BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1929.

General, Physical, and Inorganic Chemistry.

Perturbation theory in quantum mechanics. A. H. Wilson (Proc. Roy. Soc., 1929, A, **122**, 589—598).—Mathematical. It is shown that, although the series of perturbations does not in general converge, yet it usually possesses the same asymptotic character as in the classical theory, and its use can therefore be justified. The investigation is limited to systems possessing only discrete spectra, and the method does not seem adequate to deal with systems with continuous spectra. L. L. Bircumshaw.

Assignation, especially of multiplet terms to series limits. F. Hund (Z. Physik, 1928, **52**, 601—609).—A discussion of the theory of multiplet series. E. B. Robertson.

Light scattering and the hydrogen spectrum. H. S. Allen (Nature, 1929, **123**, 127).—An examination of the secondary spectrum of hydrogen suggests that many of the lines arise by light scattering, as described by Raman and Krishnan (this vol., 240). The lines of the Balmer series are emitted by atoms of hydrogen, and the neighbouring molecules are subjected to bombardment by light quanta of corresponding frequency. A. A. Eldridge.

Spectral phenomena of spark discharges. W. Clarkson (Phil. Mag., 1929, [vii], **7**, 322—331).—A general account of the electrical and optical properties of spark discharges is given and the phenomena are discussed on the basis of the dynamic principles previously laid down (*ibid.*, 1927, [vii], **4**, 849 etc.). The observed phenomena are in good agreement with the theoretical deductions. The variation of the arc and spark lines of helium with the initial condenser voltage is discussed and a double maximum in the arc intensities is attributed to a duplication of flashes. The subsequent reduction of spark intensities is attributed to the diversion of energy to other spectra derived from the activated state of the gas. With suitable corrections for these effects, the resulting intensity curve is in good agreement with the theory. A. E. Mitchell.

Absorption in excited helium. J. C. McLennan, R. Ruedy, and E. Allin (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 273—277).—The amount of light absorbed when light from a discharge tube containing helium is passed through a weakly excited column of the gas has been determined quantitatively. The percentage absorption is measured for the wavelengths 6678, 5876, 5016, 3889 Å. It is pointed out that the amount of absorption observed is a lower limit necessary for producing distinct reversals in the apparatus used. A. J. Mee.

Band spectrum of helium. W. Weizel (Z. Physik, 1928, **51**, 328—340).—Three new bands are reported at 4720, 4400, and 4140 Å.; one of these has been identified as the $2'p-4's$ band of the parasystem. It is thought the available evidence can be construed to show that the helium molecule arises from the combination of two excited metastable helium atoms, and not from one normal and one excited atom. R. W. Lunt.

New bands in the helium spectrum. W. Weizel (Z. Physik, 1928, **52**, 175—196).—Nine new bands in the He_2 spectrum between 3785 and 4470 Å. have been discovered and examined with a grating spectrograph. They are partly higher members of series already known, and exhibit to a marked degree anomalies which occur to a slight extent in bands already investigated. It appears that the band spectrum of helium gives the electronic terms required by Hund's theory of molecular spectra (A., 1927, 183, 495, 801, 809). The doubling of the rotational terms of the π and Δ levels is explained by the uncoupling of the rotational impulse of the electron from the axis, owing to rotation, and this uncoupling explains also the anomalies of many of the terms. He_2 is as yet the only case in which this kind of uncoupling is observed, and the only band spectrum in which all the terms predicted by theory are found by experiment. E. B. Robertson.

Helium bands. V. Fujioka (Z. Physik, 1928, **52**, 657—667).—The difference in the relative intensities of the helium bands when excited (*a*) in the gas at a pressure of 2·5 cm. by a condensed discharge at 20,000 volts and (*b*) in the gas at 8 mm. pressure by a direct discharge at 500 volts has been investigated. In the bands at 4650 and 4540 Å. the intensity maximum is found to lie in regions of higher rotational quantum number in the condensed than in the direct discharge. The band at 4540 Å. is relatively much stronger in the latter than in the former, although in both cases the absolute intensity of the band at 4650 Å. is much the greater. A table is given of the relative intensities of a number of ortho- and parhelium bands in the direct and condensed discharges, referred to 4650 Å. as standard.

The bands at 4950 and 5350 Å., which are relatively stronger in the negative glow of the direct discharge, have been analysed under a dispersion of 8 Å./mm., and their origin is discussed. E. B. Robertson.

