning the decrease in ultra-violet output of mercury-vapour lamps with time is reviewed and found to be very conflicting. The decrease in intensity of ultra-violet light from three atmospheric-pressure mercury-vapour lamps has been measured in terms of the photochemical reaction described above. The results obtained are so divergent that it is obvious that photochemical work should be controlled by a calibrated actinometer.

It is shown that a thickness of 2·2 mm. of the reacting solution absorbs all rays shorter than 321 $\mu\mu$,

and evidence is quoted that the method provides a means of determining the efficacy of a light source in respect of either the "stimulative" region (280—330 $\mu\mu$) of the spectrum or the "bactericidal" region (below 300 $\mu\mu$). The method has been applied to testing the fastness of coloured papers to light, with the result that fading and uroxameter titrations increased proportionately. The transparency of glasses to ultra-violet radiation has been tested and the following percentage transmission of ultra-violet light obtained : with no cover 100, with silica 0·11 inch thick 85·7, with "vitaglass" 0·065 inch thick 20·8—24·4, with window glass 0·082 inch thick 3·1, with "calorex" glass 0·208 inch thick 0, and with non-actinic glass 0·2 inch thick 0·4. These results bear out the claims made for the materials.

<div style="text-align:right">R. A. Morton.</div>

Kinetics of the photochemical formation of hydrogen chloride. N. Thon (Z. physikal. Chem., 1926, **124**, 327—351).—The rate of photochemical combination of hydrogen with chlorine in mixtures containing a considerable excess of one reactant and also in mixtures containing oxygen has been measured. Bodenstein and Dux's empirical expression for the reaction velocity, $d[HCl]/dt = k[Cl_2]^2[H_2]/([H_2]+n[Cl_2])$, (A., 1913, ii, 1039) expresses the results satisfactorily, n having the value 0·1. For mixtures containing oxygen, k is inversely proportional to the oxygen concentration, whilst n remains unchanged, from which it is concluded that the rate of reaction is given by $d[HCl]/dt = k_1[Cl_2]^2[H_2]/\{([H_2]+k_2[Cl_2])[O_2]\}$, where $k_1 = k[O_2]$, and $k_2 = n$. From the form of this expression it appears probable that the reaction is brought about by chlorine atoms or Cl_3 molecules rather than by activated normal molecules. This view is supported by the fact that no reaction occurs in yellowish-orange or orange-red light, *i.e.*, light of wave-lengths for which there is no question of the dissociation of molecules into atoms. For gas mixtures containing a considerable excess of hydrogen, the Bodenstein–Dux expression reduces to the simpler form $d[HCl]/dt = k[Cl_2]^2$. Even if the gases are in approximately the stoicheiometric proportions, the simplified formula still holds, although the order with respect to chlorine is less than 2. No evidence of a retarding effect of a considerable excess of hydrogen such as Chapman has described (J.C.S., 1923, **123**, 3062) has been observed. R. Cuthill.

Photochemical influence of bromine on ethyl maleate and ethyl fumarate. F. Wachholtz (Z. physikal. Chem., 1927, **125**, 1—48; cf. Eggert, A., 1924, i, 368).—In carbon tetrachloride solutions containing bromine, the number of molecules, φ, of ethyl maleate transformed into the fumarate per quantum of energy absorbed is independent of the concentrations of the bromine and ester; for light of wave-length 4360 Å. it is 295 at 21°. It is independent of the light intensity, but varies with the wave-length, *e.g.*; between 15° and 24° $\varphi_{4360} = 1·85\varphi_{5370}$, approximately. φ is influenced by temperature, *e.g.*; $\varphi_{25°} = 2\varphi_{21.5°}$, approximately. Mercuric bromide and mercurous nitrate and perchlorate also sensitise the photochemical change of maleic to fumaric esters. The additive reaction ethyl fumarate or maleate$+$bromine$+h\nu \longrightarrow$ dibromodiethyl succinate has also been studied. Here α, the number of added molecules of bromine per quantum absorbed, is 8·2 at 21° for light of wave-length 4360 Å. in presence of 0·1N-bromine. It is independent of light intensity and of ester concentration and also of the ratio present of fumaric to maleic ester. α varies with the wave-length ($\alpha_{4360} = 2\alpha_{5370}$, approximately) and with the temperature ($\alpha_{24.5°} = 2\alpha_{15°}$, approximately). These results are in accordance with theoretical considerations.

<div style="text-align:right">L. F. Gilbert.</div>

Photochemical decomposition of potassium persulphate. II. J. L. R. Morgan and R. H. Crist (J. Amer. Chem. Soc., 1927, **49**, 338—346; cf. this vol., 216).—Absorption data for aqueous solutions of sulphuric acid, potassium persulphate, sulphate, and hydroxide are given; with the exception of the hydroxide, the absorbed regions do not appreciably overlap the regions absorbed by the persulphate solutions. The wave-length most effective in producing photochemical decomposition of the latter is at about 230 mμ; the calculated value is 1 μ. The velocity of the decomposition is proportional to the intensity of the light, and the temperature coefficient is about 1·18, independent of any small acidity or alkalinity. These facts indicate that the reaction is purely photochemical and is unaccompanied by side or intermediate reactions.

<div style="text-align:right">S. K. Tweedy.</div>

Photolysis of potassium nitrate. D. S. Villars (J. Amer. Chem. Soc., 1927, **49**, 326—337).—The quantum efficiency of the decomposition of potassium nitrate solutions in ultra-violet light ($KNO_3 = KNO_2 + O$) is very small for wave-lengths greater than 280 $\mu\mu$; for $\lambda 254$ $\mu\mu$, it increases regularly with increasing p_H until p_H 9·9 is attained, after which it remains constant. Contrary to the statement of Anderson (A., 1924, ii, 408), the decomposition of potassium nitrate in polychromatic light proceeds at a rate which gradually diminishes with time, and there is no evidence of the attainment of equilibrium; complete decomposition can be obtained. Warburg's iodometric titration of nitrites (Z. Elektrochem., 1919, **25**, 334) gives good results if the solution is rendered completely alkaline before aëration with carbon dioxide.

<div style="text-align:right">S. K. Tweedy.</div>

Chemical actions of radiations. P. Villard (Compt. rend., 1927, **184**, 309—312).—The phenomena recorded by de Moncetz (this vol., 218) may be due to the diffusion into the spectrograph of a few rays of the ultra-violet region capable of destroying the X-ray image. Up to a point, the infra-red rays compensate for this and produce the effect of protection, but beyond this they react on the plate in an almost normal fashion. This neutralising effect between red and violet rays is supported by experimental evidence, except that here silver bromide is modified by X-rays in place of ordinary light-sensitive silver chloride or bromide. J. Grant.

Chemical actions of radiations. P. Villard (Compt. rend., 1927, **184**, 352—354; cf. preceding abstract).—Experiments are described illustrating the different natures of the latent images produced by X-rays and by ordinary light. These images may

co-exist and vary in their properties according to the atomic level influenced by the radiation, the frequency of which is the determining factor. A gelatin–silver bromide plate solarised by light is not solarised for high-frequency radiations, and retains a considerable portion of its sensitiveness for the latter.

J. GRANT.

Photographic action of β-rays. C. D. ELLIS and W. A. WOOSTER (Proc. Roy. Soc., 1927, A, **114**, 266—276).—Investigation of the blackening, D, of Ilford X-ray plates by beams of practically homogeneous particles taken from the continuous β-ray spectrum shows that the blackening is independent of the time of exposure, t, when the product It ($I =$ intensity) is constant. Thus the reciprocity law holds for homogeneous β-rays, as for heterogeneous (cf. Bothe, Z. Physik, 1922, **8**, 243). Independently of the time of development or the velocity of the β-particles, D is connected with It by the equation $D = C \log (It/\tau + 1)$, where C and τ are constants. This formula is identical with that holding for the blackening by X-rays. The effect of varying either the time of development or the velocity of the particles is only to alter the constants; it appears, moreover, that C is determined only by the time of development, and τ by the velocity of the particles. The fact that the characteristic curve is linear only up to a density of about 0·3, whereas Bothe (loc. cit.) obtained a curve linear up to $D = 1$, is discussed. L. L. BIRCUMSHAW.

Nature of base exchange. E. BIESALSKI (Z. anorg. Chem., 1927, **160**, 107—127).—A very full discussion is given of the group of phenomena classed as base exchange. Four main divisions are recognised: (1) Purely chemical; it is shown experimentally that the exchange of base of negatively-charged substrates of non-zeolitic nature is of this nature. (2) Ionic exchange, e.g., permutites; the possibility of anion exchange is demonstrated. (3) "Sorption exchange." (4) Pure adsorption.

H. F. GILLBE.

Lixiviation of copper minerals with ammonia and preparation of arsenical compounds of copper. G. FESTER and F. BERTUCCI.—See B., 1927, 143.

Existence of silver hydroxide in the solid state. H. L. RILEY (Phil. Mag., 1927, [vii], **3**, 459—464).—Precipitated silver oxide, even after prolonged desiccation, contains about 0·3% of water. Silver oxide which has been subjected to prolonged drying will combine with carbon dioxide to the extent only of about one twentieth of the equivalent. On the basis of Baker's work with dry substances, this is taken as an indication that the water present in the silver oxide cannot be free, but must be present as silver hydroxide, which probably exists as a surface film on the grains of silver oxide, and has the probable formula $3Ag_2O,2AgOH$. This view is in accord with theories of crystal structure. A. E. MITCHELL.

Sodium aurous thiosulphate. J. K. GJALDBÆK (Dansk Tidsskr. Farm., 1927, **1**, 251—297).—Sodium aurous thiosulphate, $Na_3Au(S_2O_3)_2,2H_2O$, is best prepared by a modification of the method of Fordos and Gelis, which is based on the reaction $4Na_2S_2O_3 + AuCl_3 = Na_3Au(S_2O_3)_2 + 3NaCl + Na_2S_4O_6$. A solution of hydrochloroauric acid is treated with sufficient N-sodium hydroxide solution to furnish an excess of 0·1 mol. of sodium hydroxide after the whole of the acid has been converted into the sodium salt; a greater excess of alkali is to be avoided, as it causes the product to be contaminated with sulphate, from which it is difficult to free it subsequently. The resulting solution is added in small portions to a solution of sodium thiosulphate containing an excess of 5% above the theoretical amount required by the equation. The addition of each portion of gold solution produces a brown coloration (probably due to the transitory formation of an auric sodium thiosulphate), which slowly disappears on keeping; decolorisation must take place before further portions of gold solution are added. The speed of the reaction can be accelerated by the addition of sodium iodide as a catalyst, the effect being due to the formation of aurous iodide as intermediate compound. Sodium aurous thiosulphate can also be prepared directly from aurous iodide and sodium thiosulphate, but the preparation of the former substance in a pure state is difficult. Solid sodium aurous thiosulphate (97—99% pure) is obtained in 95% yield by diluting the above solution until it contains 4—5% of the salt and adding four times its volume of 96% alcohol. The product can be further purified by dissolving in water, adding a little sodium thiosulphate, and reprecipitating with alcohol as before. In order to remove sulphate, 50 g. of the salt dissolved in 800 c.c. of water are treated with sufficient barium chloride to precipitate the sulphate, and thereafter with N-sodium carbonate, added 2 c.c. at a time, until a filtered portion gives no test for barium. From 2 to 5% of sodium thiosulphate are added to the filtrate and the salt is precipitated with 96% alcohol. The solid salt, especially if prepared by precipitation from a slightly alkaline solution containing a 5% excess of sodium thiosulphate, is quite stable. The water of crystallisation contained in the salt is completely expelled at 150—160°. Its aqueous solution is ionised almost entirely into $Na^{\cdot}$ and $Au(S_2O_3)_2'''$ ions; further dissociation into S_2O_3'' and $Au^{\cdot}$ ions takes place only to a very small extent. No metallic gold can be precipitated by ferrous sulphate, oxalic acid, or stannous chloride, but hydrogen sulphide and alkali sulphides precipitate aurous sulphide. Attempts to determine the p_H value of the solution gave results varying from 7·5 to 5·6, the irregularities being ascribed to the presence of impurities.

H. F. HARWOOD.

Formation in the unstable state of two hydrates of magnesium platinocyanide. P. GAUBERT (Compt. rend., 1927, **184**, 527—529; cf. this vol., 312).—Crystals of the hydrates of magnesium platinocyanide containing two and seven molecules of water have been prepared. The former, which are colourless, appear inside a drop of solution on the edges of which the latter are forming as a result of rapid crystallisation below 30°. The dihydrate takes up water to form the red heptahydrate, and the action is reversed in presence of a drying agent. The absence of colour from solutions of platinocyanides may be due to the presence of the dihydrate.

J. GRANT.

Soluble alkaline-earth aluminates. H. T. S. BRITTON (J.C.S., 1927, 422—424).—The hydrogen-ion concentration curves of the reactions between solutions of alkaline earths and aluminium salts show that these earth solutions dissolve aluminium hydroxide in exactly the same way as does sodium hydroxide to form soluble aluminates the compositions of which may be represented $M(AlO_2)_2$. The delayed precipitation of aluminium hydroxide from chloride solutions is due to the tendency of chlorides to promote the formation of colloidal solutions. The data are discussed in connexion with the presence of aluminium in soil solutions. W. THOMAS.

Volatility of the compounds formed by heating barium sulphate with sulphuric acid. F. KRAUSS. —See B., 1927, 139.

Formation of mercuric cobaltothiocyanate $(Hg[Co(CNS)_4])$ in presence of nitric acid as a qualitative test for mercury. B. ORMONT (Z. anal. Chem., 1927, 70, 308—310).—One part of mercury in 1250 parts of water can be detected by the blue coloration or precipitate of mercuric cobaltothiocyanate (Orlov, A., 1906, i, 406) produced when there are added to 2 c.c. of the solution 2 c.c. of concentrated nitric acid and 2 c.c. of a solution of potassium cobaltothiocyanate. This latter solution is prepared by dissolving 10 g. of cobalt nitrate hexahydrate and 10 g. of potassium thiocyanate in 30 c.c. of water. Copper and lead interfere and bismuth may cause the precipitate to be violet in colour. R. CUTHILL.

Volatility of borax. I. M. KOLTHOFF (Nature, 1927, 119, 425—426).—Although it is now admitted that fused borax is volatile (cf. A., 1926, 813; Briscoe, Robinson, and Stephenson, A., 1925, ii, 619; 1926, 1007) the loss of sodium oxide is negligible if the heating is not continued for more than 2 hrs.

A. A. ELDRIDGE.

Anhydrous borates of silver, barium, and zinc. F. DE CARLI (Atti R. Accad. Lincei, 1927, [vi], 5, 41—47).—Investigation of the temperatures of devitrification of systems composed of boric anhydride mixed with either silver oxide, or barium oxide, or zinc oxide demonstrates the existence of the following anhydrous borates : $Ag_2O,4B_2O_3$; BaO,B_2O_3 ; $BaO,2B_2O_3$; $BaO,3B_2O_3$; $BaO,4B_2O_3$; $2ZnO,B_2O_3$, and ZnO,B_2O_3. T. H. POPE.

Cobaltiboroammine. C. DUVAL (Compt. rend., 1927, 184, 333—334).—On subjecting a solution of cobalt acetate, boric acid, and ammonium acetate to a current of air and adding ammonia, the non-electrolyte *cobaltiborotriammine*, $[CoBO_3,(NH_3)_3]$, is obtained as a violet, insoluble powder. The compound, for which μ is lower than for cobaltinitrotriammine, is very stable ; at 120°, it loses ammonia to form cobalt oxides and cobaltous borate.

E. W. WIGNALL.

Action of acids and alkalis on fuller's earth. F. WELDES.—See B., 1927, 127.

Europium compounds. M. P. B. SARKAR (Bull. Soc. chim., 1927, [iv], 41, 185—189).—Some new salts of europium have been prepared. The *oxalate*, $Eu_2(C_2O_4)_3,10H_2O$, is converted into a pentahydrate at 100° ; the *nitrate* melts in its water of crystallisation

$(6H_2O)$ at 85° ; *normal tartrate*, $Eu_2(C_4H_4O_6)_3,5H_2O$; *acid tartrate* is $HEu(C_4H_4O_6)_2,2H_2O$, corresponding with the analogous bismuth and gadolinium compounds. The *acetate* $(4H_2O)$ loses $1H_2O$ when kept over sulphuric acid ; it is more soluble in water than the corresponding gadolinium salt. The *cyano-platinate* is $Eu_2[Pt(CN)_4]_3,21H_2O$; the amount of water of crystallisation is characteristic of the yttrium group, but the colour (yellow, with pale blue fluorescence) is characteristic of the cerium group. When kept in a vacuum, the salt loses $3H_2O$ and forms an unstable red salt with a green fluorescence, characteristic of the yttrium group. Prolonged desiccation produces $Eu_2[Pt(CN)_4]_3,H_2O$. The following compounds were also prepared : *citrate* $(+5H_2O)$; *acetylacetonate*, $Eu(Me·CO·CH_2·CO·Me)_3,3H_2O$; *iodate* $(+5·5H_2O)$; *carbonate* $(3H_2O)$; *orthophosphate* $(+4H_2O)$; and double *potassium europium oxalate*, $KEu(C_2O_4)_2,2H_2O$. S. K. TWEEDY.

Electrometric study of the precipitation of silicates. H. T. S. BRITTON (J.C.S., 1927, 425—436).—The reactions between silicic acid and sodium hydroxide and the alkaline earths in solution and those between solutions of metallic salts of typical bases and sodium silicate have been investigated by means of the hydrogen electrode. The reactions of silicic acid with the strong bases have a pronounced effect on the hydrogen-ion concentration of the solutions. The precipitates obtained by the interaction of a solution of sodium silicate, $Na_2O,2·16SiO_2$, and metallic salts, except that from calcium chloride, contain less silica than that required to form the metasilicates. The hydrogen-ion concentration at which these silicate precipitates begin to be formed in solutions of p_H less than 7 are approximately those at which their corresponding hydroxides separate. The silicate precipitates obtained from alkaline solutions appear when the hydrogen-ion concentrations have not been reduced to the extent required by their respective hydroxides. The results are discussed in relation to the question of soil acidity.

W. THOMAS.

Separation of metals from the gas phase. A. E. VAN ARKEL (Chem. Weekblad, 1927, 24, 90—96).—Metals of high m. p., of which easily dissociated volatile compounds are known, can be obtained in a pure coherent form by heating a filament of the metal in an atmosphere of the vapour of the compound. The best results are obtained if the compound be prepared in the evacuated apparatus in which the metal is to be deposited ; for this purpose, an excess of the (impure) metal is enclosed with the other element of the compound to be employed, which thus acts merely as a carrier to convey the metal from the impure powder to the pure deposit. Titanium, zirconium, hafnium, thorium, molybdenum, tungsten, iron, and nickel are readily purified in this way. By suitable modification, nitrides, carbides, and alloys may also be prepared. S. I. LEVY.

Constitution of titanium peroxide. R. SCHWARZ and W. SEXAUER (Ber., 1927, 60, [B], 500—502).—Titanium peroxide is prepared by the cautious addition of titanium sulphate solution to a mixture of potassium sulphate and hydrogen peroxide at 0°,

and precipitation with alcohol followed by treatment of the precipitate with ice-cold water. The product is dehydrated by the successive action of acetone, absolute ether, and light petroleum at 0°. Determinations of titanium dioxide, active oxygen, and water indicate the constitution $(OH)_2TiO\text{---}O_2H_2$ or $(OH)_2Ti:O{<}^{OH}_{OH}$ for the peroxide.   H. Wren.

Action of acetic acid on red lead. Formation of basic lead peracetate. C. Brückner.—See B., 1927, 139.

Complex salts of lead iodide and alkali halides. L. J. Burrage (Chem. News, 1927, **134**, 85—86).— Unlike the analogous double chloride and bromide, the iodide $KI,PbI_2,2H_2O$ (cf. A., 1926, 908) is very soluble in acetone. Addition of ether to the solution causes the separation of a yellow oil which coagulates to a flocculent precipitate. The latter, like the original compound, deepens in colour on keeping over calcium chloride, presumably through loss of part of the water of crystallisation; no iodine is liberated on fusion at 300°. The double *salts* $PbI_2,NH_4I,2H_2O$ and $PbI,NaI,2H_2O$, behave similarly.
S. K. Tweedy.

Oxidation of ammonium sulphide. M. P. Applebey and J. A. Lanyon.—See B., 1927, 131.

Oxidation of phosphorus vapour at low pressures. M. Bodenstein (Z. Physik, 1927, **41**, 548—550).—The experimental work of Chariton and Walta (this vol., 122) is discussed briefly, with particular reference to the significance of pressure measurements.   R. W. Lunt.

Formation of phosphorus sulphides from phosphine. L. Delachaux (Helv. Chim. Acta, 1927, **10**, 195—197).—If phosphine is heated with more sulphur than is necessary to convert the whole of the hydrogen into hydrogen sulphide, the reaction can be represented by the equation $2PH_3+nS=3H_2S+P_2S_{n-3}$, and above 450° the ratio of the pressure, P, to the temperature (Abs.), T, is constant, indicating that at this temperature the reaction is complete. With smaller relative amounts of sulphur, the ratio P/T continues to increase for some time, even at 500°, and the gaseous phase consists of a mixture of hydrogen sulphide and phosphine, and the solid phase of phosphorus, which is gradually covered with phosphorus sulphide formed by interaction between the constituents of the gas phase. The reaction between hydrogen sulphide and phosphine does not occur with any appreciable velocity below 320°, and above this temperature the ratio P/T increases continuously with the time, no equilibrium being reached. The products are hydrogen and a variable mixture of phosphorus sulphides.
R. Cuthill.

Pervanadic acid. J. Meyer and A. Pawletta (Z. physikal. Chem., 1927, **125**, 49—97).—The action of hydrogen peroxide on acidified solutions of vanadic acid has been studied by colorimetric, conductometric, and titration methods. Acidification of solutions of "*iso*polyvanadic acid" (formed by decomposing the hydrogen peroxide in a solution of vanadic acid in the former substance) results in the formation

of a pale yellow solution of VOX_3, in which vanadium acts as a cation. The further action of hydrogen peroxide causes the formation of a red solution of the salt VO_2X_3, in which the oxygen atoms are bound to the vanadium atom by the peroxide linking; this reaction is slow. A bright yellow solution of maximum conductance in the system *iso*polyvanadic acid+hydrogen peroxide contains the *ortho*-acid, $H_3[V(O_2)O_3]$, where again two of the oxygen atoms are joined to the vanadium atom by the peroxide linking. The sensitivity of the hydrogen peroxide-vanadic acid colour test is discussed (cf. A., 1926, 1020). The evidence of previous authors for the existence of " pervanadic acid," HVO_4, is adversely criticised.   L. F. Gilbert.

Activation of oxygen (especially during the oxidation of aldehydes). W. P. Jorissen and P. A. A. van der Beek (Rev. trav. chim., 1927, **46**, 42—46).—A brief discussion of the mode of activation of oxygen during various oxidation reactions.
H. F. Gillbe.

Oxidation of bivalent chromium in aqueous solution in absence of air. A. Asmanow (Z. anorg. Chem., 1927, **160**, 209—221).—Pure stable salts of bivalent chromium may be prepared as follows : an aqueous solution of chromic sulphate is reduced electrolytically at a lead cathode in an atmosphere of hydrogen. When reduction is complete, the chromous sulphate is precipitated by alcohol, washed with alcohol and ether, and dried in a current of hydrogen. The product is stable in dry air.

In presence of platinum as catalyst, the solution oxidises with evolution of hydrogen, the reaction being unimolecular. Sulphuric acid accelerates the reaction, but to a less extent than does hydrochloric acid. In absence of platinum, there is no measurable evolution of hydrogen with sulphuric acid present even in concentrations up to $10N$, although the reaction takes place to some extent in presence of hydrochloric acid. In the latter case, the oxidation is accelerated by ammonium chloride.

Very rapid oxidation takes place in ammonia solution, especially in presence of ammonium salts, which prevent the precipitation of chromous hydroxide. The reaction is then no longer unimolecular, but is autocatalysed by the chromic ion. H. F. Gillbe.

Reactions of chromates at high temperatures. II. The system $CaO\text{-}Cr_2O_3\text{-}O_2$. K. S. Nargund and H. E. Watson (J. Indian Inst. Sci., 1926, **9A**, 149—167; cf. B., 1924, 670).—The dissociation pressures of calcium chromate between 900° and 1030° are recorded. At 1030° and less than 20 mm. pressure, the *compound* $Cr_2O_3,CrO_3,3CaO$ is obtained; at about 2 mm., the *compound* $3Cr_2O_3,2CrO_3,8CaO$; at lower pressures, the final *product* is $2Cr_2O_3,CrO_3,5CaO$, which has no appreciable dissociation pressure at 1030°. The dissociation pressure of chromium trioxide increases very rapidly between 210° and 250°, exceeding 400 mm. at 250° (cf. Simon and Schmidt, A., 1926, 697). In presence of lime, calcium chromate forms a *basic chromate*, $2CrO_3,3CaO$, which is comparatively easily decomposed, yielding the *compound* $Cr_2O_3,6CrO_3,12CaO$, which has a dissociation pressure of 270 mm. at 910°, and decomposes

to the *compound* $Cr_2O_3,4CrO_3,9(?)CaO$, dissociation pressure 22 mm./920°. The latter is also formed when the oxide and chromate are heated together in air; it is black, and soluble in dilute acids, and decomposes to the *compound* $Cr_2O_3,3CrO_3,6CaO$, which has no measurable dissociation pressure at 1030°. Mixtures of calcium chromate and chromic oxide yield the *compound* $Cr_2O_3,2CrO_3,2CaO$, dissociation pressure 150 mm./1030°, the final product of dissociation being a chromite. Mixtures of lime and chromic oxide heated in a vacuum yield the *chromite*, $2Cr_2O_3,2CaO$, from which treatment with acid removes lime, yielding the *compound* $2Cr_2O_3,CaO$. Mixtures of calcium oxide and chromic oxide absorb oxygen rapidly on heating, the gas being afterwards liberated at the same temperature; it is suggested that an intermediate compound is formed and decomposed. S. I. LEVY.

Chlorides of bivalent molybdenum, tungsten, and tantalum. V. Tritantalum hexachloride or tantalum trichloride? K. LINDNER (Z. anorg. Chem., 1927, **160**, 57—63).—The formula of Ruff and Thomas (A., 1925, ii, 1187) for the oxychloride $Ta_3Cl_7O,3H_2O$ requires the tantalum to function as a tervalent element; the author's formula for the same compound, prepared in the same manner, is $H(Ta_3Cl_7,H_2O),3H_2O$, the tantalum being bivalent. Analogous oxychlorides are not found among the complexes formed by other elements in groups V and VI, and the analytical figures are more in favour of the aquo-chloro-acid formula. Although a large amount of evidence for the latter formula is put forward, the question of the valency of the tantalum in this compound cannot be regarded as settled. H. F. GILLBE.

Complex chlorides of tervalent molybdenum. W. R. BUCKNALL, S. R. CARTER, and W. WARDLAW (J.C.S., 1927, 512—521).—The ammonium, potassium, rubidium, and cæsium salts of the types R_3MoCl_6 and R_2MoCl_5,H_2O have been prepared and the above formulations confirmed. From solutions of low acid concentration a complex salt of molybdenyl monochloride, $KMoOCl_2,3H_2O$, was prepared. By the action of liquid ammonia on diammonium molybdenum pentachloride, a very unstable mono-ammine was isolated, $(NH_4)_2[MoCl_5,NH_3],H_2O$. Conductivity measurements and the preparation of the molybdenyl disalicylate, phthalate, and oxalate have been carried out to study the hydrolysis of the complex chlorides. The compound $MoCl_2OH$ is one of the products of the hydrolysis. W. THOMAS.

Reduction of alkali tungstates. W. T. SPITZIN (J. Russ. Phys. Chem. Soc., 1926, **58**, 474—490).—A brief *résumé* of former work on the preparation and properties of the alkali tungstate "bronzes." In the present work, the reduction by hydrogen of normal sodium tungstate, $Na_2WO_7,2H_2O$; sodium bitungstate, $Na_2W_2O_7$; paratungstate, $Na_{10}W_{12}O_{11},28H_2O$; tetratungstate, $Na_2W_7O_{13}$; metatungstate, $Na_2W_4O_{13},10H_2O$, and pentatungstate, $Na_2W_5O_{16}$, and the conditions governing the formation and decomposition of the blue, violet, red, and yellow sodium tungstate "bronzes" were investigated. The reduction of the acid tungstates occurs in two

stages: between 600° and 700° excess of oxygen present as tungstic oxide (WO_3) is quantitatively removed, and sodium tungstate and metallic tungsten are left. At 900°, this is further reduced, all the sodium and oxygen being volatilised. These reactions can be employed for the quantitative analysis of complex tungstates. The various bronzes can be obtained by cautiously heating the corresponding acid tungstate in hydrogen, when an atom of oxygen is removed. On further heating in hydrogen at 550°, the blue bronze loses successively 3 mols. of tungstic oxide, giving in turn the violet, red, and yellow bronzes. The theoretical equations for the various reactions are found to agree closely with the quantitative experimental results. M. ZVEGINTZOV.

True and pseudo-halides. A. HANTZSCH and H. CARLSOHN (Z. anorg. Chem., 1927, **160**, 5—26).—The halogens form true and pseudo-salts comparable with ordinary true and pseudo-acids and salts. The class to which a particular salt belongs depends on the position of the metal in the ionisation potential series. Stable pseudo-halide salts are recognised by their indifference to sulphuric acid, whereas unstable pseudo-salts react chemically in the same manner as true salts, although their physical properties are those of pseudo-salts. Metals of variable valency probably form only pseudo-salts. The limit of the ionisation potential between true and pseudo-chlorides of the univalent metals lies between sodium and lithium chlorides, whilst for iodides, and probably also for bromides, the limit is lower, on account of the greater tendency of hydriodic acid towards salt formation. The limit for iodides lies below lithium. For halides of bivalent metals, the limit is below manganese, and possibly between calcium and magnesium. Little is known with certainty about the alkaline-earth metal halides. The most positive of the tervalent metals, aluminium, and probably all ter- and multi-valent metals form exclusively pseudo-halides. Only sodium, potassium, rubidium, and cæsium give exclusively true salts. A study of the change from pseudo- to true salt in the case of the cobalt halides shows that the change is dependent on the nature of the solvent, the halogen, and the salt concentration. Of all the solvents investigated, acetone shows the least tendency to bring about the change from pseudo- to true salt. H. F. GILLBE.

Reactivity of manganese dioxide in the solid state. F. DE CARLI (Atti R. Accad. Lincei, 1926, [vi], **4**, 577—581).—Heating curves, obtained by means of the apparatus previously used (A., 1924, ii, 758), are given for mixtures of manganese dioxide with other oxides. The curve for the pure dioxide shows (1) a slight retardation beginning just above 400° and ending with a pause at 530°, and (2) a halt at 930—940°. Mixtures of 1 mol. of barium, strontium, and calcium oxide with 1, 2, or 3 mols. of the dioxide exhibit indications of exothermic reactions beginning at 150—250°. Of oxidisable oxides, cuprous oxide begins to react with manganese dioxide at 380° and stannous oxide at 180°. Chromium sesquioxide does not react, but the behaviour of other anhydrides towards the dioxide is similar to that towards lead dioxide. Magnesium, zinc, cupric,

cadmium, and lead oxides are without influence on the decomposition of manganese dioxide. From these results, together with those obtained with lead dioxide and by Hedvall with barium dioxide (A., 1919, ii, 26), it is evident that these three dioxides are able to react in the solid state with a large number of varied compounds.   T. H. POPE.

Influence of high temperatures on metallic sulphides in a carbon-tube furnace. M. PICON (Bull. Soc. chim., 1927, [iv], **41**, 189—191).—Sulphides of iron (FeS), manganese (MnS), and chromium (CrS) are more resistant to the action of carbon in a vacuum at high temperatures than the corresponding oxides. Ferrous sulphide loses its sulphur completely at 1600°; the influence of the presence of carbon on the reaction was not verified (Bogitch, B., 1926, 194). Manganese sulphide volatilises unchanged at 1375° and will dissolve up to 15% of graphite without apparent change. When this sulphide is prepared in a vacuum furnace by Mourlot's method (A., 1899, ii, 747), a product contaminated with metallic carbide is obtained; the pure substance may be obtained by the action of hydrogen sulphide on the oxide at 900°. Chromium sulphide melts with dissociation at 1550°.
                                   S. K. TWEEDY.

Behaviour of precipitated ferric hydroxide towards hydrocyanic acid ; a case of differences in reaction connected with several stages of ageing in a metallic hydroxide. E. WEDEKIND and HEINRICH FISCHER (Ber., 1927, **60**, [*B*], 541—544; cf. Wedekind and Albrecht, A., 1926, 1196). —Freshly-precipitated ferric hydroxide gradually becomes black in contact with 4% hydrocyanic acid, whilst the liquid acquires an intense reddish-violet colour, the cause of which has not been ascertained. With increasing age of the ferric hydroxide, the colour becomes less intense, and is scarcely perceptible with a preparation 20 days old. With specimens which have been preserved during 5—6 weeks, the blackening of the solid or violet colour of the solution is not observed. The black precipitate consists of a mixture of Prussian blue and ferric hydroxide; it is also formed when freshly-prepared ferric hydroxide is brought into contact with Prussian blue. The ageing of the hydroxide affects only the first phase of the change, viz., the reduction of ferric to ferrous hydroxide by hydrocyanic acid.
                                   H. WREN.

Existence and structure of the disulphides NiS$_2$ and CoS$_2$. W. F. DE JONG and H. W. V. WILLEMS (Z. anorg. Chem., 1927, **160**, 185—189).—A discussion of the existence and structure of CoS$_2$ and NiS$_2$.   H. F. GILLBE.

Reduction of ruthenium trichloride by sodium amalgam. H. REMY and T. WAGNER (Ber., 1927, **60**, [*B*], 493—499; cf. Remy, A., 1921, ii, 209).— During the reduction of ruthenium trichloride in hydrochloric acid solution by sodium amalgam, a green coloration is observed between the initial sepia-brown and ultimate dark blue, which is more pronounced as the acidity of the solution is increased. This point corresponds with the absorption of one equivalent of hydrogen for each ruthenium ion

(when allowance is made for the quantity used in the subsidiary reduction of trichloride to metal), and thus points to the existence of the dichloride in solution. Further addition of sodium amalgam causes the production of dark blue ruthenium monochloride, reaction being incomplete in strongly acid solution, but quantitative in more dilute solution. It thus appears that bivalent ruthenium as free ion and in weak complexes is very unstable and readily passes into the univalent condition, and that ruthenium dichloride, in itself colourless or feebly coloured, gives a dark green additive compound with hydrochloric acid.   H. WREN.

Dehydration of the crystallohydrates of metallic salts. M. A. RAKUSIN and D. A. BRODSKI. —See B., 1927, 187.

Preparation of pure hydrogen for hydrogen electrodes. E. BILMANN and A. L. JENSEN (Bull. Soc. chim., 1927, [iv], **41**, 147—151).—The hydrogen is prepared by the electrolysis of $4N$-sodium hydroxide solution, a gold cathode being used; the gas contains 0·129 vol.-% of oxygen, which is removed by passing over platinum gauze at 400°. If the gauze is replaced by platinised asbestos, the hydrogen is contaminated with silicon hydride. The presence of the latter probably explains some of the "active" hydrogens which have been prepared.
                                   S. K. TWEEDY.

Preparation of small quantities of potassium, rubidium, or cæsium. J. H. DE BOER, P. CLAUSING, and G. ZECHER (Z. anorg. Chem., 1927, **160**, 128—132).—A new method is described for the preparation of small quantities of potassium, rubidium, or cæsium which does not involve heating at high temperatures in metal vessels. In the usual method of preparation, by distilling a mixture of a salt of the required metal with calcium or magnesium, the product is always contaminated with the alkaline-earth metal. Barium azide, prepared by distilling azoimide into barium hydroxide solution, decomposes below 200°. By mixing solutions of barium azide and the chloride of the required alkali metal, evaporating to dryness in a vacuum, and heating the solid residue, the pure alkali metal distils over. A simple type of apparatus is described, by the use of which contamination of the distillate by barium may be avoided.
                                   H. F. GILLBE.

Manufacture of Glauber's salt and of anhydrous sodium sulphate from residue left after the concentration of potassium salts. K. KOELICHEN.—See B., 1927, 186.

Preparation and m. p. of pure phosphorus di- and tri-iodides. F. E. E. GERMANN and R. N. TRAXLER (J. Amer. Chem. Soc., 1927, **49**, 307—312).—Pure crystalline phosphorus tri-iodide, m. p. 61·0°, may be prepared by the interaction of the requisite amounts of white or red phosphorus and iodine in a carbon disulphide solution from which all free sulphur has been removed. In a similar way, using white phosphorus, the di-iodide, m. p. 124·5°, may be obtained. When free sulphur is present, the products have low m. p., probably owing to the presence of a compound which may be P$_4$S$_3$I$_2$ (cf. A., 1925, ii, 1087).   S. K. TWEEDY.

Quantitative spectral analysis. H. KONEN (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1108—1114).—A critical review. Quantitative spectral analysis may be carried out in three general ways : (a) measurements of relative intensities for one or more emission or absorption lines, (b) the variability of single known lines in respect of breadth and symmetry under defined conditions, (c) the influence of foreign substances on the spectrum of a specified element under defined conditions. The methods proposed are reviewed in some detail, and the author sees little reason to abandon the view set forth in Kayser's " Handbuch " that quantitative spectral analysis is beset with pitfalls. Many procedures have been proved to be trustworthy by actual trial, but great caution needs to be shown in attempts to extrapolate outside the tested range of validity. The great advantages and some disadvantages of the Hartley–de Gramont method of using the " ultimate " lines are pointed out. Quantitative spectral analysis still lacks a general scientific basis, although its value in practical control is emphasised.

R. A. MORTON.

Calibration in quantitative spectral analysis. A. REIS (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1114—1116).—The spark spectra above solutions of lead nitrate were photographed and the intensities of the persistent lines determined. The darkening of the plate by these lines was measured by a registering photometer, and the results were plotted against the lead content of the solutions. A series of fairly straight lines was obtained in this way in respect of the rays 4057, 3639, 2613, 2662, 3738 Å. A similar calibration showed that the conditions of excitation (which are specified) yield trustworthy information on the lead content of gold and of gold–copper alloys.

R. A. MORTON.

Quantitative X-ray spectral analysis. P. GÜNTHER (Ver. Ges. deut. Naturforsch. Aerzte, 1926, **19**, 1118—1124).—A review of methods and achievements. The method of X-ray quantitative analysis is still of specialised application, but the diverse nature of the materials for which it has been adapted makes the outlook promising. R. A. MORTON.

Solutions for colorimetric standards. I. Spectral transmission curves for some aqueous solutions containing organic indicators or inorganic salts. M. G. MELLON and F. D. MARTIN (J. Physical Chem., 1927, **31**, 161—177).—The transmittancies of various aqueous solutions have been determined, and the percentage transmittancy-wave-length curves are given for the following cases : aqueous solutions (containing 1% of hydrochloric acid) of cupric sulphate, ferric chloride, and cobaltous chloride at concentrations $M/4$, $M/8$, $M/16$, and $M/32$; aqueous solutions (containing 2·8% of ammonia) of ammonium chromate, tetramminocupric sulphate and chloropentamminocobaltic chloride, and of potassium dichromate, all in various concentrations; and aqueous solutions of the commercial indicators, methyl-orange, thymol-blue, bromophenol-blue, methyl-red, bromocresol-purple, bromothymol-blue, phenol-red, cresol-red, 2 : 4-dinitrophenol, m- and p-nitrophenols, phenolphthalein, cresolphthalein, chlorophenol-red, bromophenol-red, chlorobromophenol-blue, and bromocresol-green at various p_H values.

A discussion of the data is reserved for a future communication. L. S. THEOBALD.

Flocculation of troublesome precipitates in analysis. W. CLAYTON (Analyst, 1927, **52**, 76—77).—Such diverse systems as calcium carbonate in saturated sodium chloride solution, talc and clay suspensions in water, certain solids in strongly acid and alkaline media, and precipitates such as mercuric tungstate will give coarse flocs which settle readily if a small quantity of starch solution (1 part per 250 parts of flocculated dry solid), which is adsorbed by the floc, is added. So-called soluble starch is not suitable. Where alkalinity is not objectionable, an alkaline starch solution is recommended.

D. G. HEWER.

Qualitative chemical analysis by the dry method. D. MIGLIACCI and C. CRAPETTA (Annali Chim. Appl., 1927, **17**, 66—74).—Descriptions are given of the distinctive colorations obtained when salts of each of 32 elements are mixed with nitrate of either cobalt, nickel, or chromium and a strip of filter-paper is immersed in the mixed solution, dried, and burnt. This method of carrying out the test is preferred to that in which a stick of charcoal is used.

T. H. POPE.

Precise volumetric analysis. K. O. SCHMITT (Z. anal. Chem., 1927, **70**, 230—235).—The use of weighing burettes and weighing tubes for measuring the reacting substances and of colorimetric methods for determining the exact end-point of a titration is described, and the magnitude of, and means of correcting errors introduced by weighing in air are discussed. A. R. POWELL.

Change of p_H in buffer mixtures at varying temperatures. I. M. KOLTHOFF and F. TEKELENBURG (Rec. trav. chim., 1927, **46**, 33—41).—The p_H of a large number of acid and alkaline buffer mixtures has been determined at various temperatures between 10° and 60°. The p_H of ordinary buffer mixtures does not change appreciably over this range, except in the case of glycine–sodium hydroxide and boric acid–sodium hydroxide mixtures. H. F. GILLBE.

Influence of sodium chloride on the colorimetric determination of p_H. L. B. PARSONS and W. F. DOUGLAS (J. Bact., 1926, **12**, 263—265).—The salt error of the sulphonephthalein series of indicators has been measured at 1, 2, and 3M-salt concentrations. By subtracting 0·3 unit from the observed colorimetric p_H values, results may be obtained for solutions containing 6—18% of salt which conform with electrometric data.

CHEMICAL ABSTRACTS.

Analytical investigation of water samples from the Dead Sea. R. KOEFOED and G. HAUGAARD (Compt. rend. Lab. Carlsberg, 1926, **16**, No. 9, 3—51).—Samples from the same depth have approximately the same composition, but the values of d and solute contents appear to vary periodically during the 24 hrs. The halogen, calcium, magnesium, and potassium contents are each linear functions of d; they increase very slowly as the depth increases up to

about 20 m., then very rapidly indeed (halogen expressed as silver equivalent in g. per litre from about 380 to about 505) up to 33 m., then more slowly but more regularly (silver equivalent about 2 g. per m. depth) as the depth increases again. This supports the earlier hypothesis that the level of the lake has been slowly rising during the last century. The sulphate content increases slowly up to about 24 m. depth, and then falls rapidly; the calcium content, on the other hand, rises regularly, and the water is saturated with respect to calcium sulphate, which is precipitated towards the bottom. The water is almost saturated with oxygen near the surface; hydrogen sulphide has a maximum value (1·25 c.c. per litre) at about 25 m. depth. A single bottom sample (83 m. depth) was found to contain much solid calcium carbonate, some gypsum, and a few well-developed sodium chloride crystals.

S. I. Levy.

[Determination of water in glycerol by measuring the] conductance of potassium chloride in glycerol. N. Kameyama and T. Semba (J. Soc. Chem. Ind. Japan, 1927, 30, 10—14).—The conductance of potassium chloride in glycerol–water mixtures increases with the increasing water content in a simple manner. To glycerol (n_D^{15} 1·4716, 98·3%) a certain definite amount of potassium chloride is added; increasing amounts of water, corresponding with n c.c. of water per 100 c.c. of the original glycerol, are added step by step, and the specific conductance, K, is measured at 25°. The electrodes are of smooth platinum. For example, when the amount of potassium chloride is 471 mg. per 100 c.c. the values of n, $K \times 10^5$ (found), and $K \times 10^5$ (calc.) are, respectively, 0, 2·14, 2·24; 0·24, 2·50, 2·33; 0·47, 2·61, 2·42; 1·18, 2·73, 2·71; 2·12, 3·14, 3·10; 3·30, 3·58, 3·63; 4·24, 4·03, 4·08; 5·09, 4·52, 4·50; 6·36, 5·14, 5·17; 7·06, 5·54, 5·55; 8·24, 6·23, 6·23; 9·41, 6·94, 6·94; 10·59, 7·73, 7·66, and 11·77, 8·53, 8·49. The formula $K \times 10^5 = 2·24 + 0·38n + 0·0127n^2$ represents the experimental values within 1·5% from $n=1$ c.c. onwards. The value of the first term and the coefficient of n in the second term are larger when the amount of potassium chloride is larger, within the range of the investigation. K. Kashima.

Determination of bromates in presence of chlorates. F. Fichter and W. F. Tschudin (Helv. Chim. Acta, 1927, 10, 267—275).—For the determination of relatively large amounts of bromate in presence of chlorate, Barnebey's method (A., 1916, ii, 261) is satisfactory, but if the quantity of bromate is small, it is preferable to use Junck's method (B., 1913, 1130). Reduction of the bromate with formic acid, hydrazine, or hydroxylamine with subsequent titration of the bromide formed is satisfactory only when the quantities of bromate and chlorate are approximately equivalent. If chromate is present, it should be precipitated as barium chromate before the iodometric determination of the bromate. Amounts of bromate in chlorate greater than about 0·1% can also be determined by reducing the solution at the b. p. with metallic cadmium and acetic acid and titrating electrometrically with silver nitrate.

R. Cuthill.

Iodometric titrations. III. Reaction between atmospheric oxygen and acid iodide solutions. K. Böttger and W. Böttger (Z. anal. Chem., 1927, 70, 209—213; cf. this vol., 222).—Addition of an equal volume of hydrochloric acid (d 1·19) to an iodide solution exposed to the air results in the liberation of iodine in an amount which depends on the concentration of the iodide and on the time of action. The rate at which the iodine is liberated is considerable during the first 15 min., but then rapidly decreases. For analytical operations, using iodide in strongly acid solutions, both acid and water, therefore, should be freed from air by boiling and an atmosphere of carbon dioxide be maintained in the apparatus in which the titration is carried out.

A. R. Powell.

Microchemical analysis. V. Delicate reaction of sulphites. L. Rosenthaler (Mikrochem., 1927, 5, 27).—The solution is rendered neutral to phenolphthalein by addition of acid or alkali. A few drops of a 1% formaldehyde solution then produce a red colour, due to the liberation of alkali hydroxide by the reaction $H \cdot CHO + Na_2SO_3 + H_2O = H \cdot CH(OH)(SO_3Na) + NaOH$. A distinct rose colour is produced in the presence of 0·1 mg. of sulphite in 0·5 c.c. of $0·1N$-thiosulphate solution.

A. R. Powell.

Determination of sulphurous acid and sulphites. J. Bicskei (Z. anorg. Chem., 1927, 160, 64—66).—The ordinary iodometric determination of sulphurous acid gives inaccurate results in concentrated solution owing to atmospheric oxidation and loss of sulphur dioxide. By employing a more powerful oxidising agent, these errors may be reduced. Standard sodium hypochlorite solution is added to the sulphurous acid and the excess of hypochlorite titrated with iodine. The method is applicable to solutions of high sulphur dioxide concentration.

H. F. Gillbe.

Volumetric determination of sulphates. M. Talenti (Giorn. Chim. Ind. Appl., 1926, 8, 611—612).—Extended use of Müller's method of determining sulphates (A., 1902, ii, 425) is recommended, especially for rapid industrial controls. The benzidine solution is prepared by gently heating and shaking an approximately 2% aqueous suspension of pure benzidine, adding sufficient concentrated hydrochloric acid to give the solution a $0·25N$ acidity, and filtering the deep chestnut liquid thus obtained. The acidity of the filtrate is determined exactly by titration with sodium or potassium hydroxide in presence of phenolphthalein. Precipitation of the sulphate and titration of the filtrate with alkali, as described by Müller, is recommended, and when a heavy metal is present, this should be previously removed by suitable precipitation and filtration. T. H. Pope.

[High values for potassium dichromate in determinations of thiosulphate.] G. Bruhns (Z. anal. Chem., 1927, 70, 128). W. Böttger (Ibid., 311).—Polemical. R. Cuthill.

Determination of nitrogen in nitrates. A. Pizzarelli.—See B., 1927, 187.

Determination of small quantities of nitrate by means of "fornitral." W. Mestrezat and M.

DELAVILLE (Bull. Soc. Chim. biol., 1926, **8**, 1217—1218).—Small quantities of nitric acid may be determined by the addition of nitron formate ("fornitral") in presence of dilute sulphuric acid. The precipitate, which separates quantitatively, is collected, washed with a saturated solution of nitron nitrate, dried, and weighed.   W. O. KERMACK.

Assay of phosphoric acid and the sodium phosphates. A. F. SHIREMAN (J. Amer. Pharm. Assoc., 1926, **15**, 267—276).—Theoretically, trinitrobenzene should be a satisfactory indicator, but its colour change is too gradual. The use of calcium chloride (to precipitate $CaHPO_4$, liberating hydrogen chloride) and phenolphthalein at 55—70° is preferred.
                              CHEMICAL ABSTRACTS.

Iodometric determination of arsenic acid. B. ORMONT (Z. anal. Chem., 1927, **70**, 310—311).—A reply to Rosenthaler's criticisms (A., 1926, 702).
                              R. CUTHILL.

Toxicity of arsenobenzenes. I. Determination of arsenic. G. SENSI.—See B., 1927, 171.

Determination of boric acid in silicates. R. SCHMIDT.—See B., 1927, 189.

Determination of carbon monoxide by titration with silver solution. W. MANCHOT and O. SCHERER (Ber., 1927, **60**, [B], 326—332).—The mixture of gases is agitated with a mixture of $0.1N$-silver nitrate (50 c.c.) and $0.15N$-sodium hydroxide (50 c.c.) to which pyridine (50 c.c.) has immediately been added, thereby giving a clear solution. After contact with the reagent at about 65° during 0·5 hr. with frequent shaking, the solution is cooled, diluted somewhat, acidified with acetic acid (20%), and filtered. The filtrate is strongly acidified with nitric acid and the unused silver is titrated by ammonium thiocyanate in presence of ferric alum. The results are usually slightly low, probably owing to slight dissolution of the precipitated silver in the acetic acid. Carbon monoxide may be determined in this manner in its mixtures with air, hydrogen, methane, or ethylene.

Carbon monoxide reacts quantitatively with gold chloride at 60—70°, according to the equation $2AuCl_3+3CO+3H_2O=2Au+3CO_2+6HCl$, and may therefore be determined either by weighing the precipitated gold or reduction of the unused gold by ferrous sulphate, followed by titration of excess of the latter by permanganate in presence of phosphoric acid. The method is applicable in presence of methane. Ethylene, however, reduces the gold chloride solution, whereas hydrogen restricts the action of carbon monoxide.   H. WREN.

Determination of cyanides and thiocyanates. J. BICSKEI (Z. anorg. Chem., 1927, **160**, 271—272).—Excess of standardised sodium hypochlorite solution quantitatively oxidises a solution of cyanide or thiocyanate to cyanate or cyanate and sulphate, respectively; the excess of hypochlorite is titrated with standard iodine solution.   H. F. GILLBE.

Determination of potassium by the aid of electrometric titration. A. RAUCH (Z. anorg. Chem., 1927, **160**, 77—91).—The potassium is precipitated from a neutral or slightly alkaline solution containing about 30% of alcohol by the addition of an excess of calcium ferrocyanide solution, as the sparingly soluble potassium calcium ferrocyanide. The excess of calcium ferrocyanide is titrated electrometrically with zinc sulphate solution, which is standardised against a solution of known potassium content. The method is applicable in presence of sodium, calcium, magnesium, chloride, and sulphate ions, but cannot be employed when there are present ammonium or barium salts, nitrates, or any substances which form sparingly soluble ferrocyanides or bring about oxidation of the ferrocyanide.   H. F. GILLBE.

Diphenylbenzidine as internal indicator for the titration of zinc with potassium ferrocyanide. W. H. CONE and L. C. CADY (J. Amer. Chem. Soc., 1927, **49**, 356—360).—Diphenylbenzidine may be used as an internal indicator in the titration of zinc salts by ferrocyanides. The latter must contain a small amount of ferricyanide. The blue oxidation compound formed in presence of zinc salts is immediately decomposed when an excess of potassium ferrocyanide is added; this end-point is very sharp. The titration is rapid, and back-titrations may be carried out. No correction is necessary for the amount of indicator present. Diphenylamine may also be used, but in this case a small correction must be applied.   S. K. TWEEDY.

Qualitative micro-analysis and quantitative micro-analysis of cobalticyanides. I. Potassium cobalticyanide as a reagent for the detection of zinc and bismuth. II. The Vanino–Treubert reaction for bismuth. A. BENEDETTI-PICHLER (Z. anal. Chem., 1927, **70**, 257—288, 288—297).—The microchemical method of detecting zinc proposed by Emich ("Lehrbuch der Mikrochemie," Wiesbaden, 1911, p. 102) is best carried out as follows. By addition to the solution of potassium cobalticyanide, the zinc is precipitated as the cobalticyanide, and this is converted into Rinman's green by heating in a current of carbon dioxide. In this way, 0·08 µg. of zinc may be detected. If other metals of the ammonium sulphide group are present, the green colour may be masked. In this case, the zinc is separated by passing hydrogen sulphide into the acetic acid solution, treating the nitric acid solution of the precipitate with bromine and potassium hydroxide, and either electrolysing the alkaline solution or adding to it ammonium sulphide. Alternatively, if large quantities of chromium are not present, the original solution may be treated with an equal volume of a 30% solution of potassium hydroxide, and the centrifugate heated with bromine water, the clear solution finally being electrolysed.

Bismuth salts in nitric acid solution, and in absence of any considerable quantity of chloride ions, give a characteristic crystalline precipitate with potassium cobalticyanide, which, unlike the somewhat similar silver cobalticyanide and the flocculent mercurous salt, is not darkened by a 10% solution of potassium hydroxide, and is distinguished from the corresponding cadmium and zinc compounds in being blackened by an alkaline stannite solution. This test will detect 0·01 µg. of bismuth in absence of large

quantities of other metals. Free sulphuric acid, and mercuric, stannous, calcium, magnesium, and especially lead salts, may alter the crystalline form of the precipitate, and frequently " somatoid " forms (cf. Kohlschütter and Egg, A., 1925, ii, 1035) are produced, these being probably solid solutions. The bismuth may be separated from the mercury, lead, copper, and cadmium by a method resembling the one ordinarily used, except that, instead of precipitating the lead as sulphate, it is precipitated as hydroxide along with the bismuth, and the nitric acid solution of the hydroxides is either tested for the two metals separately, or the bismuth is separated from it as basic nitrate.

II. The separation of metallic lead when solutions containing lead are tested for bismuth with an alkaline stannite solution can be avoided if the reagent is prepared by adding to 5 c.c. of a 10% solution of potassium hydroxide 2 or 3 large drops of a freshly-reduced 15—20% solution of stannous chloride. Even then the test is uncertain if a very large excess of lead is present.

For quantitative micro-determinations, bismuth and lead may be separated from cobalt by precipitation with hydrogen sulphide, the bismuth being separated from the lead as basic nitrate and weighed as trioxide, and the lead weighed as sulphate.   R. Cuthill.

Volumetric determination of copper. D. Köszegi (Z. anal. Chem., 1927, 70, 297—300).—To 50 c.c. of the neutral aqueous solution of the copper salt, which should correspond with not more than 0·15 g. of copper, are added 10 c.c. of a solution of 4 g. of arsenious oxide in 100 c.c. of a 3% potassium carbonate solution. Sufficient of a 10% solution of potassium hydroxide just to dissolve the resulting precipitate is then added. On boiling the solution, cuprous oxide is quantitatively precipitated according to the equation $4CuO + As_2O_3 = 2Cu_2O + As_2O_5$, and after 5 min. is collected and dissolved in a warm ferric sulphate solution, which is finally titrated with permanganate.   R. Cuthill.

Use of liquid amalgams in volumetric analysis. VIII. Determination of copper and tin by reduction with bismuth amalgam. K. Someya (Z. anorg. Chem., 1927, 160, 404—408).—Agitation of a solution of stannic chloride in 5—12N-hydrochloric acid for 10—15 min. at 45° with bismuth amalgam effects complete reduction of the tin to the stannous condition. After removing the amalgam and adding manganous sulphate solution, the stannous chloride may be titrated directly with permanganate. The presence of much sodium chloride causes slightly low results to be obtained, whereas ammonium chloride gives high results. A similar procedure is available for the determination of copper, the cuprous chloride obtained by the reduction being titrated with dichromate, using diphenylamine as internal indicator. All operations should be conducted in an atmosphere of carbon dioxide.   A. R. Powell.

Spectrographic detection and determination of impurities in aluminium and its alloys. R. Adam.—See B., 1927, 143.

Volumetric determination of aluminium in aluminium salts. F. G. Germuth.—See B., 1927, 187.

Determination of alumina in silicate analysis. F. Steinbrecher.—See B., 1927, 141.

Determination of manganese in rich alloys. E. de Luisi.—See B., 1927, 191.

Interaction of manganese salts and permanganates. I. Action of potassium permanganate on manganese sulphate and determination of manganese. J. G. F. Druce (Chem. News, 1927, 134, 145—147).—A review of the literature.

Standardisation of permanganate with electrolytic iron. L. Moser and W. Schöninger (Z. anal. Chem., 1927, 70, 235—247).—Iron deposited electrolytically from solutions containing organic compounds, such as oxalates, invariably contains carbon. Pure, smooth, silver-white deposits may, however, be obtained from a solution containing 100 g. of ferrous chloride crystals, 180 g. of sodium chloride, and 5 g. of boric acid per 100 c.c. The electrolysis is carried out at 90° with a current density of 0·9—1·0 amp./dm.² at 2 volts, using a perforated platinum disc as cathode, separated by a parchment-paper diaphragm from a soft iron anode. Care must be taken that the electrolyte contains no trace of copper, arsenic, lead, manganese, or zinc, or the deposit will be contaminated. Before weighing the iron for standardising the permanganate, the cathode is washed in water, then in 0·05N-potassium hydroxide, and finally in alcohol; drying is effected by waving it over a small flame.   A. R. Powell.

Sensitive reaction for bivalent iron. F. Kröhnke (Ber., 1927, 60, [B], 527—530).—0·01N-Disodium phosphate solution is added gradually with intermittent shaking to a dilute neutral solution of a ferrous salt floating on a solution of oximinoacetophenone in chloroform (1·49 g. in 100 c.c.). The aqueous solution rapidly becomes clear and colourless, whilst a blue coloration develops in the chloroform, which is stable if the supernatant liquid is not too alkaline or acidic. The presence of 0·03 mg. of iron in a litre of water may thus be detected. Cobalt, nickel, manganese, copper, zinc, cadmium, lead, and mercury impart, respectively, reddish-yellow, brown, brown, brown, yellow, yellow, reddish-yellow, and yellow colorations to the chloroform. The cobalt complex salt is distinguished by unusual stability towards acetic acid, so that nickel and cobalt can be detected in the same solution, since initially the brown nickel coloration predominates, but gives place after addition of 25% acetic acid to the reddish-yellow tint of cobalt. The complex salts have the constitution $CH{<}^{N—O}_{CPh:O}{>}X{<}^{O—N}_{O:CPh}{>}CH$ (X=Fe) etc.). The cobalt salt is described in detail (cf. Taylor and Ewbank, this vol., 58).   H. Wren.

Iodometric titrations. IV. Determination of iron. K. Böttger and W. Böttger (Z. anal. Chem., 1927, 70, 214—226; cf. this vol., 330).—The iodometric method for determining ferric salts given in the German Pharmacopœia gives results which are 1—2% too high, owing to the action of the air on the iodide during the long period before titration (1 hr.). Using air-free solutions and working in an atmosphere of carbon dioxide, the reaction between the ferric salt

and the iodide is completed within 15—20 min., no extra iodine is liberated, there is no after-bluing, and accurate results are always obtained. Addition of copper salts does not accelerate the reaction, but leads only to disturbing side-reactions. Thiosulphate is not oxidised under any conditions to sulphate when used for titrating acid iodine solutions, but if an excess is added and this is titrated with iodate, dichromate, or permanganate, a certain amount of sulphate is formed. A solution of chloroamine, which has been recommended as a substitute for iodine in volumetric analysis, slowly loses its strength on keeping.

A. R. POWELL.

Separation of iron, chromium, nickel, manganese, tungsten, and silicon. P. WENGER and (MLLE.) E. ROGOVINE (Helv. Chim. Acta, 1927, **10**, 242—244).—The determination of the above metals when present together in alloys has been studied. If the metal can be reduced to fine shavings, the following method is applicable. The alloy is fused with sodium peroxide in a silver crucible and the product taken up with water. Manganates or permanganates are decomposed by warming with hydrogen peroxide and the solution is filtered. The iron is separated from the nickel and manganese in the hydrochloric acid solution of the precipitate by the acetate method and determined volumetrically with permanganate, and the nickel is precipitated as the glyoxime, whilst the manganese is precipitated as mangano-manganic oxide by boiling with ammonia and bromine. Silica and tungstic oxide in the filtrate are rendered insoluble in the usual way and separated with ammonia, and chromium is precipitated from the final filtrate as the hydroxide, after reduction with alcohol. If the alloy cannot be reduced to fine shavings, the above procedure must be modified as follows. The metal is treated with aqua regia, and any insoluble portion is then fused with sodium carbonate, taken up with hydrochloric acid, and added to the aqua regia solution. Silicon and tungsten are determined as before. Iron, nickel, and manganese are precipitated as the hydroxides by heating the alkaline solution with bromine, and are separated as described above. Chromium is determined in the filtrate in the usual manner.

R. CUTHILL.

Analysis of steels. W. SINGLETON.—See B., 1927, 191.

New reagent for cobalt. P. FALCIOLA (Giorn. Chim. Ind. Appl., 1926, **8**, 612).—When added either as solid or solution to a strongly ammoniacal cobalt salt solution, sodium hyposulphite produces a yellow, orange, ruby-red, or dark red coloration, or a brownish-black precipitate, according to the concentration of the cobalt. One part of cobalt per 100,000 parts of solution is thus detectable. The blue colour of an ammoniacal nickel solution is unchanged by this reagent, but when much cobalt is present, together with nickel, the ammoniacal liquid is violet-blue, and, after treatment with hyposulphite, is decolorised by formaldehyde, which may cause the green colour of the nickel ion to reappear. When the cobalt is accompanied by any of the common metals or by molybdenum, uranium, vanadium, tungsten, titanium, etc., addition of hyposulphite to the ammoniacal

solution and subsequent filtration yield a reddish-yellow liquid, which is deepened in colour by fresh addition of hyposulphite.

T. H. POPE.

Use of liquid amalgams in volumetric analysis. VII. Oxidimetric determination of chromium. K. SOMEYA (Z. anorg. Chem., 1927, **160**, 355—365; cf. A., 1926, 1116).—In 0.3—$2.5N$-hydrochloric acid solution, chromic chloride is completely reduced to chromous chloride by shaking with zinc amalgam in an atmosphere of carbon dioxide. The amalgam is removed in three portions, shaking between each operation, and the solution titrated with ferric chloride, potassium permanganate, or potassium dichromate. For the simultaneous determination of iron and chromium in the same solution after reduction with zinc amalgam, the liquid is titrated with ferric chloride, using thiocyanate as indicator, then with dichromate, using diphenylamine as indicator; the first titration gives the chromium figure and the second the sum of the iron and chromium. For the determination of chromium in steel by the above method, the steel is dissolved in hydrochloric acid, the solution reduced with zinc amalgam, and the chromous chloride titrated directly with methylene-blue. In the method previously described for the determination of chlorate (A., 1926, 1117), the titanium tetrachloride solution recommended may be advantageously replaced by potassium dichromate. Lead amalgam also quantitatively reduces chromic chloride, but only in highly concentrated acid solutions.

A. R. POWELL.

Spectrographic identification of certain elements and the possibility of determining them by the arc spectrum. IV. Tungsten. A. DONATI (Annali Chim. Appl., 1927, **17**, 14—26).—In admixture with silica, 0.01% of WO_3 is detectable with certainty by means of the region of the carbon arc spectrum of wave-lengths 4700—3800 Å. The sensitiveness of this method for detecting tungsten is diminished somewhat in the case of a high-speed steel. A five-fold reduction in sensitiveness is caused by the presence of oxides of manganese. If the material is mixed with trimanganic tetroxide and made into a paste with silica, a more regularly coloured arc is obtained. In this way, samples of Sardinian pyrolusite have been examined qualitatively and the tungsten in them has been determined.

T. H. POPE.

Determination of tin and lead in solder and of tungsten in ferrotungsten by calculations on the Archimedean principle. KOCH.—See B., 1927, 143.

Standardisation of titanous sulphate solutions. W. M. THORNTON, jun., and A. E. WOOD.—See B., 1927, 187.

Separation of titanium from uranium. A. ANGELETTI (Annali Chim. Appl., 1927, **17**, 53—54).—Cupferron (ammonium salt of nitrosophenylhydroxylamine) precipitates titanium, but not uranyl salts (cf. A., 1921, ii, 524). In determining titanium and uranium present together, the liquid is rendered acid, but not excessively so, by means of sulphuric or hydrochloric acid, and the former metal precipitated by excess of the cupferron. The precipitate is collected,

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washed with cold water under slight suction, dried, ignited, and weighed as titanium dioxide. The uranium is determined by precipitation of the filtrate with ammonia solution.　　　　T. H. Pope.

Detection of thorium in the filaments of prepared electric vacuum lamps. P. Selényi (Z. anorg. Chem., 1927, **160**, 318—322).—If the glass bulb of an electric lamp of the vacuum type is coated with tin-foil and then heated at 150° while a potential of 300 volts is maintained between the foil and the filament, the foil being the positive pole, a stream of electrons will pass from the glass towards the filament, thereby introducing into the lamp a small quantity of metallic sodium derived from the electrolytic decomposition of the glass. This sodium acts as a "getter" for the minute traces of oxygen still in the lamp, so that when the lamp is subsequently burnt with 30—40% of its specified voltage while the tin-foil is connected to the positive lead-in wire of the filament through a galvanometer, a current of several milliamp. will flow through the instrument if the filament contains thorium, owing to the electronic emission of the thoria. Non-thoriated filaments give only the slightest trace of emission under these conditions.　　　　A. R. Powell.

Spectrographic identification of certain elements and the possibility of determining them by means of the arc spectrum. III. Vanadium. C. Porlezza and A. Donati (Annali Chim. Appl., 1927, **17**, 3—14).—Application of the method employed previously for uranium (this vol., 124, 184), to mixtures of vanadium pentoxide with silica shows that, for the region of the arc spectrum from 4730 to 3795 Å., the spectrographic sensitiveness of vanadium is greater than that of uranium, two of the lines being visible when the concentration of the vanadium is only 0·001%. Quantitative application of the method to a sample of Colorado carnotite containing 5·09% of vanadium pentoxide gave the result about 5%.
　　　　T. H. Pope.

Iodometric determination of the antimonic ion. A. Travers and Jouot (Compt. rend., 1927, **184**, 605—606).—The determination of the antimonic ion according to the reaction $Sb_2O_5 + 4HI \rightleftharpoons Sb_2O_3 + 2I_2 + 2H_2O$ cannot be rendered complete by the addition of excess of hydriodic acid (produced by the action of potassium iodide and an acid solution of antimonic chloride), since the compound $SbCl_3,3KI,1·5H_2O$ is formed, which dissolves in the dilute hydrochloric acid to produce a brilliant yellow colour and renders the titration of the iodine impossible. The addition of tartaric acid to form tartar emetic is effective but slow. The addition to the solution of potassium iodide (about five times the amount required for the reaction) and about 15% of hydrochloric acid produces the complex $SbCl_3,xHCl$. This inhibits the reversal of the reaction and gives results rapidly and in good agreement with the electrolytic method. Type metal may be attacked by hydrochloric acid containing 13% of bromine.
　　　　J. Grant.

Micro-determination of bismuth. R. Strebinger and E. Flaschner (Mikrochem., 1927, **5**, 12—15).—The nitric acid solution of bismuth nitrate is treated with ammonia until a faint opalescence is produced, solid pyrogallol is added, and the mixture heated for 15 min. on the water-bath. The precipitate is collected in a filter-tube, washed alternately with water and benzene to prevent creeping, dried at 110°, and weighed (cf. Feigl and Ordelt, A., 1925, ii, 442).　　　　A. R. Powell.

Volumetric determination of bismuth, and rapid gravimetric determination of bismuth in ores. G. G. Reissaus (Z. anal. Chem., 1927, **70**, 300—308).—Metallic bismuth is precipitated from its sulphuric acid solution by means of zinc, then dissolved in ferric sulphate solution and sulphuric acid, and the ferrous sulphate formed titrated with permanganate. Alternatively, the metal may be precipitated from solution in hydrochloric acid, not more than 15 g. of bismuth being present in 1000 c.c. of solution, by boiling with copper in an atmosphere of carbon dioxide, the reaction being : $BiCl_3 + 3Cu = 3CuCl + Bi$. The cuprous chloride solution is then titrated hot with potassium bromate, using methyl-orange as indicator. Instead of titrating in this way, the metallic bismuth may be dissolved off from the unchanged copper with hot 30% nitric acid, precipitated with ammonium phosphate, and weighed as bismuth phosphate. The advantage of these methods lies in the convenience of the separation from lead.
　　　　R. Cuthill.

Electrotitration of platinum metals. W. D. Treadwell and M. Zürcher (Helv. Chim. Acta, 1927, **10**, 281—285).—Experiments have been performed on the potentiometric titration of solutions of salts of the platinum metals with a slightly acid $0·01N$-titanous chloride solution. With a solution of palladous chloride containing free chlorine there are sharp *P.D.* changes corresponding with the conversion of the free chlorine into chloride ion, and with reduction to the metal. If auric chloride is also present, there is an intermediate change due to the reduction of the auric ion to the metal. For solutions containing platinic and palladous chlorides, the reduction of the two metals separately is not indicated. The curve for hydrochloroplatinic acid shows the reduction to the metal clearly, and also gives some signs of the reduction to the platinous state, these latter being more pronounced if an alkali iodide is added to the solution. Auric chloride can be titrated in presence of hydrochloroplatinic acid if the two are present in comparable amounts.　　　　R. Cuthill.

Test for platinum. F. Durdik.—See B., 1927, 193.

Combustion furnace with electric heating. C. Gastaldi (Annali Chim. Appl., 1927, **17**, 82—83).—In a furnace of the Heraeus type having a trough 93 cm. long, the use of three movable heating elements with a total length of 76 cm. permits of the regulation of the heating of the combustion tube. T. H. Pope.

Laboratory gas-generating apparatus. W. R. Jewell (Chem. Eng. Min. Rev., 1926, **19**, 78).
　　　　Chemical Abstracts.

Device for adjusting the levelling bulb on a gas-analysing apparatus. A. M. McCollister and C. R. Wagner.—See B., 1927, 127.

Electromagnetic separator for laboratory use. C. J. KSANDA.—See B., 1927, 144.

Still for the purification of mercury. H. S. BOOTH and N. C. JONES.—See B., 1927, 193.

Nephelometric apparatus. H. KLEINMANN (Biochem. Z., 1926, **179**, 301—303).—An improvement in the nephelometer previously described (A., 1923, ii, 429) is effected by using wider glasses which are optically matched. J. PRYDE.

New type of thermometer for cryoscopy of aqueous solutions. H. MENZEL (Z. Elektrochem., 1927, **33**, 63—69).—A description of a mercury-in-glass thermometer graduated in " molar degrees " (1 molar degree=1·860°), designed to simplify work on cryoscopy of aqueous solutions. The zero is fixed at 0° and the scale extends from +0·1 to —3·0 molar degrees. The construction, calibration, and correction of the thermometer are discussed, and results obtained with aqueous solutions of hydrogen peroxide, potassium chloride, and magnesium chloride are tabulated. H. J. T. ELLINGHAM.

Sublimation apparatus. L. BENVEGNIN (Ann. Chim. Analyt., 1927, [ii], **9**, 38—39).—The metal container is held in place by the heating plates (copper plates separated by asbestos) and the weighed watch glass over it is covered by a refrigerator with a concave lower surface the same shape as the watch-glass. Two screws keep the apparatus firmly together. Heating should be so regulated that sublimation is complete in 20 min., or too much water may condense on the sides of the watch glass.
D. G. HEWER.

Apparatus for measuring the diffusion of gases and vapours through membranes. E. E. SCHUMACHER and L. FERGUSON (J. Amer. Chem. Soc., 1927, **49**, 427—428).—The membrane is held in a combined mechanical clamp and mercury seal.
S. K. TWEEDY.

Automatic low-temperature thermostat. O. MAASS and W. H. BARNES (J. Amer. Chem. Soc., 1927, **49**, 360—363).—The light petroleum cooling-bath previously described is improved by the addition of a simple device which automatically adds liquid air to the bath when necessary. Any temperature between that of the room and that of liquid air may be maintained to within 0·1° or less. S. K. TWEEDY.

Simple, automatic cryostat. A. SIMON [with O. FISCHER, R. GLAUNER, and L. EHLING] (Ber.,

1927, 60, [*B*], 568—576).—An apparatus is figured and described by means of which any desired temperature between +20° and —195° may be maintained constant over a long period by means of a liquid boiling under suitably adjusted pressure. For temperatures between +20° and —30°, ether is used, whereas from —30° to —70° ammonia is employed. Methyl chloride can be used to —95°. Acetone and carbon disulphide are unsuitable. The b. p.–pressure curves for all the solvents are given. H. WREN.

Thermal properties of gases. IV. Apparatus for determination of densities of co-existing vapour and liquid phases. E. CARDOSO. **V. Densities of co-existing phases of sulphur dioxide.** E. CARDOSO and E. SORRENTINO (J. Chim. Phys., 1927, **24**, 65—76, 77—82).—IV. The apparatus consists essentially of a calibrated capillary tube having a small bulb at the end containing a piece of iron which can be agitated by a solenoid outside; the calibrated capillary is sealed on to ordinary capillary tubing, which is bent into the form of a U some distance from the calibrated piece, and finally terminates in a large reservoir fitted with a three-way tap. Two such systems are placed side by side, and by means of the taps are connected to the same gas generating apparatus; by taking a pressure reading, the quantity of gas present in each system is determined, and the mercury is then brought to a definite point on the calibrated capillary. The mercury in the U-portions of tubing is now frozen by immersing them in a bath of solid carbon dioxide and alcohol, fluctuations in the position of the mercury meniscus due to slight temperature variations of the reservoir thus being avoided. The calibrated capillaries are now surrounded by a constant-temperature bath, and the volumes of liquid and vapour in each tube read off. Then if P and P_1 are the weights of substance in the respective tubes, V and V_1 the volumes of liquid, and v and v_1 the volumes of vapour, the liquid density $D=(v_1P-vP_1)/(v_1V-vV_1)$ and the vapour density $d=(VP_1-V_1P_1)/(v_1V-vV_1)$.

V. The densities of the co-existing liquid and vapour phases have been determined at temperatures between 13·5° and 157·3°, and the rectilinear diameter so obtained shows no sudden point of inflexion near the critical temperature, as previous workers have supposed, but only a very slight curvature. By extrapolation, the critical density of sulphur dioxide is found to be 0·5240±0·0005. S. J. GREGG.

Mineralogical Chemistry.

Density measurements of the Tyrrhenian Sea. J. THOULET (Compt. rend., 1927, **184**, 385—386).—Systematic density measurements of the Tyrrhenian Sea have shown the existence of four straits communicating it with neighbouring seas, the principal current being that from the Strait of Gibraltar. The Mediterranean Sea is a flooded basin the bed of which consists of active volcanic material constantly producing fresh or slightly salt water, carbon dioxide,

and sulphuric acid. The carbon dioxide is most abundant on the bed of the ocean. J. GRANT.

Fusion of diabase with calcium carbonate. A. S. GINSBERG and X. S. NIKOGOSIAN (Bull. Acad. Sci. Leningrad, 1926, [vi], 679—696).—Various mixtures of diabase from Lake Onega with calcium carbonate have been fused and the resulting mass has been examined on solidification. With small pro-

portions of calcium carbonate, vitreous masses were obtained, but the 1 (carbonate) : 3 (diabase) mixture yielded a glassy basic mass filled with inclusions of acicular diopside. Further increase in the proportion of the carbonate resulted in the crystallisation of melilite, particularly with the 2 : 3 mixture; this corresponds closely in composition with certain melilites and may be represented as a mixture of 53·73% åkermanite, 27·97% sarcolite, 17·06% gehlenite, and 1·26% enstatite. With the help of the diagrams of Buddington (A., 1922, ii, 155) and Scheumann (Centr. Min., 1922, 512), showing the relation between the optical properties of melilites and their compositions, the masses obtained give data agreeing closely with the actual constants for the crystals developed. Further increase in the proportion of calcium carbonate to diabase in the mixture leads to the formation of the skeleton form of melilite, anorthite (?), and rosary-like granules of a highly refractive mineral of olivine character. Commencing with the 8 : 5 mixture, the fused masses, which are homogeneous liquids at 1500°, disperse into powder on solidification, the possibility of the formation of the γ-modification of Ca_2SiO_4 being thus indicated.

Hence enrichment of a diabasic magma with limestone may lead, as Daly (" Igneous Rocks and their Origin," 1914, 29) suggests, through an intermediate nepheline phase, which reacts with augites (cf. Bowen, J. Geol., 1922, 30, Suppl. to No. 6), to the formation of melilite layers, paragenetic, and in nature often connected with nepheline and calcium olivine formations.

T. H. POPE.

Oxidation of sulphides. F. CARMICHAEL (Univ. Toronto Studies, Geol. Series, 1926, 29—36).—The amount of sulphur and metals oxidised when powdered minerals (10 g.) are agitated for 13 days with water (500 c.c.) and oxygen (760 mm., 2100 c.c.), expressed as a percentage of the original mineral, is polydymite 18·50, chalcocite 0·65, pyrrhotite (Cream Hill mine) 0·38, troilite 0·37, marcasite 0·29, pentlandite 0·26, pyrrhotite (Hybla, Ontario) 0·18, pyrite 0·13, stibnite 0·07, sphalerite 0·06, chalcopyrite 0·02, bornite 0·01, galena 0·01.

CHEMICAL ABSTRACTS.

Formulæ of certain Vesuvian silicates. G. CESÀRO (Bull. Acad. roy. Belg., 1926, [v], 12, 350—368).—The analyses of chondrodite, humite, and clinohumite, whilst not entirely accounted for by the mol. formulæ hitherto assigned, may be explained on the assumption that, besides MgF and MgOH, the group Mg_2O enters into the mol. composition. Analyses of nepheline accord with the assumption that this mineral is a basic metasilicate.

C. H. D. CLARK.

Corundum rocks of Val Sessera (Biellese Foot-alps). F. MILLOSEVICH (Atti R. Accad. Lincei, 1927, [vi], 5, 22—31).—The constitutions of various rocks of the Biellese district are described. The white veins of Monte Foggia consist of a corundum plagioclase very similar to plumasite and are associated, besides with pyrites, with an amphibole gabbro containing corundum which is termed *sesseralite* and has the composition :

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
43·18	0·51	28·40	0·98	4·15	4·07

CaO.	Na_2O.	K_2O.	H_2O-.	H_2O+.	Total.
13·82	3·07	0·80	0·27	1·21	100·46

T. H. POPE.

Pyrargyrite and proustite from Sarrabus (Sardinia). M. FENOGLIO (Atti R. Accad. Sci. Torino, 1926, 61, 357—363).—Pyrargyrite from Sarrabus, occurring in groups of blackish-grey or deep red crystals of adamantine metallic lustre, often embedded in calcite, d^{17} 5·80, gave on analysis : Ag 59·61, S 17·89, Sb 22·24, As 0·15, total 99·89%. Proustite from the same district, found in vermilion crystals associated with galena and calcite, d^{17} 5·61, gave : Ag, 65·35; S, 19·49; As, 14·99; total 99·83. Crystallographic measurements were made on both minerals.

T. H. POPE.

Organic Chemistry.

Action of the silent discharge in olefines. N. J. DEMJANOV and N. D. PRIANISHNIKOV (J. Russ. Phys. Chem. Soc., 1926, 58, 462—473).—Under a potential of 12,000—13,000 volts, ethylene yielded a yellow, mobile oil, d_4^0 0·8360, n_D^{17} 1·4580, average mol. wt. 215, consisting of unsaturated hydrocarbons, from C_6H_{12} upwards, which reacted with bromine and dissolved in concentrated sulphuric acid, together with saturated compounds. *iso*Butylene gave a product of mol. wt. 140, d_4^{20} 0·822, $n_D^{5\cdot5}$ 1·4730, containing chiefly the hydrocarbons C_8H_{16} and $C_{12}H_{24}$, with a fraction of b. p. 30—42° consisting, probably, of the compound C_5H_{10}.

M. ZVEGINTZOV.

Catalytic hydrogenation of compounds with conjugated double linkings. G. VAVON and M. JAKES (Bull. Soc. chim., 1927, [iv], 41, 81—94).—A more detailed account of work already published (A., 1926, 934).

Use of Grignard reagents in attempted syntheses of asymmetric allene bases. C. D. HURD and C. N. WEBB (J. Amer. Chem. Soc., 1927, 49, 546—559).—3-Pyridyl methyl ketone is obtained in 60% yield by hydrolysis of ethyl nicotinoacetate (cf. Pinner, A., 1900, i, 409; 1901, i, 176). When treated in ethereal solution with magnesium phenyl bromide, it yields *α-phenyl-α-3-pyridylethylene*, b. p. 204—210°/23 mm., m. p. 78—82°. Treatment of α-phenyl-α-*p*-tolylethylene with bromine in carbon disulphide affords β-*bromo-α-phenyl-α-p-tolylethylene*, b. p. 195—202°/20 mm. The action of magnesium on ethereal β-bromo-α-phenyl-α-1-naphthylethylene, with subsequent addition of *p*-dimethylaminobenzophenone, affords α-phenyl-α-1-naphthylethylene, together with unchanged reactants and a *product*, m. p. 94—105°. The preparation of the above Grignard reagent is greatly accelerated if a magnesium-copper alloy (12·75% Cu) is substituted for the pure

magnesium. When treated with 3-pyridyl methyl ketone, the Grignard reagent yields γ-hydroxy-α-phenyl-α-1-naphthyl-γ-3-pyridyl-Δ^α-butene, m. p. 159—161°. This could not be dehydrated by heating at 160—170°, and the action of acetic anhydride afforded a mixture, m. p. 55—75°, from which a definite compound could not be isolated. Preparation of the Grignard reagent from β-bromo-α-phenyl-α-p-anisylethylene is accompanied by the formation of αδ-diphenyl-αδ-di-p-anisyl-Δ^{αγ}-butadiene, m. p. 218·5—219·5°. Treatment of the Grignard reagent with 3-pyridyl methyl ketone appears to yield the corresponding vinylcarbinol or its dehydration product, the substituted allene, but this could not be purified. β-Bromo-α-phenyl-α-p-tolylethylene and magnesium yield analogously αδ-diphenyl-αδ-di-p-tolyl-Δ^{αγ}-butadiene, m. p. 207—210°. The Grignard reagent does not react with 3-pyridyl methyl ketone. Treatment of α-bromo-β-phenyl-Δ^α-propene with magnesium yields s-dimethyldiphenylbutadiene, α-phenyl-Δ^α-propene, as-phenylmethylacetylene, and solid products. β-Bromo-αα-diphenylethylene and magnesium afford the corresponding Grignard reagent in 68% yield.

F. G. WILLSON.

Derivatives of Δ^{αγε}-hexatriene. C. PRÉVOST (Compt. rend., 1927, **184**, 458—460).—Phosphorus tribromide reacts with Δ^{αε}-hexadiene-γδ-diol to form the αζ-dibromo-Δ^{ββ}-hexadiene, m. p. 85°, b. p. 128°/12 mm., described as the αγ-dibromide by Griner (cf. A., 1893, i, 241). From the dibromide, a diacetate, m. p. 25°, b. p. 155°/12 mm., is obtained, and this, on hydrolysis, gives the corresponding glycol, m. p. 106·5°, b. p. 161°/12 mm. Δ^{αγε}-Hexatriene, when brominated, yields the above dibromide (cf. Romburgh and Dorssen, ibid., 1906, i, 722).

B. W. ANDERSON.

γ-Phenylpropinene and the preparation of true acetylenes with sodamide. M. BOURGUEL (Bull. Soc. chim., 1927, [iv], **41**, 192—193).—A reply to Bert and Dorier (this vol., 47). The lower density recorded by the author for γ-phenylpropinene (A., 1923, i, 430; 1925, i, 770) cannot be due to contamination with unchanged halogen compound. Purification by means of the copper derivative is unsatisfactory, and the operation is unnecessary if the reaction is performed in a solvent (light petroleum) which commences to distil at 100°/12 mm. After decomposition of the solid reaction product with ice, about one fifth of the solvent is distilled off in a vacuum. The hydrocarbon is then liberated and distilled (b. p. 63°/12 mm.). A third hydrocarbon, d^{15} 0·938, which is also regarded as a true phenylpropinene, has recently been obtained.

R. BRIGHTMAN.

Diacetylenic acyclic hydrocarbons, C$_{13}$H$_{20}$ and C$_{20}$H$_{34}$. M. LESPIEAU (Compt. rend., 1927, **184**, 460—462).—An ethereal solution of magnesium in heptamethylene bromide was added slowly to ethereal βγ-dibromo-Δ^α-propene, yielding a dibromide, CH$_2$·CBr·[CH$_2$]$_9$·CBr:CH$_2$, b. p. 180—183°/16 mm., d^{21} 1·274, n 1·497. Alcoholic potassium hydroxide converted this into Δ^{αλ}-tridecadi-inine, b. p. 115·5°/12 mm., m. p. —2° or —3°, d^{21} 0·8262, n 1·454 (copper and silver compounds). Distillation of the tailings of the dibromide yields another dibromide, b. p. 210°/12

mm. (impure), from which a diacetylenic hydrocarbon, C$_{20}$H$_{34}$, m. p. 54—56° (silver derivative), was obtained.

B. W. ANDERSON.

Configurational relationship of d-butan-β-ol to d-lactic acid. P. A. LEVENE, A. WALTI, and H. L. HALLER (J. Biol. Chem., 1927, **71**, 465—469).—d-Butane-αγ-diol (diphenylcarbamate, m. p. 127—129°, [α]$_D^{20}$ +53·24 in alcohol), gave, with hydrogen iodide, α-iodobutan-γ-ol, b. p. 58—60°/0·4 mm., and, with hydrogen bromide, d-α-bromobutan-γ-ol, b. p. 72—76°/20 mm., [α]$_D^{20}$ +2·53°. The iodo-derivative, on reduction, yielded d-butan-β-ol, b. p. 99—104°, [α]$_D^{20}$ +3·54°; phenylcarbamate, m. p. 62°, [α]$_D^{20}$ +8·1° in alcohol. (l-Butan-β-ol gave a phenylcarbamate, m. p. 64—65°, [α]$_D^{20}$ —16·76° in alcohol.) Since d-butane-αγ-diol has already been shown (A., 1926, 937) to be configurationally related to d-lactic acid, the latter must therefore be similarly related to d-butan-β-ol.

C. R. HARINGTON.

Action of thionyl chloride on polyhydric alcohols. R. MAJIMA and H. SIMANUKI (Proc. Imp. Acad. Tokyo, 1926, **2**, 544—546).—By gently boiling ethylene glycol with 8 parts of thionyl chloride for 15 hrs. there is formed glycol sulphite, b. p. 169—172° or 64—66·5°/12 mm., and a little ethylene dichloride. αγ-Dihydroxypropane gives under the same conditions mainly trimethylene dichloride and a little trimethylene sulphite, b. p. 74—76°/14 mm. α-Monochlorohydrin sulphite (α-chloro-βγ-propylene sulphite), b. p. 100°/16 mm., from glycerol, and i-erythritol hydrogen sulphite, m. p. 94—95°, from i-erythritol, are described. l-Arabitol and d-dulcitol give chloroform-soluble products which could not be isolated. From d-mannitol there is obtained in good yield a solid trisulphite,

$$\underset{O\cdot SO\cdot O \quad O\cdot SO\cdot O \quad O\cdot SO\cdot O}{CH_2—CH·CH—CH·CH—CH_2}, b.p.220—228°/3·5mm.,$$
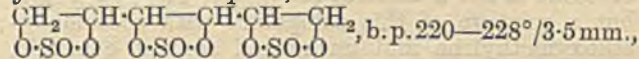
or, in the presence of pyridine after 1·5 hrs., tetrachlorohexylene sulphite, C$_6$H$_8$Cl$_4$·SO$_3$, m. p. 50·5°, b. p. 170—180°/4·5—6 mm., from which by hydrolysis with cold sodium carbonate solution is obtained tetrachlorohexylene glycol, m. p. 67—68° (+0·5H$_2$O), [α]$_D^{18·5}$ +5·9°. Inositol is unattacked by thionyl chloride alone, but in presence of pyridine it gives chloropentahydroxycyclohexane, decomp. 248°, tetrachlorodihydroxycyclohexane, m. p. 186—187°, and tri- and tetra-chloro-benzenes and -phenols.

C. HOLLINS.

Aliphatic polysulphides. D. TWISS (J. Amer. Chem. Soc., 1927, **49**, 491—494).—Treatment of potassium O-ethyl thiocarbonate, in ethereal suspension or concentrated aqueous solution, with sulphur dichloride affords ethyl formate trisulphide, S$_3$(CS·OEt)$_2$, decomp. 120—125°. Sulphur monochloride yields similarly the tetrasulphide, decomp. 120—125°. Potassium O-ethyl dithiocarbonate is converted analogously into ethyl thioformate trisulphide, decomp. 135°, and tetrasulphide, decomp. 135°. Condensation of ethyl chlorodithioformate with potassium ethyl trithiocarbonate in ethereal suspension yields ethyl dithioformate monosulphide, decomp. 100—110°, whilst oxidation of potassium ethyl trithiocarbonate with iodine (cf. Welde, A., 1877, ii, 314) affords the disulphide, decomp. 100—

110°. The *tri-* and *tetra-sulphides*, decomp. 100—110°, are obtained by the action of sulphur dichloride and monochloride, respectively, on potassium ethyl trithiocarbonate. All the above sulphides are non-distillable oils. The tri- and tetra-sulphides of ethyl formate gradually deposit sulphur, with formation of the disulphide. The sulphides of ethyl thioformate are stable, but the tri- and tetra-sulphide are slowly oxidised in air. When heated, they yield carbonyl sulphide and *O*-ethyl dithiocarbonate, but Debus' observations on the decomposition of the disulphide (Annalen, 1852, 82, 253) could not be confirmed. The solubility of the sulphides of ethyl dithioformate decreases considerably with increase in the number of sulphur atoms. The tri- and tetra-sulphides are slowly oxidised by air. When distilled in a vacuum, the tetrasulphide yields the trisulphide and sulphur. The remaining sulphides decompose when heated, mainly with formation of ethyl polysulphides and carbon disulphide. The action of alcoholic ammonia on the sulphides of ethyl formate yields ammonium *O*-ethyl thiocarbonate and ethyl urethane. The ethyl thioformate derivatives yield, similarly, ammonium xanthate and xanthamide, the latter then yielding ammonium thiocyanate. The dithioformate derivatives yield, with ammonia, chiefly ethyl polysulphides and ammonium thiocyanate, the tetrasulphide yielding the trisulphide intermediately.

F. G. WILLSON.

Compounds of bivalent carbon. II. Sodium-oxyethoxymethylene and carbon monoxide diethylacetal [diethoxymethylene]. H. SCHEIBLER (Ber., 1927, 60, [*B*], 554—557; cf. A., 1926, 711).—Contrary to the observations of Adickes (this vol., 228), the product of the action of ethyl formate on sodium ethoxide is not a uniform substance, $CH(OEt)_2 \cdot ONa$, but a mixture of this compound with sodiumoxyethoxymethylene and unchanged sodium ethoxide, which by alternate treatment with ethyl formate and evacuation at 40° loses alcohol and yields homogeneous sodiumoxyethoxymethylene, characterised by hydrolysis to carbon monoxide, sodium hydroxide, and ethyl alcohol. The compound is transformed by ethyl bromide into ethylene, carbon monoxide, and ethyl alcohol. Its transformation into diethoxymethylene by the successive action of phosphoryl chloride and sodium ethoxide (*loc. cit.*) depends on the presence of hydrogen chloride in the former reagent and a sufficient interval before the use of the second reagent. Pure phosphoryl chloride followed immediately by sodium ethoxide converts sodiumoxyethoxymethylene into ethyl phosphate. Adickes' observation that the "primary product" [?$CH(OEt)_2 \cdot ONa$, see above] is converted by water into diethoxymethylene could not be confirmed. H. WREN.

Preparation of *iso*propylidene ethers by means of acetone and zinc chloride. H. O. L. FISCHER and C. TAUBE (Ber., 1927, 60, [*B*], 485—490).—A solution of anhydrous zinc chloride in dry acetone may frequently be used with advantage for the preparation of *iso*propylidene ethers. It possesses surprising solvent power towards hydroxy-compounds, and may be used at the ordinary temperature or at the b. p. Isolation of the product affords no difficulty if the ether is insoluble in water, but is not easy when this is not the case, and the compound dissolves with difficulty in organic media; removal of the zinc chloride from its acetone solution by ammonia or pyridine is then helpful. Ethers prepared in this manner are more stable than those obtained with the aid of acids. *iso*Propylidene ethers of dihydroxyacetone, mandelic and quinic acids, mannitol, lævulose, and galactose are readily prepared, but the behaviour of dextrose is abnormal. With the tartaric acids, acetone gives *compounds*,

$$\begin{array}{c} CMe_2 \cdot O \\ O—CO \end{array}\!\!>\!\!CH \cdot CH\!\!<\!\!\begin{array}{c} CO \cdot O \\ O—CMe_2 \end{array}$$

(cf. Willstätter and Königsberger, A., 1923, i, 1172), that from the *d*-acid having m. p. 102°, $[\alpha]_D^{17}$ +63·3° in *s*-tetrachloroethane, from the *l*-acid m. p. 102°, $[\alpha]_D^{18}$ −62·6° in *s*-tetrachloroethane, from the *r*-acid, m. p. 88·5°, and from the *meso*-acid, m. p. 96—97°. Dihydroxyacetone is readily isolated from technical glycerose by means of the reagent. H. WREN.

Ethers of diacetone alcohol. A. HOFFMAN (J. Amer. Chem. Soc., 1927, 49, 530—535).—Ethers of diacetone alcohol are obtained as the result of a reversible addition of alcohol to the double linking of mesityl oxide when mixtures of mesityl oxide, an alcohol, and a mineral acid, preferably sulphuric acid, are kept for 10 days at the ordinary temperature. They are isolated by neutralisation of the reaction mixture, followed by distillation. Their probable constitution is $CMe_2(OR) \cdot CH_2Ac$. The following are described: *methyl diacetone ether*, b. p. 155—157°/760 mm.; *ethyl*, b. p. 164—166°/760 mm. (*oxime*, b. p. 103°/7 mm.; *semicarbazone*, m. p. 163—164°); *propyl*, b. p. 182—183°/760 mm. (*semicarbazone*, m. p. 139—140°); *butyl*, b. p. 198—199°/760 mm., b. p. 81—84°/7 mm. (*semicarbazone*, m. p. 134—135°); iso*butyl*, b. p. 85—87°/15 mm. (*semicarbazone*, m. p. 145°); iso*amyl*, b. p. 85—88°/6 mm. (*semicarbazone*, m. p. 142—143°); and *benzyl diacetone ether*, b. p. 153—157°/12 mm. (*semicarbazone*, m. p. 138—139°). Reduction of ethyl diacetone ether in ethereal solution with sodium and aqueous boric acid affords δ-*ethoxy-δ-methyl*-n-*pentan-β-ol*, b. p. 160—173°, d_{25}^{25} 0·868, which could not be further purified, and, when heated with concentrated sulphuric acid, yields δ-methyl-$\Delta^{\beta\delta}$-pentadiene. Oxidation of butyl diacetone ether with cold aqueous hypobromite affords chiefly β-*butoxy*isovaleric acid, b. p. 140—143°, d^{20} 1·053.

F. G. WILLSON.

Reactivity and stability of linking of organic radicals. II. Hydrolysis of esters, addition of hydrogen sulphide to nitriles, and conversion of alkyl chlorides into ethers. K. KINDLER [with A. TREU and W. FÜRST] (Annalen, 1927, 452, 90—120; cf. this vol., 55).—An extension of previous work. New members are added to the series of comparative radical tenacities as measured by the rate of hydrolysis of substituted benzoic esters; the tenacity of $X \cdot C_6H_4$ to CO_2Et increases as X is changed thus : *p*-Cl < *m*-MeO < *p*-Ph < H < *p*-MeS < *p*-Me < *p*-Et < 3 : 4-CH_2O_2 < *p*-MeO. The value for the radical *p*-diphenyl agrees well with that found by Schönberg (A., 1925, i, 557). The tenacity of *m*-MeO·C_6H_4 is very much less than that of *p*-MeO·C_6H_4. The great

variations in the recorded relative tenacities of methyl and ethyl (Meerwein, A., 1920, i, 2; Skraup and Moser, *ibid.*, 1922, i, 574; cf. von Braun, *ibid.*, 1924, i, 632) are probably due to the difference in nature of the groups to which they are attached. The present results agree with those of von Braun; in both methods a negative group is used.

The tenacity of substituted alkyl radicals towards CO_2Et increases in the order $Ph \cdot CH_2 < Me < Ph \cdot [CH_2]_2 < Et < Ph \cdot [CH_2]_3 < Pr^a$; in the substituted aromatic series, $p\text{-}Cl \cdot C_6H_4 \cdot CH_2 < p\text{-}MeO \cdot C_6H_4 \cdot CH_2 < p\text{-}Cl \cdot C_6H_4 \cdot [CH_2]_2 < p\text{-}MeO \cdot C_6H_4 \cdot [CH_2]_2$. A table is given showing the effect of the various substituents of the original series on the tenacity of Ph, $Ph \cdot CH_2$, $Ph \cdot [CH_2]_2$, and $Ph \cdot CH:CH$ towards CO_2Et. This effect is greatest with benzoic esters, least with phenylacetic esters; the same order in the series holds for all four types.

When the tenacity towards CO_2Et, determined by hydrolysis, is compared with that towards CN, determined by addition of hydrogen sulphide, or towards Cl, determined by conversion into an ethoxy-derivative by sodium ethoxide, the same order again holds. The effect of substituents is much greater with chlorides.

The increasing tenacity of alkyl radicals is compared with the decreasing dissociation constants of the corresponding acids, and that of aryl radicals with the increasing dissociation constants of the phenols.

Velocity coefficients for hydrolysis by about $N/40$-sodium hydroxide were determined for the following ethyl esters: *m*-methoxybenzoate; p-*methylthiolbenzoate*, m. p. 28° (corr.), b. p. 168°/15 mm.; p-*ethylbenzoate*, b. p. 129—130°/15 mm., *p*-phenylbenzoate, acetate, propionate, butyrate, valerate, hexoate, heptoate, octoate, phenylacetate, *p*-methoxyphenylacetate, *p*-chlorophenylacetate, *p*-nitrophenylacetate, β-phenylpropionate, β-*p*-methoxyphenylpropionate, b. p. 165°/14 mm., β-3:4-methylenedioxyphenylpropionate, β-p-*chlorophenylpropionate*, b. p. 158—159°/15 mm., γ-phenylbutyrate, cinnamate, *o*- and *p*-methoxycinnamates, 3:4-methylenedioxycinnamate, *p*-methylcinnamate, *o*- and *p*-chlorocinnamates, *o*-, *m*-, and *p*-nitrocinnamates.

Velocity coefficients are given for the addition of hydrogen sulphide to phenylacetonitrile, β-phenylpropionitrile, γ-phenylbutyronitrile, *p*-chlorophenylacetonitrile, propionitrile, butyronitrile. γ-*Phenylbutyramide*, m. p. 62° (corr.), p-*chlorophenylthiolacetamide*, m. p. 128—129° (corr.), and *thiolbutyramide*, a reddish-brown oil, are described.

Velocity coefficients are given for the replacement of chlorine by ethoxyl by means of sodium ethoxide (cf. von Braun, *loc. cit.*) in benzyl, *p*-chlorobenzyl, β-phenylethyl, and γ-phenylpropyl chlorides.

E. W. WIGNALL.

*iso*Erucic acid. T. J. MIRCHANDANI and J. L. SIMONSEN (J.C.S., 1927, 371—378).—Oxidation of ethyl *iso*erucate with ozone yields a complex product in which the dibasic acids present are identified as decane-$\alpha\kappa$-dicarboxylic acid and dodecane-$\alpha\mu$-dicarboxylic acid. These acids are also obtained together with *n*-octoic acid when methyl *iso*erucate is oxidised in acetone solution with potassium permanganate. Hence *iso*erucic acid is a non-homogeneous substance, consisting of an inseparable mix-

ture of Δ^λ-docosenecarboxylic acid and Δ^ν-docosenecarboxylic acid (cf. Mascarelli, A., 1917, i, 195). From the yields of the oxidation acids, the two acids are apparently present in approximately equal amount. Apparent homogeneity is also found in certain derivatives of *iso*erucic acid (*methyl* ester, m. p. 24—26°, resolidifying at 22°; *ethyl* ester, b. p. 243°/8 mm.; *anilide*, m. p. 77—78·5°; p-*toluidide*, m. p. 85—86°; *zinc* salt, m. p. 109°). The dibromo-derivative, however, has the appearance of a mixture, and the m. p. is not sharp (cf. Macbeth and Stewart, P., 1912, 18, 68). M. CLARK.

Synthesis of θ-, ι-, κ-, λ-, and μ-hydroxystearic acids. C. G. TOMECKO and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 522—530).—Δ^κ-*Undecenoyl bromide*, b. p. 103°/4 mm., n_D^{20} 1·4638, d_{20}^{20} 1·0295, obtained by treating the corresponding alcohol with phosphorus tribromide in toluene, is converted, successively, into the *nitrile*, b. p. 117—119°/4 mm., n_D^{20} 1·4462, d_{20}^{20} 0·8405, and Δ^κ-*dodecenoic acid*, b. p. 143—144°/3 mm., n_D^{20} 1·4510, d_{20}^{20} 0·9030 (*methyl* ester, b. p. 121—123°/3 mm., n_D^{20} 1·4414, d_{20}^{20} 0·8805). Ozonisation and subsequent hydrolysis of the ester affords *methyl Δ^ι-aldehydodecoate*, n_D^{20} 1·4430, d_{20}^{20} 0·9594 (*semicarbazone*, m. p. 114—115°). Treatment of ethyl sodiomalonate with undecenoyl bromide yields *ethyl Δ^κ-undecenoylmalonate*, b. p. 154°/2 mm., n_D^{20} 1·4450, d_{20}^{20} 0·9411, from which the corresponding *acid*, m. p. 112—113°, is obtained on hydrolysis. When heated at 150°, the latter loses carbon dioxide, with formation of Δ^λ-*tridecenoic acid*, m. p. 38—39°, b. p. 192°/20 mm., b. p. 162°/3 mm., from the *methyl* ester of which, b. p. 133°/3 mm., n_D^{20} 1·4438, d_{20}^{20} 0·8819, *methyl κ-aldehydoundecoate*, m. p. 16°, b. p. 154°/5 mm., n_D^{20} 1·4458, d_{20}^{20} 0·9504, is obtained through the ozonide. Synthesis of the following methyl hydroxystearates was effected by condensing the above aldehydo-esters with Grignard reagents according to the method of Noller and Adams (A., 1926, 712), the corresponding acids being obtained by hydrolysis: θ-*hydroxystearic acid*, m. p. 74—75° (*methyl* ester, m. p. 45—46°, b. p. 212—216°/4 mm.); ι-*hydroxystearic acid*, m. p. 81—82° (*methyl* ester, m. p. 53—54°, b. p. 213—217°/4 mm.); κ-*hydroxystearic acid*, m. p. 76—77° (*methyl* ester, m. p. 49—50°, b. p. 204—206°/4 mm.); λ-*hydroxystearic acid*, m. p. 78—79° (*methyl* ester, m. p. 50—51°, b. p. 202—204°/4 mm.); and μ-*hydroxystearic acid*, m. p. 77—77·5° (*methyl* ester, m. p. 52—52·5°, b. p. 185—189°/2 mm.). *n*-Nonyl alcohol, b. p. 205—207°, obtained by reduction of *n*-nonaldehyde, yields n-*nonyl bromide*, b. p. 88°/4 mm., n_D^{20} 1·4533, d_{20}^{20} 1·0183, when boiled with concentrated hydrobromic and sulphuric acids.

F. G. WILLSON.

Optically active compounds of aluminium. W. WAHL [with M. ANDERSIN] (Ber., 1927, 60, [*B*], 399—406).—The conception that aluminium compounds are complex substances and not double salts is established by the isolation of them in optically active forms.

The water content of ammonium and potassium aluminotrioxalates, $[Al(C_2O_4)_3]R_2$, cannot be established analytically on account of the readiness and irregularity of their efflorescence. Treatment of a

cold, saturated solution of the ammonium salt with a similar solution of strychnine sulphate or nitrate leads to the separation of *strychnine aluminotrioxalate*, $[Al(C_2O_4)_3](H,C_{21}H_{22}O_2N_2)_3,12H_2O$, $[M]_D$ $-281°$ in water. Attempts to separate this salt into fractions of differing specific rotation by crystallisation from hot water failed, owing to such extensive racemisation that the first, sparingly soluble fraction was optically inactive. The end is, however, attained by fractional extraction with water, whereby the extreme values observed for the strychnine salts of the *l*- and *d*-acid are $[M]_D$ $-281·2°$ and $+173·1°$. When preserved in the solid, moist condition, the preparations undergo marked racemisation. The strychnine salts are transformed into the corresponding ammonium salts by trituration with the calculated quantity of ammonium iodide and a little water, filtration of the strychnine hydriodide, and addition of the filtrate to a large excess of absolute alcohol. The highest value of $[M]_D$ observed for the dextrorotatory salt is $+81·2°$; in aqueous solution, the salt suffers autoracemisation.

H. WREN.

Thermal decomposition of heterocyclic oxygen rings. M. D. TILITCHEEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 447—461; cf. A., 1923, i, 1173).—The thermal decomposition of glyceryl oxalate gives a 60% yield of allyl alcohol, and no trace of *cyclo*propanol. Ethylene succinate gives mainly succinic anhydride and acetaldehyde, with some ethylene and carbon dioxide (38%). *Trimethylene oxalate*, m. p. 82—84°, prepared in 78% yield by cautiously heating methyl oxalate and trimethylene glycol, is converted by distillation in a vacuum into an *isomeride*, m. p. 186—187°. It decomposes when heated at 240—265°, evolving 46% of carbon dioxide and 54% of carbon monoxide. The residue contained propaldehyde, acraldehyde, and trimethylene glycol. *Ethylene malonate*, prepared in 95% yield as an oil by heating ethyl malonate with ethylene glycol, passes on distillation in a vacuum into a solid isomeride, m. p. 159—160°. At 205° it yields carbon dioxide (48%), acetaldehyde, ethyl acetate, ethylene acetate, and an unidentified *ester*, b. p. 148—153°/4 mm., d_4^0 1·2033, $n_D^{18·7}$ 1·4681. If the decomposition took place at 225—240°, a solid *product*, $C_9H_{10}O_5$, m. p. 108—108·5°, was also obtained. M. ZVEGINTZOV.