Triplets of helium. J. A. Gaunt (Proc. Roy. Soc., 1929, A, **122**, 513—532, and Phil. Trans., 1929,

A, 228, 151—196).—Heisenberg's calculation (A., 1927, 5), based on Schrödinger's equation, of the triplet separations of helium is open to a number of objections, the chief being that the radius of the inner orbit is neglected in comparison with that of the outer, even when the principal quantum number of the latter is only 2. The theory of an atom with two electrons is now developed on the basis of Dirac's *q*-number theory (cf. A., 1928, 344, 456), as interpreted in terms of wave-mechanics by Darwin (*ibid.*, 570). The main differences between the present method and that of Heisenberg are that (1) part of the spin effect is included from the start in Dirac's equation, whereas Heisenberg first applies the perturbation by the electrostatic interaction of the electrons with a complete neglect of spin, and then superposes the much smaller spin perturbation, and (2) the spin energies are calculated in a straightforward manner by means of integrals involving the wave-functions, and are not taken from a model built up of precessing vectors. The method of calculation for a helium atom with one excited electron is outlined and the resulting triplet separations are given. A perturbation theory is developed for nearly degenerate systems. The spin energy terms used are practically the same as Heisenberg's, with the omission of those which are already accounted for in Dirac's equation. It is shown, however, that this energy not only corresponds with classical theory, but also arises naturally from Dirac's theory. A simple formula is obtained for the mutual potential energy of two electrons. L. L. Bircumshaw.

Effect of combined electric and magnetic fields on the helium spectrum. J. S. Foster (Proc. Roy. Soc., 1929, **A, 122**, 599—603).—A study has been made of the effect of simultaneous parallel electric and magnetic fields on certain of the more intense helium lines. The light was analysed with a prism spectrograph of high dispersion (cf. A., 1924, ii, 323). Photographs are recorded showing the perpendicular components of the parhelium group $2P-5Q$ (4388 Å.) in an electric field of 63,000 volts/cm. and a magnetic field of 1650 gauss, and of the parallel and perpendicular components of the orthohelium group $2p-4q$ (4471 Å.), taken when fields of 60,000 volts/cm. and 2250 gauss were applied to the source. The expected combined effect has been found for all principal and sharp series lines which appeared on the plates (4713, 5015, 4438 Å.), and for the components of the diffuse lines which are resolved. The magnetic separation is independent of the magnitude of the Stark effect. Certain Stark components which were known to vanish in moderate fields now reappear under the action of stronger fields, as predicted in the quantum mechanical explanation of the Stark effect for helium. L. L. Bircumshaw.

Effect of electric and magnetic fields on the helium spectrum. J. S. Foster (Nature, 1929, **123**, 414).—Many lines which are not ordinary Stark components have been observed; they show no decided polarisation and are well-defined. A magnetic field of 15,000 gauss perpendicular to an electric field of 0—15,000 volts per cm. was employed.

A. A. Eldridge.

Anomalous *g*-values in the spectrum of ionised argon (A II). C. J. Bakker (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1041—1045).—Theoretical. It is found that for the Zeeman effect in the spectrum of simply ionised argon (cf. this vol., 3) the *g*-values of many terms differ from the Landé *g*-formula. The *g*-values belonging to four different coupling schemes for the terms arising from the coupling of the 4*p* and 5*s* electron are calculated and compared with those found experimentally.

N. M. Bligh.

Zeeman effect in the argon spark spectrum (A II). C. J. Bakker, T. L. de Bruin, and P. Zeeman (Z. Physik, 1928, **52**, 299—300).—In the authors' previous work on this subject (this vol., 3), in which measurements were made on the grating photographs by means of a comparator, there was apparently a slight discrepancy in the law of summation of the *g*-terms for terms of the 4*p* electron with $j=1$. The work has been checked, using a photoelectric photometer, and the discrepancies appear to have been due to errors in the optical method, too high results having been obtained for the widths of very close doublets. E. B. Robertson.

Structure of induction spectra of rare gases. A. T. Williams (Univ. nac. La Plata, estud. cien., 1928, No. 82, 253—281).—The induction method of excitation facilitates the separation of different orders of the spectra of an element. The spectra of argon, krypton, and xenon were examined. Two new lines, 3354 Å., $3(1S_3-6p_8)$ and 3355 Å., $4(1S_3-6p_9)$ in the argon spectrum are classified with Meissner's terms.

Chemical Abstracts.