Preparation of crystalline *d*-talonic acid. O. F. HEDENBURG and L. H. CRETCHER (J. Amer. Chem. Soc., 1927, **49**, 478—481).—*d*-Galactonolactone monohydrate (80 g.), pyridine (36 g.), and water (500 c.c.) are heated in a closed vessel at 100° for 115 hrs., whereby galactonic and talonic acids are obtained, which are separated from one another as their cadmium salts. Pure *d*-talonic acid has m. p. 125°, and crystallises with 0·5H₂O. It has $[\alpha]_D$ $+16·73°$ in freshly-prepared 4% aqueous solution, changing to $-21·57°$ in 240 hrs., when the solution contains 28% of acid, the remainder being present as the lactone, $[\alpha]_D$ $-41°$. The phenylhydrazide has m. p. 159°, $[\alpha]_D^{15·7}$ $-25·43°$ (cf. Levene and Meyer, A., 1917, i, 631). F. G. WILLSON.

Lactone formation of lacto- and malto-bionic acids and its bearing on the structure of lactose and maltose. P. A. LEVENE and H. SOBOTKA (J.

Biol. Chem., 1927, **71**, 471—475).—Both lacto- and malto-bionic acids when preserved in aqueous solution showed a small increase in specific rotation which was complete in 2—3 hrs., and the titration values remained constant. In view of the results of Levene and Simms (A., 1926, 1025), this indicates that these acids form only lactones with six-membered rings. Support is therefore afforded to the view that in lactose and maltose the δ-position is occupied by the linking between the two hexoses.

C. R. HARINGTON.

Synthesis of α-bromoaldehydes. A. KIRRMANN (Compt. rend., 1927, **184**, 525—527).—The author considers that the products obtained by Nef (A., 1905, i, 6) and Étard (*ibid.*, 1892, 809) were impure. The method now used consists in brominating the methyl- or ethyl-acetals by phosphorus dibromotrichloride, $CH_2R\cdot CH(OR')_2 + 2PCl_3Br_2 \longrightarrow CHRBr\cdot CHO + 2R'Br + HBr + POCl_3 + PCl_3$. In the case of propaldehyde and butaldehyde, the main reaction is accompanied by the formation of αα-dibromoaldehydes, and isolation is difficult, but the higher acetals react more smoothly. In general, the methylacetals are unstable and regenerate the unbrominated aldehyde. Ethyl bromide was isolated in the case of the ethylacetals.

The α-bromoaldehydes are colourless liquids, which may be kept for some time without darkening, form hydrogen sulphite compounds, and give Schiff's reaction. The following are described, and densities and molecular refractions are given : *α-bromopropaldehyde*, b. p. 109—110°, or 52—54°/80 mm. (cf. Nef, *loc. cit.*) ; *α-bromo*-n-*butaldehyde*, b. p. 33°/15 mm. ; *α-bromo*-n-*valeraldehyde*, b. p. 49°/12 mm. ; *α-bromo*isovaleraldehyde, b. p. 43—44°/14 mm. ; *α-bromo*-n-*heptaldehyde*, b. p. 80°/11 mm. J. M. GULLAND.

Crystalline glyceraldehyde and its transformation into dihydroxyacetone. H. O. L. FISCHER, C. TAUBE, and E. BAER (Ber., 1927, **60**, [B], 479—485).—Bimolecular glyceraldehyde is transformed in boiling pyridine into dihydroxyacetone, the highest yield observed being 49%. The reaction is most readily explained by assigning to the aldehyde the constitution $\left(\begin{smallmatrix} O \\ | \\ CH(OH) \end{smallmatrix}\!\!>CH\cdot CH_2\cdot OH\right)_2$. This conception is in harmony with the behaviour of the crystalline aldehyde when distilled in a high vacuum, with the non-success attending attempts to transform it into its *iso*propylidene ether, with the difficulty with which it adds hydrocyanic acid, and, in particular, with the indifference of its acetate towards phenylhydrazine. In contrast with the aldehyde, the corresponding acetal reacts readily with acetone in presence of copper sulphate. Lactaldehyde does not appear to be isomerised to hydroxyacetone in pyridine solution.

The following compounds are described : dibenzoxyacetone, m. p. 120·5°, and its *phenylhydrazone*, m. p. 69—70° ; *di-p-nitrobenzoxyacetone*, m. p. 197·5° (decomp.) ; *dibenzoate*, m. p. 231°, *di-p-nitrobenzoate*, m. p. 247°, and *diacetate*, m. p. 154°, of bimolecular *glyceraldehyde* ; *glyceraldehydediethylacetal* isopropylidene ether, $\begin{smallmatrix} CMe_2\cdot O \\ | \\ O-CH_2 \end{smallmatrix}\!\!>CH\cdot CH(OEt)_2$, b. p. 90—

91°/20 mm., d^{20} 0·9897, n_D^{17} 1·4208; *bimolecular lact-aldehyde acetate*, $\left(\begin{smallmatrix} O \longrightarrow \\ CHMe \end{smallmatrix}\!\!>\!CH\cdot OAc\right)_2$, m. p. 185·5°.

H. WREN.

Dioximes. XXXIX. G. B. SEMERIA and B. BOCCA (Atti R. Accad. Sci. Torino, 1926, **61**, 364—376).—See this vol., 135.

Optical enantiomeride of natural rhamnose. E. VOTOCEK and F. VALENTIN (Chem. Listy, 1927, **21**, 7—10).—See A., 1926, 940.

Oxidative decomposition of dextrose. B. BLEYER and W. BRAUN (Biochem. Z., 1927, **180**, 105—116).—Dextrose (1 mol.), when oxidised in alkaline solution with sodium *p*-toluenesulphonchloroamide, uses eight equivalents of oxygen and gives rise to 2 mols. of acetic acid and 2 mols. of carbon dioxide. It is supposed that 1 mol. of dextrose is decomposed hydrolytically into 2 mols. of methylglyoxal, which on oxidation gives 2 mols. of pyruvic acid, and on further oxidation 2 mols. each of acetic acid and carbon dioxide. P. W. CLUTTERBUCK.

Rôle of heavy metals in the autoxidation of sugars. H. A. KREBS (Biochem. Z., 1927, **189**, 377—394).—The rate of oxidation of lævulose by oxygen in feebly alkaline solution is much greater in ammoniacal solution than in phosphate or hydrogen carbonate solutions of the same hydroxyl-ion concentration. The velocity is proportional to the concentration of lævulose, ammonia, and hydroxyl ions, but is independent of the partial pressure of oxygen. The rate is increased as much as tenfold by the addition of salts of calcium and, to a less extent, of strontium or barium. Heavy metal salts (those of copper and manganese being the most effective) accelerate the autoxidation and hydrocyanic acid, pyrophosphate and hydrogen sulphide inhibit it. The effects of calcium and of the heavy metals are additive. Dextrose, mannose, galactose, and maltose are subject to the same effects at less rapid rates. The oxidation of sugars in faintly alkaline solution is attributed to the catalytic activation of oxygen by traces of heavy metals. R. K. CANNAN.

Behaviour of sugars in alkaline solution. II. Dextrose and sodium hydroxide. J. GROOT (Biochem. Z., 1927, **180**, 341—352).—The velocity constants for the rate of decline of optical rotation of dextrose in solutions of sodium and of potassium hydroxides are of the same order, increasing with the concentration of alkali up to a maximum value corresponding with the presence of alkali and dextrose in approximately molecular proportions. The temperature coefficient of the maximum velocity constant is 4·13 for a rise of temperature of 10°. The immediate depression in the rotation of dextrose produced by increasing concentrations of these hydroxides also attains a maximum value for molecular proportions of dextrose and alkali, when it amounts to 22% of the rotation of dextrose in neutral solution. The acid dissociation constant of dextrose has been determined electrometrically as $8\cdot6\times10^{-13}$. It is shown that the velocities above studied were directly proportional to the concentration of metallic glucosate present. It is suggested that the effects of alkali on dextrose may be attributed to enolisation of the glucosate molecule. R. K. CANNAN.

Crystallisation of sucrose. I. A. KUKHARENKO and M. E. VERKENTIN (Zapiski [Russia], 1926, **3**, 244—254).—At a supersaturation lower than the critical (which is 1·027, 1·031, and 1·030 for 0·5, 1·0, and 2·0% of calcium chloride, respectively), calcium chloride is a negative paralyser, the speed of crystallisation increasing with the concentration of calcium chloride in the mother-liquor. At supersaturation above the critical point, calcium chloride is a positive paralyser. CHEMICAL ABSTRACTS.

Saponin and allied substances. XVII. *Gypsophila* **saponin and its hydrolysis products. Gypsogenin and saccharides.** A. W. VAN DER HAAR (Rec. trav. chim., 1927, **46**, 85—96).—Electrodialysis of *Gypsophila* saponin by the method of Kofler and Dafert (cf. B., 1924, 73) yields free saponin together with calcium and magnesium compounds of saponin which cannot be separated by this method, but separation by means of methyl alcohol yields free saponin (ash content 0·2%) and the calcium–magnesium compound of saponin (ash content 3%). Both on hydrolysis yield the same sapogenin and saccharides. Free saponin contains water 7·2%, ash 0·2%, and on hydrolysis yields *l*-arabinose 12·2%, rhamnose hydrate 22·2%, dextrose 13·2%, *d*-galactose 17·3%, and sapogenin 21·8%. *d*-Mannose, xylose, and aldehydic acids are not produced, and only a very small quantity of lævulose was detected. The formula and m. p. 274° previously given for *Gypsophila* sapogenin (Karrer, Fioroni, Widmer, and Lier, A., 1924, i, 1091, who called it albasapogenin) are confirmed. The author assumes that free saponin is converted into the calcium–magnesium compound, in which the same sugars are combined with an altered, amorphous sapogenin, which in turn yields polysaccharides and ultimately monosaccharides. J. W. BAKER.

Structural problems of the associated lactolides and their relation to the chemistry of higher carbohydrates. M. BERGMANN (Annalen, 1927, **452**, 121—135).—A theoretical paper in which the differences between associated and polymerised molecules are examined and the criteria applied to a discussion of earlier results on the structure of ethylglycoloside, inulin, and other polysaccharides. J. W. BAKER.

Lichohexosan and lichenin. M. BERGMANN and E. KNEHE (Annalen, 1927, **452**, 151—158).—Mainly a reply to Pringsheim and Routala (this vol., 136). The authors prefer the name lichohexosan to lichosan, which is employed by Pringsheim, since the latter nomenclature suggests that it is an anhydride of the hypothetical sugar "lichose." The pure hexosan exhibits no rotation in a 2·5% aqueous solution at 20°, but at 70°, when, according to Pringsheim, deassociation is complete ($M=162$), it has $[\alpha]_D^{20}$ +8·7° (constant). Hence the optical inactivity cannot be due to the compensation of the activity of the aldehydic carbon atom by that of the four remaining carbon atoms, as assumed by Pringsheim, Knoll, and Kaston (A., 1925, i, 1385), but must be due to association. Pure lichohexosan triacetate prepared from

the hexosan has $[\alpha]_D$ $-18\cdot9°$ to $-19\cdot5°$ in chloroform (Pringsheim and Routala, *loc. cit.*, give $-21\cdot8°$ for " lichosan acetate "), whilst lichenin acetate prepared from lichenin either by the action of pyridine and acetic anhydride or sodium acetate and acetic anhydride at 60° (thus avoiding the drastic conditions employed by the other authors, *loc. cit.*), has $[\alpha]_D^{19}$ $+35\cdot6°$ in chloroform. Hence lichohexosan and lichenin cannot be identical, and the assumption that lichosan is the unit substance of lichenin (Pringsheim, Knoll, and Kaston, *loc. cit.*) cannot be upheld.

J. W. BAKER.

Individual group of amylose from potato starch. M. BERGMANN and E. KNEHE (Annalen, 1927, **452**, 141—150).—Acetylation of pure amylose prepared from potato starch by the method of Ling and Nanji (J.C.S., 1923, **123**, 2666) with pyridine and acetic anhydride for 6—7 days at the ordinary temperature yields *amylose triacetate*, $C_6H_7O_5Ac_3$, $[\alpha]_D^{16}$ $+176\cdot7°$. Further treatment of the product with pyridine and acetic anhydride for 7 days does not change its composition, and on hydrolysis with $0\cdot5N$-alcoholic potassium hydroxide it yields the original amylose, which can be reconverted into the same triacetate. The authors therefore conclude that amylose is composed of associated glucose anhydride units in the same manner as cellulose (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142), and, contrary to the conclusion of Kuhn (*ibid.*, 1925, i, 636), believe that the production of maltose occurs through the secondary union of dextrose radicals.

J. W. BAKER.

Inulin. II. L. SCHMID and G. BILOWITZKI (Monatsh., 1926, **47**, 768—789).—Inulin and water-soluble starch dissolve slightly in cold and readily in warm butylamine or piperidine. Inulin also dissolves in phenol at 100° or 180°. It is recovered from these solvents unchanged in quantity and in specific rotation. Solutions of inulin in dry phenol show practically no cryoscopic depression; this solvent, therefore, unlike liquid ammonia (A., 1925, i, 1386), does not depolymerise inulin.

H. E. F. NOTTON.

Röntgen diagram of mercerised cellulose. R. O. HERZOG (Ber., 1927, **60**, [B], 600—603).—Characteristic differences are observed between the Röntgen diagrams of fibres in the natural and mercerised condition. Since cotton which has been esterified and de-esterified without destruction of its fibrous nature gives diagrams of the first type, whereas that which has been subjected to a precisely similar chemical treatment during which it has passed into solution gives diagrams of the second type, it is considered that mercerisation involves a purely physical change, as it is improbable that the act of dissolution causes chemical alteration.

H. WREN.

Reducing action of parchment paper used in dialysis. A. GUTBIER, B. OTTENSTEIN, and W. JEHRING (Biochem. Z., 1926, **179**, 426—431).—Parchment yields on extraction with water a reducing substance, apparently of a carbohydrate nature, which may be determined by Bang's method; it reduces gold chloride and ammoniacal silver nitrate solutions. In cases where reducible metallic prepar-

ations are being dialysed, a thorough preliminary washing of the parchment paper is recommended.

J. PRYDE.

Lignin. II. Formaldehyde as product of the fission of lignin. K. FREUDENBERG and M. HARDER (Ber., 1927, **60**, [B], 581—585).—Under the conditions prescribed by Tollens for the determination of pentosans, lignin evolves formaldehyde to the extent of $0\cdot6$—$0\cdot8\%$, as deduced from its compound with barbituric acid. In like circumstances, piperonylic acid yields formaldehyde in one third the amount expected from its methylenedioxy-content, the remainder undergoing condensation with the liberated protocatechuic acid. Apparently formaldehyde is united to neighbouring hydroxyl groups in lignin as in piperonal, in which case the evolved formaldehyde represents only a portion of that present in the lignin. According to Tollens' method, the presence of pentoses or carbohydrates in " hydrochloric acid lignin " cannot be detected. Degradation of lignin by chlorine dioxide yields chlorinated, water-soluble products, whereas those derived from hexoses are insoluble in water. The presence of formaldehyde must be taken into account in the determination of pentosans in wood ; pine wood contains about $1\cdot5\%$ less pentosan than previously assumed, owing to the presence of $0\cdot20$—$0\cdot25\%$ of formaldehyde.

A modified method of isolating lignin from wood is described.

H. WREN.

Ultra-violet absorption spectrum of lignin. I. R. O. HERZOG and A. HILLMER (Ber., 1927, **60**, [B], 365—366).—The absorption spectra of sulphite waste liquor, technical ligninsulphonic acid, and Klason's α-ligninsulphonic acid resemble closely those of *iso*-eugenol and coniferin and differ widely from that of vanillin.

H. WREN.

Tetra-alkylammonium tetroxides and tetra-alkylammonium hydroxoxides. W. TRAUBE, E. BURMEISTER, and B. BLASER (Ber., 1927, **60**, [B], 439—446).—Tetramethylammonium hydroxide resembles potassium hydroxide in that its aqueous solutions when mixed with a large excess of hydrogen peroxide and evaporated to complete dryness at the atmospheric temperature under diminished pressure leave a yellow residue which dissolves in water or acid with evolution of oxygen and production of hydrogen peroxide, and hence contains *tetramethylammonium tetroxide*, $(NMe_4)_2O_4$, since the molecular ratio, $H_2O_2 : O_2$ is $1 : 1$. An occasional preponderance of hydrogen peroxide indicates incomplete transformation of the intermediate tetramethylammonium peroxide. The tetramethylammonium radical does not suffer oxidation to an appreciable extent. Tetraethylammonium hydroxide yields a similar *tetroxide*, but if a smaller excess of hydrogen peroxide is used, the product contains the *peroxide*, $(NEt_4)_2O_2,H_2O_2$.

Solid tetramethylammonium hydroxide is very readily converted by ozone into an intensely red *compound*, for which the name *tetramethylammonium hydroxoxide* is proposed. The quantity of oxygen absorbed may attain 7% of the weight of the tetramethylammonium hydroxide ; excess of ozone is quantitatively converted into oxygen by contact with the hydroxide. The hydroxoxide is decomposed by

water with evolution of "indifferent" oxygen (unable to liberate iodine from acidified potassium iodide), but without production of hydrogen peroxide. It therefore resembles closely the analogous compounds of potassium, rubidium, and cæsium, from which, however, it is distinguished by considerably greater stability (cf. A., 1916, ii, 613). H. WREN.

Derivative of αα'α''-triaminotrimethylamine. F. B. KIPPING and F. G. MANN (J.C.S., 1927, 528—530).—Bromomethylphthalimide, on treatment with gaseous ammonia in xylene solution, gives *triphthalimidotrimethylamine* (I), $(C_6H_4\!:\!C_2O_2\!:\!N\!\cdot\!CH_2)_3N$, m. p. 235° (+Me·$CO_2$H, m. p. 222—223°), which condenses with hydrazine hydrate to give (II), *triphthalylhydrazidotriaminotrimethylamine* (?),

$$N(CH_2\!\cdot\!NH\!\cdot\!C\!\!<^{C_6H_4}_{N\cdot NH}\!\!>\!CO)_3,$$ m. p. above 330°.

Hydrolysis of (I) or (II) with hydrochloric acid gives formaldehyde and ammonia. αα'α''-Triaminotrimethylamine is therefore, like methylenediamine, unstable except in the form of its acyl derivatives. Bromomethylphthalimide reacts with pyridine, giving *phthalimidomethylpyridinium bromide*, m. p. 244°, which yields on hydrolysis phthalic acid, formaldehyde, ammonia, and pyridine. Reaction with anhydrous diethylamine gives phthalimide as the main product. M. CLARK.

Constitution and synthesis of spermidine, a base isolated from animal tissues. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING (Biochem. J., 1927, 21, 97—103).—*Spermidine phosphate*, $(C_7H_{19}N_3)_2,3H_3PO_4,6H_2O$, m. p. 207—209°, is found in the mother-liquors after isolation of spermine phosphate (A., 1925, i, 294). The *picrate*, $C_7H_{19}N_3,3C_6H_3O_7N_3$, m. p. 210—212°, the *hydrochloride*, $C_7H_{19}N_3,3HCl$, slightly deliquescent, the *chloroaurate*, $C_7H_{19}N_3,3HAuCl_4$, m. p. 220—222°, and the m-*nitrobenzoyl* compound, m. p. 148—150° and 102° (probably hydrate), were prepared. The *chloroplatinate* and *mercurichloride* are very soluble.

Spermidine was proved by synthesis to be α-(γ'-aminopropylamino)-δ-aminobutane, $NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_4\cdot NH_2$, in the following way: α-(γ'-*phenoxypropylamino*)-δ-*aminobutane hydrobromide*, isolated as a by-product from the preparation of α-δ-*bis*-(γ'-*phenoxypropylamino*)*butane hydrobromide* used in the synthesis of spermine (A., 1926, 1128), was heated in a sealed tube at 100° with hydrobromic acid, yielding α-(γ'-*bromopropylamino*)-δ-*aminobutane hydrobromide*, m. p. 234—235°. Spermidine was obtained from this bromo-compound by heating the latter in a sealed tube with alcoholic ammonia and distilling the resulting solid with potassium hydroxide in steam. The picrate, hydrochloride, chloroaurate, and m-nitrobenzoyl derivative prepared from the synthetic compound were found to be identical with the corresponding derivatives from natural spermidine.

The properties of spermidine are very similar to those of spermine. It accompanies the latter base through all the stages of isolation by the three methods described by the authors (A., 1925, i, 294). Like spermine, it gives a pyrrole reaction and is optically inactive. It appears in the lysine fraction

on applying the method of Kossel and Kutscher. Its *phosphotungstate* is insoluble in acetone. S. S. ZILVA.

Action of ammonia on propylene oxide. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1927, 71, 461—463).—The aminopropanol recently prepared by the authors (A., 1926, 937) by the action of ammonia on propylene oxide, has been proved to be α-aminopropan-β-ol by the preparation of the phenylthiocarbamate, m. p. 107—108°. C. R. HARINGTON.

Synthesis of α-amino-β-hydroxy- and γ-amino-β-hydroxy-valeric acids. A. E. OSTERBERG (J. Amer. Chem. Soc., 1927, 49, 538—540).—Treatment of ethyl α-chloropropyl ether with ethyl sodiophthalimidomalonate suspended in cold benzene, followed by hydrolysis of the product with alcoholic sodium hydroxide and subsequent acidification, affords α-*amino-β-ethoxyvaleric acid*, m. p. 227°, together with a little glycine, from the former of which, by treatment with boiling hydrobromic acid, α-*amino-β-hydroxyvaleric acid*, m. p. 220°, is obtained. Reduction of β-hydroxylævulic acid oxime (cf. Wolff, A., 1891, 1185) with sodium amalgam and 50% aqueous alcohol affords γ-*amino-β-hydroxyvaleric acid*, m. p. 188°. Neither of the above aminohydroxyvaleric acids possesses the properties of Wilder's "bios" (cf. Eddy, Kerr, and Williams, A., 1925, i, 342). F. G. WILLSON.

Action of α-oxides on the esters of amino-acids. II. A. KIPRIANOV (Ukraine Chem. J., 1926, 2, 236—249; cf. A., 1926, 950).—By the action of ethylene oxide on glycine, a syrup is obtained which slowly deposits crystals of *dihydroxydiethylaminoacetic acid*, m. p. 193°. The same product is formed by distilling the residual syrup (b. p. 160—200°/5 mm. with violent decomp.) and evaporating the distillate with water to dryness. The *picrate* (+H_2O), m. p. 95°, and *dibenzoyl* derivative are described. When the acid is distilled, water is eliminated and l-*hydroxyethyl-3-morpholone*, b. p. 175—176°/5 mm., is formed [*chloroplatinate*, m. p. 190° (decomp.)]. Ethylene oxide and the ethyl ester of α-alanine yields α-*dihydroxydiethylaminopropionic acid*, m. p. 136° (*picrate*, m. p. 80—85°; *dibenzoyl* derivative, m. p. 42—43°). On distillation, water is eliminated, with formation of 2-*methyl-1-hydroxyethyl-3-morpholone*, b. p. 171°/5 mm. [*chloroplatinate*, m. p. 179—180° (decomp.)]. E. ROTHSTEIN.

Constitution of carnitine. I. Synthesis of α-hydroxy-γ-butyrotrimethylbetaine. J. W. C. CRAWFORD and J. KENYON (J.C.S., 1927, 396—402; cf. Engeland, A., 1921, i, 880).—β-Chloropropaldehyde diethylacetal, b. p. 74°/20 mm., $d_4^{18.7}$ 0.9951, $n_D^{18.7}$ 1.4206, prepared by the action of alcoholic hydrogen chloride on acraldehyde, is hydrolysed by water to β-chloropropaldehyde (*sodium hydrogen sulphite* compound). The *potassium hydrogen sulphite* compound, on treatment with potassium cyanide, gives γ-*chloro-α-hydroxy*-n-*butyronitrile*, b. p. 91.5°/3 mm., $d_4^{19.1}$ 1.0795, $n_D^{19.1}$ 1.4399 (*benzoyl* derivative, m. p. 59°, b. p. 147°/3—4 mm.; *acetyl* derivative, b. p. 116—117°/11 mm., $n_D^{20.1}$ 1.4342). The nitrile is converted by addition of trimethylamine into γ-*dimethylamino-α-hydroxy*-n-*butyronitrile methochloride*, m. p. 137°
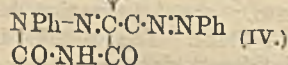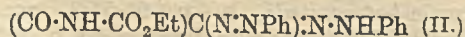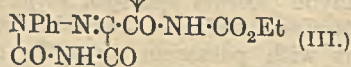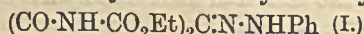
[*chloroaurate*, m. p. 95°; *chloroplatinate*, m. p. 239—240° (decomp.)], which yields on hydrolysis with hydrochloric acid the hydrochloride of α-hydroxy-γ-butyrotrimethylbetaine. This compound gives a chloroaurate, m. p. 173°, and a chloroplatinate, m. p. 216° [the *chloroplatinate* of the *ethyl* ester of *α-hydroxy-γ-butyrotrimethylbetaine* (?) has m. p. 218° (decomp.)], and is therefore identical with that described by Fischer and Göddertz (A., 1911, i, 19). Their synthesis, questioned by Engeland (*loc. cit.*), is thus confirmed. Contrary to the statement of Engeland, α-hydroxy-γ-butyrotrimethylbetaine is decomposed by sulphuric acid at temperatures up to 130°, with evolution of carbon monoxide, and cannot therefore be identical with carnitine, which loses water, yielding *apo*carnitine.

The d-*camphorsulphonate* of the synthetic betaine could not be resolved.   M. CLARK.

Isolation of histidine. H. B. VICKERY (J. Biol. Chem., 1927, **71**, 303—307).—Addition of excess of 2 : 4-dinitro-α-naphthol-7-sulphonic acid to a solution containing histidine causes, even in presence of mineral acid, almost complete precipitation of the amino-acid as the *disulphonate*, $C_6H_9N_3O_2,2C_{10}H_6O_8N_2S,0.5H_2O$, m. p. 251—254° (decomp.) after darkening at 246°; recrystallisation from water causes partial dissociation, but in presence of excess of the sulphonic acid this does not occur. The *monosulphonate* ($+3H_2O$), prepared from the theoretical amounts of histidine and the sulphonic acid in aqueous-alcoholic solution, sinters at 190° and has m. p. 212—214°. The free amino-acid can be recovered from the disulphonate by decomposition with dilute mineral acid and extraction of the sulphonic acid with butyl alcohol.

C. R. HARINGTON.

Reaction between diazonium salts and malonyl-diurethane. M. A. WHITELEY and D. YAPP (J.C.S., 1927, 521—528).—Malonyldiurethane condenses with benzenediazonium salts in presence of acetic acid, giving the *phenylhydrazone* of *mesoxalyldiurethane* (I), m. p. 203° (decomp.), the constitution of which is shown by alternative preparation from monobromo-malonyldiurethane and phenylhydrazine. In presence of sodium carbonate, the condensation yields the *urethane* derivative of *formazylcarboxylic acid* (II), m. p. 159° (decomp.). On treatment with potassium hydroxide, (I) and (II) undergo internal condensation, eliminating alcohol and yielding, respectively, the *carbourethane* (III), m. p. 203° (decomp.), and the *benzeneazo*-derivative (IV), m. p. 256° (decomp.), of 3 : 5 - *diketo* - 2 - *phenyltetrahydro* - 1 : 2 : 4-*triazine*. Hydrolysis of (II) or (IV) with hot 10% potassium hydroxide solution yields formazylcarboxylic acid.

$(CO\cdot NH\cdot CO_2Et)_2C\colon N\cdot NHPh$ (I.)

NPh–N:C·CO·NH·CO_2Et   (III.)
CO·NH·CO

$(CO\cdot NH\cdot CO_2Et)C(N\colon NPh)\colon N\cdot NHPh$ (II.)

NPh–N:C·C·N:NPh   (IV.)
CO·NH·CO

Similar condensations with the *p*-toluene- and

the *o*-nitrobenzene-diazonium salt yield both the hydrazone and the formazyl compound. The *p*-nitro-benzenediazonium salt yields the hydrazone in two isomeric forms, but no formazyl compound, and each of the isomeric hydrazones yields the same triazine compound. The *m*-nitrobenzenediazonium salt yields only the hydrazone, which could not be converted into the corresponding triazine. The following are described : o-*nitrophenylhydrazone*, m. p. 208° (decomp.), m-*nitrophenylhydrazone*, m. p. 215°, p-*nitrophenylhydrazone*, m. p. 218° (decomp.) [*isomeride*, m. p. 208° (decomp.)], and p-*tolylhydrazone*, m. p. 186°, of *mesoxalyldiurethane*; *urethane* derivative, $+Me\cdot CO_2H$, m. p. 105°, of *di-o-nitroformazylcarboxylic acid*; *urethane* derivative, m. p. 153°, of *di-p-tolylformazylcarboxylic acid*, m. p. 182°; *urethane* derivative, m. p. 205°, of 3 : 5-*diketo-2-p-nitrophenyltetrahydro-1 : 2 : 4-triazine-6-carboxylic acid*; *urethane* derivative, m. p. 218° (decomp.), of 3:5-*diketo-2-p-tolyltetrahydro-1 : 2 : 4-triazine-6-carboxylic acid*; 3 : 5-*diketo-2-o-nitrophenyl-6-o-nitrobenzeneazotetrahydro-1 : 2 : 4-triazine*, m. p. 224° (decomp.); 3 : 5-*diketo-6-p-tolueneazo-2-p-tolyltetrahydro-1 : 2 : 4-triazine*, m. p. 246°.

M. CLARK.

Decarboxylated peptides and their derivatives. I. J. VON BRAUN and W. MÜNCH (Ber., 1927, **60**, [*B*], 345—358).—Decarboxylated peptides, $NH_2\cdot CHR\cdot CO\cdot NH\cdot CH_2R'$, appear to be pharmacologically inactive (cf. Guggenheim, A., 1913, i, 773). Their *N*-monomethyl and monoethyl derivatives behave similarly, whereas the corresponding propyl and more highly alkylated compounds are so highly active that it is not possible to establish an exact relationship between degree of activity and magnitude of the alkyl group. The introduction of a second alkyl group renders the compound as inactive as the parent substance.

The decarboxylated peptides are in general prepared by introducing an α-halogenated fatty acid residue into an organic amine and treatment of the resultant halogenated amide with ammonia or a derivative thereof. Treatment of the chlorides of amino- or alkylamino-acids with organic bases offers no advantage with the simpler compounds. The reaction of primary and secondary amines on the chloroacylamides proceeds exclusively according to the scheme $NH_2R'' + Cl\cdot CHR\cdot CO\cdot NHR' \longrightarrow NHR''\cdot CHR\cdot CO\cdot NHR'$, even when R''=Me or Et. With ammonia, the change is more complex, and mixtures of primary, secondary, and tertiary products result. Increase in the weight of R favours the production of primary compounds, whilst, unexpectedly, a similar effect is produced by increase in R'. The following substances are described : *amino-acetethylamide* (*glycyldecarboxyalanine*), $NH_2\cdot CH_2\cdot CO\cdot NHEt$, b. p. 136—138°/13 mm. (*hydrochloride*, m. p. 134°; *picrate*, decomp. 162—164°); *chloroacetisoamylamide*, b. p. 134—135°/13 mm., m. p. 0°, whence *aminoacetisoamylamide*, b. p. 159—160°/11·5 mm., m. p. 26° [very hygroscopic *hydrochloride*; *picrate*, m. p. 152—154° (decomp.)], and *dimethyl-aminoacetisoamylamide*, b. p. 136—137°/12 mm., m. p. +6—8° (very hygroscopic *hydrochloride*; *picrate*, m. p. 129°); *chloroacet-β-phenylethylamide*,

m. p. 67°, b. p. 186—189°/14 mm. (slight decomp.); *aminoacet-β-phenylethylamide, hydrochloride,* m. p. 165° after softening (the free base is non-crystalline and cannot be distilled without decomposition), and the secondary *compound,*

NH(CH₂·CO·NH·CH₂·CH₂Et)₂, m. p. 109—110° (*hydrochloride,* m. p. 210°; *nitroso*-derivative, m. p. 185°), and tertiary *compound,* m. p. 111—112° (*hydrochloride,* m. p. 152°); *β-phenylethylaminoacet-β-phenylethylamide,* m. p. 35° (*hydrochloride,* m. p. 33°); *α-bromopropionisoamylamide,* b. p. 138°/12 mm., m. p. 24°; *α-aminopropionisoamylamide,* b. p. 144—145°/11 mm. (hygroscopic *hydrochloride*; *benzoyl* derivative, m. p. 112—113°), and the corresponding secondary *derivative,* m. p. 65° (*hydrochloride,* m. p. 217°); *α-methylaminopropionisoamylamide,* b. p. 145°/14 mm.; *α-ethylaminopropionisoamylamide,* b. p. 149°/13 mm.; *α-n-propylaminopropionisoamylamide,* b. p. 157°/14 mm. (*hydrochloride,* m. p. 135°; *picrate,* m. p. 86—87°); *α-n-butylaminopropionisoamylamide,* b. p. 168°/14 mm. (hygroscopic *hydrochloride*); *α-isoamylaminopropionisoamylamide,* b. p. 167—168°/10 mm. (*hydrochloride,* m. p. 193°); *α-isohexylaminopropionisoamylamide,* b. p. 182—183°/13·5 mm. (*hydrochloride,* m. p. 183°); *α-bromopropion-β-phenylethylamide,* m. p. 92°; *α-aminopropion-β-phenylethylamide,* b. p. 199—201°/13 mm., m. p. 20—21° (hygroscopic *hydrochloride*); *α-β'-phenylethylamino-β-phenylethylamide hydrochloride,* m. p. 198—199° (noncrystalline base); *α-bromoisohexomethylamide,* b. p. 142—145°/13 mm., m. p. 70—71°; *α-aminoisohexomethylamide,* b. p. 146—147°/12·5 mm. (*picrate,* m. p. 157—159°); *α-bromoisohexoethylamide,* m. p. 93°; *α-aminoisohexoethylamide,* b. p. 145—146°/12 mm. (hygroscopic *hydrochloride*; *chloroplatinate,* decomp. 195—197°), and the corresponding secondary derivative (*hydrochloride,* m. p. 215°). The following α-alkylaminoisohexoethylamides are described: *methyl,* b. p. 139°/13 mm. (hygroscopic *hydrochloride*; *picrate,* m. p. 130°); *ethyl,* b. p. 145°/11 mm. (*hydrochloride,* m. p. 139°); *diethyl,* b. p. 141°/11 mm. (hygroscopic *hydrochloride*); n-*propyl,* b. p. 152°/13 mm. (*hydrochloride,* m. p. 128°; *picrate,* m. p. 150°); n-*butyl,* b. p. 161°/13 mm. (*picrate,* m. p. 83°; *hydrochloride,* m. p. 120°); iso*amyl,* b. p. 167°/13 mm. (*hydrochloride,* m. p. 129°); di*isoamyl,* b. p. 171—174°/12 mm. (very hygroscopic *hydrochloride*); iso*hexyl,* b. p. 179°/13 mm. (*hydrochloride,* m. p. 122°); *heptyl,* b. p. 188°/13 mm. (*hydrochloride*); n-*nonyl,* b. p. 204—206°/11 mm. (*hydrochloride*). *α-Bromoisohexo-β'-phenylethylamide,* m. p. 76°, yields with ammonia *α-aminoisohexo-β-phenylethylamide hydrochloride,* m. p. 203—204° (non-crystalline *base*). *α-β''-Phenylethylaminoisohexo-β-phenylethylamide* gives a *hydrochloride,* m. p. 214°. The reaction of *α-bromo-β-phenylpropionmethylamide,* m. p. 104°, is complicated by the tendency towards intramolecular loss of hydrogen bromide with formation of cinnammethylamide, but *α-amino-β-phenylpropionmethylamide hydrobromide,* m. p. 198—200°, can be obtained in modest yield. *α-Bromo-β-phenylpropion-β'-phenylethylamide* is rather more smoothly transformed into *α-amino-β-phenylpropion-β-'phenylethylamide,* m. p. 56° (m. p. 177—178°), *cinnam-β-phenylethylamide,* m. p. 127°, being also produced. *α-β''-Phenylethyl-*

amino-β-phenylpropion-β'-phenylethylamide hydrochloride, m. p. 180°, is described. H. WREN.

Specific action of peptidases. I. Fission of amides of substituted amino-acids. E. WALDSCHMIDT-LEITZ, W. GRASSMANN, and A. SCHÄFFNER (Ber., 1927, **60**, [*B*], 359—364).—The action of peptidases towards aminoacetethylamide, α-aminopropion*iso*amylamide, α-amino*iso*hexomethylamide, α-amino*iso*hexoethylamide, aminoacetamide, α-amino*iso*hexoamide (cf. von Braun and Münch, preceding abstract), glycylarsanilic, diglycylarsanilic, triglycylarsanilic, *p*-glycyl- and di-*p*-glycyl-aminobenzoic acids (cf. Giemsa and Tropp, A., 1926, 1162) has been investigated. The substances are smoothly and completely hydrolysed by intestinal erepsin, whereas no action is observed with erepsin-free trypsin activated by enterokinase. As with the parent peptides, hydrolysis by erepsin occurs asymmetrically when an amino-acid compound of the substrate has an asymmetric carbon atom. A definite, qualitative difference in the hydrolysis of peptamines by animal and vegetable erepsin is observed, since yeast peptidase has no action. H. WREN.

Mixed aquo-ammonocarbonic acids. L. A. PINCK and J. S. BLAIR (J. Amer. Chem. Soc., 1927, **49**, 509—514; cf. A., 1926, 277).—Guanylcarbamide (dicyanodiamidine) is converted, by the action of anhydrous alcohol in presence of hydrogen chloride at 140°, into carbethoxyguanidine (cf. Nencki, A., 1875, 479). Biuret affords similarly ethyl allophanate, which, when heated with alcohol and hydrogen chloride at 156—157°, is converted into urethane. Carbethoxyguanidine is not produced by heating carbethoxycyanamide with alcohol and ammonium chloride or nitrate, by heating ammonium carbethoxycyanamide, either alone or with alcoholic ammonia, at 110°, or by the action of cyanamide on urethane. Treatment of dicarbethoxycyanamide with ammonium nitrate in absolute alcohol at 100° affords as-*dicarbethoxyguanidine,* m. p. 184°, which indicates that Bassler's dicarbethoxycyanamide is also unsymmetrical (A., 1878, 214). Treatment of sodium dicyanodiamide with ethereal ethyl chloroformate at 90—100° affords *carbethoxydicyanodiamide.* F. G. WILLSON.
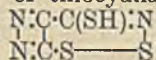
So-called " diethyl dicyanoglutaconate " and some derivatives. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 26—36).—Pure " diethyl αγ-dicyanoglutaconate " (I), prepared by condensing ethyl cyanoacetate with iodoform and sodium ethoxide, gives a colourless sodio-derivative (cf. Errera, A., 1898, i, 297, 490, 632; Ruhemann and Browning, J.C.S., 1898, **73**, 280), and agrees in composition and mol. wt. with the formula $(C_{11}H_{12}O_4N_2)_2,H_2O$. Since it does not lose water when heated at 150°, it has probably the constitution

$(C_{10}H_{12}O_4N)·CO·NH·C:(NH)(C_{10}H_{12}O_4N)$. With bromine in chloroform solution, it yields a brick-red *perbromide,* $(C_{11}H_{12}O_4N_2)_2,H_2O,HBr,Br_6$, m. p. 146—149°, which is decomposed by moist ether into *αγ-dicarbethoxyglutaconamide hydrobromide,* $C_{11}H_{16}O_6N_2,HBr$, decomp. 180°, and bromine. The corresponding *picrate,* m. p. 196·5°, may be obtained from the hydrobromide or perbromide, or directly

from (I) and picric acid in aqueous alcohol. The hydrobromide, which gives no colour with ferric chloride, is converted by boiling with dilute hydrobromic acid into a diethyl dihydroxynicotinate (Guthzeit, A., 1899, i, 450), identical with that obtained by Ruhemann on boiling an alcoholic solution of (I).　　　　　　　H. E. F. NOTTON.

Reaction of organo-magnesium compounds with nitriles. Dimethylcyanamide. L. VUYLSTEKE (Bull. Acad. roy. Belg., 1926, [v], **12**, 535—544).—Magnesium phenyl bromide reacted vigorously with dimethylcyanamide to give, on treatment with sodium hydroxide solution, *dimethylbenzamidine*, b. p. 118°/11 mm., d_4^{20} 1·0160 (*dihydrochloride*, m. p. about 250°). The product of the reaction between dimethylcyanamide and magnesium benzyl chloride yielded, on treatment with water, an analogous compound, $CH_2Ph\cdot CH\!:\!N\cdot NMe_2$, converted by 20% sodium hydroxide solution into phenylacetic acid and dimethylamine. Phenylmalononitrile, m. p. 71°, separated on treating the original aqueous mass with hydrochloric acid. Finally, by treating the original reaction product with hydrochloric acid, followed by ammonium chloride and ammonia, a *compound*, $C_{19}H_{20}N_4$, m. p. 120—121° (decomp.), was obtained, formed by the union of the acidic function of the phenylmalononitrile with the basic function of the amidine compound. From the reaction of dimethylcyanamide with magnesium ethyl bromide, no definite product could be isolated except ethane.　　　S. J. GREGG.

Two new acids of the cyanic series. B. MELIS (Annali Chim. Appl., 1927, **17**, 74—80).—The properties of ψ-thiocyanogen or perthiocyanogen, a product of the oxidation of thiocyanates, are best expressed by the formula $\begin{smallmatrix} N\!:\!C\cdot C(SH)\!:\!N \\ N\!:\!C\cdot S\!\!-\!\!-\!\!S \end{smallmatrix}$. The action of sodium hydroxide (3 mols.) on this compound (2 mols.) yields thiocyanate and two new acids : (1) stable monobasic *hydro-ψ-thiocyanic acid*,

$OH\cdot N\!:\!C\!\!<\!\!\begin{smallmatrix} C(NH)\cdot C(SH) \\ S\!\!-\!\!-\!\!-\!\!-\!\!S \end{smallmatrix}\!\!>\!\!N$; (2) the unstable dibasic

oxyperthiocyanic acid, $O\!\!<\!\!\begin{smallmatrix} NH\cdot CS \\ CS\!-\!NH \end{smallmatrix}$, which exists only in solution, but forms a stable *silver* salt.
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Colour reactions of nitroprusside. L. CAMBI (Annali Chim. Appl., 1927, **17**, 55—58).—Polemical against Tarugi (this vol., 46). The author's previous views are upheld (A., 1913, i, 606 ; 1914, i, 967) and the conclusion is reached that nitroprussides give complex salts (ferropentacyanides), often highly coloured, with all compounds containing groupings with mobile hydrogen able to react with free or combined nitrous acid to form *iso*nitroso- or nitrosoderivatives (cf. Küster, A., 1926, 821).
　　　　　　　　　　　　　　　　　T. H. POPE.

Carbimides. II. Transformations of methylcarbimide under the influence of triethylphosphine. K. H. SLOTTA and R. TSCHESCHE (Ber., 1927, **60**, [*B*], 295—301 ; cf. A., 1925, i, 1047).—Methylcarbimide, b. p. 37·4—37·8°, conveniently prepared by heating a mixture of potassium cyanate, potassium methyl sulphate, and finely-divided calcium oxide, is converted by triethylphosphine in cold, absolute

ethereal solution into a mixture of trimethyl *iso*cyanurate, 2-*methylimino*-4 : 6-*diketo*-3 : 5-*dimethyl*-1 : 3 : 5-*oxdiazine*, $MeN\!\!<\!\!\begin{smallmatrix} CO\cdot NMe \\ CO\!-\!\!-\!O \end{smallmatrix}\!\!>\!\!C\!:\!NMe$, m. p. 114°, and 2 : 4 : 6-*triketo*-3 : 5-*dimethyl*-1 : 3 : 5-*oxdiazine*, which sublimes at 255—258° (more conveniently prepared by addition of solid carbon dioxide to methylcarbimide dissolved in ether at −80°) and is hydrolysed by water to *s*-dimethylcarbamide. The methylimino-derivative is quantitatively converted by boiling water into αγε-trimethylbiuret, m. p. 126° ; prolonged ebullition in solvents of high b. p. causes conversion into trimethyl *iso*cyanurate. It is transformed by hydrogen chloride in moist carbon tetrachloride into 2 : 4 : 6-triketo-3 : 5-dimethyl-1 : 3 : 5-oxdiazine. The latter substance is transformed by methyl alcohol and potassium hydroxide into *methyl dimethylallophanate*, $NHMe\cdot CO\cdot NMe\cdot CO_2Me$, b. p. 104—105°/15 mm., m. p. 47° ; the corresponding *ethyl* ester, b. p. 105—106°/10 mm., m. p. 31°, and the *amide*, m. p. 149°, are described. *α-Nitrosoαγ-dimethylbiuret*, decomp. 101°, and *αγ-dimethylε-ethylbiuret*, m. p. 78°, have been prepared.
　　　　　　　　　　　　　　　　　H. WREN.

Carbimides. III. The principle of symmetry in the formation of trimethylcyanuric esters. K. H. SLOTTA and R. TSCHESCHE (Ber., 1927, **60**, [*B*], 301—304 ; cf. preceding abstract).—Attempts to prepare cyanuric acid derivatives containing methyl groups attached to oxygen and nitrogen within the molecule, lead, in accordance with the principle of symmetry, to compounds having the methyl groups attached exclusively to oxygen or nitrogen or to mixtures of such compounds. Thus cyanuric acid is transformed by diazomethane into the *N*-trimethyl derivative, whereas its *O*-dimethyl compound, m. p. 186°, affords the *O*-trimethyl derivative. Cyanuric chloride and sodium methoxide (1 mol.) give unchanged material and *O*-trimethyl compound. Similarly, *N*-dimethylcyanuric acid, m. p. 222° (obtained by heating methylcarbamide at 230°), is transformed by the action of methyl iodide on its silver salt into the *N*-trimethyl derivative. *N*-Dimethylcyanuric acid could not be caused to react with thionyl chloride or phosphorus pentachloride. A mixture of the *O*- and *N*-trimethylcyanuric acid appears to result from the action of methyl iodide on silver cyanate or cyanurate.
　　　　　　　　　　　　　　　　　H. WREN.

Phosphinocarboxylic acids. A. E. ARBUZOV and A. A. DUNIN (Ber., 1927, **60**, [*B*], 291—295 ; cf. A., 1914, i, 653 ; Nylén, *ibid.*, 1925, i, 1134).—Ethyl phosphinoacetate, b. p. 138·5—138·75°/10 mm., is hydrolysed by dilute hydrochloric acid at 100—120° to phosphinoacetic acid, m. p. 139·5°. β-Phosphinopropionic acid, m. p. 167—168° (Nylén, A., 1926, 826, records m. p. 178—180°), and its *barium* salt are described. α-Phosphinopropionic acid is too hygroscopic to permit analysis. Hydrolysis of ethyl phosphinoformate with concentrated hydrochloric acid yields only phosphorous acid. Ethyl phosphinoacetate resembles ethyl acetoacetate in possessing a reactive methylene group ; it is converted by sodium and methyl iodide into ethyl α-phosphinopropionate, b. p. 143—144°/12 mm.　　　　　　　H. WREN.

α-Truxillic acid, truxone, truxane, indene, and the so-called truxene. H. STOBBE and F. ZSCHOCH (Ber., 1927, 60, [B], 457—473).—Attempts are described to eliminate the uncertainties indicated in the scheme : truxillic acid $(C_9H_8O_2)_2$ [bimolecular] ⟶ truxone (probably bimolecular) ⟶ truxene (bi- or ter-molecular) ⟶ truxenequinone [tribenzoylene-benzene] (termolecular). "Bromotruxone" is converted by zinc dust and acetic acid into the colourless truxone and the colourless, so-called, "dihydrotruxone," m. p. 132°; determinations of mol. wt. in boiling alcohol as well as in benzene and acetone indicate the formula $(C_9H_8O)_2$ for the latter substance. Truxone in boiling cumene and in camphor (cf. Carlsohn, this vol., 300) is also bimolecular. "Bromotruxone" is therefore dibromotruxone, $C_{18}H_{10}O_2Br_2$, dihydrotruxone is truxanediol, and truxone has definitely the formula of a dibenzoylene*cyclo*butane,

$$\begin{matrix} C_6H_4 \cdot CH \cdot CH \cdot CO \\ CO{-}CH \cdot CH \cdot C_6H_4 \end{matrix}$$

. Truxene, prepared from truxone, indan-1-one, or β-phenylpropionic acid, forms colourless crystals, m. p. 369—370° (decomp.); it is termolecular in boiling phenol or cumene, and hence is undoubtedly tribenzylenebenzene (I). The apparently simple reduction of truxone to truxene is therefore accompanied by a change in aggregation. If truxone is heated for a considerable time with amalgamated zinc and hydrochloric acid, truxane (dibenzylene*cyclo*butane),

$$\begin{matrix} C_6H_4 \cdot CH \cdot CH \cdot CH_2 \\ CH_2{-}CH \cdot CH \cdot C_6H_4 \end{matrix}$$

, m. p. 116°, is obtained (cf. Stobbe and Färber, A., 1925, i, 19). If, however, the reduction is less prolonged, a "truxane oil" is obtained from which truxanediol separates. A similar oil is formed when the diol is converted into the corresponding iodide, which is subsequently treated with zinc and glacial acetic acid. The diol is therefore an intermediate product of the conversion of truxone into truxane. In a high vacuum, truxane can be distilled almost without decomposition, whereas when boiled under atmospheric pressure it becomes depolymerised to indene. It thus behaves similarly to many other *cyclo*butane derivatives and is to be regarded therefore as diindene. The relationship of truxane to indene is confirmed optically by observation of their absorption spectra in comparison with those of α-truxillic and *trans*-cinnamic acids. The possibility which is thus suggested that indene is a precursor of truxene is established by the formation of the latter in considerable amount when indene is heated at its b. p. for a protracted period; the trimerisation of indene is effected by condensation with loss of hydrogen, which causes "autoreduction" to hydrindene. The reaction truxone ⟶ truxene by the action of hydriodic acid and phosphorus at 180° consists of a normal production of bimolecular truxane, which becomes depolymerised at the temperature of the change to indene, from which termolecular truxene and hydrindene are derived. It is therefore proposed to substitute the name tribenzylenebenzene for truxene, reserving the latter for the unknown dibenzylene*cyclo*butadiene. Logically, the name "trux-enequinone" must be replaced by tribenzoylenebenzene.

The formation of tribenzoylenebenzene from anhydrobisindanedione is due to the initial fission of the latter compound into two molecules of indanedione, followed by condensation of three unimolecular products or of one such product with a molecule of anhydrobisindanedione to the termolecular compound. A similar explanation is advanced for the formation of tribenzylenebenzene from indanone and for that of tribenzoylenebenzene from 2 : 3-dichloroindone or the dithiin, $\begin{matrix} C_6H_4 \cdot C \cdot S \cdot C \cdot C_6H_4 \\ CO{-}C \cdot S \cdot C \cdot CO \end{matrix}$, as recorded by Brass and Mosl (A., 1926, 839); the di-indonylene of these authors is identical with tribenzoylenebenzene.

H. WREN.

Hydrogenation of xanthone. V. IPATIEV and N. ORLOV (Bull. Soc. chim., 1927, [iv], 41, 208—212).—See this vol., 251.

Acenaphthene. III. Nitro- and amino-derivatives of acenaphthenemonosulphonic acids. K. DZIEWOŃSKI and T. ORZELSKI (Bull. Acad. Polonaise, 1926, A, 347—359).—In the nitration of acenaphthene-3-sulphonic acid or in the sulphonation of 5-nitroacenaphthene, the unsubstituted ring is attacked, as in the naphthalene series. Thus with chlorosulphonic acid in nitrobenzene, 5-nitroacenaphthene affords 5 - *nitroacenaphthene* - 7 - *sulphonic acid* (*sodium* and *barium* salts; *chloride*; *methyl ester*, m. p. 146°), oxidised by sodium dichromate in acetic acid to 5-*nitro-3-sulphonaphthalene*-1 : 8-*dicarboxylic acid*. 5 - *Aminoacenaphthene* - 7 - *sulphonic acid* is obtained on reduction of the nitro-sulphonic acid; the diazonium derivative of this with sodium formate, formic acid, and copper powder affords an acenaphthenemonosulphonic acid isomeric with the known 3- and 5-monosulphonic acids (A., 1924, i, 1178), and hence *acenaphthene-4-sulphonic acid* (*sodium* and *barium* salts; *amide*, m. p. 182—183°). Sodium amalgam in aqueous solution converts it into acenaphthene. Sodium acenaphthene-3-sulphonate with nitric acid (*d* 1·38) in acetic acid (cf. Morgan and Yarsley, A., 1926, 280) affords 6-*nitroacenaphthene*-3-*sulphonic acid* (*sodium* and *barium* salts; *chloride*; *methyl* ester, m. p. 143—144°), yielding on oxidation 6-*nitro-2-sulphonaphthalene*-1 : 8-*dicarboxylic acid*. 6-*Aminoacenaphthene*-3-*sulphonic acid* with sodium amalgam in aqueous solution affords 5-aminoacenaphthene, m. p. 108°. The above reactions establish the structure of the two isomeric nitroacenaphthenesulphonic acids. 1′ - *Hydroxynaphthalene* - 4′ - *azo* - 6 - *acenaphthene* - 4 - *sulphonic acid*, violet-brown, dyeing wool in reddish-brown shades, 1′-*hydroxynaphthalene*-4′-*azo*-6-*acenaphthene*-3-*sulphonic acid*, dark violet, 7-*benzeneazo*-6-*aminoacenaphthene*-4-*sulphonic acid*, cherry-red, dyeing wool in Bordeaux-red shades, and 7-*benzeneazo*-6-*aminoacenaphthene*-3-*sulphonic acid*, dark red, are described.

R. BRIGHTMAN.

Derivatives of fluorene. A. KORCZYŃSKI, G. KARLOWSKA, and L. KIERZEK (Bull. Soc. chim., 1927, [iv], 41, 65—74).—Attempts to obtain 2 : 2′-difluorenyl by the decomposition of 2-diazofluorene or by the action of copper on 2-iodofluorene in nitrobenzene or at 300° have been unsuccessful. 2-Iodo-

fluorene affords no Grignard reagent with active magnesium in ether, and attempts to achieve the synthesis by means of the benzidine transformation also failed. *2-Iodofluorene*, m. p. 128°, obtained by the action of iodine on fluorenylhydrazine hydrochloride in aqueous potassium iodide solution, is also formed by the action of iodine on a boiling alcoholic solution of fluorene in the presence of mercuric oxide. Potassium dichromate in acetic acid oxidises it to *2-iodofluorenone*, m. p. 142—143° (*phenylhydrazone*, m. p. 146°). Bromination of 2-nitrofluorene in boiling acetic acid affords *9-bromo-2-nitrofluorene*, m. p. 143°, yielding on oxidation 2-nitrofluorenone, m. p. 222°, and on reduction in acetic acid solution with zinc and hydrochloric acid, 2-aminofluorene. With copper powder in boiling nitrobenzene, 9-bromo-2-nitrofluorene affords *2 : 2′-dinitrobisdiphenylene-ethane*, m. p. 257—258°, which is oxidised by lead oxide at 150—180° or by sodium dichromate and acetic acid to 2-nitrofluorenone; boiling in nitrobenzene converts it into *2 : 2′-dinitrobisdiphenylene-ethylene*, m. p. above 360°.

Addition of an alcoholic solution of 2-aminofluorene and potassium acetate to a concentrated aqueous solution of fluorene-2-diazonium chloride affords *2 : 2′-diazoaminofluorene*, m. p. 193°; *2 : 2′-diazoaminofluorenone*, m. p. 238—239°, is similarly prepared. *2′-Diazofluorene-2′-aminofluorenone* from aminofluorene and fluorenonediazonium chloride has m. p. 212°; prepared from fluorenediazonium chloride and aminofluorenone, it melts at 230°. It is not established whether the difference in m. p. is due to isomerism or to impurities. Fluorene-2-diazonium chloride and dimethylaniline in alcohol afford *4-dimethylaminobenzeneazo-2′-fluorene*, m. p. 227°. *4-Dimethylaminobenzeneazo-2′-fluorenone* is similarly prepared. R. BRIGHTMAN.

Fluorene series. C. COURTOT and C. VIGNATI (Compt. rend., 1927, **184**, 607—609).—The structure of the 2-bromo-7-nitrofluorene recently described (this vol., 234) has now been definitely established by conversion of the bromoaminofluorenone, m. p. 233—234°, obtained from it into 2 : 7-dibromofluorenone, m. p. 197—198° (Schmidt and Bauer, A., 1906, i, 28), by means of the Sandmeyer reaction. *2-Chlorofluorene*, m. p. 97°, is similarly obtained from 2-aminofluorene. R. BRIGHTMAN.

Electrochemical oxidation of benzene homologues. IV. o-Xylene. F. FICHTER and M. RINDERSPACHER (Helv. Chim. Acta, 1927, **10**, 40—45; cf. Law and Perkin, J.C.S., 1907, **91**, 258).—Electrochemical oxidation of *o*-xylene emulsified in $2N$-sulphuric acid with a lead dioxide anode and lead cathode, using a diaphragm, yields *o*-tolualdehyde (17—22%), *o*-toluic acid (by oxidation of the side-chain), 3 : 4-dimethylphenol (0—6%), toluquinone (7—12%), 1 : 6-dimethyl-*p*-benzoquinone (0—1·3%), and resinous matter (33—44%) probably containing a di-*o*-xylenol. The current efficiency is small. 3 : 4-Dimethylphenol dissolved in *o*-xylene is oxidised in a similar way to resinous di-*o*-xylenol (65—76%), toluquinone (16—28%), and 1 : 6-dimethyl-*p*-benzoquinone (0—6%). The formation of the last two compounds is not due to the presence of impurities

in the starting materials, but to the intermediate formation of 3 : 4-dimethyl-ψ-quinol (Bamberger, A., 1903, i, 557), which may then isomerise to the *m*-xyloquinone or lose a methyl group, giving toluquinone. The presence of 3 : 4-dimethyl-ψ-quinol is shown by the formation of an azo-compound from it with *p*-nitrophenylhydrazine. H. E. F. NOTTON.

Electrochemical oxidation of benzene homologues. V. Ethylbenzene. K. ONO (Helv. Chim. Acta, 1927, **10**, 45—52).—Electrochemical oxidation of ethylbenzene emulsified in *N*-sulphuric acid (cf preceding abstract) without a diaphragm afforded benzaldehyde (0·99%), acetophenone (0·39%), and traces of *s*-diphenyldimethylethylene glycol and ethylquinol, the greater part of the material being oxidised to carbon dioxide and water. In a mixture of acetone and $2N$-sulphuric acid, the products are acetophenone (2·42%), *p*-ethylphenol (1·78%), phenylmethylcarbinol (0·04%), *p*-benzoquinone (0·74%), ethyl-*p*-benzoquinone (3·37%), and a *diethyldiphenol* (3·59%), m. p. 131°, together with a large quantity of resin. In neither case was β-phenylethyl alcohol obtained (cf. Law and Perkin, A., 1905, i, 761). In order to elucidate the course of the reaction, *o*- and *p*-ethylphenols were oxidised in a similar way. The latter gave the diethyldiphenol, m. p. 131°, with traces of *p*-benzoquinone and acetic acid, whilst the former gave ethyl-*p*-benzoquinone (10%), identified as *ethylquinol diacetate*, m. p. 71°. The mode of formation of these products is discussed.
H. E. F. NOTTON.

Preparation of p-dinitrobenzene. G. CHAPAS (Bull. Soc. chim., 1927, [iv], **41**, 193—196).—Addition of the sodium nitrite to the diazonium salt solution before mixing with the molecular copper, and final decomposition of the excess nitrite with nitric acid (63%), afford on steam distillation slightly higher (59·5%) yields of *p*-dinitrobenzene than those obtained by Vesely and Dvořák (A., 1922, i, 690). The author concludes that neither the Sandmeyer nor the Gattermann method for the introduction of groups by the diazonium reaction is quantitative.
R. BRIGHTMAN.

Reactivity of halogenated hydrocarbons. I. Transformations with α- and β-bromonaphthalene. J. LOEVENICH and A. LOESER (Ber., 1927, **60**, [B], 320—326).—Reactivity of halogen atoms attached to the aromatic nucleus depends, not only on their tenacity, but also to a great extent on the substance with which action occurs. Bromobenzene is generally less active than the bromonaphthalenes, but a general decision cannot be made between the reactivities of the latter compounds. Bromobenzene does not react with potassium cyanide in boiling ethylene glycol, whereas α- and β-bromonaphthalenes are converted into the corresponding naphthoic acids in about 15% yield. β-Bromonaphthalene, ethyl chloroformate, and sodium amalgam give a 12·5% yield of β-naphthoic acid (after hydrolysis of the primary ester). α-Bromonaphthalene and benzamide afford benz-α-naphthalide in 51·4% yield, but reaction does not occur with salicylamide; with β-bromonaphthalene, the yields of the naphthalides are 42·3% and 18·4%, respectively, whereas with

bromobenzene the yield is about 50% of the anilide in each case. Sodium acetate converts the α- and β-bromonaphthalenes into the corresponding naphthols in 42·7% and 12% yield. Magnesium and carbon dioxide transform β-bromonaphthalene mainly into ββ'-dinaphthyl, whereas α-bromonaphthalene gives α-naphthoic acid in almost quantitative yield. In the formation of ethers from aryl halides and alkali aryl oxides, bromobenzene and α-bromonaphthalene are more reactive than β-bromonaphthalene. Benzophenone, β-bromonaphthalene, and sodium afford naphthalene (31·2%) and diphenyl-β-naphthylcarbinol (66·2%), the reaction thus resembling that of bromobenzene. H. WREN.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. I. E. DE B. BARNETT, J. W. COOK, and I. G. NIXON (J.C.S., 1927, 504—512).— *o*-Benzoylbenzoic acid is reduced with zinc dust and ammonia to *o*-benzylbenzoic acid (*methyl* ester, b. p. 320°; *ethyl* ester, b. p. 325°; *phenyl* ester), contrary to the statement of Ullmann (A., 1896, i, 563), and the reduced acid is converted quantitatively by concentrated sulphuric acid into anthrone (cf. Gresley, A., 1886, 1028). Magnesium phenyl bromide converts the esters of benzylbenzoic acid into a mixture of 9 : 9-diphenyl-9 : 10-dihydroanthracene and s-oo'-*dibenzylpinacol*, [CH₂Ph·C₆H₄·CPh(OH)·]₂, m. p. 175°; the pinacol is oxidised by chromic acid to *o*-dibenzoylbenzene. *Hydroxyphenyldimethylphthalan*, m. p. 118°, obtained from dimethylphthalide and magnesium phenyl bromide, on distillation yields o-iso*propenyl*-*benzophenone*, b. p. 208—209°/45 mm., m. p. 44°, this substance being oxidised by chromic acid to *o*-benzoylbenzoic acid. *Hydroxyphenyldiethylphthalan* has m. p. 94—95°. From *o*-dibenzoylbenzene and magnesium phenyl bromide, hydroxytriphenylphthalan is probably obtained, since heating the product at 300° yields diphenylanthrone. This last substance on reduction with zinc dust and acetic-hydrochloric acids yields *tetraphenyltetrahydrodianthryl*, $\left(\begin{smallmatrix} CPh_2 \cdot C_6H_4 \\ C_6H_4 \cdot CH- \end{smallmatrix}\right)_2$, m. p. above 340°, the same substance being produced when diphenyldihydroanthracene is heated in a current of oxygen. 9 : 9-*Di-phenyl*-10 : 10-*diphenylmethylene*-9 : 10-*dihydroanthr-acene*, $\begin{smallmatrix} CPh_2 \cdot C_6H_4 \\ C_6H_4 \cdot C:CPh_2 \end{smallmatrix}$, m. p. 286°, is obtained by heating 9 : 9-diphenyl-9 : 10-dihydroanthracene with benzophenone chloride, and 10-*chloro*-9 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*, m. p. 193—194°, is prepared by the action of hydrogen chloride on triphenyldihydroanthranol. 9 : 9 : 10-Triphenyl-9 : 10-dihydroanthracene is best obtained by reducing the anthranol with sodium and amyl alcohol. Aluminium chloride converts 9 : 9-diphenyl-9 : 10-dihydroanthracene, in carbon disulphide solution, into 9-phenylanthracene, and 9 : 10-diphenyldihydroanthracene mainly into 9 : 10-diphenylanthracene. Methyl and *ethyl tri-phenylmethane-o-carboxylates*, m. p. 69°, react with magnesium phenyl bromide, giving *diphenyl-ωω-di-phenyl-o-tolylcarbinol*, m. p. 218° (cf. Haller and Guyot, A., 1904, i, 660). H. BURTON.

Synthesis of triphenyl. R. KUHN and A. WINTERSTEIN (Ber., 1927, **60**, [B], 432—434; cf.

Pummerer and Bittner, A., 1924, i, 381).—Reduction of cinnamaldehyde by zinc–copper couple affords triphenyl (*p*-diphenylbenzene), m. p. 209—210°, in addition to hydrocinnamoin. The identity of the hydrocarbon is established by its conversion successively into *p*-phenylbenzoic acid and diphenyl. H. WREN.

Coloured hydrocarbons. IV. Dehydrogenation of the difluorenyls. V. Difulvenes and their hydrogen derivatives. VI. Absorption spectra of the difulvenes. A. A. VANSCHEIDT (J. Russ. Phys. Chem. Soc., 1926, **58**, 249—269, 269—288, 289—306).—IV. The mobile hydrogen atoms of the >CH·CH< groups of the difluorenyls can be removed by atmospheric oxidation and by the action of silver oxide and other silver salts. Difluorenyl forms an alkali derivative by the action of alcoholic potassium hydroxide. Agitation with air in cold pyridine gives the coloured bisdiphenylene-ethene and the alkali peroxide, $>CK\cdot CK< + O_2 = >C:C< + K_2O_2$. This method has been applied with success to other difluorenyl derivatives. Prolonged agitation in air gives further oxidation products. s-*Diphenylene-di-α-naphthylene-ethylene*, $\begin{smallmatrix} C_6H_4 \\ C_{10}H_6 \end{smallmatrix}>C:C<\begin{smallmatrix} C_6H_4 \\ C_{10}H_6 \end{smallmatrix}$, m. p. 317—318°, as-*diphenylenedi-α-naphthylene-ethylene*, m. p. 315°, *phenylenetri-α-naphthylene-ethylene*, m. p. about 300°, and tetra-α-naphthylene-ethylene, are described. All the above compounds can be easily reduced or oxidised to colourless substances. The hydrocarbons can also be prepared by the action of sodium on a boiling xylene solution of the difluorenyls. Prolonged action gives a brownish-red, insoluble metallic derivative, but the hydrocarbon is regenerated by vigorous agitation in air.

Silver oxide in a mixture of ammonia and pyridine or silver acetate in pyridine readily oxidises the difluorenyls. Metallic silver is precipitated. The absence of alkali hydroxides renders the resulting hydrocarbons much more stable to air. *Tetra-α-naphthylene-ethane*, m. p. 357°, can be prepared pure by this method from tetranaphthofluorenyl and silver acetate in boiling pyridine. The other difluorenyls give by this method compounds identical with those obtained by atmospheric oxidation, except bischrysofluorenyl and bisdiphenylene-ethane, which give amorphous, orange precipitates, probably further oxidation products.

Oxy-salts of copper and mercury oxidise only the highly reactive bisdinaphthofluorenyl. The action is very slow, as also when quinoline is used as a solvent.

V. The colour of the naphthodifulvenes changes from orange-red to dark green with increase in number of naphthalene nuclei. The hydrodifulvenes have a high temperature coefficient of solubility, whereas the difulvenes are readily soluble in the cold. Naphthalene nuclei depress the solubility in both classes of compounds. The difulvenes have a higher m. p. than the hydrodifulvenes, except in the case of tetraphenylene-ethene; they also differ in crystalline structure. They react readily with warm, concentrated sulphuric acid, showing the phenomena of halochromism, but are almost unaffected by alcoholic potassium hydroxide (except tetranaphthylmethene),

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whereas the hydrodifulvenes give no colour with sulphuric acid, but react with the alkali to give brown, metallic derivatives.

In pyridine, both oxidation of the hydrodifulvenes by silver salts, air, etc., and the reduction of the fulvenes by hydrogen, platinum-black, hydrogen sulphide, stibine, and ammonium sulphide are easy, especially if there are several naphthalene nuclei in the molecule. Thus the polynaphthalene derivatives lose their hydrogen when heated with the oxy-salts of copper and mercury, p-benzoquinone, or iodine.

Tetraphenylenemethene adds two atoms of bromine to the central double linking, but its naphtho-derivatives substitute bromine in the nucleus, preserving the chromophore grouping.

VI. Phenyldibenzofulvene, $CHPh{:}C(C_6H_4)_2$, and diphenyldibenzofulvene, $CPh_2{:}C(C_6H_4)_2$, were found to lack the characteristic bands in the ultra-violet of the fluorenes, but did not show a peculiar spectrum of their own, whereas the difulvenes all showed a spectrum type differing markedly from that of the fluorenes, both in the ultra-violet and also in the visible portion. The absorption bands persist even when the solution layers are reduced to 1/30 of the initial thickness, thus showing much greater absorbing power than the quinones.

The introduction of naphthalene nuclei shifts the bands towards the red, but does not alter their nature. These results show that a " difulvene " chromophore of the structure $\overset{C{:}C}{\underset{C{:}C}{{\Big\rangle}}}C{:}C\overset{C{:}C}{\underset{C{:}C}{{\Big\langle}}}$ exists. The absorption curves are very similar to those of indigotin and thioindigotin. Further analogies between the difulvene and indigotin groups are traced, which lend support to the Claaz formulation. M. ZVEGINTZOV.

Perylene and its derivatives. XII. A. ZINKE, K. FUNKE, and N. LORBER (Ber., 1927, **60**, [*B*], 577—581; cf. A., 1925, i, 383, 384).—The action of tribromophenol and aluminium chloride on perylene in nitrobenzene solution (cf. Kohn, A., 1912, i, 760) leads unexpectedly to the production of 4 : 10-dichloroperylene, identified by conversion into 4 : 10-dichlorodinitroperylene. Under certain conditions, aluminium chloride appears able to chlorinate perylene, although reaction between the compounds does not occur at 100—150°. In the presence of nitrobenzene as oxidising agent, perylene is transformed by aluminium chloride or bromide into 4 : 10-dichloroperylene or 4 : 10-dibromoperylene, m. p. 290°; if manganese dioxide is also present, 3 : 4 : 9 : 10-tetrachloroperylene is produced. Perylene and phosphorus pentachloride in nitrobenzene afford 4 : 10-dichloroperylene, whereas hexachloroperylene results from di- or tetra-nitroperylene. Dinitroperylene is obtained by the action of nitric acid (*d* 1·2) on perylene in carbon tetrachloride. Conversion of perylene into 4 : 10-dichloroperylene by nascent chlorine is effected by the addition of sodium dichromate in acetic acid to a solution of perylene and acetic acid in nitrobenzene, through which hydrogen chloride is continuously passed. 4 : 10-Dibromoperylene is analogously prepared by addition of aqueous sodium bromide and acetic acid and hydrogen peroxide and acetic acid to perylene dissolved in nitrobenzene. H. WREN.

Action of sulphuric acid on perylene. C. MARSCHALK (Bull. Soc. chim., 1927, [iv], **41**, 74—81).—Sulphonation of perylene with sulphuric and acetic acids at 75—80° affords a mixture of *perylene-3 : 9-disulphonic acid* and *perylene-3 : 10-disulphonic acid*, the former being the less soluble. Bromine in acetic acid converts both acids into the corresponding dibromoperylene, a reaction which establishes their constitution. On fusion with potassium hydroxide at 180°, the 3 : 9-disulphonic acid affords a yellow product, probably a hydroxyperylenesulphonic acid; at 250°, the mass gives an orange solution in water, with green fluorescence, from which air oxidation precipitates a brown substance differing from the violet quinone obtained by the action of sulphuric acid on 3 : 9-dibromoperylene. Perylene-3 : 10-disulphonic acid when fused with alkali at 270—280° affords a similar product, accompanied by sublimation of perylene. Aqueous sodium hydroxide (*d* 1·38) is without action on these disulphonic acids even at 200°. The *sodium* salts (greenish-yellow) of these acids are described. Perylene-3 : 10-quinone is readily obtained by the action of nitrosylsulphuric acid on perylene at 70—100°. R. BRIGHTMAN.

Thermal decomposition of benzylideneaniline. G. PYL (Ber., 1927, **60**, [*B*], 287—291).—Benzylideneaniline is decomposed by heat into benzonitrile and benzene and into phenanthridine and hydrogen. At 600°, in a porcelain tube, the formation of phenanthridine is not appreciable; maximum yields (2·3%) of the base are obtained at 800°, whereas at 900° it appears to suffer decomposition. Substitution of iron for porcelain or addition of iron turnings, iron oxide, nickel or its oxide, aluminium oxide, or ignited bauxite does not improve the yield of base, whereas iron appears to favour the production of benzonitrile. The phenanthridine does not owe its origin to benzonitrile and aniline (always produced in small amount during the change) or to benzylaniline. Nascent benzylideneaniline does not give better results than the pre-formed compound. H. WREN.

Decomposition of *O*-benzoyldibenzylhydroxylamine. S. GAMBARJAN and O. CIALTICIAN (Ber., 1927, **60**, [*B*], 390—391; cf. A., 1925, i, 1260).—*O*-Benzoyldibenzylhydroxylamine, m. p. 95·5—96·5°, prepared by the action of a slight excess of dibenzylamine on benzoyl peroxide in boiling ethereal solution, is very readily hydrolysed to dibenzylhydroxylamine and is converted in boiling xylene into benzoic acid and benzylbenzylideneamine. H. WREN.

Inhibitory effect of substituents in chemical reactions. I. **Reactivity of the amino-group in substituted arylamines.** G. M. DYSON, H. J. GEORGE, and R. F. HUNTER (J.C.S., 1927, 436—445).—Primary aromatic amines react with thiocarbonyl chloride, yielding thiocarbamyl chlorides, which in presence of water usually eliminate hydrogen chloride, giving thiocarbimides. If an inhibitory group (*e.g.*, bromine, see this vol., 141) is present in the benzene nucleus, elimination of hydrogen chloride is difficult and *s*-diarylthiocarbamides are produced instead of thiocarbimides. The results obtained show that combinations of nuclear methyl groups, hydroxy-

or alkyloxy-substituents do not affect thiocarbimide formation, whereas halogeno-, nitro-, or cyano-groups show inhibitory action, two o-chlorine atoms stopping the action completely. Sulpho- and carboxyl groups are markedly inhibitory. The results are not explicable by the steric hindrance hypothesis. The following thiocarbimides were prepared : m-xylyl-2-, b. p. 247°/760 mm.; o-xylyl-3-, b. p. 262—263°/760 mm.; o-anisyl-, b. p. 266—267°/760 mm.; m-anisyl-, b. p. 267°/760 mm.; 2 : 5-dimethoxyphenyl-, m. p. 32°; 3 : 4-dimethoxyphenyl-; o-ethoxyphenyl-, b. p. 273—275°/760 mm.; m-ethoxyphenyl-, b. p. 278°/758 mm.; o-carbethoxyphenyl-, b. p. 150—151°/1 mm.; m-carbethoxyphenyl-, b. p. 152°/10 mm.; p-carbethoxyphenyl-, m. p. 58°; p-dimethylaminophenyl-, m. p. 67°; p-acetylphenyl-, m. p. 76°; m-cyanophenyl-, an oil, decomp. at 250°; p-cyanophenyl-, m. p. 45°; 2 : 5-dicyanophenyl-, decomp. without melting; o-bromophenyl-, b. p. 257°/770 mm.; 2 : 5-dibromophenyl-, b. p. 240°; m. p. 17—18°; o-iodophenyl-, m. p. 39°; m-iodophenyl-, m. p. 46°; 3 : 5-dibromo-o-tolyl-, m. p. about 25°, b. p. 280°; 3-nitro-o-tolyl-, m. p. 69°; 2-nitro-4-ethoxyphenyl-, m. p. 78°. 2 : 6-Dichloro-, -dibromo-, -di-iodo-p-nitroanilines, 4 : 6-dibromo-o-nitroaniline, 2 : 4 : 6-tribromo-m-nitroaniline, and sulphanilic acid do not react with thiocarbonyl chloride. The thiocarbimides, on treatment with warm alcoholic ammonia, yield the following thiocarbamides : m-xylyl-2-, m. p. 190°; o-xylyl-3-, m. p. 182°; o-anisyl-, m. p. 148—149°; m-anisyl-, m. p. 160°; 2 : 5-dimethoxyphenyl-, m. p. 161°; 3 : 4-dimethoxyphenyl-, m. p. 234°; o-ethoxyphenyl-, m. p. 126°; m-ethoxyphenyl-, m. p. 167°; m-carbethoxyphenyl-, m. p. 294—295°; p-carbethoxyphenyl-, m. p. 159°; p-dimethylaminophenyl-, m. p. 190°; p-acetylphenyl-, m. p. 215° (decomp.); m-cyanophenyl-, m. p. 137°; p-cyanophenyl-, m. p. 169°; 2 : 5-dicyanophenyl-, m. p. 228°; o-bromophenyl-, m. p. 125°; 2 : 5-dibromophenyl-, m. p. 130°; o-iodophenyl-, m. p. 157°; m-iodophenyl-, m. p. 160°; and 2-nitro-4-ethoxyphenyl-, m. p. 177°. Condensation of the thiocarbimides with the corresponding arylamines yields the s-diarylthiocarbamides : s-di-m-xylyl-2-, m. p. 208°; s-di-o-anisyl-, m. p. 134°; s-di-m-anisyl-, m. p. 126°; s-bis-2 : 5-dimethoxyphenyl-, m. p. 127°; s-bis-3 : 4-dimethoxyphenyl-, m. p. 140°; s-di-o-ethoxyphenyl-, m. p. 125°; s-di-m-ethoxyphenyl-, m. p. 115°; s-di-m-carbethoxyphenyl-, decomp. without melting; s-di-p-carbethoxyphenyl-, m. p. 165°; s-di-p-acetylphenyl-, m. p. 198°; s-di-m-cyanophenyl-, m. p. 144°; s-di-p-cyanophenyl, m. p. 171°; s-di-o-bromophenyl-, m. p. 157°; s-bis-2 : 5-dibromophenyl-, m. p. 154°; and s-di-o-iodophenyl-, m. p. 164° (decomp.). s-Bis-3 : 5-dinitrophenyl-, m. p. 160°; s-di-o-carboxyphenyl-, m. p. 300° (decomp.), and s-di-p-acetamidophenylthiocarbamides, m. p. 220° (decomp.), are formed directly from the substituted aniline and thiocarbonyl chloride. The o-substituted thiocarbimides have an unpleasant, pungent odour, whilst the p-substituted have the odour of aniseed. H. BURTON.

p-Cymene. VI. 6-Nitro-2-amino-p-cymene and new azo-dyes. A. S. WHEELER and C. R. HARRIS (J. Amer. Chem. Soc., 1927, 49, 494—499).—Addition of p-cymene to concentrated nitric and

sulphuric acids (1 : 2) at below 0° affords chiefly 2 : 6-dinitro-p-cymene, m. p. 54° (cf. Alfthan, A., 1920, i, 253), together with mono- and di-nitrotoluenes. Reduction of the dinitrocymene with ammonium sulphide yields 6-nitro-2-amino-p-cymene, yellow, m. p. 53° (hydrochloride, m. p. 207—208°, slight decomp. at 175°; hydrobromide, m. p. 233° after darkening at 210—230°; sulphate, m. p. 115—140°; nitrate, m. p. 165° after darkening at 155°; acetyl derivative, m. p. 115°; benzoyl derivative, m. p. 179°). Boiling nitric acid (d 1·5) converts the dinitrocymene into 2 : 6-dinitro-p-toluic acid, whilst fuming nitric acid at 130° affords 2 : 6-dinitroterephthalic acid. The following dyes were prepared from the diazotised nitroamine and the components mentioned : phenol, claretbrown, m. p. 240°; resorcinol, red, m. p. 253°; thymol, chocolate, m. p. 242°; carvacrol, bluish-black, m. p. 216°; β-naphthol, carmine, m. p. 251°; α-naphthol-2-sulphonic acid, grenadine-red, m. p. 243°; α-naphthol-4-sulphonic acid, carmine, m. p. 256°; and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, purple, m. p. not below 325°. The shades given by these dyes on textiles are listed, as well as their colour reactions with concentrated sulphuric acid.
F. G. WILLSON.

Ammonium character of tri- and di-arylamines. II. E. WEITZ and H. W. SCHWECHTEN (Ber., 1927, 60, [B], 545—551).—The salt-like nature of triaryllaminium compounds (this vol., 49) is established further by the observation that tri-p-tolylaminium perchlorate and 1 : 1'-dibenzyl-4 : 4'-dipyridinium dichloride in concentrated alcoholic solution give an immediate precipitate of 1 : 1'-dibenzyl-4 : 4'-dipyridinium perchlorate (cf. A., 1922, i, 366), whilst the solution retains its intensely blue colour. When a solution of tri-p-tolylaminium perchlorate in methyl alcohol is diluted with the same solvent, the intensity of the colour rapidly diminishes and decomposition ensues. When, however, the solvent is methyl alcohol containing 2% of perchloric acid (70%), the solution closely obeys Beer's law. The repression of dissociation by addition of the acid is considered to exclude the possibility that the perchlorate is a quinhydrone, $2N(C_7H_7)_3,(ClO_4)_2$. Evidence is adduced in favour of the view that the compound $N(C_7H_7)_3,SbCl_5$ isolated by Wieland and the product $N(C_7H_7)_3,SbBr_5$, obtained from tri-p-tolylamine, phosphorus tribromide, and bromine, are salt-like in nature and contain quadrivalent antimony. A similar view is scarcely tenable for the compound $N(C_7H_7)_3,PCl_5$, but it is probable that this compound contains a greater proportion of chlorine. This hypothesis is strengthened by the production from ferric chloride of ferrous chloride and a complex aminium salt. Further, halides which readily form complex compounds but have no oxidising action ($HgCl_2$, $AlCl_3$, $BiCl_3$) do not give a blue coloration with tri-p-tolylamine except after addition of halogen. Treatment of di-p-tolylamine with iodine and silver perchlorate in ether or glacial acetic acid gives unstable blue solutions which doubtless contain the aminium perchlorate; the compound from di-p-tolylmethylamine is somewhat more stable. Under similar conditions, the para hydrogen atom of diphenylamine suffers replacement. H. WREN.

Preparation of 4- and 5-nitro- and -amino-hydrindene. J. LINDNER and J. BRUHIN (Ber., 1927, **60**, [B], 435.—439).—Hydrindene is converted by a mixture of nitric and sulphuric acids at −10° into a mixture of 4- and 5-nitrohydrindene, which is separated into its components by alternate fractional distillation under reduced pressure and freezing of the individual fractions. 5-Nitrohydrindene has m. p. 40—40·5°, b. p. 152°/14 mm.; 5-aminohydrindene, m. p. 37—38°, b. p. 131°/15 mm., and its acetyl derivative, m. p. 106°, are described. 4-*Nitrohydrindene*, m. p. 44—44·5°, b. p. 139°/10 mm., is reduced to 4-*aminohydrindene*, m. p. −2° to 0°, b. p. 128°/about 15 mm. (*acetyl* derivative, m. p. 126—127°). The structure of the nitro-compounds is established by their oxidation to the corresponding nitrophthalic acids. The 4-derivatives do not appear identical with those described by Borsche and John (A., 1924, i, 723). H. WREN.

New transformation of naphthylamine-sulphonic acids. A. WAHL and G. VERMEYLEN (Compt. rend., 1927, **184**, 334—336).—When α-naphthylamine-8-sulphonic acid is agitated with excess of concentrated sulphuric acid at 75—80° for some hrs., it is converted into the 4-sulphonic acid, identified by conversion into 1 : 4-dichloronaphthalene. The transformation may be explained by hydrolysis of the 8-acid, followed by normal sulphonation in the 4-position. The 8-acid hydrolyses more readily than the 4-acid. E. W. WIGNALL.

Additive compounds between quadri- and bivalent metals and organic bases. Probable nature of secondary valencies. G. SCAGLIARINI (Atti R. Accad. Lincei, 1926, [vi], **4**, 574—576).—Debye and Hückel's theory of solutions is discussed in relation to the compositions of the complex compounds formed by treatment of halides of tin, titanium, cobalt, or nickel with organic bases in various solvents. A rational explanation of the formation of such compounds may be reached on the assumption that the secondary valencies are identical with the residual affinities due to their electric moments.
T. H. POPE.

Manufacture of nitro-derivatives of aromatic amines. J. W. LEITCH AND CO., LTD., and A. E. EVEREST.—See B., 1927, 101.

p-Cymene. VII. **Bromination of 2 : 6-di-amino-*p*-cymene.** A. S. WHEELER and E. DE W. JENNINGS (J. Amer. Chem. Soc., 1927, **49**, 572—575).—The bromination of 2 : 6-diacetamido-*p*-cymene (cf. Alfthan, A., 1920, i, 253) in cold carbon tetrachloride yields 3-*bromo*-2 : 6-*diacetamido-p-cymene*, m. p. 261°, from which 3-*bromo*-2 : 6-*diamino-p-cymene*, m. p. 99—100°, is obtained by hydrolysis with boiling aqueous hydrochloric acid [*monohydrochloride*, m. p. 162—168° (decomp.); *dibenzoyl* derivative, m. p. 257°]. Bromination of free 2 : 6-diamino-*p*-cymene in cold carbon tetrachloride yields 3 : 5-*dibromo*-2 : 6-*diamino-p-cymene dihydrobromide*, m. p. 136° (decomp.) after darkening at 125°. The *diacetyl* derivative, m. p. 232°, and *dibenzoyl* derivative, m. p. 215°, of the dibromo-*p*-cymylenediamine are described. F. G. WILLSON.

Action of nitrobenzene on aromatic diamines. G. B. CRIPPA [with P. CASTELLI] (Gazzetta, 1927, **57**, 15—19).—When a nitrobenzene solution of a phenylenediamine containing sodium carbonate is subjected to prolonged boiling, the amine reacts with the solvent, giving an aminoazo-derivative. In this way, *p*-phenylenediamine yields *p*-aminoazobenzene, a small proportion of azoaniline, and a black, vitreous mass. For the formation of *p*-aminoazobenzene, two mechanisms are possible : (1) $NH_2 \cdot C_6H_4 \cdot NH_2 +$ $Ph \cdot NO_2 = H_2O + NH_2 \cdot C_6H_4 \cdot N \vdots NPh \vdots O \xrightarrow{-O}$ $NH_2 \cdot C_6H_4 \cdot N \vdots NPh$; (2) $Ph \cdot NO_2 \xrightarrow{-O} Ph \cdot NO$ and $NH_2 \cdot C_6H_4 \cdot NH_2 + Ph \cdot NO = H_2O + NH_2 \cdot C_6H_4 \cdot N \vdots NPh$. The azoaniline formed is doubtless a bimolecular oxidation product of the *p*-phenylenediamine. The black compound resembles aniline-black and may consist of polynuclear oxidation products derived from tetra-aminodiphenylbenzoquinonedi-imine formed initially. T. H. POPE.

Nickel and cobalt arylazo-β-naphthylamine compounds. G. B. CRIPPA (Gazzetta, 1927, **57**, 20—25).—Unlike copper and iron (A., 1926, 307), powdered nickel and cobalt yield compounds of the type $Ni(or\ Co)(R \cdot N_2 \cdot C_{10}H_6 \cdot NH_2)_2$ when boiled with arylazo-β-naphthylamines in aniline or nitrobenzene solution. If the boiling is prolonged for several hrs., the catalytic action of the metal comes into play and the corresponding triazoles are gradually formed. The nickel arylazo-β-naphthylamines crystallise in green needles, are highly stable towards alkalis, and are readily decomposed by dilute acid with liberation of the arylazo-β-naphthylamines. The cobalt compounds have similar properties and are violet-brown. When the amino-group of the azo-derivative is not in the *ortho*-position, the linking with the metal is unstable and the compound cannot be isolated.

[With E. VIGEVANI.]—Nickel (cobalt) *compounds* of the following azo-derivatives were prepared : benzeneazo-β-naphthylamine, m. p. 260° (265°); *o*-tolueneazo-β-naphthylamine, m. p. 245° (215—217°); *m*-toluene-azo-β-naphthylamine, m. p. 267° (220°); *p*-toluene-azo-β-naphthylamine, m. p. 281° (281°); ψ-cumene-azo-β-naphthylamine, m. p. 264—266° (268°); *p*-chlorobenzeneazo-β-naphthylamine, m. p. 271—272° (215—217°); *p*-bromobenzeneazo-β-naphthylamine, m. p. 262—263° (235—237°); *p*-acetophenone-1-azo-β-naphthylamine, m. p. 285° (270°); α-naphthalene-1-azo-β-naphthylamine, m. p. 271°. Cobalt α′-naphthalene-1-azo-β-naphthylamine has m. p. 250°. T. H. POPE.

Constitution of the diazonium derivative of 1-amino-2-naphthol-4-sulphonic acid. M. BATTEGAY and J. SCHMIDT (Bull. Soc. chim., 1927, [iv], **41**, 205—208).—Of the alternative formulæ for the diazonium derivative of 1-amino-2-naphthol-4-sulphonic acid, (II) is dismissed as improbable, since the presence of the strongly basic diazonium hydroxide group with the sulphonic group in the same molecule would probably lead to internal salt formation. The resultant betaine structure (IV) is not consistent with the formation of definite sodium, magnesium, or zinc salts by precipitation from the neutral diazonium

solution. The quinonoid structure (III) is rejected on account of the stability of the diazonium compound towards potassium iodide solutions, no oxidising
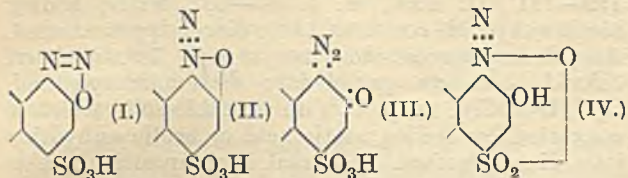
power being observed. The adopted formula (I) is further supported by the isolation of an acidic *copper* compound, $(C_{10}H_7O_5N_2S)_2Cu,6H_2O$, brown crystals with a metallic lustre, which gives no precipitate with sodium hydroxide and yields a yellow solution with ammonia.　R. BRIGHTMAN.

Cold oxidation (decolorisation) of colouring matters in acid media by sodium hypochlorite. A. SEYEWETZ and E. CHAISE (Bull. Soc. chim., 1927, [iv], **41**, 196—205).—The action of cold sodium hypochlorite on suspensions of nitrophenols and nitroamines in dilute hydrochloric acid at 15—20° has been examined. Nitro-phenols and -naphthols undergo chlorination in the first stage of the reaction and are subsequently oxidised, the final products being carbon dioxide, chloropicrin, and nitric acid. Chlorination takes place first in all cases when the phenol contains a free *meta* position with respect to the nitro-group. In the case of picric acid, in which the *meta* positions are occupied, reaction is very slow, and affords mainly chloropicrin and carbon dioxide, with formation of picryl chloride as a side reaction. The latter compound is not attacked under the conditions described. The presence of a *p*-nitro-group appears to favour the formation of chloro-quinones. Thus *p*-nitrophenol affords more chloranil and nitric acid, although the main oxidation products are chloropicrin and carbon dioxide; 2-chloro- and 2 : 6-dichloro-4-nitrophenol are formed initially. 2 : 4-Dinitrophenol behaves similarly, affording 6-chloro-2 : 4-dinitrophenol initially, and chloranil as an oxidation by-product. With 2 : 4-dinitro-α-naphthol, 2-chloro-α-naphthaquinone is first formed and subsequently oxidised to phthalic and oxalic acids. 2 : 4-Dinitro-1-naphthol-7-sulphonic acid (naphthol-yellow *S*) is rapidly oxidised to 4-sulphophthalic acid and chloropicrin. With nitro-amines, chlorination takes place unaccompanied by oxidation. Thus *p*-nitroaniline affords 2-chloro- and 2 : 6-dichloro-4-nitroaniline, *o*-nitroaniline gives 4 : 6-dichloro-2-nitroaniline, *m*-nitroaniline affords a mixture, and dinitroaniline a *chloronitroaniline*, m. p. 145—146°. 2 : 4 : 6-Trinitroaniline, picramic acid, and di-, tetra-, and hexa-nitrodiphenylamines are unattacked. *o*-Nitrophenol is attacked much more slowly than the *p*-isomeride; 4 : 6-dichloro-2-nitrophenol is formed initially and subsequently oxidised to carbon dioxide, chloropicrin, and nitric acid.
　R. BRIGHTMAN.

Reduction of *o*-nitrophenyl*iso*diazomethanes. F. D. CHATTAWAY and A. J. WALKER (J.C.S., 1927, 323—333; cf. A., 1925, i, 1193; 1926, 169).— 1-2′ : 4′-Dibromophenyl-3-*o*-nitrophenyl*iso*diazometh-

ane is reduced by boiling alcohol or stannous chloride to cycloazi-2 : 4-*dibromophenylbenztriazone* (I, R=$C_6H_3Br_2$), m. p. 178°,

which on further reduction with tin and hydrochloric acid in the cold gives o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine*, m. p. 184° (o-*acetyl* derivative, m. p. 210°; o-α-*diacetyl* derivative, m. p. 184°), identical with the reduction product of β-o-*nitrobenzoyl*-2 : 4-dibromophenylhydrazine, m. p. 180°. Alcoholic potassium hydroxide converts (I) into *potassium* 2 : 4-*dibromodiazoaminobenzene-2′-carboxylate*, m. p. 230—240° (decomp.) [*acid*, m. p. 151° (decomp.)], and an isomeric compound isolated as an *acid*, $C_{13}H_9O_2N_3Br_2$, m. p. 275°. By similar methods, cycloazi-p-*bromophenylbenztriazone*, m. p. 197°; cycloazi-2 : 4-*dichlorophenylbenztriazone*, m. p. 167° (labile), 157° (stable); and cycloazi-2 : 4 : 6-*trichlorophenylbenztriazone*, m. p. 258°, were obtained. Hydrolysis of the cycloazi-2 : 4-dichloro-compound gives 2 : 4-*dichlorodiazoaminobenzene-2′-carboxylic acid*, m. p. 163—167° (decomp.), and an *acid*, $C_{13}H_9O_2N_3Cl_2$, m. p. 275°.

To show that the cycloazi-benztriazones had constitution (I) and not (II), there were prepared p-*bromophenylbenztriazone* (II, R=C_6H_4Br), m. p. 196°, from methyl *p*-bromodiazoaminobenzene-*o*′-carboxylate by oxidation with alcohol; and 2 : 4-*dibromophenylbenztriazone*, m. p. 136°.

Hydrolysis of the last substance with alcoholic potassium hydroxide gave 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid as the sole product. H. BURTON.

[Nuclear condensation of phenols with nitriles.] K. HOESCH (Ber., 1927, **60**, [*B*], 389; cf. Houben, this vol., 143).—A question of priority.
　H. WREN.

Terpenes and related compounds. III. Isomerisation of safrole under reduced pressure. N. HIRAO (J. Soc. Chem. Ind. Japan, 1927, **30**, 81—82).—A mixture of 3 parts of powdered potassium hydroxide and 100 parts of safrole is heated to boiling for 3·5 hrs. under 13—18 mm. pressure, and 94% isomerisation is obtained without resinification. When the amount of alkali is reduced to 2 parts, the mixture has to be heated for 5 hrs. to complete the reaction. The reaction is retarded by the presence of a small amount of water, but it can be completed by protracting the time of heating. The isomerisation is unsatisfactory when sodium hydroxide is used.　K. KASHIMA.

3-Nitro-*p*-phenetidine. F. REVERDIN (Helv. Chim. Acta, 1927, **10**, 3—4).—D.R.-P. 101778/1898 states that the nitration of *p*-ethoxyacetanilide dissolved in sulphuric acid with nitric and sulphuric acids at 5° yields a yellow product which is hydrolysed by 25% sulphuric acid to 2-nitro-4-aminophenetole, m. p. 170°. It is now shown that pure 2-nitro-4-acetamidophenetole, m. p. 123°, prepared by this method, is almost colourless, and is hydrolysed to 2-nitro-4-aminophenetole (3-nitro-*p*-phenetidine), m.p. 40°.　H. E. F. NOTTON.

Electrochemical oxidation of phenols. *m*-Xylenol, thymol, and potassium *iso*eugenyl sulphate. F. FICHTER and M. RINDERSPACHER

(Helv. Chim. Acta, 1927, **10**, 102—106).—Electrochemical oxidation of an emulsion of *s-m*-xylenol in 2*N*-sulphuric acid affords *m*-xyloquinone and a dixylenol resin. The same products were obtained, in 30% and 11% yield, respectively, in sulphuric acid–acetone solution. The resin is obtained in larger quantities when the xylenol is dissolved in *o*-xylene; it gives, on distillation in a high vacuum, a fraction, b. p. 185—190°, which has the composition of a dixylenol. Further experiments on the electrochemical oxidation of thymol (cf. A., 1914, i, 946) have resulted in the isolation of pure dithymol as its hydrate, m. p. 140° (cf. A., 1908, i, 84), in addition to thymoquinone and much resinous matter. A solution of potassium *iso*eugenyl sulphate in aqueous sodium carbonate is oxidised in a similar way to vanillin (50%), vanillic acid (4%) (A., 1925, i, 813), and a brown, amorphous *substance* (20%), probably a divanillic acid.   H. E. F. NOTTON.

Action of nitrous acid on *ar*-tetrahydro-α-naphthol and on 5 : 8– and 5 : 6(or 7 : 8)-dihydro-α-naphthols. F. M. ROWE and E. LEVIN (J.C.S., 1927, 530—531).—Schroeter's statement (A., 1922, i, 130) that nitrous acid converts *ar*-tetrahydro-α-naphthol into 4-nitroso-*ar*-tetrahydro-α-naphthol (cf. J.C.S., 1918, **113**, 965) is confirmed, since the product is identical with that obtained by interaction of *ar*-tetrahydro-α-naphthaquinone and hydroxylamine. Oxidation of the nitroso-compound with dilute nitric acid yields 4-*nitro*-ar-*tetrahydro-α-naphthol*, m. p. 123°. The products of interaction of phenylhydrazine and *ar*-tetrahydro-α-naphthaquinone, of aniline and 4-nitroso-*ar*-tetrahydro-α-naphthol, and of diazobenzene chloride and *ar*-tetrahydro-α-naphthol are also identical. The compounds previously described as 4-nitro-5 : 8-dihydro-α-naphthol and 4-nitro-5 : 6-(or 7 : 8)-dihydro-α-naphthol (*ibid.*, 1921, **119**, 2024) are shown by analysis to be 4-nitroso-5 : 8- and 5 : 6-(or 7 : 8)-dihydro-α-naphthols.   M. CLARK.

Acetylbenzoyl derivatives of 7-amino-β-naphthol. L. C. RAIFORD and W. F. TALBOT (J. Amer. Chem. Soc., 1927, **49**, 559—561).—Treatment of 7-amino-β-naphthol with acetic anhydride in pyridine solution affords the *diacetyl* derivative, m. p. 156°, which, on hydrolysis with alcoholic sodium hydroxide, yields the corresponding acetamidonaphthol, m. p. 232° (cf. Kehrmann and Wolff, A., 1900, i, 449), from which 7-*acetamido-β-naphthyl benzoate*, m. p. 177°, is obtained by benzoylation in alkaline solution. On hydrolysis, the latter loses the benzoyl group. 7-Benzamido-β-naphthyl benzoate, m. p. 181° (cf. Sachs, *ibid.*, 1906, i, 829), affords 7-*benzamido-β-naphthol*, m. p. 243—246°, on hydrolysis, and this, on acetylation, yields 7-*benzamido-β-naphthyl acetate*, m. p. 177°. No rearrangement characteristic of acetylbenzoyl derivatives of *o*-aminophenols (cf. Raiford and Coutare, A., 1924, i, 1304) was observed.   F. G. WILLSON.

Aromatic thionyl and chlorothionyl derivatives. I. Thionylpyrocatechol and dichlorothionylquinol. A. GREEN (J.C.S., 1927, 500—504).—Thionylpyrocatechol, $C_6H_4\!\!<\!\!^O_O\!\!>\!\!SO$, b. p. 137—138°/105 mm., is best obtained by treating pyro-catechol with thionyl chloride in carbon disulphide–pyridine solution. Boiling acetic acid with a trace of pyridine converts it into *monoacetylpyrocatechol*, b. p. 189—191°/102 mm., m. p. 57—58°, whilst boiling acetic anhydride converts it into diacetylpyrocatechol. *Acetylbenzoylpyrocatechol* has m. p. 78°. Thionyl chloride converts quinol into *dichlorothionylquinol*, $C_6H_4(O\cdot SOCl)_2$, m. p. 75°, an unstable solid which is converted by boiling acetic acid or acetic anhydride into diacetylquinol. Thermal decomposition yields *p*-benzoquinone together with other products.

H. BURTON.

Action of chlorosulphonic acid on phenols. IV. J. POLLAK and E. GEBAUER-FÜLNEGG (Monatsh., 1926, **47**, 537—558).—Phloroglucinol reacts with ten times its weight of chlorosulphonic acid at the ordinary temperature to yield the trisulphonic acid, which, however, could not be freed from inorganic acids, and was isolated as its *ammonium* salt, $+1\cdot5H_2O$, decomp. 272—275° (depending on manner of heating). The crude acid treated with potassium hydroxide and methyl sulphate is not methylated, but yields only its *potassium* salt, $+1\cdot5H_2O$, and the action of bromine followed by potassium acetate yields only 2 : 4 : 6-tribromophloroglucinol. Either the free acid or its ammonium salt when heated with phosphorus pentachloride for 4 hrs. at 130° yields Δ^2-octachloro*cyclo*hexenone. The acid when heated in ether solution with aniline yields only aniline sulphate, but when heated with the free base it yields *s*-trianilinobenzene. When the acid is heated with *p*-aminophenol for 0·5 hr. at 105—110°, only the sulphate of the base is obtained, but in boiling nitrobenzene the product is 2 : 4 : 6-*tri-p-hydroxyanilinophloroglucinol*, decomp. above 350°. These reactions show the ease with which the sulphonic acid groups are removed, and short heating with hydrochloric acid (1 : 1) effects their removal quantitatively, a little phloroglucide also being formed. At higher temperatures (110°) or with 20—50 times the quantity of chlorosulphonic acid, phloroglucinol yields *phloroglucinol-2 : 6-disulphonyl chloride*, m. p. 184°, which when treated with aniline in ether solution yields the *anilide*, decomp. 275°, but when heated with aniline without a solvent it yields trianilinobenzene. The chlorosulphonyl groups are quantitatively eliminated by heating with hydrochloric acid, but the anilide is relatively stable towards acids. The potassium salt of the disulphonic acid, treated with 6 mols. of chlorosulphonic acid, is converted into the trisulphonic acid. Conversely, long treatment of the latter with a large excess of chlorosulphonic acid converts it into the disulphonyl chloride. At 150—160°, the reaction between phloroglucinol and chlorosulphonic acid yields pentachlorophenol and hexachlorobenzene.

[With O. LITVAY.]—The action of chlorosulphonic acid on pyrogallol for 0·75 hr. at 100° yields the *disulphonyl chloride*, m. p. 178° (decomp.), identical with that obtained by the action of chlorosulphonic acid on the disulphonic acid obtained by Delage (A., 1901, i, 274). By the action of phosphorus pentachloride at 140° or of thionyl chloride at 100° on pyrogalloldisulphonyl chloride, 1-*chloro-2 : 6-dihydroxybenzene-3 : 5-disulphonyl chloride*, decomp. 187—189°, is obtained, whilst at a higher temperature penta-

chlorophenol and hexachlorobenzene are the sole products. The last two products are also obtained by the action of chlorosulphonic acid on pyrogallol at higher temperatures.

[Correction.]—The compound to which the constitution *p*-dichlorobenzodiquinone was previously assigned (Pollak and Gebauer-Fülnegg, A., 1926, 1244) is now shown to be chloranilic acid.　　　J. W. BAKER.

Benzyl δ-chlorobutyl ether : a new unsymmetrical derivative of tetramethylene glycol. G. M. BENNETT and A. L. HOCK (J.C.S., 1927, 472—476).—Benzyl chloride reacts with the sodium derivative of trimethylene glycol, yielding *benzyl γ-hydroxypropyl ether*, b. p. 155°/23 mm., 172°/43 mm., d_4^{20} (vac.) 1·0474, n_a^{20} 1·5128, which on treatment with thionyl chloride furnishes *benzyl γ-chloropropyl ether*, b. p. 129°/16 mm., d_4^{20} (vac.) 1·0706, n_a^{20} 1·5102. This chloro-ether is converted by aqueous-alcoholic sodium cyanide into *γ-benzyloxybutyronitrile*, b. p. 157°/12 mm., 166°/16 mm., d_4^{20} (vac.) 1·026, n_a^{20} 1·5005, which on hydrolysis and esterification gives *ethyl γ-benzyloxybutyrate*, b. p. 160°/14 mm., d_4^{20} (vac.) 1·036, n_a^{20} 1·4930. *Ethyl β-benzyloxyethylmalonate*, b. p. 213°/22 mm., d_4^{20} (vac.) 1·0795, n^{20} 1·4908, obtained by condensing benzyl β-chloroethyl ether with ethyl sodiomalonate, on hydrolysis and thermal decomposition gives *γ-benzyloxybutyric acid*, which on esterification yields the above ethyl ester. This ester on reduction in toluene solution with sodium and ethyl alcohol yields *benzyl δ-hydroxybutyl ether*, b. p. 157°/12 mm., d_4^{20} (vac.) 1·029, n_a^{20} 1·5107, which is converted by thionyl chloride into *benzyl δ-chlorobutyl ether*, b. p. 135°/12 mm., d_4^{20} (vac.) 1·0572, n_a^{20} 1·5083. *Benzyl β-iodoethyl ether* has b. p. 148—149°/14 mm.; it reacts with magnesium, giving a Grignard reagent.　　　H. BURTON.

Diphenylphenylacetylenylcarbinol [triphenylpropargyl alcohol]. III. Esters. IV. Attempts to obtain the free radical, triphenylpropargyl, $CPh:C\cdot CPh_2$. C. MOUREU, C. DUFRAISSE, and A. S. HOUGHTON (Bull. Soc. chim., 1927, [iv], 41, 53—56, 56—58).—III. The following esters of triphenylpropargyl alcohol have been obtained by treating the chloride (cf. A., 1923, i, 921; 1925, i, 136) with the appropriate silver salt in benzene : *acetate*, m. p. 93—94° ; *propionate*, m. p. 83—84° ; *butyrate*, m. p. 73—74° ; *benzoate*, m. p. 95—100°. The esters are stable in a vacuum, especially over sulphuric acid, and are hydrolysed by alcoholic but not by aqueous potassium hydroxide. With methyl or ethyl alcohol, they afford the corresponding triphenylpropargyl ether.

IV. Treatment of triphenylpropargyl chloride with iron in glacial acetic acid in a current of carbon dioxide at 40° affords *αγγδδζ-hexaphenyl-Δ^{αε}-hexadiinene*, $(CPh:C\cdot CPh_2\cdot)_2$, m. p. 179°, together with a yellow substance, m. p. 245°. The corresponding bromide with magnesium in ether affords the same products.　　　R. BRIGHTMAN.