Intensities of the light of the oxygen green line in the night sky. J. C. McLennan, J. H. McLeod, and H. J. C. Ireton (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 397—412).—In order to obtain some information on the origin of the excitation of the non-polar aurora and on the composition and physical state of the upper atmosphere, some experiments were made to determine whether the intensity of the oxygen green line varied during a single night. The apparatus is fully described. There was no regular diminution in intensity immediately after sunset, but it reached a maximum about an hour after midnight, and then diminished until sunrise. Measurements on the total intensity of the green line radiation for a series of successive moonless nights showed large variations. The origin of the maximum value attained about midnight is associated with solar radiation. It may be that when oxygen in the upper atmosphere is irradiated with light of very short wave-length it passes into the atomic state from which spontaneous transitions take place, giving rise to the green line. Light of longer wave-length may inhibit the process and prevent the accumulation of oxygen in the atomic state. In order to explain the time of maximum intensity, it is possible that the upper atmosphere may be irradiated at night with solar light refracted or scattered laterally into it from beams that are projected over the earth and graze its surface. The ratio of the energy of scattered solar light waves of wave-length less than 2070 Å. to that of those longer than 2500 Å. would, in the region of very low pressure,

increase after sunset up to midnight and then decrease. If this view is true the upper atmosphere must always be glowing more or less feebly with a faint green light.
A. J. Mee.

Arc spectrum of nitrogen in the extreme ultra-violet. K. T. Compton and J. C. Boyce (Physical Rev., 1929, [ii], **33**, 145—153).—Lines in the arc spectrum of nitrogen excited by controlled electron impact were photographed in a vacuum spectrograph in the region from 500 to 1200 Å. These lines, together with all other available data, are tabulated and used for a fairly complete analysis of the spectrum, in good agreement with the predictions of the Hund theory. A Grotrian diagram of the nitrogen atom is constructed. The ionisation potential is 14·48 volts, and the metastable levels ^2D and ^2P have energies corresponding with 2·37 and 3·56 volts, respectively, in good agreement with the predictions of Kaplan and Cario from a study of active nitrogen (cf. A., 1928, 683).
N. M. Bligh.

Excitation of the aurora green line in active nitrogen. J. Kaplan (Physical Rev., 1929, [ii], **33**, 154—156; cf. A., 1928, 566).—The auroral green line has been excited in the nitrogen afterglow when oxygen was present in the discharge in which the active nitrogen was produced and observed. The interpretation of the phenomenon is based on Kaplan and Cario's explanation of active nitrogen (cf. preceding abstract).
N. M. Bligh.

Arc spectrum of chlorine. K. Majumdar (Nature, 1929, **123**, 131).—Lines which Laporte (A., 1928, 805) ascribed to the transition $4M_2$ ($N_1 \longleftarrow N_2$) are attributed to $4M_2$ ($N_1 \longleftarrow O_2$), and the ionisation potential of chlorine is estimated to be about 13 volts.
A. A. Eldridge.

Analysis of first spark spectrum of sulphur. D. K. Bhattacharyya (Proc. Roy. Soc., 1929, A, **122**, 416—429; cf. Ingram, A., 1928, 1068).—Saha's extension of the irregular doublet law, which shows that, knowing the spectra of two elements in any group of successive elements which are reduced by electric discharge to the same electronic constitution, then the spectra of the remaining elements can be predicted (cf. A., 1928, 209), has been successfully applied to the analysis of the first spark spectrum of sulphur, and 59 lines are classified. In an attempt to identify the doublet spectrum of S II, 84 lines have been measured in the region 5712—7715 Å., a pure sulphur tube of Wood type being employed. With two exceptions, none of the lines agrees with those previously found by Bungartz (A., 1925, ii, 609), who apparently used a lower excitation and did not get lines of S II. An interesting band spectrum of sulphur was observed in the near infra-red, extending from 7574 to 7057 Å., the bands having a close resemblance to the A, B, α, α', α'' bands of oxygen.
L. L. Bircumshaw.

Polarisation of resonance radiation and the breadth of spectral lines. A. Ellett (Proc. Iowa Acad. Sci., 1927, **34**, 283).—Observations on the polarisation of the D-line resonance radiation of sodium indicate that the transition probabilities for the various components of the Zeeman pattern are substantially in agreement with the predictions of the summation rule. The distribution of energy in the exciting line is due practically entirely to the Doppler effect.
Chemical Abstracts.

Magneto-optical determination of the intensity of the first two members of the principal series of potassium and the vapour pressure of potassium. J. Weiler (Ann. Physik, 1929, [v], **1**, 361—399).—See A., 1928, 1067. The ratio of the first to the second member (temp. 253—296°) is now given as 98·5 : 1±5%, and the formula for the vapour pressure as log $pT = -20{,}590/4{\cdot}571T + 10{\cdot}133$ or $-21{,}100/4{\cdot}571T + 10{\cdot}37$ according to the method used.

Beryllium spectrum in the region λ 3367—1964 Å. S. N. Bose and S. K. Mukherjee (Phil. Mag., 1929, [vii], **7**, 197—200).—The lines of beryllium at 2351, 2175, 2126, 2056, and 2033 Å., reported as singlets by Bowen and Millikan (A., 1926, 985), are shown to be doublets of approximate wave-number difference 2·6. These are probably triplets due to the triplet P-terms, but it was impossible to separate the P_2 and P_3 lines. The earlier results of Rowland and Tatnall and of Glaser (A., 1922, ii, 675) have been verified. Four new lines, a doublet at 3019, a triplet at 2986, and singlets at 3110 and 2738 Å., have been discovered. By feeding a large quantity of the metal or its salt into an arc the lines at 3321, 2651, 2494, and 2175 Å. have been obtained in reversal, indicating the common origin of the lines in the p-level as classified by Bowen and Millikan. The vacuum spark spectrum comprises ten bands degraded towards the red. The measurements of the edges vary over the range 2474·2—2189·0 Å.
A. E. Mitchell.

Transition probabilities in the Ca II spectrum. A. Zwann (Naturwiss., 1929, **17**, 121—122).—If f denotes the strength of a spectral line expressed as a ratio of the dispersion or absorption of the line to the dispersion or absorption of an elastic and isotropic electron, vibrating with the same frequency and defined according to the classical theory, then f for the two components of the calcium line 2^2S-2^2P together equals 1·08 and for the three components of the line 3^2D-2^2P together, equals 0·09. The corresponding values of Einstein's A are $1{\cdot}55\times10^8$ and $1{\cdot}3\times10^7$, respectively.
W. E. Downey.

Fine structure of the principal series of cæsium and rubidium. A. Filippov and E. Gross (Naturwiss., 1929, **17**, 121).—The cæsium lines 4593 and 4555 Å. have been examined in absorption by means of an echelon grating of 30 plates. Each line shows two components. The rubidium emission lines at 4215 and 4201 Å. also show two components each.
W. E. Downey.

First spark spectrum of mercury, Hg II. F. Paschen (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 536—546).—An apparatus is described for investigating the first spark spectrum of mercury, Hg II. The wave-lengths of a large number of lines are given and a term table is drawn up. The spectrum is discussed.
A. J. Mee.

Second spark spectrum of mercury, Hg III. J. C. McLennan, A. B. McLay, and M. F. Crawford

(Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 247—251).—The extreme ultra-violet spectrum of a mercury spark in hydrogen has been reinvestigated, wave-length measurements being made in the range 1935—1350 Å. A zinc–aluminium spark was used as a comparison spectrum. The spectrum of an alternating discharge through mercury vapour in a vacuum was also studied. By the use of an inductance in series with the discharge the number of lines between 1750 and 700 Å. was reduced considerably. The lines classified in this region appeared in the lower excitation discharge spectrum, so that they probably belong to the Hg^{++} spectrum and not to any more highly ionised mercury spectrum. In the analysis Carroll's wave-lengths are used below 1350 Å. There is similarity between the Au II and Hg III spectra.
A. J. Mee.

First spark spectrum of thallium, Tl II. J. C. McLennan, A. B. McLay, and M. F. Crawford (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 241—245).—The spectrum of the thallium spark has been investigated and analysed, aluminium and zinc spark spectra being used as standards. A table giving frequency, intensity, and term combination of each line is drawn up. The intensities of all the classified lines are in good agreement with theory. A comparison of the ^3P and ^3D intervals of Ga II, In II, Tl II, and Hg I is made, and indicates points of similarity between these spectra. The relative positions of the singlet and triplet term systems of Tl II agree well with those of the corresponding systems of Zn I, Cd I, and Hg I.
A. J. Mee.

Wave-length measurements in the vacuum spark spectrum of lead from 2200 to 5000 A. S. Smith (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 331—335).—The work of Carroll on wave-lengths of the vacuum spark spectrum of lead up to 1936 Å. is extended to 5000 Å. A table of wave-lengths is given. (Cf. A., 1926, 214.)
A. J. Mee.

Black body [radiation] at the m. p. of palladium by the tube method. G. Ribaud and S. Nikitine (Compt. rend., 1929, **188**, 618—620).—Measurements on an electrically-heated palladium tube, 80×1·5 mm., by 0·5 mm. thickness, and with a cavity 0·3 mm., give constant values for the filament current when the mechanical tension of the tube is below 2·5 g./mm.^{2}; at higher tensions the temperature of rupture is lowered sharply 8°, and the phenomenon is attributed to an allotropic transformation of palladium 8° below its m. p. The tube method gives an excellent pyrometric bench mark, since the temperature can be followed closely to the fusion point.
R. Brightman.