Influence of the sulphur atom on the reactivity of adjacent atoms or groups. I. Qualitative comparison of reactivities of chlorine and hydroxyl in α-, β-, γ-, and δ-positions to a sulphur atom. G. M. BENNETT and A. L. HOCK (J.C.S.,

1927, 477—483).—*γγ'-Dibenzyloxydipropyl sulphide* and *δδ'-dibenzyloxydibutyl sulphide*, obtained by the action of aqueous-alcoholic sodium sulphide on the corresponding chloro-ethers, are converted by cold, fuming hydrobromic acid into *γγ'-dihydroxydipropyl sulphide* (*di-p-nitrobenzoyl* derivative, m. p. 104—105°) and *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide*, $(C_4H_8S\cdot[CH_2]_4\cdot OH)Br$ (I) [*picrate*, m. p. 189—190° ; *bromoplatinate*, decomp. without melting at 165—170° ; *bromoaurate*, m. p. 65—70° (decomp.)]. Decomposition of (I) by heat furnishes tetrahydrothiophen [*methiodide*, m. p. 195—197° (decomp.) (von Braun and Trümpler, A., 1910, i, 275, give m. p. 185—190°) ; *mercurichloride*, m. p. 127—133° (decomp.) (Grischkevitsch-Trochimovski, A., 1917, i, 153, gives m. p. 124·5—125·5°) ; *bromoplatinate*, decomp. 236—238°]. *Tetrahydrothiophen-δ-bromobutylsulphonium bromide* (*picrate*, m. p. 92—96°) was produced from (I) by keeping it in a vacuum for several weeks.

A study of the reactivities of the hydroxyl groups or chlorine atoms in the α-, β-, γ-, and δ-positions to the sulphur atom (cf. A., 1926, 146 ; 1923, i, 734) gives the following order of reactivity : α>β>γ<δ. The reactivity of the sulphur atom, involving addition of methyl iodide or oxygen, varies in the order α<β<γ. An explanation of these results is founded on the electronic theory of valency, and it is suggested that the high reactivity of the hydroxyl group in the δ-position is due to transmission of the polar effect of the sulphur atom through space, not along the carbon chain.　　　H. BURTON.

Constitution and colour. XIII. Constitution of triphenylmethane dyes. F. KEHRMANN, H. GOLDSTEIN, and A. VON SALIS (Helv. Chim. Acta, 1927, 10, 33—39).—A close parallelism exists between the absorption spectra of corresponding mono-, di-, and tri-acid salts of malachite-green, $NMe_2\cdot C_6H_4\cdot CPh:C_6H_4:NMe_2Cl$, and Bindschedler's green, $NMe_2\cdot C_6H_4\cdot N:C_6H_4:NMe_2Cl$, between those of corresponding mono- and di-acid salts of fuchsonimine and *N*-phenylbenzoquinonedi-imine ; and between those of dimethylfuchsonimonium salts, $CPh_2:C_6H_4:NMe_2X$, and phenylbenzoquinoneiminedimethylimonium, $NPh:C_6H_4:NMe_2X$, salts. Corresponding compounds differ only in the replacement of the ·CPh: group by ·N: and, since the quinoneimine derivatives undoubtedly possess a *p*-quinonoid structure, the triphenylmethanes must be similarly constituted.　　　H. E. F. NOTTON.

Condensation of substituted anilines with *cyclo*pentanonecyanohydrin. Derivatives of 1-anilino*cyclo*pentane-1-carboxylic acid. S. H. OAKESHOTT and S. G. P. PLANT (J.C.S., 1927, 484—493).—A mixture of *o*-toluidine and *cyclo*pentanone in acetic acid, when treated with potassium cyanide, yields 1-*o*-*toluidino*-1-*cyano*cyclo*pentane*, m. p. 68°, which is hydrolysed by cold, concentrated sulphuric acid to 1-*o*-*toluidino*cyclo*pentane*-1-*carboxylamide*, m.p. 122° (*hydrochloride*). Further hydrolysis of the amide gives 1-*o*-*toluidino*cyclo*pentane*-1-*carboxylic acid*, m. p. 128°. By a similar reaction there were prepared the following derivatives of 1-*cyano*cyclo*pentane* : 1-*o*-*anisidino*- ; 1-m-*anisidino*-, m. p. 132° ; 1-p-

anisidino-; 1-*veratrylamino*-, m. p. 98°; 1-mm'-*dimethoxyanilino*-, m. p. 150°; 1-o-*chloroanilino*-; 1-m-*chloroanilino*, m. p. 47°; 1-p-*chloroanilino*-, m. p. 73°; 1-o-*bromoanilino*-; 1-m-*bromoanilino*-; 1-p-*bromoanilino*-, m. p. 69°; 1-m-*nitroanilino*-, m. p. 95°; 1-p-*nitroanilino*-, m. p. 165°; 1-o-*carboxyanilino*-, m. p. 122°; 1-m-*carboxyanilino*-, m. p. 153°; and 1-p-*carboxyanilino*-, m. p. 189—190°. o-Nitroaniline does not furnish a cyano*cyclo*pentane, and it is found that the rate of formation of these nitriles is dependent on the position of the substituent in the benzene nucleus. The corresponding nitriles on hydrolysis yield the following derivatives of *cyclo*pentane-1-carboxylic acid : 1-p-*anisidino*-, m. p. 160° (*amide*, m. p. 81—82°); 1-o-*chloroanilino*-, m. p. 145° (*amide*, m. p. 113°); 1-m-*chloroanilino*-, m. p. 112° (*amide*, m. p. 118°); 1-p-*chloroanilino*-, m. p. 144° (*amide*, m. p. 132°); 1-o-*bromoanilino*-, m. p. 140° (*amide*, m. p. 128°); 1-m-*bromoanilino*-, m. p. 130° (*amide*, m. p. 126°); 1-p-*bromoanilino*-, m. p. 130° (*amide*, m. p. 145°); 1-m-*nitroanilino*-, m. p. 137° (*amide*, m. p. 144°); 1-p-*nitroanilino*-, m. p. 187° (*amide*, m. p. 231°); and 1-p-*carboxyanilino*-, m. p. 225° (decomp.) (*amide*, m. p. 272°). 1-o-Anisidino-1-cyano*cyclo*pentane on treatment with sulphuric acid is hydrolysed and sulphonated, *sodium* 1-o-*anisidinocyclopentane-1-carboxylamide-5'-sulphonate* (I), being isolated. 1-o-*Carboxy*- and 1-m-*carboxy-anilinocyclopentane-1-carboxylamides* have m. p. 225° and 153°, respectively.

1-o-Toluidino*cyclo*pentane-1-carboxylic acid on heating at 270—320° with potassium hydroxide and sodium ethoxide yields 1-methylcarbazole, which is further evidence for the view that the carbazoles are formed by the enlargement of the *cyclo*pentane ring (see A., 1925, i, 1271; 1926, 843). 3 : 5-*Dimethoxyaniline*, b. p. 178°/20 mm. (*acetyl* derivative, m. p. 157°), is obtained by reducing 3 : 5-dimethoxynitrobenzene, the preparation of which from s-trinitrobenzene is given.　　　　　H. BURTON.

Three-carbon system. XI. Mechanism of isomeric change in unsaturated acids. R. P. LINSTEAD (J.C.S., 1927, 362—371).—In an endeavour to show that the mechanism of tautomeric change in unsaturated acids in the presence of alkali is explained by the system $>CH \cdot C(OH) \cdot CH \cdot CO_2H \rightleftharpoons$ $>CH \cdot C{:}C \cdot CO_2H \rightleftharpoons >C{:}C \cdot CH \cdot CO_2H$, a quantitative study of the action of potassium hydroxide solutions of varying concentration at different temperatures, on *cyclo*hexylacetic acid, *cyclo*hexylideneacetic acid, and Δ^1-*cyclo*hexenylacetic acid was made. The results show that the rate of isomeric change depends on the concentration of alkali, although the position of equilibrium of the unsaturated acids does not. The equilibration of the three acids is shown by the author's bromine addition method (cf. *ibid.*, 355) to be a unimolecular reversible reaction. It is concluded that the isomeric change of unsaturated acids is tautomeric and does not depend on the addition and removal of water. *Sodium* cyclo*hexylideneacetate* has m. p. 276° (decomp.).　　　　H. BURTON.

Action of benzoyl peroxide on benzene at low temperatures and in the presence of iron and aluminium chlorides. A. F. A. REYNHART (Rec. trav. chim., 1927, 46, 54—61).—The action of benzoyl peroxide on benzene in the presence of aluminium and ferric chlorides at various temperatures from —30° to +50° has been investigated. With either catalyst, the main primary products formed are benzoic acid and phenyl benzoate, small quantities of carbon dioxide and diphenyl also being produced, the quantities of these increasing with rise in temperature. Since, however, aluminium chloride forms a stable molecular complex with phenyl benzoate, an equimolecular quantity of the catalyst must be employed for the complete decomposition of the peroxide. With ferric chloride the reaction is slower, but 0·2 mol. is sufficient to complete the decomposition, since the molecular complex with phenyl benzoate is unstable. With an excess of ferric chloride, the phenyl benzoate further reacts with benzene and ferric chloride to yield benzoic acid, and a brown, complex product containing iron. The same products are obtained when benzene is added to the complex formed by the addition of ferric chloride to phenyl benzoate in carbon disulphide solution, the peroxide not being attacked by ferric chloride under the same conditions. Even at 50°, the reaction, $(Ph \cdot CO_2)_2 + C_6H_6 \longrightarrow Ph \cdot Ph + CO_2 + Ph \cdot CO_2H$, observed by Gelissen and Hermans (A., 1925, i, 545) is only a subsidiary one.　　　　J. W. BAKER.
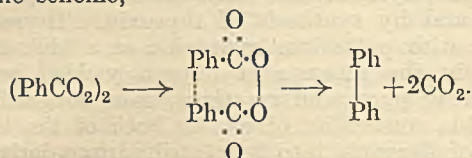
Action of benzoyl peroxide on chlorides and oxychlorides of phosphorus and antimony. A. F. A. REYNHART (Rec. trav. chim., 1927, 46, 62—67).—Antimony pentachloride accelerates the decomposition of benzoyl peroxide in petroleum (b. p. 40—60°) at 10°, the products being phenyl benzoate and carbon dioxide. The only definite products which can be isolated when the peroxide is decomposed with an equimolecular quantity of phosphorus pentachloride in petroleum (b. p. 80—100°) at 100° are carbon dioxide and benzoyl chloride, but when the two substances are cautiously heated together at 96—98° without solvent (the reaction tends to become explosive), the products are benzoyl chloride, chlorobenzene, carbon dioxide, and phosphoryl chloride, the quantities of each obtained being approximately those required by the equation $(Ph \cdot CO_2)_2 + PCl_5 \longrightarrow Ph \cdot COCl + PhCl + CO_2 + POCl_3$. Phosphoryl chloride at its b. p. (107°) has no effect on the thermal decomposition of the peroxide, which proceeds normally, yielding mainly phenyl benzoate and carbon dioxide, but with a large excess of phosphoryl bromide at its b. p. (194°), 1 mol. of carbon dioxide is liberated, and benzoic acid and bromobenzene could be isolated, after treatment with ice, from the products of the reaction, which probably proceeds in accordance with the equations $(Ph \cdot CO_2)_2 + POBr_3 \longrightarrow Ph \cdot CO_2POBr_2 + CO_2 + PhBr$: $Ph \cdot CO_2POBr_2 + 3H_2O \longrightarrow Ph \cdot CO_2H + H_3PO_4 + 2HBr$.　　　　J. W. BAKER.

Decomposition of benzoyl and succinyl peroxides at a high temperature and without solvents. A. F. A. REYNHART (Rec. trav. chim., 1927, 46, 68—71).—Thermal decomposition (at

about 300°) of benzoyl peroxide in an apparatus specially designed so that the diphenyl formed is rapidly removed before it has much opportunity of itself reacting with the peroxide, gives a 68% yield of this compound. Since no trace of bromobenzene is obtained when the decomposition is carried out in the presence of bromine vapour, it follows that free phenyl radicals are not produced at any period of the reaction, the 2 mols. of carbon dioxide being liberated at the moment of formation of diphenyl in accordance with the scheme,

$$(PhCO_2)_2 \longrightarrow \begin{matrix} O \\ \| \\ Ph \cdot C \cdot O \\ | \\ Ph \cdot C \cdot O \\ \| \\ O \end{matrix} \longrightarrow \begin{matrix} Ph \\ | \\ Ph \end{matrix} + 2CO_2.$$

Thermal decomposition of succinyl peroxide under the same conditions yields adipic acid and carbon dioxide. J. W. BAKER.

Action of chlorinated hydrocarbons on benzoyl peroxide with or without the presence of aluminium chloride. A. F. A. REYNHART (Rec. trav. chim., 1927, 46, 72—76).—Carbon tetrachloride has no action on benzoyl peroxide in the presence of aluminium chloride at 0°, but in chloroform solution at the same temperature the main products formed are benzoyl chloride, benzoic acid, and carbonyl chloride, no trace of p-trichloromethylbenzoic acid being detected. The reaction is represented by the equation $(Ph \cdot CO_2)_2 + CHCl_3 \longrightarrow Ph \cdot CO_2H + Ph \cdot COCl + COCl_2$. At the same time, a secondary reaction, $(Ph \cdot CO_2)_2 + CHCl_3 \longrightarrow C_6H_6 + CO_2 + Ph \cdot CO_2CCl_3$ $(=Ph \cdot COCl + COCl_2)$, yields a small quantity of benzene. This secondary reaction is favoured at 50°, but the benzene reacts under the catalytic influence of the aluminium chloride with the benzoyl chloride and carbonyl chloride to yield, respectively, benzophenone and a further quantity of benzoyl chloride. The action of an excess of tetrachloroethylene at its b. p. on benzoyl peroxide yields chlorobenzene, $\alpha\beta\beta$-trichlorostyrene (40% yield), and carbon dioxide, but when the tetrachloroethylene is not in excess, hexachloroethane and some high-boiling, chlorinated products are also obtained. Aluminium chloride has no catalytic effect on this reaction. J. W. BAKER.

Metallic derivatives of the enolic forms of monocarbonyl compounds. V. Interaction of phenylacetylene with ethyl potassiophenyl-acetates. VI. Action of alkali metals on ethyl phenylacetate. H. SCHEIBLER and A. Z. MAHBOUB (Ber., 1927, 60, [B], 558—564; 564—568).—V. Ethyl potassiophenylacetate is converted by phenylacetylene at 125—130° into 2 : 5-diphenyl-3 : 6-dibenzyl-p-benzo-quinone, m. p. 156° (corr.); if the potassium derivative formed during the condensation is decomposed by dry carbon dioxide instead of by water, a colourless compound separates which passes gradually into the yellow quinone. The latter is unusually stable towards reducing agents, but is converted by zinc dust and glacial acetic acid into the corresponding quinol, m. p. 111·5° (corr.). The quinone is transformed by sodium ethoxide or by alcoholic potassium hydroxide into a substance, $C_{66}H_{54}O_5$, m. p. 256° (corr.). In addition to the quinone, a compound, $C_{32}H_{24}O_2$, m. p. 208° (corr.) (2 : 4-diphenyl-1-benzyl-Δ^1-cyclopentene-3 : 5-dione), is occasionally obtained during the action of phenylacetylene on ethyl potassio-phenylacetate; it is derived from ethyl $\alpha\gamma$-diphenyl-acetoacetate.

VI. During the action of potassium on an ethereal solution of ethyl phenylacetate, the changes (1) $CH_2Ph \cdot CO_2Et + K = CHPh:C(OEt) \cdot OK + H$ and (2) $CHPh:C(OEt) \cdot OK + CH_2Ph \cdot CO_2Et + K = CH_2Ph \cdot C(OK):CPh \cdot CO_2Et + EtOK + H$ occur simultaneously. Since the velocity of (1) greatly exceeds that of (2), the main product is ethyl potassiophenyl-acetate, provided that an excess of ester is not present during or after dissolution of the metal. In the preparation of ethyl potassiophenylacetate, it is advisable to work as rapidly as possible with a slight deficiency of the metal, and to finish the preparation without delay. If ethyl potassiophenylacetate covered by ether is treated with a small quantity of ethyl phenylacetate, solution follows with formation of ethyl potassio-$\alpha\gamma$-diphenylacetoacetate. This is due to decomposition of ethyl potassiophenylacetate by liberated ethyl alcohol (cf. equation 2), whereby ethyl phenylacetate is regenerated, thereby allowing the change to continue until formation of ethyl potassio-$\alpha\gamma$-diphenylacetoacetate is almost quantitative. The corresponding sodium derivatives do not differ so widely in their solubilities as the potassium compounds, so that the initial precipitate does not become completely dissolved when an excess of ethyl phenylacetate is present. Ethyl $\alpha\gamma$-diphenyl-acetoacetate, m. p. 78—79°, and the potassium derivatives of ethyl phenylacetate and $\alpha\gamma$-diphenyl-acetoacetate are described. H. WREN.

Xanthophanic acids. II. Production of naphthalene compounds from derivatives of aceto-acetic esters. F. FEIST, H. JANSSEN, and C. A. CHEN (Ber., 1927, 60, [B], 199—208; cf. this vol., 151).—The by-product, $C_{20}H_{22}O_5$, isolated by Liebermann during the preparation of diethylxanthophanic acid according to Claisen is formed by fission of the latter acid by ozone or, with great readiness, by means of boiling alcohol or the protracted action of alcohol at the ordinary temperature. It is identified as ethyl acetyl-1 : 6-dimethylnaphthalenedicarboxylate, since it is hydrolysed to a dibasic acid, m. p. 273°, which is converted by distillation with lime into 1 : 6-di-methylnaphthalene and passes at 350° into acetyl-1 : 6-dimethylnaphthalenemonocarboxylic acid, m. p. 184°. The formation of the "by-product" from ethyl acetoacetate and ethyl ethoxymethylene-acetoacetate depends on the primary formation of ethyl methenyldiacetoacetate (cf. loc. cit.), which, under the influence of alkali (derived from ethyl sodioacetoacetate), becomes decarboxylated to ethyl diacetylcrotonate; the latter substance is readily converted by loss of water into the naphthalene derivative. Acetyl-1 : 6-dimethylnaphthalenedicarb-oxylic acid is oxidised by permanganate in alkaline solution to 1 : 6-dimethylnaphthalene-2 : 4 : 7-tricarboxylic acid, m. p. 360° (also hemihydrate); the silver salt and the triethyl ester, m. p. 75—76°, are described.

The *diethyl* ester, m. p. 231—232°, of the tricarboxylic acid is obtained by treatment of the " by-product " with boiling nitric acid (31%), together with two neutral nitrogenous *compounds*, $C_{20}H_{21}O_6N$, m. p. 131—132°, and (?) $C_{20}H_{19}O_5N$, m. p. 75—85°; all three substances are converted by alkali hydroxide into 1 : 6-dimethylnaphthalene-2 : 4 : 7-tricarboxylic acid. H. WREN.

Reaction of lactones and of furan derivatives with aromatic hydrocarbons and aluminium chloride. E. J. KING (J. Amer. Chem. Soc., 1927, 49, 562—566).—When treated with phthalide and aluminium chloride, benzene and naphthalene yield, respectively, *o*-benzylbenzoic acid, m. p. 114°, and *o*-β-naphthylmethylbenzoic acid, m. p. 136—137°. In benzene solution, phenylphthalide, naphthalene, and aluminium chloride yield only triphenylmethane-2-carboxylic acid, but in carbon disulphide solution 2-phenyl-4-β-naphthylmethylbenzoic acid is obtained. No reaction was observed between diphenylphthalide, benzene, and aluminium chloride. Coumarin, benzene, and aluminium chloride yield α-phenyl-αβ-dihydrocoumarin, whilst coumarilic acid and benzene yield similarly *α-phenyl-αβ-dihydrocoumarilic acid*, m. p. 147—147·5° (*silver* salt; *methyl* ester, m. p. 68—69°). Bromination of the latter in carbon disulphide affords a *monobromo*-derivative, m. p. 241°, whilst bromination in chloroform yields an *isomeride*, m. p. 127°, which is converted into the isomeride of higher m. p. when its sodium salt is boiled in aqueous or alcoholic solution. Coumarilic acid and toluene yield analogously *α-p-tolyl-αβ-dihydrocoumarilic acid*, m. p. 165—165·5° (*methyl* ester, m. p. 87—88°; β-*bromo*-derivative, m. p. 260°). Pyromucic acid, benzene, and aluminium chloride yield what is presumably β-*phenyl-αβ-dihydropyromucic acid*, m. p. 159° (*silver* salt), which, on bromination in chloroform, affords the δ-*bromo*-derivative, m. p. 251°.

F. G. WILLSON.

Compounds of sexavalent uranium with aromatic hydroxy-acids. R. WEINLAND and K. HAGER (Z. anorg. Chem., 1927, 160, 193—208).— The following compounds are described : *uranyl methyl salicylate* ($+C_5H_5N$), *aniline* and *piperidine disalicylatouranates*, *ammonium tribenzoatouranate*, *ammonium* ($+3H_2O$), *aniline* ($+4H_2O$), *o-toluidine* ($+3H_2O$), *pyridine* ($+4H_2O$), and *piperidine* ($+3H_2O$) *tri-p-hydroxybenzoatouranates*, *pyridine* ($+7H_2O$) and *aniline tri-m-hydroxybenzoatouranates*, *pyridine* ($+H_2O$), *triethylamine*, *o-toluidine*, *m-nitroaniline*, *toluylenediamine*, *methylamine* ($+5H_2O$), *guanidine* ($+6H_2O$), *potassium* ($+9$ and $13H_2O$), *ammonium* ($+9$ and $13H_2O$), and *barium* ($+10$ and $14H_2O$) *trisalicylatouranates*. The variety of complexes which may be formed is due to the amphoteric nature of uranyl hydroxide, which is thus able to react with both the carboxyl and phenolic groups. The structure of the compounds is discussed from the point of view of residual valency. H. F. GILLBE.

Purification of *o*-methoxybenzoic acid. E. CATTELAIN (Bull. Soc. chim., 1927, [iv], 41, 114—115).—The crude *o*-methoxybenzoic acid is dissolved in water with a slight excess of sodium hydroxide, the solution neutralised with acetic acid, and after addition of a little sodium acetate acidified with acetic acid. The *o*-methoxybenzoic acid is precipitated, salicylic acid remaining in solution, and is filtered cold and washed with a little water.

R. BRIGHTMAN.

Thyroxin. III. Constitution and synthesis of thyroxin. C. R. HARINGTON and G. BARGER (Biochem. J., 1927, 21, 169—183; cf. A., 1926, 644, 724).—The orientation of the iodine atoms in the tetraiodo-derivative of the *p*-hydroxyphenyl ether of tyrosine (thyroxin) has been established by degradation and by synthesis of thyroxin. Thyroxin on fusion with potassium hydroxide at a high temperature in the absence of oxygen yielded products exhibiting pyrogallol reactions, thus suggesting the probable conversion of one or both of the benzene rings of thyroxin into 3:4:5-trihydroxy-derivatives. It was also found that the colour reaction of thyroxin with nitrous acid and ammonia (Kendall and Osterberg, A., 1920, i, 180) was also given in general by benzene derivatives containing two iodine atoms in the *ortho*-positions to a hydroxyl or an amino-group, which suggested that thyroxin contained a similar grouping. By exhaustive methylation of thyroxin with methyl iodide after boiling the product with alcoholic potassium hydroxide, an unsaturated *acid*, $C_{16}H_{10}O_4I_4$, melting indefinitely above 290°, was obtained. On oxidising this acid with potassium permanganate, an *aldehyde*, $C_{14}H_8O_3I_4$, m. p. 198°, was obtained, which by further oxidation gave an acid, $C_{14}H_8O_4I_4$, m. p. 283°, *methyl* ester, m. p. 233°, *ethyl* ester, m. p. 171·5°. The acid was shown to be 3 : 5-*di-iodo*-4-(3':5'-*di-iodo*-4'-*methoxyphenoxy*)*benzoic acid* by synthesis in the following way :

3 : 5-*Di-iodo*-4-(4'-*methoxyphenoxy*)*nitrobenzene*, yellow, m. p. 144°, was prepared by boiling a solution of quinol monomethyl ether and 3 : 4 : 5-tri-iodo-nitrobenzene in methyl ethyl ketone with dry potassium carbonate. The *aniline*, m. p. 121—122°, was then obtained by reducing the above nitro-compound in glacial acetic acid with stannous chloride and hydrogen chloride (*hydrochloride*, m. p. 216°; *sulphate*, m. p. 201°). The base was converted by Sandmeyer's reaction into 3 : 5-*di-iodo*-4-(4'-*methoxyphenoxy*)*benzonitrile*, m. p. 167—169°. The nitrile when boiled with a mixture of hydriodic and acetic acids underwent simultaneous hydrolysis and demethylation, yielding 3 : 5-*di-iodo*-4-(4'-*hydroxyphenoxy*)*benzoic acid*, m. p. 252—254°. The latter compound on treatment in concentrated ammonia with iodine in potassium iodide yielded 3 : 5-*di-iodo*-4-(3' : 5'-*di-iodo*-4'-*hydroxyphenoxy*)*benzoic acid*, m. p. 255°. Finally, by methylating the last compound it was converted into the methoxy-derivative, which was found to be identical with the above acid product, $C_{14}H_8O_4I_4$, obtained by degradation of thyroxin.

The starting point in the actual synthesis of thyroxin was 3 : 5-*di-iodo*-4-(4'-*methoxyphenoxy*)*benzaldehyde*, m. p. 121°, obtained from the nitrile by a modification of Stephen's method (A., 1925, i, 1131). From this compound the *azlactone*, yellow, m. p. 211°, was prepared by heating a mixture of the aldehyde and sodium acetate with hippuric acid and acetic anhydride. The *azlactone* was converted into *ethyl* 3 : 5-*di-iodo*-α-*benzamido*-4-(4'-*methoxyphenoxy*)-

cinnamate, m. p. 203°, by warming with absolute alcohol containing 10% of sulphuric acid. The cinnamic ester when boiled with hydriodic acid and red phosphorus yielded α-*amino*-β-3 : 5-*di-iodo*-4-(4'-*hydroxyphenoxy*)*phenylpropionic acid*, which on iodination in ammoniacal solution gave α-*amino*-β-3 : 5-*di-iodo*-4 - (3' : 5'- *di - iodo* - 4'-*hydroxyphenoxy*)*phenylpropionic acid*, identical chemically and physiologically with thyroxin isolated from the thyroid gland.

S. S. ZILVA.

Constitution in the acenaphthene and naphthalene series. K. DZIEWOŃSKI, (MLLE.) H. GALITZERÓWNA, and A. KOCWA (Bull. Acad. Polonaise, 1926, *A*, 209—242).—The monosulphonic acid (I) obtained from acenaphthene and sulphuric acid at 100° (cf. A., 1924, i, 1178) is oxidised to a sulphonaphthalic acid (II), from which, on alkaline fusion at 250°, a compound, m. p. 257°, previously supposed to be identical with 4-hydroxynaphthalic anhydride (Graebe, A., 1903, i, 408), is obtained. Since, however, it has the formula $C_{12}H_6O_3$, gives β-naphthol when distilled with calcium hydroxide, and forms 1 : 8-phenylpyridazone-2-naphthaquinone, m. p. 238—240° (A., 1924, i, 1199) without loss of carbon dioxide, it must be 7-*hydroxy*-1-*naphthoic acid* (*benzoyl* derivative, m. p. 194°; *methyl ether*, m. p. 167·5°, and its *silver* salt). Accordingly, (II) is 2-sulphonaphthalic acid (2-sulphonaphthalene-1 : 8-dicarboxylic acid) and (I) is acenaphthene-3-sulphonic acid. The second acenaphthenesulphonic acid (amide, m. p. 222—223°) is therefore the 5-derivative. Acenaphthene behaves on sulphonation in the same way as naphthalene, substitution taking place in the α-(5)-position at lower, and in the β-(3)-position at higher temperatures. 2-*Hydroxynaphthalic anhydride*, m. p. 242°, is obtained by fusing (II) with potassium hydroxide at 150°. Acenaphthene-5-sulphonic acid is oxidised to 4-sulphonaphthalic acid, from which 4-*chlorosulphonylnaphthalic anhydride*, m. p. 191—193° (corresponding *sulphonamide*, m. p. 316°, and *methyl sulphonate*, m. p. 210°), is prepared. Further evidence for the constitution of 4-hydroxynaphthalic anhydride (III), m. p. 350—351°, obtained by fusing the sulphonic acid with potassium hydroxide at 240°, is furnished by its conversion into α-naphthol when distilled with calcium hydroxide and by the preparation of yellowish-brown 3-*nitroso*-4-*hydroxynaphthalic anhydride*, m. p. 230° (red *zinc* salt, dark green *iron* lake). The following derivatives of (III) are described : the *methyl ether*, m. p. 257°; *acetyl* derivative, m. p. 188—189°; *benzoyl* derivative, m. p. 235—236°; colourless *potassium* salt; *phenylhydrazone*, m. p. 335—336°; *oxime*, m. p. above 350° (red *sodium* salt); *mononitro*-derivative, m. p. 222°; also 4-*hydroxynaphthalimide*, m. p. above 300°; *ammonium* 4-*aminonaphthalate*, m. p. 222° (decomp.), and 4-*aminonaphthalic anhydride*, m. p. above 350°, which may also be prepared by reducing Graebe's 4-nitronaphthalic anhydride.

1 : 8-Phenylpyridazone-4-naphthaquinone, m. p. 201—202° (*loc. cit.*); 1 : 8-(p-*nitrophenylpyridazone*)-4-*naphthaquinone*, m. p. 305—307°, and 1 : 8-α-*naphthylpyridazone*-4-*naphthaquinone* are formed from (III) and the appropriate diazonium salt. 4-Hydroxynaphthalic anhydride condenses with resorcinol in presence of zinc chloride to 4-*hydroxynaphthafluorescein*, orange-red, which dyes dark reddish-brown on a chromium mordant.

H. E. F. NOTTON.

Application of the Perkin reaction to phenolic aldehydes. S. OGAWA (Bull. Chem. Soc. Japan, 1927, **2**, 20—26).—The uncertain m. p. of the products previously obtained by means of the Perkin reaction from phenolic aldehydes (Tiemann, A., 1877, 893; 1878, 579; Vörlander, *ibid.*, 1906, i, 317) were due to the presence of by-products. Vanillin gives, in addition to 4-acetoxy-3-methoxycinnamic acid, 4-(4'-*acetoxy*-3'-*methoxycinnamoxy*)-3-*methoxycinnamic acid* (*acetylferuloylferulic acid*), m. p. 250° (decomp.) (*methyl* ester, m. p. 204—205·5°), which may also be prepared from 4-*acetoxy*-3-*methoxycinnamoyl chloride*, m. p. 133—134°, and 4-hydroxy-3-methoxycinnamic acid, in presence of pyridine. Similarly, the product from *p*-hydroxybenzaldehyde contains 4-*p-acetoxycinnamoxycinnamic acid*, m. p. 222—223° (*methyl* ester, m. p. 166—167°), and a *substance*, $C_{29}H_{22}O_8$, m. p. 231° (decomp.) (*methyl* ester, m. p. about 200°), probably p-(4-p'-*acetoxycinnamoxycinnamoxy*)*cinnamic acid*, as well as pure *p*-acetoxycinnamic acid, m. p. 205—205·5°. Experiments with veratraldehyde and acetylvanillin show that only aldehydes with a free hydroxyl group give these complex products. 4-*p*-Acetoxycinnamoxycinnamic acid is also obtained from p-*acetoxycinnamoyl chloride*, m. p. 118—119°, and *p*-hydroxycinnamic acid in pyridine solution.

H. E. F. NOTTON.

Compounds similar to chaulmoogric acid. I. G. A. PERKINS and A. O. CRUZ (J. Amer. Chem. Soc., 1927, **49**, 517—522).—Treatment of ethyl Δ²-*cyclo*pentenylmalonate (cf. Noller and Adams, A., 1926, 1137) with powdered sodium in toluene, followed by addition of an alkyl halide, affords the corresponding ethyl Δ²-*cyclo*pentenylalkylmalonates, from which the corresponding disubstituted malonic acids are obtained on hydrolysis. The following were prepared : Δ²-*cyclopentenylethylmalonic acid*, m. p. 156° (decomp.); Δ²-*cyclopentenyl-n-propylmalonic acid*, m. p. 153° (decomp.); Δ²-*cyclopentenylisopropylmalonic acid*, m. p. 178° (decomp.); Δ²-*cyclopentenylallylmalonic acid*, m. p. 146° (decomp.); Δ²-*cyclopentenyl-n-butylmalonic acid*, m. p. 134° (decomp.); and di-Δ²-*cyclopentenylmalonic acid*, m. p. 184° (decomp.). When heated at the m. p., the above acids lose carbon dioxide, with formation of the following respective acids : α-Δ²-*cyclopentenyl-butyric*, b. p. 145—150°/20 mm.; -n-*valeric*, b. p. 150—160°/20 mm.; -*isovaleric*, b. p. 158—161°/20 mm.; -α-*allylacetic*, b. p. 158—160°/20 mm.; -*hexoic*, b. p. 167—169°/20 mm.; and di-Δ²-*cyclopentenylacetic acid*, b. p. 185—187°/20 mm. All the above substituted acetic acids decomposed when kept.

F. G. WILLSON.

New method of preparation of methyl phenylethylmalonate. M. M. RISING and T.-W. ZEE (J. Amer. Chem. Soc., 1927, **49**, 541—545).—α-Phenylbutyronitrile (cf. Bodroux and Taboury, A., 1910, i, 557) is converted, by treatment with sodium in dry ether, into the sodio-derivative, which is condensed with ethereal methyl chloroformate, giving *methyl* α-*cyano*-α-*phenylbutyrate*, b. p. 180—192°/17 mm. Treatment of the latter with hydrogen chloride

in absolute methyl alcohol and ether affords the corresponding *iminohydrochloride*, m. p. 102°, which, on hydrolysis, yields methyl phenylethylmalonate, m. p. 39·5° (cf. Rising and Stieglitz, A., 1918, i, 271). The reactions of the above sodio-compound suggest the existence of the *tautomeride*, CEtPh:C:NNa.

F. G. WILLSON.

Bromine derivatives of some δ-ketonic esters. G. A. HILL (J. Amer. Chem. Soc., 1927, **49**, 566—571).—Treatment of benzylidenepinacolone with ethyl malonate and sodium ethoxide in alcohol affords *ethyl β-pivalyl-α-phenylethylmalonate*, $CH_2(CO \cdot CMe_3) \cdot CHPh \cdot CH(CO_2Et)_2$, m. p. 44·5°. On bromination in carbon tetrachloride, this yields a *monobromo*-derivative, m. p. 80—81°, which is unchanged after an hour at 200°. *Methyl β-pivalyl-α-phenylethylmalonate*, m. p. 82·5°, is obtained analogously, together with the *monomethyl* ester, m. p. 103°. Bromination of the former in carbon tetrachloride affords a *monobromo*-derivative, m. p. 83·5°, together with an *isomeride*, m. p. 85°, the ratio of the former to the latter being 2 : 1. In methyl alcohol, the isomeric bromo-derivatives are produced in equal quantities. Further bromination of the isomeride of lower m. p. could not be satisfactorily effected. Treatment of this isomeride in benzene with methyl-alcoholic sodium methoxide affords *methyl 3-pivalyl-2-phenyl*cyclo*propanedicarboxylate*, m. p. 86°, this compound being obtained from the isomeride of m. p. 85° by the action of sodium methoxide, *p*-toluidine, or ammonia. The isomeride of m. p. 83·5° is unaffected by methyl-alcoholic potassium iodide and by methyl-alcoholic hydrogen bromide, whilst the latter reagent converts the isomeride of m. p. 85° into the derivative of lower m. p. The latter yields, when heated for an hour at 250°/35 mm., *γ-pivalyl-α-carbomethoxy-β-phenylbutyrolactone*, m. p. 128°. The last is obtained from *β-pivalyl-α-phenylethylmalonic acid*, m. p. 137°, by bromination in chloroform, followed by treatment with sodium carbonate and esterification of the product with methyl alcohol and hydrogen chloride. When boiled with water, β-pivalyl-α-phenylethylmalonic acid is converted into *γ-pivalyl-β-phenylbutyric acid*, m. p. 122°. The above bromo-derivative, m. p. 85°, yields, when heated for an hour at 150°/25 mm., an isomeric *γ-pivalyl-α-carbomethoxy-β-phenylbutyrolactone*, m. p. 103·5°, which, on hydrolysis with sodium methoxide, yields a *γ-pivalyl-α-carboxy-β-phenylbutyrolactone*, m. p. 135°, the latter being reconverted, on esterification, into the original ester, m. p. 103·5° (cf. Kohler, A., 1922, i, 552).

F. G. WILLSON.

Opianyl chloride. A. KIRPAL (Ber., 1927, **60**, [B], 382—383; cf. Rodionov and Fedorova, this vol., 151).—Opianyl ψ-chloride, m. p. 94°, prepared by the action of phosphorus pentachloride on opianic acid at 80°, is converted by methyl alcohol at the atmospheric temperature into the corresponding ψ-ester, m. p. 105°, which is transformed by prolonged contact with methyl-alcoholic hydrogen chloride into the normal ester, m. p. 83°.

H. WREN.

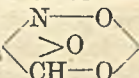**Complex compounds from pyromellitic anhydride.** R. SEKA and H. SEDLATSCHEK (Monatsh., 1926, **47**, 511—517).—Pyromellitic anhydride combines with various phenol ethers to form coloured additive compounds, containing 1 mol. of each component. These are produced by simple crystallisation of the anhydride from excess of the ether, or by mixed fusion, and readily decompose into the original constituents in a vacuum at 100°. The following *compounds* are obtained : from anisole, yellow laminæ, m. p. 250—260°; from veratrole, orange-red, m. p. 195—200°; from quinol dimethyl ether, crimson, m. p. 180—185°; from tetralin, yellow, m. p. 215—220°. Pyromellitic anhydride may either be regarded as a combination of two furanquinones (if the benzene nucleus is given its centric formula) or as a combination of maleic anhydride and a fulgide system (if the Kekulé phase is used) (cf. Pfeiffer, A., 1922, i, 341; Stobbe and Dietzel, ibid., 1923, i, 39), the formation of complex compounds with only 1 mol. of the phenol ether supporting the latter view.

J. W. BAKER.

Condensation products of pyromellitic anhydride. R. SEKA, O. SCHMIDT, and K. SEKORA (Monatsh., 1926, **47**, 637—641).—Pyromellitic anhydride condenses with commercial xylene in the presence of aluminium chloride to yield a mixture of the isomeric *dixyloylbenzenedicarboxylic acids* in 65·9% yield. Fractional crystallisation from acetic acid yields a sparingly soluble portion, m. p. 312°, and a readily soluble one, m. p. 283°. Reduction of the mixture gives a mixture of the isomeric *lactones*, $C_{26}H_{22}O_4$, m. p. 105—110°, in 90% yield. Similar condensation with *p*-cymene yields a mixture of isomeric p-*cymoylbenzenedicarboxylic acids*, m. p. 295° after crystallisation, in 52·5% yield. 5 : 7 : 12 : 14-Dinaphthanthradiquinone-1 : 4 : 8 : 11-tetracarboxylic acid (Philippi and Seka, A., 1923, i, 576), on treatment with phosphoryl chloride and phosphorus pentachloride, yields the *chloride*, decomp. 320° (in a sealed tube), which, heated for 12 hrs. with methyl or ethyl alcohol, yields the *tetramethyl* and *tetraethyl* esters, respectively, the former decomp. 370°.

J. W. BAKER.

Compound derived from *o*-nitrobenzaldehyde and diazomethane and its transformation products. F. ARNDT and W. PARTALE (Ber., 1927, **60**, [B], 446—456).—*o*-Nitrobenzaldehyde is readily converted by an ethereal solution of diazomethane at

−10° into the *compound*, $C_6H_4\begin{smallmatrix} N-O \\ CH-O \end{smallmatrix}>O>CH_2$, m. p. 65°, b. p. 144°/10 mm., 150°/15 mm., for which the non-committal name "*nitraldin*" is proposed; *o*-nitroacetophenone is not formed to a considerable extent, if at all. Nitraldin does not react with acetic anhydride, phenylcarbimide, semicarbazide, or *o*-nitrophenylhydrazine. It explodes by contact with sulphuric acid, and decomposes violently at 200° with evolution of formaldehyde. It is transformed by very cautious treatment with formic acid into the *nitroso*-derivative, $NO \cdot C_6H_4 \cdot CH \begin{smallmatrix} O \\ O \end{smallmatrix} > CH_2$, m. p. 103—104° (decomp.), which is converted by warm 2N-hydrochloric acid into formaldehyde and *methylenedibenz-isooxazolone*, $CO \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > N \cdot CH_2 \cdot N \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > CO$, which

is also derived by the action of mineral acids on nitraldin. The constitution of the latter substance is established by its production from benz*iso*oxazolone and formaldehyde in presence of 2N-hydrochloric acid and from hydroxymethylbenz*iso*oxazolone and acid with evolution of formaldehyde. Benz*iso*oxazolone is converted by boiling aqueous formaldehyde into *hydroxymethylbenzisooxazolone*, m. p. 116—117°, which, in solution, appears to be in equilibrium with the compounds from which it is derived. In neutral media, the equilibrium is greatly in favour of the hydroxymethyl compound, so that it may be crystallised from water or acetic anhydride. In alkaline solution, equilibrium is in favour of the components, so that benzoyl chloride and alkali hydroxide convert it into *N*-benzoylbenz*iso*oxazolone and ammonia (which combines with the formaldehyde) transforms it into benz*iso*oxazolone. For a similar reason, its conversion into methylenedibenz*iso*oxazolone (*v. s.*) by hydrochloric acid is prevented by the addition of a large excess of formaldehyde.
H. WREN.

Condensation products from o-aminobenzaldehyde. Preparation of the aldehyde. E. BAMBERGER (Ber., 1927, 60, [*B*], 314—319; cf. Seidel, A., 1926, 1140; Weitnauer, Diss., Zurich, 1904).—Anhydrotris-*o*-aminobenzaldehyde, (?)

$$CH{<}^{C_6H_4\cdot NH}_{N-C_6H_4}{>}CH\cdot NR\cdot C_6H_4\cdot CHO,$$ (R=H), m. p. 230—251°, according to the mode of heating, is obtained when *o*-aminobenzaldehyde is preserved in aqueous or ethyl-alcoholic solution or, more slowly, when the solid aldehyde is kept in a closed vessel. It is converted by *p*-nitrophenylhydrazine in feebly acid solution into the *p*-nitrophenylhydrazone of *o*-aminobenzaldehyde. The action of methyl-alcoholic hydrogen chloride on *o*-aminobenzaldehyde gives *methylanhydrotris-o-aminobenzaldehyde* (R=Me), m. p. 240° (decomp.); the corresponding *ethyl* and n-*propyl* derivatives, m. p. 200° and 216—217°, respectively, are analogously prepared. *o*-Aminobenzaldehyde and β-phenylhydroxylamine give the *compound*, $C_{27}H_{22}ON_4$, m. p. 215—229° (decomp.), according to the manner of heating.

Improved directions are given for the preparation of *o*-amino- from *o*-nitro-benzaldehyde. H. WREN.

Chlorovanillin and some of its derivatives. R. M. HANN and G. C. SPENCER (J. Amer. Chem. Soc., 1927, 49, 535—537).—A chlorovanillin, presumably 5-chloro-4-hydroxy-3-methoxybenzaldehyde, m. p. 165°, is obtained by the action of chlorine on vanillin in glacial acetic acid at the ordinary temperature (cf. Menke and Bentley, A., 1898, i, 661). The *oxime*, m. p. 172—173° [*hydrochloride*, m. p. 168—169° (decomp.); *hydrobromide*, m. p. 153—154° (decomp.)], *hydrazone*, m. p. 248—249° (decomp.), *phenylhydrazone*, m. p. 106—107°, *diphenylhydrazone*, m. p. 155—156°, *semicarbazone*, m. p. 198—199° (decomp.), and *thiosemicarbazone*, m. p. 216—217°, are described. Condensation of chlorovanillin with ethyl cyanoacetate in presence of piperidine affords the *ethyl* ester, m. p. 201°, of 5-*chloro-4-hydroxy-3-methoxy-α-cyanocinnamic acid*, yellow, m. p. 233—234° (decomp.), whilst treatment with aniline and β-naphthylamine in alcohol

yields, respectively, *chlorovanillylideneaniline*, m. p. 160° [*picrate*, m. p. 226—227° (decomp.)], and chlorovanillylidene-β-naphthylamine, m. p. 130—131° [*dibromide*, m. p. 150—155° (decomp.); *picrate*, brickred, m. p. 214° (decomp.)].
F. G. WILLSON.

Synthesis of p-hydroxybenzophenone. W. T. MINAEV (J. Russ. Phys. Chem. Soc., 1926, 58, 307—313).—The various methods for the preparation of the aromatic polyhydroxy-ketones are discussed from the point of view of their value in dye chemistry. Döbner's method of condensing the phenol with benzoyl chloride in presence of zinc chloride was adopted. On gently warming the mixture of phenol and benzoyl chloride, hydrogen chloride is evolved quantitatively, and the phenolic ester, $Ph\cdot CO_2Ph$, is formed. Further action of benzoyl chloride at 180° in presence of zinc chloride gives a 93% yield of the *para*-benzoylated ester, $Ph\cdot CO\cdot C_6H_4\cdot CO_2Ph$, which, on prolonged hydrolysis with alkali, gives an extremely small yield (7%) of the impure *p*-hydroxyketone.

It was found that the action of alkali, zinc chloride, or hydrochloric acid on the pure *p*-hydroxy-ketone gave tars. On completion of the second stage of the synthesis, therefore, the *p*-benzoylated ester was separated from the zinc chloride, and repeatedly hydrolysed with small quantities of alkali, the crystals of the *p*-hydroxy-ketone which separated being removed in each case. A 51·5% yield of pure ketone m. p. 133·8—133·9°, was obtained.

The possibility of a migration to the nucleus of the benzoyl group, $Ph\cdot CO\cdot O\cdot Ph \longrightarrow Ph\cdot CO\cdot C_6H_4\cdot OH$ is discussed.
M. ZVEGINTZOV.

Reactions of hydrazines with hydroxymethylene-ketones and their derivatives. I. K. VON AUWERS and H. MAUSS (Annalen, 1927, 452, 182—210).—The intermediate products in the production of 1 : 3- and 1 : 5-diphenylpyrazoles from hydroxymethyleneacetophenone and phenylhydrazine (Auwers and Schmidt, A., 1925, i, 585) are now shown not to be hydrazones, but hydrazides of the composition $CHBz{:}CH\cdot NPh\cdot NH_2$ (I) (25%) and $CHBz{:}CH\cdot NH\cdot NHPh$ (II) (75%), which on distillation yield 1 : 3- and 1 : 5-diphenylpyrazoles in the proportions stated. The latter intermediate, 1-*phenyl*-2-*β-benzoylvinylhydrazine*, m. p. 126°, when shaken with air in alcoholic sodium hydroxide solution, is oxidised to β-*benzoylvinylazobenzene* (III), m. p. 50—60°. The sodium salt of the ketone reacts with phenylhydrazine to yield *s*-formylphenylhydrazine, small quantities of (II) and (III), and acetophenone. Hydroxymethyleneacetophenone benzoate (the ketonic structure of which is proved by its oxidation to phenylglyoxylic acid with potassium permanganate in aqueous acetone solution), on treatment with phenylhydrazine yields two initial products, m. p. 120° and 164°, respectively, which are found to be isomorphous forms of 1-*phenyl*-1-β-*benzoylvinylhydrazine* (I), the ring structure previously ascribed (*loc. cit.*) to the one m. p. 164° being incorrect. On oxidation with potassium permanganate, either form yields the anilide of hydroxymethyleneacetophenone, identical with a synthetic specimen, which with phenylhydrazine yields 1 : 5-diphenylpyrazole. Both forms

when treated with p-nitrobenzaldehyde yield the p-*nitrobenzylidene* derivative, CHBz:CH·NPh·N:CH·C$_6$H$_4$·NO$_2$, m. p. 173—174°, identical with a synthetic specimen prepared from hydroxymethyleneacetophenone and p-nitrobenzylidenephenylhydrazine; and with p-nitrobenzoyl chloride both yield an N-p-*nitrobenzoyl* derivative, CHBz:CH·NPh·NH·CO·C$_6$H$_4$·NO$_2$, m. p. 205°, identical with a specimen obtained from the sodium salt of hydroxymethyleneacetophenone and p-nitrobenzoylphenylhydrazine. Hence it is the substituted aminogroup of phenylhydrazine which reacts with esters and ethers of the hydroxymethylene-ketone. With s-formylphenylhydrazine, the ketone yields the α-*phenyl*-β-*formylhydrazide*, m. p. 148—149°, which when heated with 2N-hydrochloric acid for 15 min. yields 1 : 3-diphenylpyrazole. The sodium salt of the ketone reacts with p-nitrophenylhydrazine hydrochloride to yield the p-*nitrophenylhydrazide*, m. p. 156—157°, which when heated for 15 min. with acetic acid yields 1-p-*nitrophenyl*-5-*phenylpyrazole*, m. p. 117—118°, b. p. 240—242°/14 mm. (also obtained directly when the benzoate of the ketone is used). This compound, on reduction with stannous chloride and hydrochloric acid, yields 1-p-*aminophenyl*-5-*phenylpyrazole*, m. p. 148·5—149·5°, which yields 1 : 5-diphenylpyrazole when the amino-group is removed. The benzoate of the ketone reacts with p-nitrophenylhydrazine in propyl alcohol at the ordinary temperature to yield the nitrodiphenylpyrazole directly, together with a *compound*, m. p. 208—209°. In boiling propyl alcohol a bis-p-*nitrophenylhydrazine* derivative, NO$_2$·C$_6$H$_4$·NH·N:CPh·CH:CH·NH·NH·C$_6$H$_4$·NO$_2$, was obtained, red, m. p. 170—172° (+1 mol. of acetone), yellow, m. p. 195—200° (changing into the red form on heating), which after long heating on a waterbath yields 1-p-*nitrophenyl*-3-*phenylpyrazole*, m. p. 169—169·5°, giving on nitration with nitric acid for 0·5 hr. on a water-bath 1 : 3-*dinitrodiphenylpyrazole*, m. p. 226—228°, identical with the product obtained by direct nitration of 1 : 3-diphenylpyrazole. The constitution CHBz:CH·NH·NMe·CH:CHBz is now assigned to the compound, m. p. 138°, obtained from hydroxymethyleneacetophenone and methylhydrazine. On methylation with methyl sulphate, it yields s-*dimethyldi*-β-*benzoylvinylhydrazine*, m. p. 175—176°, identical with the compound obtained from s-dimethylhydrazine and the sodium salt of hydroxymethyleneacetophenone. When heated with hydrochloric acid, it yields s-tribenzoylbenzene. Treated with methylhydrazine and p-nitrobenzaldehyde, the benzoate of the ketone yields 1-p-*nitrobenzylidene*-2-*methyl*-2-β-*benzoylvinylhydrazine*, m. p. 207°.

J. W. BAKER.

Theory of colour lakes. Optically active, internally complex salt of pæonol. P. PFEIFFER, S. GOLTHER, and O. ANGERN (Ber., 1927, 60, [B], 305—313; cf. A., 1911, i, 819; 1913, i, 879).—The internally complex structure of lakes is established by the resolution of such substances containing a metallic atom of constant co-ordination number into their optical antipodes; the cobalt derivatives of pæonol (2-hydroxy-4-methoxyacetophenone) being selected. Pæonol is converted by chloropentamminecobaltic chloride in boiling aqueous solution into the *compound* Co(C$_9$H$_9$O$_3$)$_3$ (also +CHCl$_3$), which is not suitable for purposes of resolution. The ketone is transformed by hydroxoaquodiethylenediaminecobalt bromide (cf. Werner and Matissen, A., 1918, i, 379) or by chloroaquodiethylenediaminecobalt sulphate into the *bromide*, [Co en$_2$(C$_9$H$_9$O$_3$)]Br,H$_2$O, from which the corresponding *iodide* (monohydrate and anhydrous), *chlorate*, *perchlorate*, and *dithionate* are derived. Resolution of the bromide is effected by treatment with silver d-tartrate and evaporation of the filtrate to a syrup from which the d-*tartrate* of the l-base separates, [α]$_{red}^{19}$ −139·4° in water. Treatment of the tartrate with sodium bromide affords the corresponding active *bromide*, [α]$_{red}^{19}$ −175·7° in water. Pæonol is converted by treatment with copper or nickel sulphate and ammonia into the *compounds* Cu(C$_9$H$_9$O$_3$)$_2$ and Ni(C$_9$H$_9$O$_3$)$_2$, which give additive *derivatives* with pyridine (2 mols.) or aniline (1 mol.). Amended directions are given for the preparation of carbonatodiethylenediaminecobalt nitrate and the corresponding bromide. H. WREN.

Preparation of alizarin from phthalic anhydride and o-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1927, 49, 473—478).—When phthalic anhydride (0·2 mol.) is heated with o-dichlorobenzene (1 mol.) and aluminium chloride (0·3 mol.) at 100° for about 14 hrs., o-3 : 4-*dichlorobenzoylbenzoic acid*, m. p. 191·2°, is obtained in 70% yield. When heated with 4 parts of concentrated sulphuric acid at 150° for 4 hrs., the latter affords a practically quantitative yield of 2 : 3-dichloroanthraquinone, and this, when heated with an equal weight of water and 4 parts of potassium hydroxide at 225°, is converted into alizarin (yield, 31·2%). The formation of β-chloroanthraquinone from phthalic anhydride and o-dichlorobenzene (Sprent and Dodd, E.P. 204,528) could not be confirmed. F. G. WILLSON.

Polyhydroxyanthraquinones. VII. Structure and synthesis of hydroxyanthrarufin and of rufiopin. S. V. PUNTAMBEKER and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 486—491; cf. A., 1925, i, 1076).—Treatment of 2'-hydroxy-3 : 4-dimethoxydiphenylmethane-2-carboxylic acid (cf. A., 1925, i, 272) with concentrated sulphuric acid and boric acid at the ordinary temperature, followed by addition of phosphorus pentoxide, affords 5-*hydroxy*-1 : 2-*dimethoxy*-9-*anthrone*, which, on oxidation with chromic acid in glacial acetic acid, yields 5-*hydroxy*-1 : 2-*dimethoxyanthraquinone*, orange, m. p. 230·5—231·5°, and this, on demethylation with hydrobromic acid in acetic acid, is converted into 1 : 2 : 5-*trihydroxyanthraquinone*, brownish-red, m. p. 273—274° (*triacetate*, m. p. 238—239°), identical with hydroxyanthrarufin. Condensation of p-bromoguaiacol with opianic acid in presence of concentrated sulphuric acid yields 5 : 6-*dimethoxy*-2-(5'-*bromo*-2'-*hydroxy*-3'-*methoxyphenyl*)*phthalide*, m. p. 163—164°, which, on reduction with zinc and sodium hydroxide, affords 2'-*hydroxy*-3 : 4 : 3'-*trimethoxydiphenylmethane*-2-*carboxylic acid*, m. p. 155—156°. Bromination of the latter in glacial acetic acid yields 5'-*bromo*-2'-*hydroxy*-3 : 4 : 3'-*trimethoxydiphenylmethane*-2-*carboxylic acid*, m. p. 168—169°, whilst treatment with concentrated

sulphuric acid in presence of boric acid affords 5-*hydroxy*-1 : 2 : 6-*trimethoxy*-9-*anthrone*. On oxidation, the latter is converted into 5-*hydroxy*-1 : 2 : 6-*trimethoxyanthraquinone*, orange, m. p. 245—246°, and this, on demethylation, yields 1 : 2 : 5 : 6-*tetrahydroxyanthraquinone*, red, m. p. 316—318° (*tetra-acetate*, m. p. 237—238°), identical with rufiopin.

F. G. WILLSON.

Reduction products of dinaphthanthradiquinone. R. SEKA and K. SEKORA (Monatsh., 1926, 47, 519—528).—Reduction of dinaphthanthradiquinone with alkaline hyposulphite and benzoylation of the product yields the *dibenzoyl* derivative of the monoquinol, $C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{C(OBz)}_{C(OBz)}{>}C_6H_4$, decomp. 350° (cf. Philippi, A., 1913, i, 627), which, on further reduction and acetylation with zinc dust, acetic anhydride, and sodium acetate, yields the *monobenzoyltriacetyl* derivative of dinaphthanthradiquinol, decomp. 283—285°. The corresponding *tetraacetyl* derivative, decomp. 295°, is obtained by similar treatment of the original diquinone. The diquinone, treated in acetic acid suspension with granulated tin and fuming hydrochloric acid, yields *dinaphthanthradiquinol*, decomp. 340—343°, which on acetylation yields the tetra-acetyl derivative already described. On oxidation, either with nitrobenzene or chromic acid, it is reconverted into the diquinone. A preliminary account of the reduction with zinc dust in ammoniacal solution is given. J. W. BAKER.

Nitro-derivatives of dinaphthanthradiquinone and their reactions. R. SEKA and O. SCHMIDT (Monatsh., 1926, 47, 619—626).—Nitration of dinaphthanthradiquinone with potassium nitrate and sulphuric acid yields two isomeric *mononitro*-derivatives, one soluble with difficulty in nitrobenzene, decomp. above 400° (39·7%), and the other easily soluble in the same solvent, decomp. 310° (36·9%). Nitration with nitric acid (d 1·52) at the temperature of the water-bath yields two *dinitro*-derivatives (cf. Phillipi and Seka, A., 1923, i, 577), which are separated by the same method, the one sparingly soluble, decomp. above 400° (40·9%), and the other, decomp. 340° (45·6%). Long heating of the sparingly soluble dinitro-compound with aniline or *p*-toluidine causes replacement of both nitro-groups with the formation of *dianilino*- and di-*p*-*toluidino*-derivatives, decomp. above 400° and decomp. 420°, respectively. The readily soluble dinitro-compound similarly yields an isomeric *dianilino*-compound, decomp. 320°. The sparingly soluble nitro-compound heated with aniline for 3 hrs. yields, not a mono-, but a *di-anilino*-derivative, decomp. 330°. These compounds all give intensely coloured bluish-grey to black dyes when heated with fuming sulphuric acid. J. W. BAKER.

Amino-derivatives of dinaphthanthradiquinone. R. SEKA and O. SCHMIDT (Monatsh., 1926, 47, 627—634).—Treatment of 2-benzoylanthraquinone-3-carboxylic acid (Phillipi, A., 1913, i, 627) with concentrated sulphuric acid yields dinaphthanthradiquinone in 52·8% yield (calculated on the original dibenzoylbenzenedicarboxylic acids). On nitration with nitric acid (d 1·52), 2-*dinitrobenzoylanthraquinone-3-carboxylic acid*, m. p. 170°, is obtained, which on

reduction with ferrous sulphate yields the corresponding *diamino*-compound, m. p. 170°. These compounds on heating with sulphuric acid (d 1·83) yield, respectively, *dinitro*- and *diamino-dinaphthanthradiquinone*, both decomp. 400°. The dinitro-compound exhibits the same colour reactions as the compound obtained by the direct nitration of the diquinone (preceding abstract), but reduction of the latter (decomp. above 400°) with stannous chloride in alkaline solution yields a *diamino*-compound, decomp. 450°, which contains two atoms of hydrogen more than the diaminodiquinone. J. W. BAKER.

Nitriles of the benzanthrone series. KALLE & Co., A.-G.—See B., 1927, 101.

Manufacture of *iso*dibenzanthrones. BADISCHE ANILIN- & SODA-FABRIK.—See B., 1927, 101.

Vat dyes of the *iso*dibenzanthrone series. BADISCHE ANILIN- & SODA-FABRIK.—See B., 1927, 101.

Manufacture of 1 : 4-diarylamino-5 : 8-dihydroxyanthraquinones. I. G. FARBENIND. A.-G.—See B., 1927, 136.

Menthol studies. I. Menthyl esters of the nitro- and amino-cinnamic acids. K. L. McCLUSKEY and B. C. SHER (J. Amer. Chem. Soc., 1927, 49, 452—457).—The following menthyl esters were prepared by treating the appropriate acids with thionyl chloride and heating the resulting crude acid chlorides with menthol at 130°: p-*nitrocinnamate*, m. p. 92·5°, $[M]_D^{19}$ −224·00°; m-*nitrocinnamate*, m. p. 85°, $[M]_D^{19}$ −233·61°; o-*nitrocinnamate*, m. p. 49·5°, $[M]_D^{19}$ −209·75°; cinnamate, b. p. 174°/3 mm., $[M]_D^{19}$ −218·46°; benzoate, b. p. 173°/12 mm., $[M]_D^{19}$ −238·17°; and *p*-nitrobenzoate, m. p. 62°, $[M]_D^{19}$ −271·13°. Treatment of menthyl *p*-nitrocinnamate with pyridine dibromide–hydrobromide in glacial acetic acid affords *menthyl* αβ-*dibromo-β-p-nitrophenylpropionate*, m. p. 48° (cf. Rosenmund and Kuhnhenn, A., 1923, i, 782). Addition of bromine to menthyl o-nitrocinnamate in chloroform solution yields *menthyl* αβ-*dibromo-β-o-nitrophenylpropionate*, m. p. 93—93·5°, $[M]_D^{33}$ −76·03°; *menthyl* αβ-*dibromo-β-phenylpropionate*, m. p. 83·5°, $[M]_D^{30}$ −202·11, was prepared analogously. Reduction of the nitro-derivatives with iron powder affords the corresponding amino-compounds : *menthyl* p-*aminocinnamate*, m. p. 122°, $[M]_D^{19}$ −219·30°; m-*aminocinnamate*, b. p. 230°/2 mm., $[M]_D^{19}$ −209·14°; o-*aminocinnamate*, m. p. 85°, $[M]_D^{19}$ −182·32°; and p-*aminobenzoate*, m. p. 88°, $[M]_D^{19}$ −250·53 [*nitrate*, decomp. 150—156; *hydrochloride*, m. p. 196° (decomp.)]. *Menthyl* p-*dimethylaminocinnamate*, m. p. 99°, $[M]_D^{19}$ −220·67° (*methiodide*, decomp. above 140°, $[M]_D^{19}$ −177·68°), was prepared by condensation of *p*-dimethylaminobenzaldehyde with menthyl acetate in presence of sodium. All the above specific rotations were determined in 5% benzene solution. The following *dyes*, obtained by coupling the components mentioned, are described : menthyl *p*-aminocinnamate and β-naphthol, red ; menthyl *p*-aminocinnamate and R-salt, maroon ; menthyl *m*-aminocinnamate and β-naphthol, orange ; menthyl *p*-aminobenzoate and β-naphthol, orange-red ; and menthyl *p*-aminobenzoate and F-salt, orange, m. p. 287—288°.

F. G. WILLSON.

Decomposition products of menthyl esters of sulphonic acids. T. S. PATTERSON and (MISS) I. M. McALPINE (J.C.S., 1927, 349—353; cf. *ibid.*, 1906, **89**, 332).—Menthyl benzenesulphonate, naphthalene-β-sulphonate, and naphthalene-α-sulphonate (m. p. 116·5°, $[\alpha]_{5461}^{17\cdot5}$ —114·8°) decompose when distilled at 4 mm. into menthene and benzene sulphonic acid or naphthalene-β- or -α-sulphonic acids. When, however, the decomposition is carried out at about 120° in sealed tubes (no pressure), secondary reactions take place with the formation of hexahydrocymene, dimenthene, an unrecognised gelatinous substance (cf. Tolloczko, A., 1899, i, 440; Kanonnikov, *ibid.*, 1900, ii, 134), and the corresponding sulphonic acid. Decomposition of the esters in nitrobenzene or xylene at about 120° yields only dimenthene and the corresponding sulphonic acid.

J. M. GULLAND.

γ-Terpinene. F. RICHTER and W. WOLFF (Ber., 1927, **60**, [*B*], 477—479).—In striking contrast to the oil from the cultivated plant, that from wild *Crithmum maritimum* (Linn.) contains little dill-apiol; on distillation, it readily yields a terpene hydrocarbon, b. p. 69—73°/20 mm., d_{16}^{19} 0·8515, n_D^{19} 1·4785, α_D +2·5° (in 1 dm. tube), which is identified as $\Delta^{1\cdot4}$-p-menthadiene. The identity of the substance with crithmene (Francesconi and Sernagiotto, A., 1913, i, 636) and moslene (Murayama, *ibid.*, 1921, i, 875) is established.

H. WREN.

Production of camphene from pinene hydrochloride. H. GAMMAY.—See B., 1927, 156.

Camphor and terpenes. V. Addition of hydrocyanic acid to camphorimine, fenchimine, menthimine; cyanohydrins of camphor and menthone. J. HOUBEN and E. PFANKUCH (Ber., 1927, **60**, [*B*], 586—600; cf. A., 1926, 1251).—The action of potassium or silver acetate on 2-*endo*chlorocamphane-2-carboxylamide or of silver acetate on the corresponding nitrile leads to loss of hydrogen chloride and production of camphene-1-carboxylamide and camphene-1-nitrile, respectively, thus excluding the possibility of preparing camphorcyanohydrin from these initial materials. Camphorimine readily adds hydrogen cyanide, giving 2-*aminocamphane-2-nitrile*, m. p. 170—171° (decomp.) [*hydrochloride*, m. p. about 270° (decomp.)], which is converted by concentrated hydrochloric acid into camphor. It is transformed by sodium nitrite into *camphorexocyanoendohydrin*, m. p. 159°, $[\alpha]_D^{19}$ —32·2° in alcohol, which with hydrochloric acid yields optically inactive 2-*endochlorocamphane-2-nitrile*, m. p. 181—182°, identified by conversion into 2-chlorocamphane-2-carboxylamide. The action of potassium cyanide on camphornitroimine gives the isomeric camphor*endocyanoexohydrin*, m. p. 209—210°, $[\alpha]_D^{19}$ +32° in glacial acetic acid (cf. Passerini, A., 1925, i, 1290), thus affording a remarkable instance of the isolation of two optically different compounds from the same initial material. The constitution of Passerini's compound is established by converting it by means of phosphorus pentachloride and phosphoryl chloride into the chloronitrile, which is transformed with difficulty into camphene-1-carboxylic acid in addition to (?) *bornylenecarboxylamide*, m. p. 218—

219°. Fenchimine is converted by aqueous hydrocyanic acid into *cyanofenchylamine*, m. p. 111° (*hydrochloride*; *acetyl* derivative, m. p. 200—201°), which appears to be converted by nitrous acid into a fenchenenitrile. *Menthimine*, b. p. 94°/12 mm., prepared by the action of ammonia on menthonenitroimine, adds anhydrous hydrocyanic acid with formation of cyanomenthylamine [*hydrochloride*, m. p. about 150° (decomp.), $[\alpha]_D^{19}$ +24·2° in water], which could not be transformed into menthonecyanohydrin. The latter *compound*, m. p. 144—145°, $[\alpha]_D^{19}$ +82·7° in alcohol, is obtained by the action of potassium cyanide on menthonenitroimine. It is hydrolysed by potassium hydroxide apparently to a menthenecarboxylic acid (*amide*, m. p. 122°).

H. WREN.

***apo*Cyclene.** I. S. S. NAMETKIN and Z. P. ALEXANDROVAVA (J. Russ. Phys. Chem. Soc., 1926, **57**, 395—398).—*apo*Cyclene (I) first obtained by Komppa and Roschier (A., 1922, i, 1167) as one of the products of the dehydration of camphenol by the xanthate method, yields, on hydration, various products of doubtful constitution. The hydration could be 1 : 6 (yielding alcohols derived from camphenilone and α-*iso*camphenilone; cf. A., 1925, i, 1079), 1 : 2 (yielding products derived from *apo*camphor), or 2 : 6 (yielding products derived from camphenilol and *apo*camphor). Actually, an alcohol derived from *apo*camphor was obtained by the authors, and the addition cannot be 1 : 6 [cf. below]. Komppa and Roschier (*loc. cit.*) found as one of the products α-*iso*camphenilol. The authors prepared *apo*cyclene by the oxidation of the hydrazone of camphenilone, m. p. 39—40°, b. p. 136·5—137°/748 mm. (compare Komppa and Roschier, *loc. cit.*). Hydration with glacial acetic acid and sulphuric acid yielded an *ester*, b. p. 104—105°/21 mm. Hydrolysis gave an *alcohol*, m. p. 51—60°, b. p. 100·5—101°/19 mm.; this on oxidation yielded a mixture of ketones, $C_9H_{14}O$, which on further oxidation were converted into *apo*camphoric acid, m. p. 204—205°.

E. ROTHSTEIN.

Constituents of oil of Supa. New natural source of copaene. G. G. HENDERSON, W. McNAB, and J. M. ROBERTSON.—See B., 1927, 172.

Vat dyes of the 2-thionaphthen-2-indoleindigo series. R. HERZ and J. MÜLLER.—See B., 1927, 136.

Reduction of quinoline-2 : 4-dicarboxylic acid. T. NOZOE (Proc. Imp. Acad. Tokyo, 1926, **2**, 541—543).—Reduction of quinoline-2 : 4-dicarboxylic acid with sodium amalgam gives the di- or tetra-hydroacid, isolated as *copper* salt (*benzoylated acid*, $C_{18}H_{13 \text{ or } 15}O_5N,2H_2O$, decomp. 170°), whilst by reduction with hydrogen and platinum-black in acetic acid a quantitative yield of *decahydroquinoline-2 : 4-dicarboxylic acid*, which decomposes at 286—286·5° or, with 1·5AcOH, has m. p. 137° (decomp.). The *sodium* (+4H$_2$O), *barium* (+6H$_2$O), *copper* (+5H$_2$O), and *silver* salts and the low-melting *ethyl* ester (*chloroplatinate*, decomp. 225°) are described. Methylation of the decahydro-acid with methyl-alcoholic potassium hydroxide and methyl iodide

gives the *methylbetaine*, $CO_2H \cdot C_9H_{11}NMe_2{<}^{CO}_{O}$ (*chloro-aurate*, decomp. 195—196°). If 10% aqueous potassium hydroxide is used in the methylation, the product is a *betaine* with probably a dipeptide structure,

$$CO_2H \cdot C_9H_{14}N \cdot CO \cdot C_9H_{11}(CO_2H)NMe_2{<}^{CO}_{O}$$ (*chloro-aurate*, decomp. 178—179°). C. HOLLINS.

Syntheses of hæmopyrrolecarboxylic acid. H. FISCHER and A. TREIBS (Ber., 1927, **60**, [*B*], 377—381).—4-Methylpyrrole-3-propionic acid is converted by treatment with hydrogen cyanide and hydrogen chloride in ether–chloroform followed by hydrolysis of the imine hydrochloride into *5-aldehydo-4-methylpyrrole-3-propionic acid*, m. p. 152° (corr.), which decomposes above its m. p. with formation of porphyrin and is converted by boiling concentrated hydrochloric acid into a *methene* derivative, decomp. 170° after darkening at 140°. It is transformed by treatment with hydrazine hydrate and sodium alkoxide into 4 : 5-dimethylpyrrole-3-propionic acid (hæmopyrrolecarboxylic acid), m. p. 130°. 2 : 4 : 5-Trimethylpyrrole-3-propionic acid (cf. Fischer and Nenitzescu, A., 1924, i, 1233) is converted by phthalic anhydride in glacial acetic acid at 185—195° into the phthalide of 4 : 5-dimethylpyrrole-3-propionic acid, which is hydrolysed to the *phthalidic acid*, m. p. 205° (corr.), converted by glacial acetic and hydriodic acids into 4 : 5-dimethylpyrrole-3-propionic acid. H. WREN.

Transformation products of tetrabromopyrocatechol. F. ZETZSCHE and S. SUKIENNIK (Helv. Chim. Acta, 1927, **10**, 91—102).—The yellowish-brown *monopyridine* salt of 2 : 5 : 6-*tribromo-3 : 4-dihydroxyphenylpyridinium bromide*, $C_{11}H_7O_2NBr_4,C_5H_5N$, decomp. 155—157°, separates slowly when tetrabromopyrocatechol is treated with dry pyridine at 40°. If the pyridine is slightly moist, the red *dipyridine* salt, m. p. above 260°, is also obtained. When either of these is treated with hydrobromic acid (*d* 1·15), 2 : 5 : 6-*tribromo-3 : 4-dihydroxyphenylpyridinium bromide*, m. p. 242—243° (decomp.), is formed. The pyridine ring in this compound is not opened by aniline or by phenylhydrazine as in the case of dinitrophenylpyridinium chloride (A., 1906, i, 454), but aqueous solutions of bases convert it, through an unstable violet intermediate compound, into 2 : 5 : 6-*tribromo-3 : 4-dihydroxyphenylpyridinium betaine*, $C_5H_5N \cdot C_6(OH)Br_3 \cdot O$, m. p. 208—209°. This is analogous to the 2 : 4-dinitro-5-hydroxyphenylpyridinium betaine described by Zincke and Weispfenning (A., 1910, i, 585). It is reconverted by pyridine and hydrogen bromide into the red dipyridine salt, and by acids into 2 : 5 : 6-tribromo-3 : 4-dihydroxyphenylpyridinium salts (*sulphate*, m. p. 255°; *chloride*, m. p. 220—222°; *glycerol-β-phosphate*). All the above compounds are oxidised by nitric acid to the corresponding quinone, red 2 : 5 : 6-*tribromo-3 : 4-diketo-3 : 4-dihydrophenylpyridinium nitrate*, decomp. indefinitely, when heated. This and the corresponding *bromide* give a green colour with alcoholic ferric chloride and are decomposed by alkali with liberation of pyridine. Attempts to prepare compounds of a similar type from tetrabromopyrocatechol with other bases were unsuccessful. Pure tetrabromoveratrole, m. p. 151—152° (Brüggemann, A., 1896, i, 356, gives 118°), does not combine with pyridine. When tetrabromopyrocatechol, in 10% sodium hydroxide solution, is oxidised by the air, a red substance is precipitated which contains sodium bromoanilate and gives 2 : 5-dibromo-3 : 6-dihydroxy-*p*-benzoquinone on acidification. H. E. F. NOTTON.

Synthesis of 5 : 6-dimethoxyindole and its 2-carboxylic acid. A. E. OXFORD and H. S. RAPER (J.C.S., 1927, 417—422).—The first stage in the oxidation of tyrosine to 5 : 6-dihydroxyindole and its 2-carboxylic acid by tyrosinase (cf. Raper, this vol., 278) is the production of 3 : 4-dihydroxyphenylalanine, and this is suggested as a possible method by which certain pyrocatechol derivatives may arise in nature.
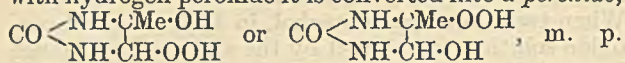
Condensation of 6-nitrohomoveratrole with ethyl oxalate (cf. Blaikie and Perkin, A., 1924, i, 547) yields 2-*nitro-4 : 5-dimethoxyphenylpyruvic acid*, m. p. 193—194° [*phenylhydrazone*, m. p. 170° (decomp.)], which is oxidised by alkaline hydrogen peroxide to 2-*nitro-4 : 5-dimethoxyphenylacetic acid*, m. p. 202—204°. The latter when reduced with ferrous sulphate and ammonia yields 5 : 6-dimethoxyindole-2-carboxylic acid, which at its m. p. (202—203°) passes into 5 : 6-dimethoxyindole, m. p. 154—155°, b. p. 198°/8 mm. (1-*acetyl* derivative, m. p. 150—152°). Colour reactions of these compounds are described, but neither the indole nor its acetyl derivative gives the brucine reaction (cf. Lions, Perkin, and Robinson, A., 1925, i, 831; Perkin and Rubenstein, *ibid.*, 1926, 394). J. M. GULLAND.

Quinolines. M. WYLER (Ber., 1927, **60**, [*B*], 398; cf. Maschmann, this vol., 158).—Quinolines are readily purified by means of their double salts with zinc chloride $(Base,HCl)_2,ZnCl_2$, from which they are regenerated by treatment with alkali and steam or (as hydrochlorides) by dry distillation. 2 : 8-Dimethylquinoline has m. p. 27°. Distillation of the double salt from 2-methylquinoline under greatly diminished pressure affords occasionally a *chloro-2-methylquinoline*, m. p. 94·5° (*hydrochloride*, m. p. 165°; *picrate*, m. p. 213—214°). H. WREN.

Oxidation of 5-aminouracil. O. BAUDISCH and D. DAVIDSON (J. Biol. Chem., 1927, **71**, 497—499).—Treatment of 5-aminouracil, in alkaline solution, with potassium ferricyanide gave *diuracilpyridazine*, m. p. above 300°. On the analogy of the previously observed oxidation of *iso*barbituric acid (A., 1925, i, 1188) it is thought that the reaction proceeds through the stage of 5 : 5'-diaminouracil. C. R. HARINGTON.

Action of methylglyoxal on carbamide. L. SEEKLES (Rec. trav. chim., 1927, **46**, 77—84).—Carbamide reacts with methylglyoxal to yield *methylacetylenediureine*, m. p. 274° (decomp.), as a final product. An intermediate *product*, (I) or (II), m. p. 193° (decomp.), can be isolated. On treatment with fuming nitric acid, both the diureine and its inter-

(I.) $^{HO \cdot CMe \cdot NH}_{NH_2 \cdot CO \cdot NH \cdot CH-NH}{>}CO$

(II.) $^{NH_2 \cdot CO \cdot NH \cdot CMe---NH}_{CH(OH) \cdot NH}{>}CO$

mediate product yield nitropyruvic ureide. On hydrolysis in presence of phenylhydrazine, the intermediate product yields methylglyoxalosazone, and with hydrogen peroxide it is converted into a *peroxide*,

$$CO\underset{NH\cdot CH\cdot OOH}{\overset{NH\cdot CMe\cdot OH}{<}} \text{ or } CO\underset{NH\cdot CH\cdot OH}{\overset{NH\cdot CMe\cdot OOH}{<}}, \text{ m. p.}$$

146° (decomp.). This peroxide is unstable both in the dry state and in solution. Treated with fuming nitric acid, it yields nitropyruvic ureide, with potassium permanganate followed by phenylhydrazine it yields methylglyoxalosazone, and with hydrogen peroxide, acetylcarbamide is obtained. On treatment with hot water, intramolecular oxidation occurs, yielding a *substance*, m. p. 167°, probably pyruvic acid monoureide, $Ac\cdot CO\cdot NH\cdot CO\cdot NH_2$. This yields a *phenylhydrazone*, m. p. 160—162° (resinifying on exposure to air), which is also obtained by the action of phenylhydrazine on the peroxide.　　J. W. BAKER.

Relative stability of cyclic bases. XIII. J. VON BRAUN and O. GOLL (Ber., 1927, **60**, [*B*], 339—345; cf. A., 1926, 739).—The systems derived by the insertion of one or two methylene groups in the piperazine ring resemble piperazine itself in stability and thus find their place among the least stable cyclic systems.

Tetrahydro*iso*quinoline is converted by trimethylene bromide into α*γ*-ditetrahydro*iso*quinolyl-*n*-*propane*, b. p. 265—270°/14 mm. (slight decomp.), 230°/1 mm., m. p. 55—56° (hygroscopic *hydrochloride*, decomp. 230—232°; *picrate*, m. p. 190°). The new base is transformed by trimethylene bromide into *ditetrahydro*iso*quinoliniumditrimethylenininimium brom-*

ide, $C_9H_7N\underset{\underset{Br}{|}}{\overset{CH_2\cdot CH_2\cdot CH_2}{\underset{CH_2\cdot CH_2\cdot CH_2}{<}}}NC_9H_7$, m. p. 225°

(corresponding *chloride*, decomp. 219—220°; *chloroaurate*, decomp. 158°, after darkening at 140°; *chloroplatinate*, decomp. 220—222°). The diquaternary bromide is converted by tetrahydro*iso*quinoline and a little water at 200° into α*γ*-ditetrahydro*iso*quinolylpropane in 80% yield, whereas with piperidine under similar conditions it affords α*γ*-ditetrahydro*iso*quinolyl-*n*-propane, α*γ*-dipiperidino-*n*-propane, and α-*piperidino-γ-tetrahydro*iso*quinolyl-*n*-*propane*, b. p. 230—240°/14 mm. (very hygroscopic *hydrochloride*; *picrate*, m. p. 190°).

The action of trimethylene bromide on αβ-dipiperidinoethane or of ethylene bromide on α*γ*-dipiperidino-*n*-propane affords dipiperidiniumhomopiperazinium bromide, which does not melt below 300° (corresponding *chloride*, m. p. 290—300°, after darkening at 280°, according to the rate of heating; *chloroaurate*, m. p. 212°; *chloroplatinate*, decomp. 285°, after darkening at 250°). The bromide is converted by piperidine at 200° into αβ-dipiperidinoethane and α*γ*-dipiperidino-*n*-propane; with tetrahydro*iso*quinoline, the products are αβ-ditetrahydro*iso*quinolylethane, α*γ*-ditetrahydro*iso*quinolyl-*n*-propane, αβ-dipiperidinoethane, α*γ*-dipiperidino-*n*-propane, and an inseparable mixture of *γ*-piperidinopropyl- and β-piperidinoethyl-tetrahydro*iso*quinoline. *Ditetrahydro*iso*quinoliniumhomopiperazinium* bromide, m. p. 279—280° (decomp.) (corresponding *chloride*, m. p. 272°), is transformed by tetrahydro*iso*quinoline into an equimolecular mixture of αβ-ditetrahydro*iso*-

quinolylethane and α*γ*-ditetrahydro*iso*quinolyl-*n*-propane. With piperidine, it affords a little dipiperidinoethane and -propane containing tetrahydro*iso*quinoline, mainly β-piperidinoethyl- and *γ*-piperidinopropyl-tetrahydro*iso*quinoline, and small amounts of ditetrahydro*iso*quinolyl-ethane and -propane.　H. WREN.

Isomerism of reduced derivatives of quinoxaline. II. Stereoisomeric 2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines. C. S. GIBSON (J.C.S., 1927, 342—349; cf. *ibid.*, 1923, **123**, 1570).— 2 : 3-Dimethylquinoxaline, m. p. 104·5—105·5° (cf. Gabriel and Sonn, A., 1908, i, 60), crystallises +3H_2O. When reduced with sodium and alcohol, it yields a mixture of meso-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* (75%), m. p. 111—112° (crystallographic data given), and dl-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 101—102°, which is probably a pseudo-racemic mixture. The following derivatives of the *meso*-base are described : 1 : 4-*diacetyl*, m. p. 145—146°; 1 : 4-*dibenzoyl*, m. p. 218·5—219·5°; 1-*benzoyl*, m. p. 137—138° (*nitroso*-compound, decomp. 140°, and *hydrochloride* described); 1 : 4-*di*-m-*nitrobenzoyl*, m. p. 243—244°; 1-p-*nitrobenzoyl*, m. p. 167°; 1-p-*toluenesulphonyl*, m. p. 183—184°; 1 : 4-*diphenylcarbamyl*, m. p. 190—191°; 1-*carbamyl*, m. p. 162—163° (crystallographic data given). Resolution of the *dl*-base by *d*- and *l*-tartaric acids yields d-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 94·5°, $[\alpha]_{5461}$ +112·3° (crystallographic data given; l-*tartrate*, $[\alpha]_{5161}$ +49·9°; l-*benzoyl* derivative, m. p. 233—234°, $[\alpha]_{5461}$ −369·1°), and l-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 94·5°, $[\alpha]_{5461}$ −112·0° [d-*tartrate*, decomp. 149°, $[\alpha]_{5461}$ −50·2°; 1-*benzoyl* derivative, m. p. 233—234° (decomp.), $[\alpha]_{5461}$ +369·7°; 1-p-*toluenesulphonyl* derivative, m. p. 172°, $[\alpha]_{5461}$ +66·9°].　J. M. GULLAND.

Preparation of a respiration model with a complex iron compound of indigotin. K. KUNZ and A. J. KRESS (Ber., 1927, **60**, [*B*], 367—376).— Iron pentacarbonyl slowly evolves carbon monoxide when warmed in anhydrous pyridine at 70—80°, apparently forming the compound, $Fe_2(CO)_7$. In the same solvent, indigotin is transformed by iron pentacarbonyl into the additive *compound*, $(C_{16}H_{10}O_2N_2)_2,Fe(CO)_5,2C_5H_5N$, which is readily decomposed by water and acids with re-formation of indigotin, but is not sensitive towards oxygen, since the iron atom is shielded by carbon monoxide. If, however, the green solution of the compound is warmed with an excess of iron pentacarbonyl, exactly 5 mols. of carbon monoxide are evolved and the red *substance*, $(C_{16}H_{10}O_2N_2)_2Fe$, is produced. The rôle of the nitrogen atoms in this compound is established by the observation that thioindigotin gives an analogous additive compound with iron pentacarbonyl, but cannot react with iron or other heavy metal alone. The carbonyl group of indigotin is not mainly responsible for the formation of the compound, since di-indolidenemethane gives analogous complex derivatives. It must therefore be assumed that the iron atom is united by four subsidiary valencies to the nitrogen atoms of the four pyrrole nuclei, although participation of the carbonyl oxygen is not absolutely excluded. A parallel is therefore drawn between

the indigotin derivative, hæmoglobin, and chlorophyll. The red compound regenerates indigotin when treated with acids. It is very sensitive towards oxygen and, like hæmoglobin, absorbs exactly 1 mol. of oxygen for each atom of iron. If anhydrous hydrogen cyanide is added to the red solution, the power of absorbing oxygen is lost, and only becomes restored gradually as the hydrogen cyanide is removed in a stream of oxygen. Union of the compound with oxygen is initially feeble; the absorbed oxygen is evolved in a vacuum and the red colour returns to the solution. After a short time at the atmospheric temperature, or more rapidly when warmed, the red colour reappears, the liberated oxygen being used in the oxidation of part of the indigotin. Renewed addition of oxygen renders the solution again green, and the process may be repeated until the indigotin is completely oxidised, whereby considerable heat is evolved. If, however, the green solution is preserved at 0°, the oxygen becomes more firmly united, with production of a *compound*, $(C_{16}H_{10}O_2N_2)_2FeO_2$, which does not evolve oxygen when warmed in a vacuum, but decomposes into indigotin, isatin, and a colourless by-product when warmed in anhydrous media in an atmosphere of nitrogen. In analogy with hæmoglobin, the indigotin derivative might be expected to absorb carbon monoxide, but the result has not been realised experimentally, probably owing to the inhibitive action of pyridine, the only available solvent. Nitric oxide reacts readily, probably forming initially a bluish-green additive compound containing 1 mol. of nitric oxide for each atom of iron. With excess of gas, 5 mols. of nitric oxide are absorbed and indigotin separates. Carbon dioxide does not affect the indigotin compound.

H. WREN.

Synthesis of derivatives of 1 : 8-naphthyridine. G. KOLLER (Ber., 1927, **60**, [*B*], 407—410; cf. Seide, this vol., 62).—Methyl 2-aminopyridine-3-carboxylate, m. p. 84—85°, is converted by ethyl malonate and ethyl-alcoholic sodium ethoxide at 145—150° into *methyl 2 : 4-dihydroxy-1 : 8-naphthyridine-3-carboxylate*, which softens at 236° (*sodium* salt); the basicity of the nitrogen atoms appears so depressed by their proximity and the presence of the hydroxy-groups that the substance is incapable of forming a stable salt. The ester is converted by dilute potassium hydroxide into 2 : 4-*dihydroxy-1 : 8-naphthyridine*, which, with phosphorus pentachloride and phosphoryl chloride, affords 2 : 4-*dichloro-1 : 8-naphthyridine*, m. p. 125—126° [*gold* salt, $(C_8H_4N_2Cl_2)_2,HAuCl_4$, m. p. 210—212° (decomp.) after softening at 200°]. H. WREN.

Producing amines, their substitution products, nitriles, and tetrazoles. KNOLL & Co., and K. F. SCHMIDT.—See B., 1927, 172.

Structure of furazan oxides. C. R. KINNEY and H. J. HARWOOD (J. Amer. Chem. Soc., 1927, **49**, 514—516).—Oxidation of the four dioximes of camphorquinone yields but one and the same furazan oxide, which has thus probably the symmetrical structure suggested by Green and Rowe (J.C.S., 1913, **103**, 897) and Forster and Fierz (*ibid.*, 1918). Further evidence for the symmetrical structure is afforded by the ozonisation of diphenylfurazan oxide, the chief product of which is benzoic acid, indicating an ethylenic linking between the carbon atoms of the furazan oxide ring. F. G. WILLSON.

New transformation of tertiary heterocyclic bases into secondary dealkylated bases. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1927, **184**, 331—333).—Previous methods of removing an *N*-alkyl group from a heterocyclic base to give the "nor" base have been unsatisfactory. A new method giving good yields from alkaloid bases which are not readily oxidised consists in treating the *N*-alkyl amine oxide with excess of acetic (or benzoic) anhydride; this gives the *N*-acetyl derivative of the nor-base, which is also acetylated at any hydroxyl group present. Saponification removes first *O*-acetyl, then combined acids (*e.g.*, tropic acid), and finally *N*-acetyl. The following compounds are obtained by this method: tropidine *N*-oxide gives *N*-acetylnortropidine, $C_7H_{10}NAc$, a neutral oil soluble in water, and thence nortropidine; tropine oxide gives *ON*-diacetyltropigenine, $C_7H_{11}ONAc_2$, by saponifying *N*-acetyltropigenine, m. p. 124° (hydrochloride, m. p. 162°), and tropigenine, or, with benzoic anhydride, *N*-benzoyltropigenine; *apo*atropine oxide gives *N*-acetylnor*apo*atropine, $C_7H_{11}(CO_2C_8H_7)NAc$, m. p. 114° (hydrochloride, m. p. 140°), saponified to *N*-acetyltropigenine and tropigenine; hyoscyamine oxide gives *ON*-diacetylnorhyoscyamine, $C_7H_{11}(CO_2C_9H_8)ONAc_2$, $[\alpha]_D$ −30°, and thence *N*-acetylnorhyoscyamine, m. p. 158°, $[\alpha]_D$ −15°, *N*-acetyltropigenine, and tropigenine; atropine oxide gives the same derivatives; hyoscine oxide gives *ON*-diacetylnorhyoscine, and thence *N*-acetylnorhyoscine, m. p. 130°, $[\alpha]_D$ −27° (hydrochloride, m. p. 205°), *N*-acetyloscine, and noroscine; N-*methylgranatoline oxide*, m. p. 218°, gives *ON*-diacetylgranatoline, m. p. 80°, and thence *N*-acetylgranatoline, m. p. 120°, and granatoline. Work on ψ-pelletierine, tropinone, alkylpiperidines, and alkaloids of the morphine, eserine, and nicotine groups is announced. E. W. WIGNALL.

***iso*Quinoline series and synthesis of papaverine.** K. W. ROSENMUND, M. NOTHNAGEL, and H. RIESENFELDT (Ber., 1927, **60**, [*B*], 392—398).—ω-Bromostyrene is converted by potassium phthalimide in presence of cuprous bromide or copper bronze at 195° into *ω-phthalimidostyrene*, m. p. 188—189°, which adds hydrogen bromide in glacial acetic acid solution, yielding the *compound* $C_{16}H_{12}O_2NBr$, m. p. 107—108° (decomp.), and is hydrolysed by alcoholic potassium hydroxide to the corresponding *phthalamic acid*, m. p. 169°; attempts to isolate the unsaturated amine were unsuccessful. Benzamide, ω-bromostyrene, potassium carbonate, and copper acetate in boiling *p*-cymene afford *benzoylphenylvinylamine*, CHPh:CH·NHBz, m. p. 161°; *benzoyl-3 : 4-methylenedioxyphenylvinylamine*, m. p. 159°, and *benzoyl-p-anisylvinylamine*, m. p. 169°, are similarly prepared. Benzoylphenylvinylamine is converted by aluminium oxide in boiling decahydronaphthalene into 1-*phenyliso*quinoline, m. p. 94° (*picrate*, m. p. 164°), but the success of the operation depends greatly on the quality of the oxide, for the

preparation of which a trustworthy method has not been found.

β-Nitrodimethoxystyrene (cf. Rosenmund, A., 1911, i, 34) is converted by a solution of sodium in methyl alcohol into *methyl β-nitro-α-3 : 4-dimethoxyphenylethyl ether*, m. p. 106°; *methyl β-nitro-α-3 : 4-methylenedioxyphenylethyl ether*, m. p. 62°, is described. β-Methoxy-β-3 : 4-dimethoxyphenylethylamine, b. p. 170°/13 mm. (*hydrochloride*, m. p. 185°), yields a *benzoyl* derivative, m. p. 124°, which is converted by phosphoric oxide in boiling toluene into 6 : 7-dimethoxy-1-phenyl*iso*quinoline, identified as the *picrate*, m. p. 250°. β-*Methoxy-β-3 : 4-methylenedioxyphenylethyl-amine hydrochloride*, m. p. 162°, is described. β-Methoxy-β-3 : 4-dimethoxyphenylethylamine is transformed by homoveratryl chloride into the *amide*, $C_6H_3(OMe)_2 \cdot CH(OMe) \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot C_6H_3(OMe)_2$, m. p. 147—148°, which with phosphoric oxide affords papaverine, m. p. 146·5—147°. H. WREN.

Alkaloids of the *Calumba* root. VI. Corydalis alkaloids. VIII. Synthesis of tetrahydrojatrorrhizine, tetrahydrocolumbamine, and corypalmine. E. SPÄTH and E. MOSETTIG (Ber., 1927, 60, [*B*], 383—389; cf. A., 1926, 963, 965).—The base (I) (R=R'=H), obtained by the action of phloroglucinol and sulphuric acid on *r*-tetrahydroberberine (*loc. cit.*), is converted by partial methylation with diazomethane in methyl-alcoholic solution into tetrahydropalmatine (R=R'=Me), tetrahydrojatrorrhizine (R=H, R'=Me), and tetrahydrocolumbamine (R=Me, R'=H), together with unchanged material. The mono- and di-phenolic bases are separated from one another by means of their hydrochlorides. Partial methylation of the dextrorotatory form of base (I) affords *d*-tetrahydropalmatine and a mixture of phenolic bases from which corypalmine is isolated by fractional extraction of the chloroform solution with dilute hydrochloric acid. H. WREN.

(I.)
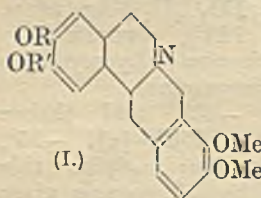
Derivatives of dibenzoarsenole [*oo'*-diphenylylenearsine]. H. GOTTLIEB-BILLROTH (J. Amer. Chem. Soc., 1927, 49, 482—486).—In the preparation of 3 : 3'-dimethoxydiphenyl from *o*-dianisidine by treatment of the tetrazo-hydrochloride with alcohol, the yield of the former is increased to 60% if a trace of copper powder be added previously to the alcohol, but there are formed, at the same time, small proportions of 4-*chloro-3 : 3'-dimethoxydiphenyl*, m. p. 74°, and 4 : 4'-*dichloro-3 : 3'-dimethoxydiphenyl*, m. p. 130°. When boiled with arsenious chloride, 3 : 3'-dimethoxydiphenyl yields 3 : 6-*dimethoxy-9-chloro-oo'-diphenylylenearsine* (I), m. p. 198—199°. This is unattacked by molecular silver in xylene at 100°, but yields, on oxidation with hydrogen peroxide in pyridine, 3 : 6-*dimethoxy-oo'-diphenylylenearsinic acid*, decomp. 220°, whilst

(I.)

treatment with 10% aqueous sodium hydroxide for 6 hrs. at 150—160° affords an amorphous *substance*, softening at about 85°, apparently isomeric with the corresponding dimethoxy-*oo'*-diphenylylenearsenious oxide. Nitration of the above arsinic acid with concentrated nitric and sulphuric acids at the ordinary temperature yields 2 : 4 : 5 : 7-*tetranitro-3 : 6-dimethoxy-oo'-diphenylylenearsinic acid*, yellow, decomp. 265°, which turns reddish when exposed to light (cf. Aeschlimann, A., 1925, i, 319). F. G. WILLSON.

Reaction between Grignard reagents and 10-chlorophenoxarsine or 10-chloro-5 : 10-dihydrophenarsazine. J. A. AESCHLIMANN (J.C.S., 1927, 413—417; cf. Roberts and Turner, A., 1926, 852).—An extension of previous work (A., 1925, i, 706). 10-*Methylphenoxarsine*, b. p. 185°/20 mm., yields a *dihydroxide*, m. p. 94°, with hydrogen peroxide, and reacts with bromoacetic acid to give 10-*methyl-10-carboxymethylphenoxarsonium bromide*, m. p. 199°. 10 : 10-Dimethylphenoxarsonium iodide has m. p. 225° when heated quickly (cf. Roberts and Turner, *loc. cit.*). 10-*Ethylphenoxarsine sulphide*, m. p. 109°, is formed by the action of sulphur in carbon disulphide, or from the corresponding oxide and hydrogen sulphide. 10-*Phenylphenoxarsine*, m. p. 107°, b. p. 270°/30 mm., forms a *hydroxide*, m. p. 93°, and an *oxide*, m. p. 184°. 10-*Phenyl-10-methyl-phenoxarsonium iodide* has m. p. 175°.

10-*Methyl-*, m. p. 105° (*acetyl* derivative, m. p. 154°); 10-*ethyl-*, m. p. 75°; and 10-*phenyl-5 : 10-dihydro-phenarsazine*, m. p. 142°, react with 1 mol. of methyl iodide only, even at 100°, to give the corresponding *dihydrophenarsazonium iodides* : 10 : 10-*dimethyl-*, m. p. 259° (slow heating) or 268° (rapid heating), which regenerates the dihydrophenarsazine when heated in a vacuum; 10-*methyl-10-ethyl-*, m. p. 229° or 236°; 10-*phenyl-10-methyl-*, m. p. 158° (decomp.). J. M. GULLAND.

Types of linking in the protein molecule. W. S. SADIKOV (Biochem. Z., 1926, 179, 326—331). —An investigation of suggested types of linkings between amino-acids based on a study of the stability or otherwise of collagen, glutin (from gelatin), keratin, and peptone towards pepsin and trypsin. Collagen is labile to pepsin, stable to trypsin, glutin is labile to both pepsin and trypsin, keratin is stable to pepsin and to trypsin, whilst peptone is stable to pepsin and labile to trypsin. It is suggested that pepsin attacks ether, ester, or anhydride linkings, whilst trypsin acts on peptide linkings. J. PRYDE.

Determination of halogens and sulphur in organic substances. A. RECSEI (Chem.-Ztg., 1927, 51, 96).—Sulphur and halogens are determined in non-volatile substances by the methods of Asboth (A., 1896, ii, 448) and of Warunis (A., 1911, ii, 927) respectively, using in each case 50—60 parts of a mixture of 2 parts of potassium sodium carbonate and 1 part of sodium peroxide. C. IRWIN.

Determination of acetoacetic acid. L. LORBER. —See this vol., 372.

Biochemistry.

Fœtal blood-gas tensions and gas transfusion through the placenta of the goat. A. S. HUGGETT (J. Physiol., 1927, **62**, 373—384).—The oxygen and the carbon dioxide dissociation curves of the maternal and fœtal blood of the goat have been determined. The difference in oxygen tension between maternal arterial and fœtal venous blood was 45 mm. for oxygen and 18 mm. for carbon dioxide. The gradient for carbon dioxide can be reversed by asphyxiation of the mother. Diffusion of blood gases across the placenta satisfactorily explains these results.
R. K. CANNAN.

Uptake of dyes by red blood-corpuscles. P. J. JURISIC (Biochem. Z., 1927, **181**, 17—29).—The uptake of any given basic or acidic dye by red blood corpuscles, over a definite period, is proportional to the concentration of the dye in the solution; in general, the basic dyes are taken up to a greater extent from an isotonic sodium chloride solution than from one containing sucrose, the reverse being the case with the acidic dyes. In the case of two acidic dyes soluble in diamylamine, the uptake of the dye by the blood-corpuscles, especially from dilute solutions, was almost complete in experiments of long duration, indicating adsorption. The rate of uptake of the dyes was increased by a rise in temperature. C. R. HARINGTON.

Spectrophotometric study of blood solutions. R. P. KENNEDY (Amer. J. Physiol., 1927, **79**, 346—361).—The determination of the hæmoglobin in blood solutions by measurement of the light absorption has been controlled by determinations of the oxygen capacity by the Van Slyke method. The absorption ratio of hæmoglobin has been determined over the visible spectrum. Precautions and limits of error in spectrophotometric measurements are discussed.
R. K. CANNAN.

Spectrophotometric studies on blood pigments and their derivatives. V. ZILZER (Biochem. Z., 1926, **179**, 348—363).—From the fact that the specific extinction coefficients of oxyhæmoglobin, hæmin, and hæmatoporphyrin increase with increasing thickness of solution, but with constant concentration, or with constant layer thickness and increasing concentration, it is inferred that the pigment molecules disperse as well as absorb light and that they follow in these respects different laws. When concentration and layer thickness are altered in opposite but equal senses, the specific extinction coefficients are unaltered and the Beer law holds. The spectrophotometric determination of these blood pigments will therefore be beset with inaccuracies until the laws of light dispersion as applied to them are more fully elucidated.
J. PRYDE.

Biochemistry of sulphur. I. Identity of ergothioneine from ergot with sympectothion and thiasine from blood. B. A. EAGLES and T. B. JOHNSON (J. Amer. Chem. Soc., 1927, **49**, 575—580). —Sympectothion (Hunter and Eagles, A., 1926, 85) and thiasine (Benedict, A., 1926, 421) are both identical with Tanret's ergothioneine (the betaine of thiolhistidine) (A., 1909, i, 671; cf. Barger and Ewins, J.C.S., 1911, **99**, 2336). F. G. WILLSON.

Ammonium salts in circulating blood. J. K. PARNAS (Bull. Soc. Chim. biol., 1927, **9**, 76—90).— It is reaffirmed that a small but definite quantity of ammonium salts exists in the circulating blood (cf. Parnas and Heller, A., 1925, i, 323, 454; Fontès and Yovanovitch, ibid., 1926, 85; Parnas and Klisiecki, ibid., 536; Fontès, ibid., 968). F. L. HEWITT.

Ammonia content and formation in blood. VII. Ammonia formation in physiologically stagnant blood. A. KLISIECKI, W. MOZOLOWSKI, and M. TAUBENHAUS. **VIII. Is the ammonia content of the blood connected with the presence of cyanates?** W. MOZOLOWSKI and M. TAUBENHAUS (Biochem. Z., 1927, **181**, 80—84, 85—95).— VII. Blood obtained by producing a contraction in the resting spleen has a higher content of ammonia than systemic blood, whilst that obtained by allowing the spleen to fill with blood again and immediately producing a second contraction contains the same concentration of ammonia as the systemic blood. Ammonia must therefore accumulate during the physiological stagnation of the blood in the spleen.

VIII. Observation of the formation of ammonia in shed blood or in protein-free blood filtrates, with and without the addition of cyanates, affords no support to the view that the latter are present in normal blood and form the source of the ammonia which is produced. C. R. HARINGTON.

Blood-ammonia. D. ADLERSBERG and M. TAUBENHAUS (Arch. exp. Path. Pharm., 1927, **121**, 35—66; cf. A., 1926, 855).—The blood-ammonia in normal and pathological subjects, and the effect on the normal value of varying conditions, have been determined. The normal actual ammonia-nitrogen content of circulating blood is less than 0·05 mg. %. This value is increased temporarily by intravenous injection of sodium dihydrogen phosphate or by greatly increased breathing. No alteration occurs during short periods of breathing mixtures poor in oxygen. Pathological conditions, with the exception of severe diabetic acidosis, show normal values. With rabbits, cutting off the kidneys from the circulation causes a gradual rise in the ammonia of the peripheral blood and a similar rise in the blood of the hepatic vein. After cutting off all the abdominal organs, no alteration occurs in the blood-ammonia, but a gradual rise in the precursor of ammonia results. Normal fresh rabbit's bile always contains ammonia, the value varying from 0·023 to 0·07 mg. %. Fresh human cerebrospinal fluid contains no ammonia. A. WORMALL.

Determination of plasmal in blood-serum. R. FEULGEN and K. IMHÄUSER (Biochem. Z., 1927, **181**, 30—48; cf. Pflüger's Arch., 1924, **206**, 389).— Blood-serum is treated with Schiff's reagent and with sufficient sulphur dioxide in aqueous solution to liberate the plasmal from its precursor; the solution so obtained is compared colorimetrically with another obtained by similar treatment of a second sample

of serum which contains, in colloidal solution, a known amount of plasmal thiosemicarbazone; by the use of Bürker's colorimeter (A., 1923, ii, 694) the plasmalogen in the second sample of serum can be compensated for and that in the first sample calculated. Considerable variations were found in the plasmal content of the blood-serum of various species.

C. R. HARINGTON.

Plasmalogen. I. Occurrence of plasmalogen in body-fluids. W. STEPP, R. FEULGEN, and K. VOIT (Biochem. Z., 1927, **181**, 284—288).—A method is given for the detection of plasmalogen with fuchsin–sulphurous acid. Serum, saliva, the stromata of red blood-corpuscles, amniotic fluid, and pus gave a positive, cerebrospinal fluid, urine, and aqueous humour a negative reaction. With hen's eggs, the white gives a faint reaction, but the yolk is rich in plasmalogen. Milk gives a positive reaction, but colostrum is much richer. P. W. CLUTTERBUCK.

Decolorisation of light-green by male and female sera. H. B. VAN DYKE and A. SCHURMEYER (Biochem. Z., 1927, **180**, 353—356).—Contrary to Manoiloff and Ssentjurin, there is no specific sex difference in the rates of decolorisation of light-green by male and female sera of animals or man.

R. K. CANNAN.

Effect of potassium oxalate on electrolytes of blood and plasma. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 587—604).—Variations, which were outside the limits of experimental error, but were inconsistent in magnitude and direction, were observed between oxalated and defibrinated samples of the same blood, particularly in the electrolyte content and the carbon dioxide absorption curve. The hæmatocrit values of the oxalated blood were always lower than those of the defibrinated blood. The variations were present whether the blood was treated anaërobically or in the air; they were independent of the time which had elapsed since the addition of the oxalate, and they were not the same as those produced by an equivalent amount of sodium chloride. In view of these results, defibrination is recommended in preference to treatment with oxalate for the prevention of coagulation in blood required for accurate work on the concentration of electrolytes.

C. R. HARINGTON.

Anaërobic defibrination of blood. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 607—609).—A sampling bulb provided with a stopcock at either end, and connected at one end to a levelling bulb, is completely filled with mercury; blood is allowed to flow into the bulb until nearly all the mercury is displaced, the stopcocks are closed and the bulb is shaken; the fibrin adheres to the fine globules of mercury and the blood is readily separated. C. R. HARINGTON.

Determination of partition of phosphorus in blood. M. MÂCHEBŒUF (Bull. Soc. Chim. biol., 1927, **9**, 94—98).—Determination of the total phosphorus of whole blood, serum, and corpuscles, and of the inorganic phosphates of the serum may be carried out, using 10 c.c. of blood. For inorganic phosphate determination in serum, proteins are removed from 3 c.c. of serum by trichloroacetic acid; sulphuric acid, ammonium nitrate, and ammonium molybdate are added to the filtrate, the phosphomolybdate is collected, and the amount of standard sodium hydroxide required to displace the ammonia is determined, using phenolphthalein as indicator. Fractionation of the proteins with ammonium sulphate indicated that in 1 c.c. of horse serum, containing 0·077 mg. of total phosphorus, the inorganic phosphates accounted for 0·025 mg., the albumin contained 0·035 mg., and the globulin 0·014 mg. L. F. HEWITT.