Intensities of some Fe$^+$ multiplets in the arc and chromosphere spectra. W. Clarkson (Phil. Mag., 1929, [vii], 7, 98—105).—Intensity measurements of the $2^4F-2F'$ and 2^4F-2^4D multiplets for ionised iron, the iron arc, and the chromosphere have been examined. In all cases there are wide divergences from the theoretical intensities of individual lines. In each multiplet there is one line 4520 and 4549 Å., which is abnormal relative to the others. Ionised iron is similar to ionised nickel and cobalt in that the multiplet summation rules apply only when extended to cover the total series of both multiplets. The total summation rule shows the iron arc spectrum to be free from self-absorption whilst it demonstrates the self-reversal of the solar spectrum.
A. E. Mitchell.

Predicted lines of Cr II in the spectra of the sun and of α Persei. T. Dunham, jun., and C. E. Moore (Astrophys. J., 1928, **68**, 37—41).

Influence of a hydrogen atmosphere on the arc spectra of certain metals. H. Crew (Phil. Mag., 1929, [vii], 7, 312—316).—Many of the effects of a hydrogen atmosphere on arc spectra previously observed (A., 1901, ii, 81) are attributed to pole effects in the apparatus employed. A new apparatus eliminating pole effects has been devised and by its use many of the effects previously observed have disappeared. Some notable results attendant on the change of atmosphere round an arc from air to hydrogen are recorded in the arc spectra of magnesium, zinc, aluminium, cadmium, and carbon. The general effects are the broadening of certain reversals, the reduction in intensity of most of the lines, particularly triplets, the reduction in intensity of lines due to impurities in magnesium and zinc, and the enhancement of such lines in the spectra of aluminium, cadmium, and carbon.
A. E. Mitchell.

***K*-Radiation of the lightest elements.** M. Södermann (Z. Physik, 1929, **52**, 795—807).—By using an optical glass grating with 220 lines per mm., the wave-lengths of the *K*-series *X*-ray spectral lines of the elements from beryllium to aluminium have been measured. The results obtained are compared with those of previous investigators.
J. W. Smith.

Absorption spectra of the vapours of tin, silver, and manganese between 5500 and 2140 Å. R. G. Loyarte and A. T. Williams (Physikal. Z., 1929, **30**, 68—75).—The absorption spectra of tin, silver, and manganese vapours have been obtained at temperatures between 1200° and 2200°. For tin and manganese the results of Zumstein (A., 1926, 107, 453) and of McLennan, Young, and McLay (A., 1925, ii, 454) are confirmed. Lines corresponding with the ionised atom have been observed in the spectrum of silver. The results are in agreement with Hund's theory as to the relation between the deeper atomic levels and absorption spectra. The equation $N'/N=e^{-E/RT}$, N' being the number of excited atoms, N the total number of atoms, has been applied to the data on tin with satisfactory results.
R. A. Morton.

Series of the arc spectrum of tin. A. T. Williams and F. Charola (J. Phys. Radium, 1928, [vii], 9, 377—385).—A number of hitherto unclassified terms in the arc spectrum of tin have been investigated and identified and origins are assigned to them. A table is given in which all the known terms are summarised, and this is illustrated by a Grotrian diagram. It is shown that the structure of the spectrum is in accord with the theory of Hund.
J. L. Buchan.

Intercombinations in the arc spectrum of carbon. D. S. Jog (Nature, 1929, **123**, 318).—In a heavy arc spectrum of Acheson graphite in the region 2000 Å. the following inter-combination lines were identified : 51313, ${}^1\bar{D}_2-{}^3\bar{P}_1$ $(2L_2\longleftarrow L_2M_1)$; 51356, ${}^1\bar{D}_2-{}^3\bar{P}_2$ $(2L_2\longleftarrow L_2M_1)$; 39862, ${}^1\bar{S}_0-{}^3\bar{P}_1$ $(2L_2\longleftarrow L_2M_1)$, whence ${}^3\bar{P}_1-{}^1\bar{S}_0=20474$, corresponding with λ 4884·2 Å., which was not observed in the coronal spectrum. A. A. ELDRIDGE.

Relative intensities of the Stark effect components of the [Balmer] H_β and H_γ lines. H. MARK and R. WIERL (Z. Physik, 1929, **53**, 526—541).—A more detailed account of work already published (A., 1928, 1168).

Critical potential of the Geiger point counter. O. KLEMPERER (Z. Physik, 1928, **51**, 341—349; cf. Geiger and Klemperer, *ibid.*, 49, 753).—For all dimensions of the counter and gas pressures the initial potential at which the current in the point counter increases from 10^{-13} to 10^{-10} amp. is dependent on only two constants: the number of positive ions required to liberate an electron from a metal surface and the range of the electrons. It was the same for air, hydrogen, and carbon dioxide. Variations from this condition appear only at very high ionic velocities. J. W. SMITH.

Ionisation potentials of the rare-earth elements in relation to their position in the periodic system. L. ROLLA and G. PICCARDI (Phil. Mag., 1929, [vii], 7, 286—301).—A method for the determination of the ionisation potential of a metal, based on the measurement of the current flowing between two electrodes in a gas flame in which a salt of the metal is being volatilised, has been developed and shown to yield results in agreement with those calculated from spectroscopic data. The method is applied to determinations of the ionisation potentials of the rare-earth metals, which are shown to lie between 5·49 volts for lanthanum and 7·06 volts for yttrium. Comparison with the other elements places the rare-earth metals at the end of the fifth period of the periodic system, a result in general agreement with their chemical properties. With the exception of cerium the ionisation potentials increase regularly with increasing atomic number. Gadolinium exhibits no special peculiarities, indicating that such peculiarities must have their origin in the inner zones of the atomic structure. The results indicate that, with the possible exception of cerium, the external electronic shell is the same for all the rare elements. The ionisation potential of cerium, 6·91 volts, is attributed to the less basic character of this element. A. E. MITCHELL.

Photo-electric effect at low temperatures. J. C. MCLENNAN, L. A. MATHESON, and C. D. NIVEN (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 279—287).—When a potassium photo-cell is cooled to liquid air temperatures the emission for all wave-lengths of incident light is decreased, that for longer wave-lengths being affected most. The measurements have been extended with potassium down to the temperature of liquid hydrogen (—252°), and the current is still found to decrease. The results are discussed. It is possible that an electrical double layer at the surface of the potassium is responsible to a large extent for the change. The temperature variation of the threshold frequency may be related to the Thomson coefficient in metallic conduction. Also a change in the absorption coefficient with temperature may be partly responsible for the change in emission, but this cannot be the sole cause. A. J. MEE.

Influence of adsorbed gas on the photo-electric sensitivity of coconut charcoal. O. VON AUWERS (Z. Physik, 1928, **51**, 618—637).—The photo-electric sensitivity of coconut charcoal to mercury arc light has been determined in relation to the nature of the adsorbed gas; the effects due to hydrogen, nitrogen, and air have been examined. Only small differences are found between these gases. The sensitivity of the charcoal surface diminishes as the adsorbed gas is removed, and its value in the presence of adsorbed gas is approximately independent of the pressure of the gas. R. W. LUNT.

Oscillations in ionised gases. L. TONKS and I. LANGMUIR (Physical Rev., 1929, [ii], **33**, 195—210).—Langmuir's theory of electronic and ionic oscillations in an ionised gas is developed, and experimental investigation is made over a frequency range of 1—1000 megacycles. The very rapid electronic oscillations leave the heavier positive ions unaffected, whilst the ionic oscillations are so slow that the electron density has its equilibrium value at all times. They vary in type according to wave-length, from the shorter ones similar to the electron vibrations to the longer ones similar to sound waves, an approximate transition range being established. N. M. BLIGH.

Characteristic oscillation of free electrons in a constant magnetic field. S. BENNER (Naturwiss., 1929, **17**, 120—121).—The theory of Appleton and Barnett (Electrician, 1925, **94**, 398) has been experimentally proved. W. E. DOWNEY.

Influence of the level of origin of the photo-electrons on the distribution in space of their initial directions. P. AUGER (Compt. rend., 1929, **188**, 447—550; cf. A., 1926, 1188).—Electrons from the *K*-level behave as if they possess no motion before their photo-electric expulsion, whilst those from the *L*-level show a considerable supplementary dispersion, appreciable even for low values of this level, which indicates the existence of electronic motion in the atom itself before excitation. J. GRANT.

Diffraction of electrons by crystalline powders. Electronic analysis. M. PONTE (Compt. rend., 1929, **188**, 244—246).—A stream of electrons produces diffraction phenomena with crystalline powders analogous to those of *X*-rays. It is shown that in the case of zinc oxide, with the ordinary *X*-ray apparatus for crystal analysis, electronic analysis gives results in a short time with the expenditure of little energy, and having a maximum deviation from Broglie's law of 2%. J. GRANT.