Gasometric determination of p_H of blood. A. J. EISENMAN (J. Biol. Chem., 1927, **71**, 611—628). —Serum is separated from blood anaërobically and its carbon dioxide content determined; other samples of the same serum are saturated at known (higher and lower) tensions of carbon dioxide, and the resulting carbon dioxide content is determined; by means of the logarithmic chart of Peters (A., 1923, i, 1249), the carbon dioxide absorption curve of the serum is constructed from the last two observations; the first observed carbon dioxide content can then be located on the line so obtained and the corresponding p_H read off. By employing an experimentally-determined average value of 5·6 vol.-% to represent the difference in carbon dioxide content of the serum at 60 and 30 mm. tension of carbon dioxide, the method requires the determination of only one point on the curve; this modification is less accurate, since the above-mentioned average value is subject to variations which could not be definitely accounted for.

C. R. HARINGTON.

Micro-colorimeter. H. KLEINMANN (Biochem. Z., 1926, **179**, 276—286).—A description of the construction and method of using a micro-colorimeter made on the Duboscq principle and requiring only 1 c.c. of the solution. Depths up to 60 mm. are available, the angle of the field of view is 4·5°, and the error of the instrument is 0·5—1%.

J. PRYDE.

Micro-colorimetric determination of nitrogen. Total and residual nitrogen of blood-drops. H. KLEINMANN (Biochem. Z., 1926, **179**, 287—300).— A micro-Kjeldahl apparatus is described together with its application, in conjunction with the Nessler technique and the micro-colorimeter (see preceding abstract), to the determination of the total and residual nitrogen of minute quantities of blood (0·1—0·2 c.c.). J. PRYDE.

Nephelometric determination of neutral fat+ cholesterol of the blood by Bing and Heckscher's method. H. HECKSCHER (Biochem. Z., 1927, **181**, 444—487).—Pure cholesterol suspensions are not suitable for nephelometric determination by the method of Bing and Heckscher (cf. A., 1925, i, 995, 999), but mixtures of triolein and cholesterol containing more than 10% of triolein can be determined quantitatively. In carrying out the method, temperature variations within 10° and 20° are unimportant, and the degree of cloudiness is constant from 15 to 45 min. after formation of the suspension. Further details are given in respect to the taking of samples of blood, drying, preserving, and extraction, and in this modified form the method gives results comparable with those obtained by Bang's method.

P. W. CLUTTERBUCK.

Determination of minute quantities of quinine in the blood. A. C. Roy (Indian J. Med. Res., 1926, **14**, 129—133).—Acidified $0.01N$-iodine solution detects a difference of 0.002 mg. of alkaloid between 0.03 and 0.045 mg. per 5 c.c., and a difference of 0.001 mg. between 0.03 and 0.001 mg. With a total volume of 5 c.c. or 2 c.c., 0.0005 mg. or 0.0001 mg., respectively, can be detected by matching against saturated ammonium sulphate solution.
CHEMICAL ABSTRACTS.

Lithium citrate as anticoagulant in blood investigations. Systematisation of blood micro-analysis. G. DE TONI (Biochem. Z., 1927, **181**, 289—295).—The determination of inorganic phosphorus, sodium, potassium, calcium, and magnesium in blood by the methods of Kramer and Tisdall (A., 1921, ii, 412, 595, 463) and of Kramer and Gittleman (A., 1925, i, 180) is not interfered with by the presence of lithium citrate, which can therefore be used to prevent clotting when the samples are taken.
P. W. CLUTTERBUCK.

Bile salt hæmolysis. I. Fixation of bile salts by serum as an absorption phenomenon. J. L. DONELLY and A. G. MITCHELL (Amer. J. Physiol., 1927, **79**, 297—304).—The amounts of bile salts which fix increasing volumes of serum are given by $K = X^n/C$, where X is the weight of bile salts, C is the volume of serum, and $n = 2.175$. When a given addition of bile salts is spread over a period of time, more remains free than when the entire quantity is added at once.
R. K. CANNAN.

Calcium and halogen content of an organism during gestation. H. VIGNES and COISSET (Compt. rend., 1927, **184**, 472—474).—Determination of the calcium and chlorine content of pregnant guinea-pigs showed progressive decalcification throughout the period of gestation. There were slight indications of a corresponding increase in chlorine.
B. W. ANDERSON.

Combined cholesterol of the brain. L. GASSNER (Biochem. Z., 1927, **180**, 359—362).—Practically the whole of the cholesterol of the brain is in the free state. The higher proportions of cholesterol esters hitherto reported may be due to the fact that precipitation of cholesterol by digitonin is not complete without long keeping. Drying brain tissue at 100° with calcium sulphate leads to a loss of 30% of the total free cholesterol.
R. K. CANNAN.

Chemistry of the brain. I. Nitrogen distribution in the fractions of horse brain soluble in light petroleum. K. SINGER (Biochem. Z., 1926, **179**, 432—442).—The choline, total amino-, cerebroside, and residual nitrogen values of light petroleum extracts of horse brain have been determined. It is intended to apply the method to the brains of normal and mental (e.g., progressive paralysis) cases.
J. PRYDE.

Characteristics of unvarying lipins. E. F. TERROINE and P. BELIN (Bull. Soc. Chim. biol., 1927, **9**, 12—48).—The fatty acid content of the brain does not depend on the diet, but that of all other tissues may be divided into two classes, one part affected by and the other independent of the diet. The variable portion disappears during starvation. The ratio of unvarying fatty acids to lipin phosphorus is constant, practically the same for all animals, and identical with that of lecithin. The iodine value of the unvarying fatty acids is higher than that of the variable acids and of the fat deposits. It is suggested that linoleic acid is a constituent of the extracellular phosphatides of the lungs and linolenic acid of the liver and kidneys. In the muscles, the phosphatides probably consist of two saturated and two unsaturated fatty acids, one of the latter being linolenic acid and the other a similar acid with four unsaturated linkings.
L. F. HEWITT.

Spectrochemical detection and identification of the natural porphyrins. O. SCHUMM (Z. physiol. Chem., 1927, **164**, 143—158).—Methods by which the natural animal porphyrins can be differentiated are described. The complex iron compounds of the porphyrins, which have very similar spectrochemical properties, are freed from iron and the porphyrin mixture is examined.
A. WORMALL.

Determination of the nucleic acid content of organs. N. ALDERS (Biochem. Z., 1927, **181**, 400—409).—The method of determination of the nucleic acid content of organs from their purine base content is critically examined and a new method described in which the nucleic acid content is obtained from a determination of the phosphorus remaining after the organ had been extracted continuously with ether to remove soluble phosphatides and subjected to repeated extraction with warm, very dilute acetic acid to remove inorganic phosphates. The method gives higher values than the purine base method and appears to be more trustworthy.
P. W. CLUTTERBUCK.

Constitution and synthesis of spermidine. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING. —See this vol., 343.

Inorganic constituents of the pancreas and suprarenals. H. MARX (Biochem. Z., 1926, **179**, 414—425).—The ratio of potassium to calcium in the pancreas is much higher than that of the suprarenals. Magnesium is present in the former organ in greater amount than in the latter.
J. PRYDE.

Vaso-dilator constituents of certain tissue extracts. C. H. BEST, H. H. DALE, H. W. DUDLEY, and W. V. THORPE (J. Physiol., 1927, **62**, 397—417). —Histamine and choline have been isolated from alcoholic extracts of fresh liver and lung in quantities sufficient to account for the immediate vaso-dilator effects of such extracts. Anomalous chemical behaviour of these bases when present in crude tissue extracts has been demonstrated. The average amounts of histamine isolated were 1.58 mg. per kg. of liver and 27.64 mg. per kg. of lung. The physiological significance of the occurrence of histamine in the tissues is discussed.
R. K. CANNAN.

Ovarian residue. II. Alcohol-insoluble, water-soluble nitrogeneous extractives. F. W. HEYL and B. FULLERTON (J. Amer. Pharm. Assoc., 1926, **15**, 549—556).—The basic fraction (0.51%) from ovarian residue which has been extracted with ethyl alcohol and ether contains 0.098% of basic nitrogen, including 0.009% of creatinine nitrogen.

Adenine, arginine, and lysine were separated; a substance, not xanthine, having the formula $C_5H_4O_2N_4$ and possibly a trace of histidine were isolated.　　　　　　　　　CHEMICAL ABSTRACTS.

Glucosamine compounds. Y. KOMORI (J. Biochem. [Japan], 1926, **6**, 1—20).—(1) Shells of cicad larvæ were decalcified with hydrochloric acid and well washed, the protein then being destroyed by boiling with 20% potassium hydroxide solution. The residue, decolorised by means of 0·5% potassium permanganate followed by oxalic acid, contained 0·13% of ash, 46·09% C, 6·76% H, 6·50% N. The hydrolysed substance contained 59·70% of acetic acid, equivalent to 2 acetyl groups per nitrogen atom. The glucosamine content of the ash-free material was 85·13% (N : glucosamine= 1 : 1·02); the glucosamine was obtained by boiling with concentrated hydrochloric acid (osazone, m. p. 203°). (2) Ovomucoid was digested with trypsin (2%) at 38°. After removal of tyrosine by evaporation and filtration, leucine was removed after precipitation with mercuric chloride and lead acetate. Decomposition of the lead precipitate afforded a substance containing 4·59% of ash, 44·46% C, 6·77% H, 7·55% N. When hydrolysed with hydrochloric acid and stannous chloride, it yielded 27·5% of glucosamine; the acetic acid content of the ash-free substance was 37·54% (N : AcOH=1 : 1·15). (3) The fluid from the egg-sac of gastropods, when boiled with a slight excess of acetic acid, yielded a substance containing 17·75% of ash and 8·08% of nitrogen. It contained 51·24% of acetic acid and yielded glucosamine hydrochloride by the above method.　　　　　　　　　CHEMICAL ABSTRACTS.

Proximate composition of Pacific Coast crabs. C. R. FELLERS and C. F. PARKS (Univ. Wash. Pub. Fish., 1926, **1**, No. 7, 130—156).—*Cancer magister* and *Paralithodes camtschatica* contain 102 and 362 " parts per billion " of iodine, respectively; both contain struvite ($MgNH_4PO_4,6H_2O$) crystals. Fresh crab flesh contains tyrosinase; blue discolorations are probably due to the interaction of biuret and copper, both from the blood, and ammonia. The decomposition of the meat is investigated.
　　　　　　　　　CHEMICAL ABSTRACTS.

Chemical composition of the cerebrospinal fluid. H. B. WILCOX, J. D. LYTTLE, and J. E. HEARN (Amer. J. Dis. Children, 1926, **30**, 513—540).—The normal chloride content of cerebrospinal fluid is 690—720 mg. %, low values being obtained in acute and tuberculous meningitis; the normal protein content is 30—80 mg. %, high values being obtained in inflammations of the meninges and brain substance. The normal sugar value is 40—60% of that of the blood, abnormal values being obtained in certain pathological conditions.　　CHEMICAL ABSTRACTS.

Determination of pepsin in gastric juice. H. CITRON (Deut. med. Woch., 1926, **52**, 1781—1782).—Pepsin is allowed to act on fibrin, dyed with carmine, and the resulting colour compared with that obtained from a standard pepsin preparation of known composition.　　　　　　　　　CHEMICAL ABSTRACTS.

Liver function. VI. Determination of cholesterol and alcohol-soluble and -insoluble bile pigments of the duodenal contents. C. W.

McCLURE and M. HUNTSINGER (Boston Med. Surg. J., 1926, **194**, 811—814).　　CHEMICAL ABSTRACTS.

Individual differences in the isoelectric point of the caseinogen of human milk. F. TRENDTEL (Biochem. Z., 1927, **180**, 371—376).—The p_{II} of maximum flocculation of the caseinogen of human milk varies in different women, but is constant in any one subject. The addition of 5% of sodium chloride shifts the isoelectric point towards the alkaline side, but the individual differences persist.
　　　　　　　　　R. K. CANNAN.

Iodine and milk secretion. V, VI. Administration of small doses to goats. **VII, VIII.** Administration to cows. K. SCHARRER (Biochem. Z., 1927, **180**, 300—306, 307—312, 313—333, 334—340).—V. [With A. STROBEL.] The daily administration of 7·5 or 15 mg. of iodine to goats was without striking effect on the milk yield or its fat content.
VI. [With J. SCHWAIBOLD.] The milk of normal goats contains traces of iodine. Study was made of the rate of secretion in the milk of small doses of iodine administered as sodium iodide.
VII. [With A. STROBEL and W. SCHROPP.] VIII. [With J. SCHWAIBOLD.] Similar studies to the above were carried out on cows.　　R. K. CANNAN.

Enzymes of cow's milk. I. Effect of diet. II. Diastase of the milk in disease. T. CHRZASZCZ and C. GORALOVNA (Biochem Z., 1927, **180**, 237—262, 263—271).—I. The diastase, catalase, peroxydase, and aldehydase (determined by the nitrate method) are but little affected by the feed of the cow. The first three enzymes are found chiefly in the cream.
II. The diastase and catalase activities are notably increased in milk of unhealthy cows. The former increase may be found to be of diagnostic value.
　　　　　　　　　R. K. CANNAN.

Bacteriological detection of the sugars in urine. M. BENJASCH (Deut. med. Woch., 1926, **52**, 1733).—A discussion of the method of Klein and Soliterman (*ibid.*, 959). Parallel determinations with *Bacillus coli* and *B. typhosus* allow a differentiation of dextrose and lactose. The method is inapplicable to urine in cases of icterus. Phloridzin sugar is fermented more slowly than diabetic.
　　　　　　　　　CHEMICAL ABSTRACTS.

Semi-micro-method of determining orthophosphoric acid applied to urine. R. F. LE GUYON (Bull. Soc. Chim. biol., 1927, **9**, 59—75).—Organic matter in the urine is destroyed by treating with nitric acid and magnesium nitrate, the liquid is neutralised, a known amount of $0·1N$-silver nitrate and sodium acetate added, the precipitated silver phosphate is filtered off, dissolved in dilute nitric acid, and the silver determined by titration with potassium thiocyanate. Phosphates may be determined simultaneously with the chlorides by measuring the amount of silver nitrate employed, the excess of silver in the filtrate, and the amount in the dilute nitric acid solution. Five c.c. of urine are sufficient for a determination.　　　　　　　　　L. F. HEWITT.

Determination of acetoacetic acid. L. LORBER (Biochem. Z., 1927, **181**, 366—374).—Acetoacetic

acid is determined by a macrotitrimetric method, in which the acid is exactly neutralised and heated with excess of standard sulphuric acid, when the difference in titre before and after warming gives the acetoacetic acid value, and by a microcolorimetric method which is an adaptation of the Rothera test and is applied to its determination in urine and blood.

P. W. CLUTTERBUCK.

Quantitative proportion of acetone and aceto-acetic acid in urine as obtained by qualitative tests. L. LORBER (Biochem. Z., 1927, **181**, 375—382).—The nitroprusside test and Lieben's test detect in so-called acetone-containing urine, not acetone, but acetoacetic acid. Lieben's test is modified to detect acetone and the method of using Gerhardt's test is specified. P. W. CLUTTERBUCK.

Tautomeric enol and keto-forms of aceto-acetic acid. L. LORBER (Biochem. Z., 1927, **181**, 383—390).—The nitroprusside and the ferric chloride tests on acetone urines yield completely parallel results, both tests detecting the enol form of aceto-acetic acid, which form is predominantly present both in pure solutions of the acid and in urine. Quantitative determination by Gerhardt's method of aceto-acetic acid in pure solutions and in urine is described.

P. W. CLUTTERBUCK.

Spectrophotometric analysis of blood-serum in normal and pathological conditions. I. T. B. MAGATH and C. SHEARD (Arch. Int. Med., 1927, **39**, 214—225).—A large number of sera have been examined by spectrophotometric methods, and in all cases the type of curve is like that of bile, and corresponds with the spectral analysis of bilirubin. This yellow pigment is present in normal serum and in the sera of patients suffering from slight anæmia, malaria, pernicious anæmia, hæmolytic icterus, and obstructive jaundice. The bilirubins in the sera appear to be identical, and the amount present is least in the normals and increases in the order named. An increased destruction of erythrocytes, a diminished excretion of bile, or a combination of these two factors leads to a retention of bilirubin in these pathological conditions. A. WORMALL.

Catalase content of blood in experimental anæmia. A. BERNSTEIN (Biochem. Z., 1926, **179**, 304—312).—In experimental anæmia, produced in rabbits by injection of phenylhydrazine hydrochloride, the catalase content of the blood is diminished, whilst the catalase index is increased. The increase in the latter value is more marked than, but runs parallel to, that of the colour index. The change of the catalase index in simple anæmia is much less than that in phenylhydrazine anæmia. J. PRYDE.

Influence of muscular work on blood lactic acid, alkali reserve, acidity of the urine, etc. in circulatory diseases. B. GROAG and H. SCHWARZ (Arch. exp. Path. Pharm., 1927, **121**, 23—34).—Experiments carried out on the fasting patients showed a definite rise in the blood lactic acid after muscular exercise, in some cases up to double the resting value, in contrast to normals, where the rise was extremely small. At the same time, a distinct lowering of the alkali reserve occurred, but there was no absolute relationship between this fall and the rise

in lactic acid. The urine, under these conditions, became slightly more acid and there was a slight decrease in the ammonia excretion. The significance of these results, in the light of the theories of muscle contraction and the possibility of a decreased buffering power of muscle in circulatory diseases, is discussed. A. WORMALL.

Unknown substance in urine from a case of diabetes insipidus. A. B. ILLIEVITZ (J. Biol. Chem., 1927, **71**, 693—694).—On long keeping, under sterile conditions in the cold, of the urine from a case of diabetes insipidus, an ether-soluble purple pigment was produced; it was soluble in alkalis, insoluble in acids, showed no characteristic absorption spectrum, and could not be related to indican.

C. R. HARINGTON.

Existence of insulin-like material in fuso-cellular sarcoma of white rats. A. H. ROFFO and L. M. CORREA (Rev. Soc. Argentina Biol., 1926, **2**, 567).—In a preliminary investigation, insulin-like material equivalent to 8—12 clinical units was obtained from 500 g. of the sarcoma.

G. W. ROBINSON.

Post-mortem blood-sugar determinations. J. R. PAUL (Bull. Ayer Clin. Lab. Penn. Hosp., 1926, **10**, 34—43).—Within 2 hrs. after sudden death, the dextrose content of the blood was 73—143 mg. per 100 c.c. (4 cases). In a series of general hospital cases, it was below 60 mg. in 14 cases, below 40 mg. in 8 cases, below 10 mg. in 4 cases, below 1 mg. in 1 case, and 0 in 2 cases. In 2 cases, the dextrose content of blood drawn 0·5 hr. after death was 100 mg. less than that drawn 8 hrs. before death. The results suggest the rather frequent occurrence of terminal or agonal hypoglycæmic states in a wide variety of conditions. CHEMICAL ABSTRACTS.

Metabolism of transplanted tissues and their growth in the absence of oxygen and carbo-hydrate. F. WIND (Biochem. Z., 1926, **179**, 384—399).—Rous sarcoma can grow temporarily under anaërobic conditions in Carrel's culture medium. Normal 5- to 10-day embryonic heart cells, spleen cells, and monocytes may also grow under anaërobiosis, but not so well as sarcoma cells. On removing dextrose from the culture media by dialysis, anaërobic growth ceases. Rous sarcoma is not more sensitive to anaërobic conditions than is yeast. J. PRYDE.

Inorganic salt metabolism of dogs. III. Deposition and resorption of bone. M. R. JONES (Amer. J. Physiol., 1927, **79**, 694—705).—A study is reported of the bone changes in puppies in relation to the calcium, phosphorus, and alkali of the diet. By sufficient increase in the alkali of a diet on which calcification was efficient, a resorption of bone may be induced. Metabolism and blood studies indicate that the cause lies in the metabolism within the cells. Calcification is primarily dependent on the inherent metabolic state of the animal modified by any factor—e.g., diet—which influences the metabolism of the bone cells so as to alter the balance of ions between the cells and the surrounding medium. R. K. CANNAN.

Calcification. I. Pigs fed different protein supplements. II. Rats fed menhaden oil and

various menhaden fish meals. L. A. MAYNARD and R. C. MILLER (Amer. J. Physiol., 1927, 79, 615—625, 626—632).—I. Calcification was measured by the ash content of the femurs. Fish meal or a mixture of blood meal and caseinogen (which required to be enriched by the addition of calcium and phosphate) were better protein supplements than linseed oil meal.

II. Both meal and oil of menhaden fish contain the calcifying factor. R. K. CANNAN.

Lactic acid formation in red and white muscle of birds. C. SCHMITT-KRAHMER (Biochem. Z., 1927, 180, 272—287).—The post-mortem production of lactic acid by various red and white muscles of the hen and pigeon has been determined. The amount is related to the functional activity rather than to the colour of the muscles, the least active muscles giving the highest values. Striated muscle of these birds gave values exceeding those for frog's muscle and approximating to those for mammalian muscle.

R. K. CANNAN.

Decomposition of β-hydroxybutyric acid in the liver. I. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1927, 181, 410—417).—After perfusing dog's liver with blood to which β-hydroxybutyric acid has been added, almost the whole of the acid may be recovered from the blood and liver (16—32% as acetoacetic acid). A considerable amount of β-hydroxybutyric acid is adsorbed by the liver tissue, which after perfusion contains about four times as much acid as would be expected from the β-hydroxybutyric acid content of the blood in the liver. The possibility that the liver decomposes some of the acid is not excluded, since the normal liver perfused with normal blood forms small amounts (50 mg.) of acetoacetic and β-hydroxybutyric acids, but the amount recovered from both liver and blood never exceeds the amount added.

P. W. CLUTTERBUCK.

Decomposition of acetoacetic acid during liver perfusion. I. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1927, 181, 418—424).—The amount of ketonic substances found in the blood and liver of a dog after perfusion with normal blood to which acetoacetic acid had been added was, in five experiments, 77, 128, 91, 87, 103% of the added amount, the greater part (50—60%) being present as β-hydroxybutyric acid. A considerable amount of the β-hydroxybutyric acid formed is adsorbed by the liver-tissue, the amount present in the liver after perfusion being 4—9 times the liver-blood content. The power of the surviving liver to reduce acetoacetic acid is great, but its power to break it down further is small.

P. W. CLUTTERBUCK.

Citric acid metabolism. E. B. WOODS (Amer. J. Physiol., 1927, 79, 321—340).—On prolonged feeding with citric acid, the pig develops remarkable powers of oxidation. The total organic acid, calcium, and phosphorus excretion bear no simple relation to the citric acid or acetone excreted. There is no evidence of a direct antiketogenic action of citric acid. R. K. CANNAN.

Behaviour of alanine and pyruvic acid in the surviving diabetic liver. V. LAUFBERGER (Biochem. Z., 1927, 181, 220—224).—On perfusion, in solution in ox-blood, through the surviving liver of a diabetic dog, neither alanine nor pyruvic acid is converted into lactic acid, as is the case with the normal liver. The values observed for the acetone of the blood in these experiments were very low, which is ascribed to the anti-ketogenic action of the alanine and pyruvic acid. C. R. HARINGTON.

Fate of glycuronic and galacturonic acids in the animal organism. R. HÜRTHLE (Biochem. Z., 1927, 181, 105—108).—Administration of glycuronic acid to dogs and rabbits in amounts greater than 0·2 g. per kg. leads to excretion of a large part of the substance unchanged. A dog failed to oxidise as little as 0·06 g. per kg. of galacturonic acid.

C. R. HARINGTON.

Relation between the excretion of urinary phosphorus and the consumption of carbohydrates. G. PIAZZA (Arch. Farm. sperim., 1926, 42, 85—92).—The results of experiments on dogs and on a diabetic patient show that, contrary to the conclusions of various authors, the urinary excretion of phosphorus in normal animals bears no relation to the amount of carbohydrate consumed, and that the increased tolerance towards carbohydrates induced in diabetics by insulin therapy leads to diminution in the excretion of urinary phosphorus. T. H. POPE.

Behaviour of glycæmia and of phosphorus content of the blood during muscular work. G. PIAZZA (Arch. Farm. sperim., 1926, 42, 93—96).—The performance of either moderate or severe work is accompanied usually by a very slight diminution of the proportion of inorganic nitrogen in the blood, although in one case a slight increase occurred. The acid-soluble phosphorus shows no regular change in either direction, but the free sugar of the blood tends to increase (cf. Embden and Grafe, A., 1921, i, 529; Heinelt, Deut. Ges. inn. Med., 1925, 396).

T. H. POPE.

Physiological value of five carbohydrates based on growth and fæcal analysis. H. S. MITCHELL (Amer. J. Physiol., 1927, 79, 537—541, 542—544).—I. The intestinal flora of rats fed on a diet containing 60% of lactose changed from the putrefactive to the aciduric type. The growth of the rats was poor, owing to excessive diarrhœa. With lactose and other sugars there was a close relation between the loss of carbohydrate in the fæces and the predominance of the aciduric type in the fæces.

II. Normal growth together with a change of the fæcal flora to the aciduric type was effected by feeding 30% of lactose in the diet. R. K. CANNAN.

Nutritive value of malt. M. RUBNER and A. SCHITTENHELM (Biochem. Z., 1927, 180, 426—453).—In metabolism studies on men and on dogs the meat of a normal diet was replaced by a mixture of yeast and malt. The absorption, partition in the urine, and the nutritive balance of nitrogen were followed and observations are recorded on the phosphorus, carbohydrate, and fat metabolism.

R. K. CANNAN.

Nutritive value of dried yeast preparations. A. SCHITTENHELM, MASSATSCH, and WARNAT (Biochem. Z., 1927, 180, 453—470).—Dried yeast preserved its nutritive value after roasting. The protein was

good and the vitamin value high. The growth of the feathers of young pigeons as an index of general growth (Abel) is confirmed as a method of testing for vitamin. R. K. CANNAN.

Diet and body fat. L. B. MENDEL and W. E. ANDERSON (Science, 1926, **64**, 384—386).—Starvation of rats, after feeding soya-bean oil, largely removes the "soft" oily fat, permitting the deposit of a "hard" fat. A. A. ELDRIDGE.

Has the actual reaction of the urine any influence on the extent of synthesis of hippuric acid? C. E. KOCH (Arch. exp. Path. Pharm., 1927, **121**, 83—88).—Subcutaneous injection into a rabbit of 1 g. of sodium benzoate, dissolved in physiological saline, results in the excretion in the urine of an amount of hippuric acid which is independent of the reaction of the urine, the range of the latter being p_H 5·5—8·2. With dogs, the excretion of hippuric acid after injection of 2 g. of sodium benzoate was somewhat greater in the more alkaline urines, but this is attributed to the fact that starved dogs were used to give an acid urine. Thus the extent of synthesis of hippuric acid in dogs, as in rabbits, is independent of the p_H of the urine. Part of the benzoic acid administered to dogs is excreted in combination with glycuronic acid. A. WORMALL.

Influence of nutrition on the synthesis of hippuric acid in man. E. M. P. WIDMARK (Biochem. Z., 1926, **179**, 272—275).—In the human subject receiving sodium benzoate *per os*, the hippuric acid : benzoic acid ratio of the urine falls markedly when carbohydrate is excluded from the diet, but returns to a normal value on restoration to a full *régime*. J. PRYDE.

Comparative metabolism of aromatic acids. XII. Fate of triphenylacetic acid, triphenylmethane, and triphenylcarbinol in the animal body. S. R. MIRIAM, J. T. WOLF, and C. P. SHERWIN (J. Biol. Chem., 1927, **71**, 695—698).—After feeding triphenylacetic acid to rabbits and dogs, 30—65% was recovered unchanged from the urine; a small quantity of triphenylmethane was found in the fæces. After feeding triphenylmethane, the unchanged material was recovered to the extent of 30%; triphenylcarbinol was more completely oxidised. *Triphenylacetylglycine* has m. p. 202—204°. C. H. HARINGTON.

Skatoxylsulphuric acid in urine. G. SCHEFF (Biochem. Z., 1926, **179**, 364—375).—The organic sulphates of dog's urine are increased by the administration of skatole. J. PRYDE.

Intermediate purine metabolism. I. Enzymic formation of uric acid precursors in the blood. W. A. ENGELHARDT (Biochem. Z., 1927, **182**, 121—130).—On keeping rabbit's blood, substances are formed which, under the action of oxido-reducing enzymes, give rise to uric acid. The formation of these precursor substances, which takes place in the corpuscles, is not observed at 0°, is most rapid at 37°, and diminishes at 56°. The process is not appreciably affected by the addition to the blood of fluoride, oxalate, or cyanide, nor by hæmolysis. It is suggested that the same process may lie at the basis of the formation of ammonia and inorganic phosphoric acid when blood is kept *in vitro*. J. PRYDE.

Static effort and the excretion of uric acid. R. C. GARRY (J. Physiol., 1927, **62**, 364—372).—Static effort and ordinary muscular exertion increase the excretion of uric acid. The increase extends over the two days following the work. The output of total nitrogen is similarly increased. R. K. CANNAN.

Physiological effect of massage. F. A. CAJORI, C. V. CROUTER, and R. PEMBERTON (Arch. Int. Med., 1927, **39**, 281—285).—Vigorous muscular and abdominal massage, under fasting conditions following a standard meal, leads to no appreciable alteration in the excretion of nitrogenous and other constituents in the urine. The benefits of massage appear to result from changes in the circulation, and not from any specific effect on general metabolism. A. WORMALL.

Action of physiologically equilibrated salt solutions. D. L. RUBINSTEIN (Biochem. Z., 1927, **182**, 50—64).—The sodium ion when present alone in solution has a double toxic action on turbellariæ, polychætes, and crabs. Potassium antagonises the one, and calcium the other, of these two toxic actions, but their behaviours in this respect are independent and do not summate. J. PRYDE.

Carbon monoxide poisoning in the absence of hæmoglobin. J. B. S. HALDANE (Nature, 1927, **119**, 352).—Experiments with the wax-moth, *Galleria mellonella*, and the cress plant, *Lepidium sativum*, suggest that oxygen, before it can be utilised for at least some of the oxidative processes in the cell, must combine with a substance possessing a smaller but well-marked affinity for carbon monoxide, these two gases combining with the same group in its molecule. The substance is probably a nearly universal cell constituent. A. A. ELDRIDGE.

Cytolysis of tissue-cells. V. LAUFBERGER. **Conditions of tissue cytolysis.** F. HORA (Biochem. Z., 1927, **181**, 225—229, 230—249).—Addition of small amounts of potassium cyanide, of formamide, or of saccharin to aqueous suspensions of normal cells caused a more or less extensive cytolysis of the latter within 24 hrs. Numerous other substances were found to be devoid of this effect. The cytolytic activity of the three compounds mentioned is thought to be connected with their high dielectric constant.

The cytolytic activity can be inhibited by addition of a variety of salts and other compounds, but neither the activity of the original substance nor the inhibition caused by the added substance is dependent on the concentration, the curves relating degree of cytolysis to concentration of cytolytic agent or of inhibitor showing a succession of maxima and minima. The inhibitors lose their characteristic effect on keeping in contact with the cells for 24 hrs. C. R. HARINGTON.

Physiological action of alcohol. I. Alcoholic content of the blood of a fasting man following ingestion of alcoholic liquor. II. Variations of glycæmia and alcoholæmia following ingestion of alcoholic liquors and of sucrose. S. BAGLIONI,

L. Bracaloni, and A. Galamini (Atti R. Accad. Lincei, 1926, [vi], 4, 545—551; 1927, [vi], 5, 34—39).—I. The course followed by the curve expressing the proportion of alcohol in the blood as a function of the time reckoned from the consumption of alcoholic liquor is different according as the subject is a habitual drinker or not. In the former event, the alcohol content of the blood reaches a maximum, and also vanishes, more rapidly than with an abstainer.

II. Experiments on human beings disclose a connexion between glycæmic and alcoholæmic variations which appears to support the view that sugar in the organism ultimately undergoes alcoholic scission.
T. H. Pope.

Action of narcosis on the chemical composition of the brain. M. Serejski (Biochem. Z., 1927, 182, 188—192).—Chloroform narcosis in dogs leads to an increase in the lipin content of both the white and the grey matter of the brain. The white matter shows a greater increase in cholesterol and unsaturated phosphatides than the grey matter. The total nitrogen of the white and grey matter is not significantly altered, but there is a slight tendency to increase.
J. Pryde.

Toxicity of local anæsthetics administered intra-arterially. T. Kuroda (Biochem. Z., 1927, 181, 172—175).—The toxicity of anæsthetics of the cocaine group is less after intra-arterial than after intravenous administration, probably owing to a detoxication during passage through the capillary plexus.
C. R. Harington.

Blood reactions of the alkaloids of *Ceanothus americanus*. C. E. Tharaldsen and J. Krawetz (Amer. J. Physiol., 1927, 79, 545—552).—Both *in vitro* and when administered orally or subcutaneously, these alkaloids reduced the clotting time of blood. Their influence was probably on the action of the thromboplastin.
R. K. Cannan.

[Pharmacology of] quinine. G. Weiss and R. A. Hatcher (J. Pharm. Exp. Ther., 1927, 30, 327—333).—The toxicity of quinine is dependent on the rate of its intravenous injection. For the cat, the fatal dose of the hydrochloride falls from 140 mg. per kg. body-weight to 100 mg. as the rate of injection is increased from 2 to 5 mg. per kg. body-weight per min. Cats recover within about 3 hrs. from the toxic effects of 70% of the fatal dose. The exclusion of the kidneys from the circulation has little influence on the rate of recovery, and perfusion experiments show that the greater part of an intravenous dose is probably destroyed in the liver.
E. A. Lunt.

[Pharmacology of] quinine. R. A. Hatcher and H. Gold (J. Pharm. Exp. Ther., 1927, 30, 347—350).—Quinine is eliminated practically completely from human blood in 6—20 min. after intravenous injection.
E. A. Lunt.

[Pharmacology of] quinidine. S. Weiss and R. A. Hatcher (J. Pharm. Exp. Ther., 1927, 30, 335—345).—The toxicity of quinidine sulphate varies with the rate of intravenous injection. The average fatal dose for the cat, when injected at the rate of 5 mg. per kg. body-weight per min., is about 80 mg. per kg. About 95% of an intravenous dose leaves the blood within 5 min.; the elimination is practically complete in 3—4 hrs. Perfusion experiments indicate that the liver of the cat destroys quinidine and quinine at practically the same rates. The quinidine was determined by titration with bromine water.
E. A. Lunt.

Nephelometric determination of small quantities of arsenic. M. Delaville and J. Belin (Bull. Soc. Chim. biol., 1927, 9, 91—93).—A mixture of 5 c.c. of the fluid investigated with 5 c.c. of a reagent containing sodium hyposulphite (10%) in hydrochloric acid is boiled and cooled, and the turbidity compared in a nephelometer with that of a standard arsenic solution. The error is $\pm 6\%$, using solutions containing 0·0005 mg. of arsenic per c.c. In biological fluids, organic matter is destroyed first by a mixture of nitric and sulphuric acids; the liquid is then evaporated and diluted.
L. F. Hewitt.

Detection of small quantities of lead in organs by chemical and spectrographic means. M. Klostermann (Ver. Ges. deut. Naturforsch. Aerzte, 1926, 3, 1116—1118).—Lead is obtained as dioxide by ordinary methods, and the formation of a deep blue colouring matter by the interaction of tetramethyldiaminodiphenylmethane, lead dioxide, and glacial acetic acid gives a colorimetric criterion for the quantity of lead present. The method has been calibrated by the addition of known amounts of lead to various organs and determining its quantity by the procedure described. The lead may be reconverted into the dioxide and then determined spectrographically.
R. A. Morton.

Kinetics of the action of carboxylase. E. Hägglund and T. Rosenquist (Biochem. Z., 1927, 181, 296—301).—The optimal phosphate concentration for the extraction of carboxylase from yeast is 0·3—0·35M, such extracts being four times as active as an aqueous extract. The variation of reaction velocity with concentration of substrate and with amount of enzyme is studied.
P. W. Clutterbuck.

Catalase. I. H. von Euler and K. Josephson (Annalen, 1927, 452, 158—181).—By a modification of the method of Hennichs (A., 1926, 756), the authors have obtained an exceedingly active preparation of catalase from horse-liver. The first extraction of the liver with water does not remove all the enzyme, a second extraction yielding a solution practically identical with the first. Only a single precipitation of the combined extracts with a half volume of alcohol should be employed. The solution (C.F. 1500) so obtained was adsorbed with aluminium hydroxide and the enzyme eluted with 0·02N-ammonia solution, 46% of the activity being obtained. Dialysis of this solution (C.F. 7500) for 60 hrs. resulted in no loss of activity, and yielded a product with C.F. 14,600. Elution with sodium hydrogen phosphate removes only 29% of the activity together with a much larger amount of blood pigment, and in this case a loss of activity occurs during dialysis, the final product having C.F. 4600. After dialysis of the solution obtained from the ammonia elution, the enzyme was adsorbed on kaolin in a medium having p_H 5, and again eluted with 0·02N-ammonia.

The solution (C.F. 26,000) after dialysis through a collodion membrane at 0° for 110 hrs. yielded a preparation having C.F. 43,000, which could be concentrated under diminished pressure without loss of activity. In agreement with Hennichs, it was found that there is no relation between the activity of the preparations and the percentage of iron present. Two preparations having C.F. 43,000 and 40,000, respectively, contained N 14·72 and 15·06%; S 0·78 and 1·25%; Fe 0·63 and 0·15%, respectively (phosphorus absent), the ash content of the two samples being only 1·4 and 0·94%, respectively.

J. W. Baker.

Collagen-dissolving enzyme (collagenase). W. S. Sadikov (Biochem. Z., 1927, **181**, 267—283). —Whereas freshly-prepared trypsin does not, many commercial preparations (especially when old) do attack tendon collagen. When minced pancreas is digested with 20% glycerol at the ordinary temperature for 24 hrs., an extract is obtained which attacks both fibrin and collagen, and the gland residue if further digested for 24 hrs. at 40° with glycerol gives an extract which attacks only collagen. Attempts were made to purify collagenase by adsorption methods. The enzyme is not precipitated by safranine, but it is adsorbed by kaolin (distinction from fibrinase). Charcoal adsorbs fibrinase partly, but does not adsorb collagenase. Kaolin and charcoal adsorbates of pepsin contain an enzyme which in acid solution converts collagen into a glue, but cannot further digest it (glutinase). When an old pancreatic solution was fractionated with kaolin and charcoal, whilst with charcoal no selective adsorption occurred, with kaolin the collagenase was destroyed. Collagenase is not injured by alcohol (distinction from trypsin). Collagen which has been treated with picric acid withstands the action of pepsin and trypsin, but is attacked by collagenase. Collagen and fibrin pretreated with formaldehyde are completely resistant to collagenase and trypsin, but fibrin, so treated, is attacked by pepsin. Glycerol extracts of spleen attack fibrin and collagen in alkaline solution and sodium carbonate extracts contain glutinase. Glycerol and sodium carbonate extracts of pancreas act equally well on collagen and fibrin, but those of liver are inactive. Pure pancreatic juice without addition of enterokinase digests fibrin both in acid and alkaline solution, but acts only faintly on collagen. In presence of enterokinase, collagen is attacked in both acid and alkaline solution, but fibrin only in alkaline solution. Enterokinase alone possesses to a slight extent the properties of collagenase and glutinase. Glycerol extracts of the fæces of various animals were shown to contain tryptase, collagenase, α-glutinase (glutinises in acid solution), and β-glutinase (glutinises in alkaline solution). Diphtheria toxin contains α-glutinase, but no collagenase, peptase, or tryptase.

P. W. Clutterbuck.

Glycerophosphatase. H. Kobayashi (J. Biochem. [Japan], 1926, **6**, 261—274).—The optimum acidity for the activity of glycerophosphatase is at p_H 5·56. The rate of hydrolysis of glycerophosphate is proportional to the enzyme quantity, i.e., the time necessary for equal degrees of hydrolysis is inversely proportional to the amount of enzyme. The affinity between the enzyme and the substrate is not influenced by the acidity of the medium.

Chemical Abstracts.

Peroxydase. IV. Influence of the substrate on the optimum p_H. H. Ucko and H. W. Bansi (Z. physiol. Chem., 1927, **164**, 52—57).—Horseradish peroxydase has different optimum reactions for the substrates, pyrogallol, guaiacol, and o-cresol (cf. A., 1926, 1275). The activity–p_H curve and the optimum p_H are not specific properties of an enzyme, but depend on the substrate.

A. Wormall.

Stereochemical specificity of lipases. Effect of poisons on fat-splitting enzymes. P. Rona and R. Ammon (Biochem. Z., 1927, **181**, 49—79).— The course of hydrolysis of various esters by different preparations of lipase was followed electrometrically, periodic measured additions of alkali being made in sufficient amount to maintain a constant p_H; in all cases the course of reaction was linear. When the substrate was r-methyl mandelate, the lipases from pig- and ox-liver and from taka-diastase attacked the d-ester preferentially, whilst those from human liver, guinea-pig serum, and pig-pancreas attacked the l-ester first (cf. Willstätter, A., 1924, i, 1144). The lipase from pig-liver behaved abnormally in that it hydrolysed the pure l-ester more rapidly than the pure d-ester, although its action on the r-ester was to bring about a preferential hydrolysis of the d-form; on further purification, this enzyme tended to lose its optical specificity. Whilst the concentration of enzyme had little effect on the hydrolysis of tributyrin by pig-liver lipase, it had a large effect on the rate of hydrolysis of the mandelic esters; further, methyl mandelate was hydrolysed much more rapidly than ethyl mandelate. The inhibiting effect of various alkaloids, of atoxyl, of trypaflavine, and of adrenaline on these enzymes is described.

C. R. Harington.

Influence of the quinine group on enzymic functions of the organism. VI. Dependence on the p_H **of the action of quinine and carbamide on pancreatic lipase.** J. A. Smorodincev and V. A. Danilov (Biochem. Z., 1927, **181**, 149—157). —Quinine accelerates the hydrolysis of triacetin by pancreatic lipase over the range p_H 4·5—6·0, but retards it at p_H 8, which, under normal conditions, is the optimum reaction for this enzyme. Carbamide has no effect on the enzyme at any reaction; carbamide nitrate has no action beyond that due to its effect on the p_H of the solution.

C. R. Harington.

Papain. H. Kraut and E. Bauer (Z. physiol. Chem., 1927, **164**, 10—36; cf. A., 1924, i, 467; 1925, i, 739).—The adsorption curves of papain and invertase on alumina show significant differences. Small amounts of the adsorbent remove a relatively large amount of papain and a small amount of invertase, but with further additions the amount of the former decreases, whilst that of the latter increases. Simple peptides are not integral constituents of papain, but it is not possible to separate the peptones and polypeptides from the enzyme.

Crude papain contains an inhibitory substance, which is probably a peptide, since digestion with crepsin leads to an increase in activity. Substances associated with the enzyme act as stabilisers and as co-adsorbents, for purified papain is much less readily adsorbed than the original preparation. Purification results in the removal of nine-tenths of the original impurities, and the methods of purification include extraction with chloroform, precipitation of part of the impurities with lead phosphate, adsorption on alumina, and elution with dilute acetic acid. Yeast-gum is added as a stabiliser and co-adsorbent. Dialysis causes a loss in activity, probably due to the loss of a specific stabiliser with buffer properties. Some chemical properties of the preparation are given. Millon's reaction becomes somewhat stronger during the course of purification, whilst Molisch's and the ninhydrin reactions remain fairly constant. A study of the stability at different hydrogen-ion concentrations shows that there is a maximum stability at p_H 5—6, approximately the same as the optimum reaction. A. WORMALL.

Influence of the reaction on the proteolytic power of papain. II. W. E. RINGER and B. W. GRUTTERINK (Z. physiol. Chem., 1927, **164**, 112—142; cf. A., 1926, 977).—A purified water-soluble papain shows two optimum reactions (p_H 2·5 and 11·3) for the dissolution of fibrin. Similar optima are found when heat-coagulated egg-white and serum proteins are used as substrates, although the optimum on the acid side varies somewhat with the protein. The influence of electrolytes on this action depends on the p_H of the medium, for small quantities of a large number of anions and cations have a strong inhibitory action, except in neutral or faintly acid solutions, where they have a strong activating action. Variations in the amount of electrolyte, with constant p_H, produce alterations in the velocity of the reactions, and also in the range of p_H, over which the action takes place. The further digestion of serum proteins by papain in neutral solution, as measured by the liberation of amino-nitrogen, is also accelerated by electrolytes. Papain and serum proteins appear to form compounds in neutral solution. A. WORMALL.

Purification and properties of pepsin. J. C. FORBES (J. Biol. Chem., 1927, **71**, 559—585).—On treatment of an aqueous solution of commercial pepsin with safranine, the enzyme was quantitatively precipitated; the precipitate was dissolved in 20% alcohol containing a little oxalic acid and the dye removed by extraction with butyl alcohol. In this way, enzyme preparations were obtained having twenty times the activity of the original material. Such an active preparation had C 45·24, H 6·19, N 11·50, S 1·79%; figures are given for the nitrogen distribution; traces only of purine derivatives were found. The isoelectric point was at p_H 2·5; the preparation had no immediate effect when added to dilute hydrochloric acid, but on prolonged incubation of such a solution a decrease was observed both in the conductivity and the hydrogen-ion concentration. Extraction of the dried preparation with ether left the enzymic activity unchanged; addition of alcohol and ether to aqueous solutions of the pepsin caused

inactivation when the concentration of acid was high, but had little or no effect when it was low. C. R. HARINGTON.

Intensification of enzymic action by minimal amounts of known substances. M. JACOBY (Biochem. Z., 1927, **181**, 194—206).—The activity of urease is increased by the presence of as little as 0·0001 mg. of potassium cyanide, or by even less of acetaldehydecyanohydrin; the activating effect is independent of the p_H. Urease which has been inactivated by mercuric chloride can be reactivated by treatment with cyanide. The action of urease is also accelerated by very small amounts of histidine, histamine, and hæmoglobin; arginine and lysine have a slight accelerating effect, whilst other amino-acids have practically no effect. Histidine, therefore, apparently belongs to a second group of accelerating substances of the same order of activity as cyanides. C. R. HARINGTON.

Fermentations with yeast regarded from the biological point of view. II. Fermentability of glyceraldehyde and dihydroxyacetone by living yeast. H. HAEHN and M. GLAUBITZ (Ber., 1927, **60**, [B], 490—493).—Pure glyceraldehyde is not fermented by bottom beer yeast, top yeast M, or *Saccharomycodes Ludwigii* in 1% solution or in a solution of p_H 7·37—7·73, and only slightly if boiled previous to the addition of the yeast. The yeast-cells become damaged to some extent. Pure dihydroxyacetone is vigorously fermented by *S. Ludwigii* after a pronounced period of induction, but not by the other two varieties of yeast. With technical, bimolecular dihydroxyacetone, the action is somewhat less vigorous. The yeast-cell does not suffer damage in any case. H. WREN.

Fermentability of free and phosphorylated hexoses and a polarimetric proof of their fixation in the yeast-cell. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **179**, 451—458).—Robison's hexosemonophosphate and the two monophosphates prepared by Neuberg—one by partial hydrolysis of hexosediphosphate, the other by hydrolysis of synthetic sucrosemonophosphate—are all fermented by top and bottom yeasts, but more rapidly by yeast juice. In no case is the fermentation as rapid as that of dextrose and lævulose. Lævulose shows an increased lævorotation, and hexosemonophosphate (Robison's and that from the diphosphate) an increased dextrorotation when they are added to yeast juice which has lost its fermentative power through keeping. It is suggested that a combination of sugar or sugar phosphate with yeast protein or protein degradation products may lie at the basis of this phenomenon (see also Neuberg and Kobel, A., 1926, 151, 1061). J. PRYDE.

Phosphorylation and oxido-reduction [in fermentation]. R. NILSSON and T. LÖVGREN (Z. physiol. Chem., 1927, **164**, 61—68).—The addition of small quantities of methylene-blue to dried bottom yeast H in a phosphate solution containing sugar decreases considerably the induction of the fermentation process as measured by the evolution of carbon dioxide, but subsequently the fermentation curves, with and without methylene-blue, are approximately

parallel. Large quantities of methylene-blue, however, entirely suppress the evolution of carbon dioxide. The action of small amounts of methylene-blue, by which the induction period is shortened, is attributed to the participation of this substance in the oxido-reduction reactions. Addition of methylene-blue also increases the rate of disappearance of inorganic phosphate from the solution during the first stages.
A. WORMALL.

Fermentation of dextrose and pyruvic acid. E. HÄGGLUND and L. AHLBOM (Biochem. Z., 1927, **181**, 158—171).—The relative rates of fermentation of dextrose and of pyruvic acid by yeast and yeast extracts vary with the nature of the enzyme preparation. Acceptance of the theory that the action of carboxylase on pyruvic acid is an essential part of yeast fermentation involves the further assumption of the existence of a co-enzyme which renders the pyruvic acid susceptible to the action of carboxylase, and, in those cases in which pyruvic acid is not fermented, must have been inactivated. No evidence of the existence of such a co-enzyme has so far been obtained.
C. R. HARINGTON.

Velocity of fermentation of pyruvic acid and the theory of fermentation. C. NEUBERG (Biochem. Z., 1927, **180**, 471—490).—Living yeast ferments dextrose more rapidly than pyruvic acid. With dry yeast, acetone yeast, and maceration juice, on the other hand, pyruvic acid is the more rapidly fermented in acetate buffers at p_H 4·8—5·0. The pyruvic acid theory of fermentation finds further support in these results. The fermentation of pyruvic acid and of dextrose in alkaline solution is discussed, and it is suggested that the inability of yeast to ferment added pyruvic acid in alkaline media may find explanation in the selective permeability of the yeast and the effect of the hydrogen-ion concentration on the ionisation and enolisation of pyruvic acid.
R. K. CANNAN.

Pyruvic acid as an intermediate product of alcoholic fermentation. F. TRAETTA-MOSCA (Annali Chim. Appl., 1927, **17**, 59—60).—Rimini's results (this vol., 279) are criticised (see A., 1926, 978).
T. H. POPE.

Inactivation of some yeast enzymes by zinc and cadmium salts. S. KOSTYTSCHEV and G. MEDVEDEV (Z. physiol. Chem., 1927, **164**, 77—102).—Invertase and reductase of dried yeast are both inhibited by small amounts of zinc and cadmium salts, the reductase action being measured by the reduction of added acetaldehyde. Concentrations of these salts as low as $M/25,000$ decrease the activities of the two enzymes. The velocity coefficient is greatly reduced in both cases, but the reaction curve is unaltered in form. The velocity coefficient for inversion is approximately inversely proportional to the logarithm of the concentration of the zinc or cadmium salt. This inhibitory effect is due to a specific action of zinc and cadmium ions, since the anions of their salts have no effect, and also salts of magnesium, calcium, strontium, and barium have little or no inhibitory influence on the enzymes concerned. The significance of these results in relation to the effect of zinc and cadmium salts on the form-

ation of acetaldehyde during fermentation of dried yeast is discussed. The salts of bivalent metals have no specific action on the carboxylase of dried yeast, although there is a decreased liberation of carbon dioxide in the first stages. A. WORMALL.

[Determination of] cytochrome in yeast cells. H. VON EULER and H. FINK (Z. physiol. Chem., 1927, **164**, 69—76).—The hæmochromogen in a pyridine extract of yeast can be determined by utilising the spectrophotometric method of Odencrants, which is described. A pyridine solution of hæmin is used as standard, and a quantitative comparison is made of the absorption of light at the main band (about 557 mμ). A. WORMALL.

Changes in hydrogen-ion concentration of natural waters produced probably by the growth of bacteria. V. ENEVOLDSEN (Biochem. Z., 1927, **181**, 251—266).—Considerable changes in the p_H of sea-water were observed while travelling through the Cattegat and up the Baltic and also in the pools near Roskilde. Investigations of the changes of p_H of sea-, fresh-, and ditch-water show that any such change of p_H is followed by a period of compensation. Sterilised sea-water after being kept for 8 days with frequent shaking, on inoculating with sea-water bacteria, shows changes of p_H daily.
P. W. CLUTTERBUCK.

Formation of carbamide by bacteria. II. N. N. IVANOV and M. I. SMIRNOWA (Biochem. Z., 1927, **181**, 8—16).—Both in the case of bacteria which form carbamide in a gelatin–peptone medium and in the case of those which do so only in presence of free arginine, the carbamide production is completely inhibited by the introduction of carbohydrates or of mannitol into the medium. Urease could be detected in all organisms which fail, under any conditions, to produce carbamide. It is thought, therefore, that production of carbamide is dependent on more or less complete absence of urease, and that the synthesis of the latter enzyme may be favoured by the presence of carbohydrate. C. R. HARINGTON.

Biochemistry of asymmetry (asymmetric dismutation). C. NEUBERG and E. SIMON (Biochem. Z., 1926, **179**, 443—450).—dl-Methyl-n-butaldehyde is converted by *Bacterium pasteurianum*, and by acetone extracts of the bacteria, into the corresponding dextrorotatory amyl alcohol and optically active valeric acid (cf. Neuberg and Simon, A., 1926, 1062).
J. PRYDE.

Tissue-digesting enzyme (histase) of streptococci. M. FOBISHER (J. Exp. Med., 1926, **44**, 777—785).—The extracellular proteolytic enzyme, *histase*, present in many strains of beta-type, aërobic and facultative hæmolytic streptococci, is partly inactivated in about 45 min. at 60°. It is present in sterile filtrates of cooked meat cultures. No correlation was found between hæmolysis and proteolysis. The enzyme resembles trypsin in its action.
CHEMICAL ABSTRACTS.