Motion of slow electrons in the rare gases. F. VON KÖRÖSY (Z. Physik, 1928, **51**, 420—428).—The work of Ramsauer and Meyer is considered from the point of view that the maximum effective target area is to be anticipated for that electron velocity which is equal to the orbital velocity of the electrons in the outermost shell. Approximate calculations of the orbital velocities are given which agree satisfactorily with the observed maxima. R. W. LUNT.

Groups of electrons in the Geissler discharge. K. G. Emeléus and W. L. Brown (Phil. Mag., 1929, [vii], 7, 17—31).—The previous work of Emeléus (A., 1927, 293) and of Emeléus and Harris (A., 1927, 490) has been extended. Measurements of the collector characteristics in the Geissler discharge from a cold cathode in argon, neon, hydrogen, and oxygen at about 0·1 cm., under conditions approximating to the normal cathode potential drop, have been made. The results indicate that in the negative glow and in the Faraday dark space there is a group of fast electrons with approximately Maxwellian velocity distributions and an average energy of about 25 volts. The initial production of these is attributed to the passage of electrons into the negative glow from the cathode dark space and persistence by reason of a process the reverse of ionisation by collision. The persistence of two groups of slow electrons in the discharge is attributed to an effect of the Ramsauer minimum of the free paths of electrons.

A. E. Mitchell.

Three-dimensional motion of an electron in the field of a non-neutral atom. M. A. Higab (Phil. Mag., 1929, [vii], 7, 31—52).—Mathematical.

A. E. Mitchell.

Radiometer effect of positive ions. C. T. Knipp and W. S. Stein (Phil. Mag., 1929, [vii], 7, 70—79).—The effects of a stream of positive ions on an aluminium vane 0·1 mm. thick in residual air at 0·0003 mm. have been investigated. There is definitely both a radiometer and a mechanical effect, the energy loss in the apparatus being accounted for approximately as residual air effect 4%, mechanical effect 68%, and radiometer effect 28%. At a pressure of 0·009 mm. the distribution is roughly residual air effect 32%, mechanical effect 39%, and radiometer effect 28%.

A. E. Mitchell.

Electronic charge *e*. R. T. Birge (Nature, 1929, **123**, 318).—The evaluation of *e* is discussed.

A. A. Eldridge.

Internal energy of electron evaporation in the electron emission of silver. J. M. Adams (Z. Physik, 1929, 52, 882).—It is pointed out that the result obtained by Rosenfeld and Witmer (A., 1928, 936), who calculated from the energy of evaporation of electrons from a silver surface that the number of valency electrons of this element was 3, is quite possible, since several examples are available of silver in a bivalent or tervalent state.

J. W. Smith.

Electron scattering in helium. E. G. Dymond and E. E. Watson (Proc. Roy. Soc., 1929, **A**, **122**, 571—582; cf. Dymond, A., 1927, 392).—The velocity distribution and angular distribution of electrons from a tungsten filament scattered by single collisions in helium have been measured, using an apparatus very similar to that previously employed. With the object of reducing stray effects due to electrons being scattered by the walls of the collision chamber, this was lined with thin aluminium sheet at all points where the main electron beam might strike. The gas pressure varied from 0·08 to 0·12 mm. of mercury. Curves are reproduced showing the velocity distribution of electrons scattered through 10° for initial velocities of 102, 226, and 386 volts. For each curve, besides the peak corresponding with elastic collisions, two others appear, due to excitation and ionisation of the atom, respectively. That due to excitation reaches its maximum value at 21—22 volts, indicating that the excitation of the triplet system, requiring 19·8 volts, is very small at these high velocities. The effect of ionisation is at a maximum relative to that of excitation in the neighbourhood of 200 volts. It was found previously (*loc. cit.*) that the curve did not drop after the ionisation point, but even tended to rise. It is now found that the continuous loss of energy in the curves is much smaller, and is substantially the same, relative to the loss due to excitation, at 382 as at 226 volts. There seems to be no reason why it should not be attributed to the normal processes of ionisation. The scattering curves of both elastic and inelastic collisions (energy loss 21 volts) for an initial velocity of 210 volts are also reproduced. At large angles, many more elastically reflected electrons occur than inelastically reflected electrons, but for smaller angles they approximate in number, and for higher initial velocities (400 volts) the inelastic group may considerably exceed the elastic group for 5° angle of scattering. The reasons for the discrepancies between the present results and those found in previous work are discussed. The peaks in the curves relating scattered intensity with angle of scattering were most probably due to reflexion at the glass walls.