Mixed acid fermentation. Fermentative sugar dissimilation by micro-organisms of the coli group. W. C. DE GRAAF (Nederland. Tijdschr. Hyg. Microbiol. Serol., 1926, **1**, 43–70).—A discussion.
CHEMICAL ABSTRACTS.

Reduction of *l*-cystine by *Bacillus coli*. H. YAOI and S. HOSOYA (Japan Med. World, 1926, **6**, 81—83).—When *B. coli communis* is incubated in protein-free synthetic media containing *l*-cystine, cysteine is produced by reduction. The daily increase reaches the optimum after the 15th or 18th day. Anaërobic conditions yield larger quantities of cysteine than aërobic conditions. CHEMICAL ABSTRACTS.

Effects of alkylresorcinolcarboxylic acids and their dependence on the constitution of the alkyl side-chains. L. BLEYER (Biochem. Z., 1927, **181**, 350—365).—Suspensions of gram-negative cells (*Bacillus coli*, *dysenteriæ*, *proteus*, *prodigiosus*, *pyocyaneus*, etc.) were homogenised by sodium hexyl- and heptyl-resorcinolcarboxylates, but gram-positive cells (staphylococcus, pneumococcus, *B. diphtheriæ*, etc.) were unaffected. Red blood-corpuscles were hæmolysed and coagulated opaque serum-protein was clarified. Toxins were deprived of their toxicity and of their antigenic function, 0·25—0·5% of the hexyl compound producing this effect with the toxins of dysentery and tetanus. Diphtheria toxin was, however, more resistant. The reaction depends on the size of the alkyl group. The sodium salt of resorcinolcarboxylic acid and its ethyl derivative have little or no effect, the cytolytic, toxin-destroying, and homogenising power first appearing in the amyl derivative and increasing in the hexyl and heptyl derivatives. P. W. CLUTTERBUCK.

Cystine content of peptones for bacteriological use. H. YAOI (Japan Med. World, 1926, **6**, 114—116).—Commercial peptones vary greatly as to cystine content : Witte contains most, Difco least. Some samples of gelatin also contain cystine in minute amounts. CHEMICAL ABSTRACTS.

Use of saponin in protection of insulin against enzymes. F. LASCH and S. BRÜGEL (Biochem. Z., 1927, **181**, 109—116).—The physiological activity of solutions of insulin to which small amounts of saponin had been added was not affected by exposure to the action of pepsin or of trypsin. It is suggested that this observation may form the basis of a method for the oral administration of insulin.
C. R. HARINGTON.

Replacement of sugar by other substances in the removal of hypoglycæmic symptoms caused by insulin. F. SILBERSTEIN, J. FREUD, and T. RÉVÉSZ (Biochem. Z., 1927, **181**, 327—332).—Administration of dihydroxyacetone and especially of alanine, either perorally or subcutaneously, prevents hypoglycæmic symptoms after insulin. Lactates proved untrustworthy, and acetaldehyde, salts of pyruvic acid, glycerol, and alcohol were also unsuitable. P. W. CLUTTERBUCK.

Action of insulin on enzymes. U. SAMMARTINO (Arch. Farm. sperim., 1926, **42**, 17—27).—Experiments made with a more highly purified insulin confirm the previous conclusion (Atti R. Accad. Lincei, 1923, [v], **32**) that insulin has no influence on the velocity of reaction of enzymes such as diastase, catalase, and lipase. T. H. POPE.

Variations in the phosphorus content of muscular tissue during insulin hypoglycæmia.

G. PIAZZA (Arch. Farm. sperim., 1926, **42**, 28—32).—No increase in the inorganic phosphorus content is detectable in muscle during hypoglycæmia produced by administration of insulin. No hydrolysable phosphorus fraction exists in muscle either before or after the action of insulin. Insulin hypophosphatæmia cannot be due to displacement of phosphorus or a phosphorus compound from the blood into the muscular tissue. T. H. POPE.

Influence of insulin on the mammalian heart. M. B. VISSCHER and E. A. MULLER (J. Physiol., 1927, **62**, 341.—348).—Insulin has no intrinsic effect on the oxygen consumption of the heart in the heart–lung preparation. R. K. CANNAN.

Sugar, inorganic phosphorus, and lactic acid of blood after administration of insulin and dextrose. I. KATAYAMA and J. A. KILLIAN (J. Biol. Chem., 1927, **71**, 707—722).—Both in rabbits and in normal and diabetic human beings, insulin in large doses causes an increase in the lactic acid of the blood ; the increase is, however, small in comparison with the fall in concentration of dextrose. A similar, but less marked, rise in concentration of lactic acid follows ingestion of dextrose. The fall in the inorganic phosphorus of the blood, which follows administration of insulin, precedes the rise in the lactic acid content. The rise in lactic acid is greater in the normal than in the diabetic subject, and the results, in general, are in favour of the view that the lactic acid is an intermediate product in the utilisation of carbohydrate under the influence of insulin. C. R. HARINGTON.

Blood calcium and tolerance for magnesium. Hypercalcæmia induced by the parathyroid hormone. S. A. MATTHEWS and W. C. AUSTIN (Amer. J. Physiol., 1927, **79**, 708—718).—From studies of the fatal dose of magnesium sulphate when injected into normal and parathyroidectomised dogs and into dogs injected with parathyroid extract, it was concluded that the toxicity of magnesium sulphate is closely proportional to the calcium concentration in the blood. The effect of the parathyroid hormone on the heart and vascular system is antagonised by magnesium sulphate. R. K. CANNAN.

Action of iodine and iodine preparations, thyroidectomy, and administration of thyroid gland on blood catalase *in vitro* and *in vivo*. A. TIMOFEJEWA (Biochem. Z., 1927, **180**, 35—45).—A relationship exists between the functioning of the thyroid gland and the catalase activity of the blood. This is not a direct effect, since iodine, iodide ions, iodised protein, and active thyroid extracts do not increase catalase activity *in vitro*. On the other hand, catalase is activated or mobilised by feeding with thyroid extract or by pretreatment for some time with iodine or potassium iodide. P. W. CLUTTERBUCK.

Thyroxin. III. Constitution and synthesis. C. R. HARINGTON and G. BARGER.—See this vol., 358.

Diuretic-antidiuretic action of pituitary. R. L. STEHLE (Amer. J. Physiol., 1927, **79**, 289—296).—Urine secreted after pituitary injection is extraordinarily rich in phosphorus, calcium, potassium, and magnesium, which presumably arise from the

cells. It is suggested that the antidiuretic action of pituitary is due to increased capacity of the cells to hold water as a result of electrolyte changes. The diuretic effect is a salt effect due to the necessity for the kidney to excrete the salts thrown into the blood by the cells. R. K. CANNAN.

Internal secretions of the ovary. IV. A. S. PARKES and C. W. BELLERBY (J. Physiol., 1927, **62**, 385—396).—Details are given of the extraction and the yields of œstrus-producing hormone from placenta, uterus, fœtus, and amniotic fluid. It is improbable that the hormone is elaborated in the placenta.
R. K. CANNAN.

Cell respiration. VI. Function of the suprarenal cortex and the substance C_{XII}. A. VON SZENT-GYÖRGYI (Biochem. Z., 1927, **181**, 433—437). —A substance, C_{XII}, having the properties of a thiophenol derivative, is isolated from the suprarenal cortex. It is soluble in acetone, water, and methyl alcohol, slightly soluble in ether, insoluble in light petroleum. It gives no nitroprusside reaction, reduces iodine, p-phenylenediamine, neutral silver nitrate, and ferric salts, and gives colour reactions with ferrous and ferric salts. It does not reduce permanganate (cf. A., 1925, 93, 708; 1926, 99).
P. W. CLUTTERBUCK.

Function of the suprarenal cortex. I. Blood changes following bilateral suprarenalectomy in cats. II. (With A. J. EISENMAN.) Acid–base equilibrium. W. W. SWINGLE (Amer. J. Physiol., 1927, **79**, 666—678, 679—688).—I. The blood becomes more concentrated, resulting in a rise in the concentration of protein, non-protein nitrogen, and carbamide. The blood-sugar falls to a level characteristic of insulin hypoglycæmia. There is albuminuria and a diminished secretion of urine. Death may be attributed either to hypoglycæmia or to acid intoxication.

II. There is a fall in the p_H, carbon dioxide tension, and total acid of the blood and in the serum hydrogen carbonate. There is evidence of an uncompensated acidosis due to phosphoric and organic acids.
R. K. CANNAN.

Cellular oxidation in certain tissues of dogs deprived of suprarenals. O. P. ESTRADA and S. M. NEUSCHLOSZ (Rev. Soc. Argentina Biol., 1926, **2**, 597—598).—The oxidative power of different tissues of dogs was determined after extirpation of the suprarenals. There was a general diminution in the case of muscular tissues which was compensated by addition of cortical substance. Addition of thyroid from normal animals caused compensation, but the thyroid from animals deprived of suprarenals had the contrary effect. Cortical substance slightly inhibits oxidation by normal muscle. The effect of suprarenal extirpation in the case of organs was slight, but there was an inconstant increase in the oxidative power of the pancreas.
G. W. ROBINSON.

Disappearance of intravenously injected dextrose, formation of glycogen, and arterial and venous sugar content in dogs deprived of suprarenals. O. P. ESTRADA (Rev. Soc. Argentina Biol., 1926, **2**, 544—547).—Dogs from which the suprarenals

had been removed showed a decrease in blood-sugar content in the first 4 hrs. after removal. The blood-sugar was then maintained at 0·05—0·085% for some time, subsequently falling to 0·025—0·055% at death. The disappearance of sugar was delayed by intravenous injection of dextrose in four cases out of five, and the subsequent hypoglycæmia did not occur. Hepatic and myocardial glycogen were greatly diminished. A less evident diminution in muscular glycogen took place. Hepatic glycogen was not increased by injection of dextrose, but there was an increase in myocardial and muscular glycogen which did not, however, reach the normal figure. Removal of the suprarenals tended to cause the sugar content of venous blood to equal and exceed that of arterial blood. The effect still persisted after injection of dextrose. G. W. ROBINSON.

Effect of irradiation on vitamin-A. S. G. WILLIMOTT and F. WOKES (Pharm. J., 1927, **118**, 217—218).—Cod-liver oil, rich in vitamin-A, was irradiated in an open evaporating basin 3 inches from a quartz mercury vapour lamp. The temperature of the oil rose from 20° to 70° in 90 min. Data are given showing the diminution in vitamin-A content with time in an oil irradiated under these conditions. The determinations were made in a Lovibond tintometer, using the arsenious chloride and antimony chloride tests. One third of the vitamin was destroyed in the first hr., and the whole in 2 hrs.; irradiation of the oil for a few min. results in the subsequent slow destruction of the vitamin over a long period.
E. A. LUNT.

Feeding of xanthophyll to rats on a diet deficient in vitamin-A. S. G. WILLIMOTT and T. MOORE (Biochem. J., 1927, **21**, 86—88).—Pure crystalline xanthophyll prepared from nettle leaves cannot replace vitamin-A in the diet of rats.
S. S. ZILVA.

Absorption spectrum of cholesterol and its biological significance with reference to vitamin-D. I. I. M. HEILBRON, E. D. KAMM, and R. A. MORTON (Biochem. J., 1927, **21**, 78—85).—In the fractional crystallisation of cholesterol (from brain and from cod-liver oil) from ethyl acetate a small quantity of a compound accumulates in the least soluble fraction which shows well-defined absorption bands at 293 $\mu\mu$, 280 $\mu\mu$, and 269 $\mu\mu$. Cholesterol itself shows only general absorption. These bands disappear on irradiation with ultra-violet light. The unknown substance is therefore closely connected with the precursor of vitamin-D. S. S. ZILVA.

Relation of cholesterol to vitamin-D. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1927, **21**, 127—129).—Cholesterol purified by way of the dibromide shows no longer the absorption spectrum in the ultra-violet region characteristic of ordinary cholesterol (cf. preceding abstract) and cannot be activated antirachitically by irradiation with ultra-violet light. Ergosterol (or some similar sterol) is the parent substance of vitamin-D. S. S. ZILVA.

Antirachitic value of fresh spinach. M. H. ROSCOE (Biochem. J., 1927, 21, 211—215).—A slight but definite influence upon calcification is demonstrated by introducing fresh green leaves of summer

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spinach into the diet of young rats and rabbits (cf. Chick and Roscoe, A., 1926, 437; Boas, *ibid.*, 437). The effect is more marked in the case of the rabbits.
S. S. ZILVA.

Effect of excessive irradiation with ultra-violet light upon the growth of rats. J. L. LEIGH-CLARE (Biochem. J., 1927, **21**, 208—210).—Provided that the eyes are shielded, exposure of young growing rats to ultra-violet radiation for periods up to 30 min. daily has no deleterious effect on growth and well-being of the rats. An exposure for 30 min. is no more beneficial than that for shorter periods.
S. S. ZILVA.

Antirachitic value of cod-liver oil concentrate injected subcutaneously. B. KRAMER, S. D. KRAMER, D. H. SHELLING, and M. J. SHEAR (J. Biol. Chem., 1927, **71**, 699—706).—The unsaponifiable fraction of cod-liver oil, after removal of cholesterol, cured rickets in rats when injected subcutaneously in ethereal solution, but was inactive when injected in solution in palmitin.
C. R. HARINGTON.

Isolation of the anti-beri-beri vitamin. B. C. P. JANSEN and W. F. DONATH (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1390—1400).—A method is described for extracting from fine rice polishings the vitamin which protects rice-birds and pigeons from polyneuritis. From 100 kg. of the rice polishings a residue of 1·4 g. was obtained which appeared to contain about one quarter of the vitamin originally present. The product was apparently the hydrochloride of a base, possibly $C_6H_{10}ON_2,HCl$. Its chemical behaviour suggests the presence of a glyoxaline nucleus.
M. S. BURR.

Gaseous metabolism in the initial stages of *B*-avitaminosis in birds. B. A. LAVROV and S. N. MATZKO (Biochem. Z., 1926, **179**, 332—347).—From experiments on hens kept on a diet deficient in vitamin-*B* it is concluded that the specific effects of lack of the latter are not related to the lowered oxidative processes of the organism. The drop in gaseous metabolism in *B*-avitaminosis appears only when symptoms of starvation have set in.
J. PRYDE.

Influence of nutrition on the blood catalase content. A. BERNSTEIN (Biochem. Z., 1926, **179**, 313—325).—The catalase content of pigeon's blood is less than that of other animals, but in different animal species it is found to vary within wide limits, up to 1000%. In a single animal species variations up to 50% may be encountered. In starvation and during lack of vitamin-*B*, the catalase content does not fall below normal values. The catalase content of the organism cannot serve as an index of the total metabolism.
J. PRYDE.

Serum-calcium in vitamin-*B* deficiency. A. UNGAR (Biochem. Z., 1927, **180**, 357—358).—The serum-calcium of normal and of beri-beri pigeons showed no differences sufficient to support the view that beri-beri convulsions are due to a deficiency in the secretion of the parathyroid. R. K. CANNAN.

Water-soluble vitamins-*B* and -*C* in malt and malt extract. L. RANDOIN and R. LECOQ (Bull. Soc. Chim. biol., 1927, **9**, 49—58).—Malt and malt extract do not possess anti-scorbutic activity, but they contain vitamin-*B*, and hence promote growth and alleviate polyneuritic symptoms of pigeons and rats. The beneficial effect of malt extract in human scurvy is attributed to the high content of vitamin-*B*, thus partly replacing vitamin-*C*. L. F. HEWITT.

Can administration of sodium hydrogen carbonate or active iron oxide influence the course of avitaminosis in pigeons? D. BANERJEE (Biochem. Z., 1927, **180**, 27—29).—The course of avitaminosis is unaffected by administration of these substances. P. W. CLUTTERBUCK.

Relation between vitamin-*C* content of diet and milk in the cow. J. S. HUGHES, J. B. FITCH, H. W. CAVE, and W. H. RIDDELL (J. Biol. Chem., 1927, **71**, 309—316).—No relationship could be observed between the vitamin-*C* content of the cow's food and that of its milk. C. R. HARINGTON.

Protoplasm. II. Chemical constituents of the plasmodium of *Lycogala epidendron* and alterations during spore differentiation. A. KIESEL (Z. physiol. Chem., 1927, **164**, 103—111).—The methods used are those previously described (A., 1926, 204). Tables are given showing the various constituents present in the dry material, and a complete analysis has been made of the ether-soluble matter, which represents more than one third of the dry substance. Cholesterol is present to the extent of 2·97% of the fat soluble in light petroleum. The unsaturated fatty acids include much oleic acid, a smaller quantity of linoleic acid, and unsaturated hydroxy-acids, whilst the saturated fatty acids include those from C_{16} to C_{20}. Spore differentiation is accompanied by appreciable decreases in the percentages of protein, glycogen, and fatty substances, and increases in plastein and myxoglucosan.
A. WORMALL.

Action of amino-acids on the germination of *Phycomyces nitens*, Kunze and Schmidt. D. TITS (Bull. Acad. roy. Belg., 1926, [v], **12**, 545—554).—Using solutions of graded alkalinity containing 2% of peptone, germination took place only in those containing less than 0·1% of potassium hydroxide, the optimum solution containing 0·1% of tartaric or 0·5% of citric acid. With a series of solutions each containing 1% of tartaric acid and 0·7% of sucrose, together with 1% of one of a selected number of amino-acids, no germination was produced until 5 parts per 100,000 of peptone were added. The latter acted catalytically, since the minimum quantity producing germination in the absence of the amino-acids is 7 parts per 100,000. The activity of the amino-compounds in producing germination is in the descending order leucine, glutamic acid, histidine, cystine, and glucosamine. S. J. GREGG.

Acid formation by fungi. W. S. BUTKEWITSCH (Biochem. Z., 1927, **182**, 99—109).—Gluconic acid, as well as citric and oxalic acids, is formed by *Aspergillus* from sugars, and when nitrogen is lacking or in the presence of calcium carbonate, it is produced in larger amounts than the two last-mentioned acids. In cultures of *Mucor stolonifer*, under the same

conditions, only fumaric and oxalic acids were found.
C. R. HARINGTON.

Two kinds of carbamide formation in mushrooms. N. N. IVANOV and A. TOSCHEVIKOVA (Biochem. Z., 1927, **181**, 1—7).—On keeping cut mushrooms for some days with the cut end of the stem dipping into solutions containing ammonium carbonate or arginine nitrate, an increase in the carbamide content of the cap of the mushroom was observed; the expressed juice of mushrooms caused a formation of carbamide when added to a solution containing arginine, but not when added to one of ammonium carbonate. The formation of carbamide from the latter would therefore seem to be a function of the living cell.
C. R. HARINGTON.

Fungus chitin. DOUS and ZIEGENSPECK (Arch. Pharm., 1926, **264**, 751—753).—*Boletus edulis* was dried, ground, extracted with alcohol and ether, then with alcoholic potassium hydroxide, washed with cold 4% alcoholic hydrochloric acid, warmed with 0·5% aqueous hydrochloric acid to remove hemicelluloses and glycogen, washed with boiling water, and finally with alcohol and ether. The product contained 2·09% N. Crab shells were similarly treated to provide material for comparison, and the product contained 6·05% N. The two substances were subjected to hydrolysis with 1%, 5%, and 10% sulphuric acid. Differences were shown in the proportion of nitrogen removed and in the amounts of reducing sugar formed. The authors conclude that the product from *Boletus* is not chitin, and, following Ilkewitsch, term it mycetin. When mycetin is hydrolysed with fuming hydrochloric acid, it yields *mycetosamine,* which is different from the chitosamine obtained from crab chitin. The corresponding sugars are also different. Mycetosamine yields a methylpentose, termed *mycetose.* Chitosamine hydrochloride has $[\alpha]+87\cdot4°$; mycetosamine hydrochloride has $[\alpha]+70\cdot2°$.
W. A. SILVESTER.

Bio-radioactivity of plants. E. BURKSER, I. BRUN, and K. BRONSTEIN (Biochem. Z., 1927, **181**, 145—148).—Only insignificant radium emanations could be detected in the fresh leaves and stems of various plants, and none at all in the dried material; the radium content of the ash of plants was also found to be very small except in the case of the grape. Thorium could not be detected in the ash of any plant.
C. R. HARINGTON.

Constancy of the chemical composition of plants. N. N. IVANOV (Biochem. Z., 1927, **182**, 88—98).—The seeds of pea, lentil, and vetch plants grown under very variable conditions of soil, moisture, and climate contain the same constant amount of protein, carbohydrate, and ether-soluble material. The nitrogen intake of these plants is independent of the soil nitrogen. In contrast to other cereals, and in resemblance to these *Leguminosæ,* maize, which can utilise atmospheric nitrogen fixed by soil bacteria, shows the same stability with regard to chemical composition under varying conditions of growth.
J. PRYDE.

Cell-membrane of plants. E. SCHMIDT, K. MEINEL, and E. ZINTL (Ber., 1927, **60**, [B], 503—526).—The cell-membrane of archegoniates and phanerogams is composed of cellulose, hemicellulose, and incrustation. Repeated treatment of it alternately with chlorine dioxide and sodium sulphite results in the isolation of a cellulose–hemicellulose complex which is not further affected by the reagents, and therefore appears to pre-exist in the cell-membrane, and hence is termed " skeleton substance," whereas the incrustation and a portion of the hemicellulose are removed. The existence of two types of hemicellulose, differentiated also by varying stability towards oxidising agents, is therefore postulated. Glycuronic acid occurs among the products of hydrolysis of the hemicellulose of flax, hemp, wheat straw, beech (cf. A., 1925, i, 1370), fern, spruce, pine, etc.; and since these are systematically very distinct members of the series of archegoniates and phanerogams, it seems reasonable to conclude that a carboxylated polysaccharide (the precursor of glycuronic acid) is common to both series. Free glycuronic acid cannot, however, be present in the skeleton substance, since it cannot be removed by treatment with sodium hydrogen carbonate or sodium sulphite and hence an ester-like union of cellulose, acid, and hemicellulose is assumed. The method of Tollens and Lefèvre (determination of carbon dioxide liberated by the action of 12% hydrochloric acid) is not applicable to the polyglycuronic acids such as are derived from *Fucus serratus* (A., 1926, 939), but trustworthy results are obtained by treatment of the skeleton substance with $N/15$- or $N/10$-alkali hydroxide, followed by conductometric titration of the solution with $N/10$-hydrochloric acid. The results are independent of the presence or absence of the skeleton substance in the liquid during titration and, further, under the experimental conditions pure cellulose does not absorb appreciable quantities of alkali hydroxide. The form of the titration curves cannot be due to the production of alkoxides, to the presence of strong acids, or to adsorption phenomena at the solid phase. The presence of acids of medium strength must be postulated which with respect to dissociation constant are comparable with lactic acid, and considering the nature of the skeleton substance these can only be carboxylic acids. Treatment of the skeleton substance of beech with $N/10$-sodium hydroxide causes a loss in weight of 12·53%, whereas titration experiments indicate the presence of 12·86% of acid calculated as glycuronolactone. It is therefore probable that only the acid is removed from beech by the alkaline treatment, and this is confirmed by the observation that nothing further can be extracted by a fresh treatment. In the skeleton substance, the acid is regarded as present in esterified form. Further treatment with more concentrated alkali hydroxide causes the removal of the pentosans, so that by using alkali hydroxide of different concentrations it is possible to determine separately the polymeric acids and the acid-free pentosans. Pine does not suffer loss in weight when treated with $N/10$-alkali, although titration discloses the formation of acid. With 5% alkali hydroxide, acid and hemicelluloses are simultaneously removed, so that a more stable union of acid and hemicellulose in pine than in beech must be assumed. The behaviour of oxycellulose is similar to that of pine.
H. WREN.

Cell respiration. V. Mechanism of some plant oxidations. A. von Szent-Györgyi (Biochem. Z., 1927, **181**, 425—432).—The fruits, tubers, or roots of thirteen plants are divided by means of the guaiacum reaction into three groups, first, those which blue guaiacum directly, secondly, those which give only a blue colour after adding also pyrocatechol, and thirdly, those which do not blue guaiacum even in presence of pyrocatechol. The results are discussed in relation to the constitution of the plant oxidation systems. The browning of slices of plants in air is conditioned by the presence of tyrin, which, as with guaiacum, is not directly oxidised by the oxydase, but only by the o-quinone arising by the action of the oxydase. P. W. Clutterbuck.

Plant oxidation : nature and reactions of the substance "tyrin." B. S. Platt and A. Wormall (Biochem. J., 1927, **21**, 26—30).—The oxidative properties of the preparation "tyrin" of Szent-Györgyi (A., 1926, 99) are due to the presence in it of free or combined amino-acids. It does not function as a respiratory pigment. The ether extract of potato oxydase after it has acted on a pyrocatechol solution for 10 min. yields a substance which gives a blue coloration with guaiacum and benzidine. Hydrogen peroxide is formed in addition to this oxidation product. This confirms Szent-Györgyi's hypothesis (loc. cit.) of the mechanism of the blueing of guaiacum by the pyrocatechol–oxydase system (cf. Onslow and Robinson, A., 1926, 1176). S. S. Zilva.

Relationship between catalase activity and seed vitality. M. Gracanin (Biochem. Z., 1927, **180**, 205—210).—Further determinations of the catalase activity of seeds (cf., A., 1926, 432) show that the catalase content cannot always serve as an index of the vitality of a plant. The catalase activity of *Pisum sativum, Lupinus angustifolius, Zea mays,* and *Triticum vulgare* decreases with age, and etiolated leaves of *Beta vulgaris, Juglans regia,* and *Althœa officinalis* contain but little catalase compared with green leaves. On the other hand, both green and etiolated leaves of *Papaver somniferum, Daucus carota,* and *Sinapis alba* contained the same amount of catalase. Leaves of *Mnium undulatum, S. alba, P. sativum, Secale cereale,* and *Medicago sativa,* dipped in distilled water, $0.05M$-sodium chloride, or $0.001M$-zinc sulphate showed high catalase activity, in $0.001M$-copper sulphate a less activity, and in $0.001M$-ferric chloride or iodine no activity. It appears, therefore, that concentrations of sodium chloride and zinc sulphate which can kill these plants have but little effect on their catalase activity. P. W. Clutterbuck.

Effect of juice of potato-tubers on biological reduction of o-dinitrobenzene. A. Pietsch (Biochem. Z., 1927, **181**, 183—191).—The reduction of o-dinitrobenzene by potato-tubers themselves, by the higher plants, and by the muscles of animals, is inhibited by the juice of potato-tubers, whilst the reduction by yeast and by bacteria is stimulated by the tuber juice. The reduction by yeast is stimulated by 5% dextrose, whilst that by potato-tubers is inhibited by 5—10% dextrose ; the dextrose content of the tuber juice may therefore account for its effect on the reduction. The reduction is, in general, retarded by 0.1% of camphor and completely inhibited by 0.1% of mercuric chloride. C. R. Harington.

Yield of carbon compounds in photosynthesis under natural conditions. S. Kostytschev, K. Bazyrina, and G. Vassiliev (Biochem. Z., 1927, **182**, 79—87).—The method of investigating photosynthesis in a stream of atmospheric air suffers from the disadvantage that the velocity of the air current in relation to the leaf surface and the capacity of the leaf container is too low. This is regarded as explaining the discrepancies between the amount of photosynthesis as observed in the above methods and in the indirect method (Blatthälftenmethode of Sachs, Arb. bot. Inst., Würzburg, 1884, **3**, 1). With increase in the velocity of the air-stream, increasing synthesis is observed, rising eventually to the high values obtained by the indirect methods. J. Pryde.

Influence of potassium and sodium salts on the metabolism of reserve materials in young barley plants grown in darkness. A. Bobrownicka-Odrzywolska (Bull. Acad. Polonaise, 1925, **B**, 801—846).—Utilisation of the reserve materials of the seed by young barley plants has been studied by comparing the composition of the seed with that of plants grown in darkness to the point of exhaustion of the reserve materials, in culture solutions without nitrogen, and with and without sodium and potassium. In presence of potassium, a smaller amount of carbohydrate is required for the formation of a unit of cellulose. Sodium has a similar effect if accompanied by other necessary mineral salts. Potassium also reduces the loss of organic matter and the percentage of starch decomposed for respiration processes. The young plants made poorer growth in pure potassium or sodium chloride solutions than in distilled water ; none the less, in pure potassium chloride solution, a smaller percentage of starch was decomposed for respiration than in distilled water. Plants grown in solutions of mineral salts including potassium always contained more nitrogen than when potassium was withheld. In pure potassium or sodium chloride solutions, there was a greater loss of "unidentified" material, but no greater loss of nitrogen, than in the other culture solutions. C. T. Gimingham.

Nitrate utilisation by asparagus in the absence of light. G. T. Nightingale and L. G. Schermerhorn (Science, 1926, **64**, 282).—Quantitative experiments indicate that asparagus can take up nitrates in the dark, and that so long as there is a carbohydrate supply present, plants are able to build up nitrates to higher forms of nitrogen compounds. The assimilation of nitrates occurs as rapidly in the dark as in the light. A. A. Eldridge.

Specificity of proteins in different rice varieties. T. Tadokoro (Proc. Imp. Acad. Tokyo, 1926, **2**, 498—501).—It is reported that samples of oryzanin prepared from common and from glutinous rice vary in isoelectric point, in nitrogen, sulphur, and phosphorus content, in free amino-nitrogen, in optical activity and refractive index, and in other ways. No experimental data are given. E. A. Lunt.

Bacterial decomposition of tobacco as leading to the formation of bases in presence of water. A. FAITELOWITZ (Biochem. J., 1927, **21**, 262—264; cf. Fodor and Reifenberg, A., 1925, i, 1519).—The formation of pyridine and amino-bases from nicotine with resulting basic reaction does not occur to any appreciable extent in the dry fermentation process. In presence of moisture, on the other hand, the decomposition of tobacco leads to a basic reaction. This change is most probably due to bacterial decomposition. S. S. ZILVA.

Relation of nitrates to tobacco frenching. W. D. VALLEAU and E. M. JOHNSON (Science, 1926, **64**, 278—279).—Frenching of tobacco plants appears to occur when the rate of carbohydrate metabolism proceeds relatively more rapidly than nitrogen absorption. Leaf-tissue is thus produced which, in the absence of sufficient available nitrogen, cannot sufficiently rapidly develop chlorophyll and other essential cell constituents; hence the new leaves of diseased plants are chlorotic. A. A. ELDRIDGE.

Changes in fresh and dried tobacco leaves before and during fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **179**, 459—490).—In fresh tobacco leaves small quantities of acetaldehyde and ethyl alcohol are present. Treatment of the fresh leaves with steam liberates methyl alcohol from the pectic esters present. In a pulp of fresh leaves digested with calcium hydrogen sulphite the amount of acetaldehyde is considerably increased. Very active invertase, amylase, hexosediphosphatase, and aldehyde-mutase are present in a pulp of the fresh leaves. The last-mentioned enzyme converts phenylglyoxal into *l*-mandelic acid. Air-dried leaves and trade tobacco contain furoid substances in the form of pectins, and the fresh, dried, or fermented leaves all yield furfuraldehyde and carbon dioxide when treated with hydrochloric acid. The presence of uronic acids is inferred. Of the methyl alcohol which is liberated from fresh tobacco leaves, some 7—9% is present in the form of esters, the dried leaves contain some 30% more of the ester form than do fresh leaves, whilst dark (cigar) tobaccos contain only 1%, and light (cigarette) tobaccos 5—7%. In ungerminated tobacco plant seeds, phosphatase and aldehyde-mutase are present. It is concluded that a part of the carbohydrate exchange of the tobacco leaf is produced by self-contained agents. J. PRYDE.

Rôle of boron in the growth of plants. W. E. BRENCHLEY and K. WARINGTON (Ann. Bot., 1927, **41**, 167—187; cf. Warington, A., 1923, i, 1274).—The necessity of small quantities of boron for the growth of certain plants is evident in sand as well as in water cultures, and is independent of the composition and p_H value of the nutritive solution and of the conditions of aëration at the roots. Of 52 other elements tested, none proved capable of replacing boron for plants which require it. Boron is shown to be essential for a number of species of *Leguminosæ* and for melon, whereas various cereals and some other plants completed development in its absence. If the nutritive solution is frequently or continuously renewed, evidence of boron deficiency is considerably delayed and the total quantity required is lessened. The concentration, if not high enough to be toxic, appears to be of little importance. The boron is actually absorbed and does not act as an ordinary catalyst; it appears to be associated with absorption or utilisation of calcium. C. T. GIMINGHAM.

Chemical stimulants of plant growth. A. ZLATAROFF (Bull Soc. Chim. biol., 1926, **8**, 1198—1207).—The effects of chlorides, oxidising and reducing compounds, amines, and uranyl acetate on plant growth are described. Seeds were immersed in a dilute solution of the compound to be tested and then allowed to germinate; in most cases a stimulating effect was observed. W. O. KERMACK.

Relation of leaf area to growth and composition of apples. M. H. HALLER and J. R. MAGNESS (Proc. Amer. Soc. Hort. Sci., 1925, 189—196).—A higher percentage of dry weight, sugars, and acids is associated with apples grown with a large leaf area as compared with those of the same variety grown with a small leaf area. CHEMICAL ABSTRACTS.

Carbon dioxide nutrition of the forest. D. FEHÉR (Biochem. Z., 1927, **180**, 201—204).—The carbon dioxide content of the air in woods, being conditioned by the simultaneous respiration of the soil, decreases from the soil upwards and is considerably influenced by the acidity of the soil; the greater the acidity, the greater the effect on soil bacteria and the lower the soil respiration and carbon dioxide content of the air. The optimal soil respiration and carbon dioxide content of the air are obtained during rainy periods. P. W. CLUTTERBUCK.

Respiration processes in different varieties of potatoes. K. G. SCHULZ (Landw. Versuchs-Stat., 1926, **105**, 23—73).—The rate of uptake of oxygen by tubers of late varieties of potatoes was greater than in early varieties. Absorption of oxygen remained fairly steady over a period of 3 months. Individual tubers of the same variety showed considerable variation in respiratory activity. The rate of elimination of carbon dioxide from the leaves of growing potato plants per unit surface exposed was greater for late than for early varieties. Respiration was irregular, but appeared to bear a relationship to the rate of development of leaf-surface. A general uniformity existed between the rate of oxygen uptake by the tubers and the rate of carbon dioxide elimination from the leaves of different varieties. No relationship was apparent between the intensity of the respiratory changes and the size and number of sprouts developing from the tubers. A. G. POLLARD.

Water-soluble content of calcium and phosphorus in cabbage. W. H. PETERSON and C. B. PETERSON (J. Agric. Res., 1926, **33**, 695—699).—In samples of cabbage grown on two types of soil, the average percentage of calcium in the fresh material was 0·046, and of phosphorus, 0·028; 60% of the total calcium and 61% of the total phosphorus were soluble in water. The proportion of water-soluble calcium and phosphorus decreased as the plants matured. C. T. GIMINGHAM.

Ether-soluble substances of cabbage-leaf cytoplasm. I. Preparation and general characters. II. Calcium salts of glyceridephosphoric acids. A. C. CHIBNALL and H. J. CHANNON (Biochem. J., 1927, 21, 225—232, 233—246).—I. The minced leaves are extracted with water and the aqueous extract is coagulated by heating at 70°. The residue is then pressed out in a Buchner press until no more liquid is expressed and extracted with ether for 40 hrs. The crude extract is evaporated to dryness in a vacuum and extracted again with dry ether. The fat constants of several such preparations from cabbage leaves are given.

II. On adding acetone to an ethereal solution of the ether-soluble substances of the cytoplasm from the leaf cells, no phospholipins are precipitated. All the phosphorus of this fraction is present in combination with calcium, glycerol, and fatty acids. Nitrogen is virtually absent. The main constituent was identified as the calcium salt of a *diglyceridephosphoric acid*, which pre-exists in the leaf cell and is a product of phospholipin decomposition. The preparation and properties of the free acid (decomp. 100°) and of its *calcium*, *lead*, and *barium* salts are given. Since the acid on boiling with barium hydroxide yields an optically active barium glycerophosphate, it is concluded that the phosphoric acid is in the α-position. Indication of the possible presence of the calcium salt of a monoglyceridephosphoric acid has also been obtained.   S. S. ZILVA.

Myrosin and sinigrin. A. HEIDUSCHKA and C. PYRIKI (Arch. Pharm., 1926, 264, 692—698).—Guignard's method of extracting myrosin from white mustard seed is improved by carrying out the digestion at 40° instead of at 70°. The myrosin is precipitated from the aqueous extract by alcohol, and so is obtained in much higher yield and of considerably greater activity. The products were tested by their action on sinigrin and the allylthiocarbimide obtained was determined by the German official method. Myrosin can be purified by repeated reprecipitation from aqueous solution by alcohol, followed by dialysis; the product so obtained is nearly twice as active as the original material. The purified substance still contains 4·09% of ash; corrected for this, it has the composition C, 43·52%; H, 6·33%; N, 14·96%; S, 2·62%; P, 1·21%. A number of *Cruciferæ* have been examined touching their content of myrosin and sinigrin. *Brassica Rapa esculenta*, Koch, *Brassica Napus esculenta*, DC., *Cochlearia Armoracia*, L., *Raphanus sativus*, L., v. *niger*, DC, and *ibia*, v. *alba*, DC. all contain allylthiocarbimide and myrosin, but no sinigrin. The amounts vary according to the species, *Cochlearia* containing the most, both of enzyme and allylthiocarbimide. *Beta vulgaris* contains neither sinigrin nor myrosin.   W. A. SILVESTER.

Soluble enzymes contained in black mustard (*Brassica nigra*, K.). A. ASTRUC and M. MOUSSERON (Compt. rend., 1927, 184, 126—128).—Black mustard seeds are shown to contain, in addition to myrosin, easily detectable quantities of invertase, amylase, maltase, emulsin, and an anaërobic oxydase. Sucrose is present, but no raffinose or stachyose.
C. HOLLINS.

Rubichloric acid and asperuloside. H. HÉRISSEY (Bull. Soc. Chim. biol., 1926, 8, 1208—1210; cf. Annalen, 1851, 80, 321; A., 1925, i, 1369; 1926, 547).—Rubichloric acid obtained by Rochleder in an impure condition from madder root is considered very probably to be identical with the glucoside, asperuloside, which has been isolated from odoriferous *Asperula* and from *Galium Aparine*.
W. O. KERMACK.

Chemistry of oleander. H. TAUBER and J. ZELLNER (Arch. Pharm., 1926, 264, 608—693; cf. Straub, A., 1918, i, 368).—Air-dry oleander leaves contain a paraffinic *hydrocarbon*, $C_{34}H_{70}$, m. p. 70°, resembling that found in *Alchemilla* by Vogl (A., 1923, i, 990), together with fats the isolated acids of which form a mixture of m. p. 55—60° and acid value 190. These substances are soluble in light petroleum; the original treatment of the plant material with trichloroethylene also extracted an amorphous resin *compound* (C, 66·76%; H, 9·76%), m. p. 245° (decomp.), insoluble in light petroleum (amorphous *nitro*-derivative, decomp. 185°).

When the dry leaves are extracted with water, the chief product is a glucoside " Oleandrin-6." This compound (cf. Straub, *loc. cit.*) crystallises in prisms and has the composition $C_{24}H_{34}O_7$, m. p. 230° (in a sealed tube filled with carbon dioxide). It gives the reactions of digitalis strongly; it is not hydrolysed by emulsin, but when treated with sulphuric acid (0·5%) it is resolved into a brown, resinous *compound* and an unidentified dextrorotatory sugar which reduces Fehling's solution but neither yields glucosazone nor gives the reactions of a pentose.

" Oleandrin-4 " (Böhringer & Söhne) was not isolated in the above extraction of oleander leaves, but is obtained by this firm by a method of which a description is given. It differs from " Oleandrin-6 " in being insoluble in a mixture of ether and alcohol, also in crystal form and composition; thus it forms leaflets of m. p. 224–225° (in sealed tube) and has the composition $C_{33}H_{46}O_8$ or $C_{33}H_{48}O_8$. This difference from " Oleandrin-6 " is not due to water or alcohol of crystallisation. Moreover, whereas " Oleandrin-6 " is decomposed when heated with acetic anhydride, " Oleandrin-4 " yields a (*tri-* or *tetra-*)*acetyl* derivative (m. p. 210°). The motherliquors of the above separation yield a mixture (m. p. 98—120°) which may or may not contain a third glucoside of the same group. Besides the above compounds, oleander leaves contain tannin-like substances.   W. A. SILVESTER.

Plant chemistry. XVII. *Rhododendron hirsutum*. E. FEYERTAG and J. ZELLNER (Monatsh., 1926, 47, 601—609).—The leaves of *Rhododendron hirsutum* have been examined by the usual methods. The light petroleum extract on hydrolysis with alcoholic potassium hydroxide yields a portion not hydrolysed from which were isolated a *hydrocarbon*, m. p. 65°, a *resin alcohol*, m. p. 226—227°, and a *substance* $C_{30}H_{52}O$, m. p. 205°, $[\alpha]_D + 63·9°$ (in chloroform), which could not be acetylated, and for which full crystallographic data are given. Acidification of the hydrolysed portion gave only resin acids. The small ether extract gave a *substance*, m. p. 234°. The

water-soluble portion of the alcohol extract yielded a tannin which on treatment with 3% sulphuric acid in a current of carbon dioxide gave a phlobaphen, the analytical data for both, however, not agreeing with that of Rochleder and Schwarz ("Phytochemie," 1854, p. 168). The water-insoluble portion yielded a natural phlobaphen, invert-sugar, and choline. Distillation of the leaves with steam yields an oil, d^{21} 0.8780, n_D^{20} 1.4807, $[\alpha]_D -29.0°$ (in ether), which consists, in all probability, of the *hydrocarbons* $C_{10}H_{18}$ and $C_{10}H_{16}$. J. W. BAKER.

Plant chemistry. XV. Chemistry of barks. V. J. ZELLNER [with K. KNIE, E. ROSENBLÜH, M. STEIN, and J. RICHLING] (Monatsh., 1926, **47**, 659—679).—The light petroleum extract (2.10%) of the bark of *Acer pseudoplatanus*, L., contains ceryl alcohol and an inactive phytosterol similar to that of elm-bark (A., 1926, 646), but differing from it in crystalline form. On hydrolysis, the saponifiable material yields glycerol and palmitic, stearic, arachidic (?), and phosphoric acids. Hydrolysis of the ether extract (0.94%) gives resin acids, ceryl alcohol, and a *resin alcohol*, $C_{32}H_{54}O_3$, m. p. 175—176°, but no octadecyl alcohol (cf. A., 1924, i, 814). The alcohol extract (11.50%) contains phlobaphens, tannin (3.47%), and invert-sugar. The water-soluble matter (20.66%) contains mineral matter (3.10%). Free acid (as KOH), 1.23%; soluble polysaccharides, 0.69%; crude fibre, 50.50%; pentosans, 11.39%; total ash, 10.54%; and total nitrogen, 1.99%, are also present.

The unsaponifiable portion of the light petroleum extract of *Crataegus oxyacantha*, L., contains compounds (*a*), m. p. 75°, probably impure ceryl alcohol, and (*b*), m. p. 212°, $[\alpha] +25°$ (acetyl derivative, m. p. 216°), probably identical with lupeol (A., 1922, i, 826); the saponifiable fraction contains stearic and palmitic acids. The ether extract yields, on hydrolysis, alniresinol (*loc. cit.*), a *substance*, $C_{26}H_{44}O_2$(?), m. p. 170°, and a substance, $C_{22}H_{38}O_3$, m. p. 278°, previously obtained from lime-bark (A., 1926, 983), together with amorphous resin acids. The bark also contains phlobaphens, pyrocatechol-tannins, invert-sugar, water-soluble polysaccharides, oxalates, and tartrates.

The bark of *Pavia rubra*, Lam., yields: light petroleum extract, 3.91%; ether extract, 2.53%; alcohol extract, 18.46%; water-soluble matter, 28.94%; soluble polysaccharides, 2.33%; free acid (as KOH), 3.23%; reducing sugar, 2.67%; soluble mineral matter, 0.54%; total ash, 5.83%; total nitrogen, 1.96%; crude fibre, 30.22%. The light petroleum extract contains a *hydrocarbon*, m. p. 74°, ceryl alcohol, almost pure sitosterol, and saponifiable matter which yields myristic and oleic acids. The alcohol extract contains phlobaphens, tannins, aesculin, and dextrose. Enzymes were present in the cold aqueous extract.

The water-soluble portion of an alcoholic extract of the bark of *Picea excelsa*, Lk., contains tannins and invert-sugar. The insoluble portion, freed from terpenes by steam distillation, contains an *ester* (?), m. p. 116°; ceryl alcohol, and a *substance*, m. p. 70—71°. Arachidic acid and smaller amounts of palmitic and stearic acids are present, principally

as glycerides. The large resin acid fraction contains a small quantity of a *substance*, m. p. 105—107°. Sterols appear to be completely absent.

H. E. F. NOTTON.

Chemistry of halophytes. J. ZELLNER (Monatsh., 1926, **47**, 611—618).—Complete analyses of the mineral matter present in various plants which grow in soils containing more salts than is usual have been carried out. The following summary gives, respectively, the water content, amount of mineral matter in the fresh plant and in the dried plant, for the examples studied: *Salicornia herbacea*, 76.58, 5.02, 21.42; *Suæda salsa*, 75.94, 5.74, 23.86; *Scorzonera parviflora*, 86.98, 2.23, 16.98; *Plantago maritima*, 80.46, 2.85, 14.58; *Aster Tripolium*, 73.15, 2.80, 10.43; *Erythræa tinariæfolia*, 61.87, 1.65, 4.32%. Determination of the osmotic pressure in the cells by the depression of the f.-p. method shows that this is exceedingly high, the value for *Salicornia* being 35 atmospheres, and for *Aster*, 16.4 atmospheres.

J. W. BAKER.

Philippine ginger. P. VALENZUELA (J. Amer. Pharm. Assoc., 1926, **15**, 652—661, 734—744).—Fresh specimens of *Zingiber officinale* Roscoe contained: moisture 79.5, 80%; ash 6.29, 6.10%; acid-insoluble ash 2.3, 2.4%. The cortex was the most pungent and the parenchyma the least. The volatile oil had: acid value 2.22, ester value 32.8, ester value after acetylation 88.3. Aldehydes were present, but phenols were absent; a semicarbazone, m. p. 144—145°, was obtained. The residue after distillation with steam had d^{20} 1.0694, saponification value 41.41. From the fatty acids, oleic, linoleic, and stearic acids were obtained. A small quantity of vanillyl alcohol was obtained; the presence of melissyl alcohol was suggested. About 0.14% of dextrose was isolated.

CHEMICAL ABSTRACTS.

Histochemical detection of santonin. E. HERNDLHOFER (Mikrochem., 1927, **5**, 21—26).—For the detection of santonin in parts of a plant, the crushed substance is extracted with a few c.c. of benzene under a reflux condenser and the filtered extract is evaporated to dryness. The residue is heated in the Klein–Werner sublimation apparatus and the sublimate is again extracted with benzene. In the presence of santonin evaporation of this solution yields yellow columnar crystals (m. p. 171°); these crystals yield characteristic greenish-brown cubes or plates (m. p. 113°) when treated with hydriodic acid containing iodine. Of the varieties of *Artemisia* tested only *A. cina* Berg and *A. cœresculens* contained santonin in the flowers and seeds.

A. R. POWELL.

Kirondrin, toxic principle from seeds of *Perriera madagascariensis* (*Simarubaceæ*). VOLMAR and SAMDAHL (Compt. rend., 1927, **184**, 393—395).—*Kirondrin*, the bitter, toxic principle of seeds of *Perriera madagascariensis*, is extracted by alcohol and occurs to the extent of 0.75% in the seeds; α- and β-kirondrin, m. p. 220—221° and 237—240°, respectively, have been isolated by fractional crystallisation and are similar in properties. The principle contains no nitrogen, sulphur, or halogen, but gives alkaloidal reactions, reduces Fehling's reagent, but does not give a phenylhydrazone, even after hydrolysis.

Subcutaneous injection of 4 mg. produces death of mice in 10 hrs.　　　　　　　L. F. HEWITT.

Pine wood lignin. E. HÄGGLUND and T. ROSENQVIST (Biochem. Z., 1926, **179**, 376—383).—Lignin prepared by the action of hydrochloric acid on pine wood, when distilled with 12% hydrochloric acid, yields about 3% of a volatile substance, similar to, but distinct from, furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde. The usual methods for determining pentosans in lignins therefore give high results. Lignin prepared by alkali treatment also yields on distillation with hydrochloric acid, in addition to furfuraldehyde, volatile substances forming phloroglucides. Lignosulphonic acid precipitated by β-naphthylamine yields no substances which condense with phloroglucinol. Neither pine wood nor the lignin prepared from it contains methylpentosans. Friedrich's primary lignin contains ethoxyl groups. Lignin yields but small quantities of vanillic acid or vanillin.　　J. PRYDE.

Origin of humic matter. C. E. MARSHALL and H. J. PAGE (Nature, 1927, **119**, 393).—The view that humic matter is derived from lignins is supported. By means of aqueous sulphur dioxide under pressure, a true fractionation of humic and hymatomelanic acids of natural origin is effected; the substances dissolved are closely analogous to the lignosulphonic acids obtained from wood pulp. The close relationship between natural humic acids and lignins may, however, be due to the presence of unchanged lignins in natural humic acid preparations.
　　　　　　　　　　A. A. ELDRIDGE.

Source of trilaurin : Mahuba seed, *Acrodiclidium Mahuba,* A. J. Sampaio. E. ANDRÉ (Compt. rend., 1927, **184**, 227—229).—Extraction of the seed with light petroleum and crystallisation of the crude product from ether yields trilaurin (45—50% of the weight of the seed).
　　　　　　　　　　J. W. BAKER.

Distribution of dihydrositosterol in plant fats. R. J. ANDERSON, F. P. NABENHAUER, and R. L. SHRINER (J. Biol. Chem., 1927, **71**, 389—399; cf. A., 1924, i, 1153).—Dihydrositosterol has been isolated from the unsaponifiable matter of the oils from rice bran, maize, and wheat germ, but not from cotton-seed or linseed oils. The various preparations had m. p. 141—146°, $[\alpha]_D$ +23—25°; the *acetyl* derivative had m. p. 137—141°, $[\alpha]_D$ +13—14°.
　　　　　　　　　　C. R. HARINGTON.

Distribution of saponins and tannins in plants. G. LUFT (Monatsh., 1926, **47**, 259—284).—An investigation of the occurrence of saponins, tannins, and other pharmaco-dynamic materials in the leaf, stem, and bark of the members of various families of plants.　　　　　　　W. ROBSON.

Nutrition and statistical variations. IV. Chemical properties of various sorts of wheat. L. BERCZELLER and H. WASTL (Biochem. Z., 1927, **181**, 117—132).—Statistical comparison of the variations in content of protein, cellulose, fat, and ash of different wheats over a period of 5 years indicates, in general, that the nature of the season has a greater influence than the species in determining the chemical composition of wheat. As between the different species of wheat, the greatest variations were observed in the content of cellulose and the least in that of fat.
　　　　　　　　　　C. R. HARINGTON.

Potential differences in the apple. L. JOST (Biochem. Z., 1926, **179**, 400—409).—Electro-potential concentration effects are observed in living and dead apples. In the former instance, the cell protoplasm forms the best membrane; in the latter, the cell membrane of the parenchymatous cells and the cuticle. Beutner's views are criticised. J. PRYDE.

Digestion of starch in vegetable cells. A. MAIGE (Compt. rend., 1927, **184**, 391—393).—Two modes of digestion of starch grains in vegetable cells, viz., peripheral and internal, are ascribed to the existence of stromata. In peripheral digestion, the amylase remains on the edge of the starch granule, whilst in internal digestion either the amylase penetrates the cortex or else the cortex is already destroyed. Heating at 55—60° destroys the vitality of the stroma and converts peripheral into internal digestion.
　　　　　　　　　　L. F. HEWITT.

Effect of eosin on the growth of roots. F. BOAS (Ber. deut. bot. Ges., 1927, **45**, 61—64).—Seeds of *Sinapis alba, Lupinus luteus, L. angustifolius, Vicia faba,* and *Zea mays* after being soaked for 17 hrs. in solutions of eosin (0·1, 0·01, and 0·001%, respectively) were planted in soil. On germination of the seeds, the roots grew at first perpendicularly out of the soil.
　　　　　　　　　　G. W. ROBINSON.

Colorimetric micro-determination of iron. L. LORBER (Biochem. Z., 1927, **181**, 391—394).—A micro-colorimetric method for the determination of iron in tissues, based on the yellow colour obtained with iron, sulphosalicylic acid, and excess of ammonia, is described and used to determine both inorganic and organically bound iron.　　P. W. CLUTTERBUCK.

Colorimetric determination of silicon in tissues by Isaacs' method. J. H. FOULGER (J. Amer. Chem. Soc., 1927, **49**, 429—435).—The work of Isaacs (Bull. Soc. Chim. biol., 1924, **6**, 157) is confirmed. The reduction of silicomolybdates by sodium sulphite is retarded by a sufficiently high concentration of phosphate; when this concentration is low (*e.g.*, in the ash from animal tissue) this inhibition may be prevented by slightly increasing the acidity of the system (cf. Bertrand, *ibid.*, 656).　S. K. TWEEDY.

Gasometric micro-Kjeldahl determination of nitrogen. D. D. VAN SLYKE (J. Biol. Chem., 1927, **71**, 235—248).—The nitrogenous material is incinerated with a mixture of sulphuric and phosphoric acids and potassium persulphate; the resulting solution is neutralised, transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), and treated with sodium hypobromite; the liberated nitrogen is determined gasometrically. The error of the method is ±1%.　　　　　　　C. R. HARINGTON.

Apparatus for rapid dialysis. L. AMBARD (Bull. Soc. Chim. biol., 1926, **8**, 1219—1221).—An apparatus is described in which dialysis can be carried out much more rapidly than with a simple collodion sac.
　　　　　　　　　　W. O. KERMACK.