L. L. Bircumshaw.

Probability of excitation by electron impact in neon. R. d'E. Atkinson (Proc. Roy. Soc., 1929, A., **122**, 430—442).—The recent data of Townsend and McCallum (A., 1928, 567) allow an estimate to be made of the " average of the sum of all probabilities " of the excitation of a quantum jump by electron impact in the case of neon. From the point of view of the quantum theory, a method is developed of analysing the results obtained by the Townsend type of experiment, in which currents of the form $i = i_0e^{\alpha x}$ are found on varying the distance x between two parallel plates in a gas at comparatively high pressures. By assuming the first critical potential and the ionisation potential to be already known, the mean probability that at potentials in the range between them a collision, if it occurs, will be inelastic can be approximately evaluated. The chief uncertainty is due to the difficulty of calculating the total number of collisions that occur, since the Hertz formula, $\nu dx = 3x/\lambda^2 . \log a/x . dx$, rests on two assumptions, neither of which is fulfilled in the present case (Z. Physik, 1925, 32, 305). It is calculated that the average value of the sum of all excitation probabilities is about 5% in neon, and evidence is adduced in support of this figure. The relation between the Townsend theory of ionisation by collision and the general scheme provided by the quantum theory is discussed. It is shown that some modification is required in the definition of the quantity α (on which the Townsend collision formula rests) as " the average number of new ions produced per ion per cm. in the direction of the field." The measured α of the curves and the " average number of ions per ion per cm." would be identical only on the assumption that the probability of ionisation is independent of the distance travelled since the last ionisation, *i.e.*, of the energy of the electron. L. L. Bircumshaw.

Diffraction of electrons at ruled gratings. B. L. Worsnop (Nature, 1929, **123**, 164—165).

Eddington's hypothesis and the electronic charge. E. Bäcklin (Nature, 1929, **123**, 409—410).—The distribution of individual values of the electronic charge, *e*, obtained by Millikan, Wadlund, and the author, respectively, is examined, and the probable error is estimated. It is not possible to decide whether 136 or 137 is the better value for Eddington's relation $hc/2\pi e^2$ (this vol., 231).

A. A. Eldridge.

Angular distribution of Compton recoil electrons. D. Skobeltzyn (Nature, 1929, **123**, 411—412).

Attachment of electrons to the molecules HCl and NH_3. V. A. Bailey and A. J. Higgs (Phil. Mag., 1929, [vii], **7**, 277—286).—The method of Bailey (A., 1925, ii, 1019) has been extended to an examination of electron attachment in hydrogen chloride and in ammonia. The probability of attachment is shown to be proportional to the electric moment of the molecule (cf. this vol., 231).

A. E. Mitchell.

Efficiency of electron impact leading to resonance in helium. G. Glockler (Physical Rev., 1929, [ii], **33**, 175—188; cf. A., 1926, 552).—The efficiency of resonance impact between electrons and helium atoms was studied as a function of the energies of the impinging electrons. The transition investigated is $1^1S \longrightarrow 2^3S$ leading from normal parahelium to metastable orthohelium, from 19·77 to 20·55 volts. The efficiency of inelastic electronic impacts rises to a maximum estimated to be 0·002 at 0·18 volt beyond the resonance potential of 19·77 volts and then decreases. The measurements were carried out by comparing the velocity distribution of the electrons leaving an equipotential surface, with the drop in current as observed in the inelastic impact method of Franck, and by comparing the velocity distribution of the electrons with the distribution of the positive current caused by them in a Lenard experiment. Both types of measurement gave similar results. N. M. Bligh.

Mobility of positive ions in flames. H. E. Banta (Physical Rev., 1929, [ii], **33**, 211—216).—The mobility of positive ions of potassium, rubidium, and cæsium in the Bunsen flame was calculated from measured values of the current density, cathode drop of potential, and the thickness of the layer at the cathode in which the potential varies rapidly. The excess of ionisation over recombination in the layer was assumed to be proportional to $(1 - x/x_1)^m$, where x is the distance from the cathode, x_1 the thickness of the layer at the cathode, and m is a constant. The calculated mobility depends on the value assumed for m, and is 1·8 when $m = 2$ and 1·07 cm./sec. per volt/cm. when $m = 3$, and is known from other investigations to be approximately 1 cm./sec. per volt/cm. The mobility is found to be the same for salts of the three metals, and is independent of the concentration of the salt, but a small increase with electric intensity is indicated. N. M. Bligh.

Ion mobilities using the Erikson method on gases of controlled purity. J. J. Mahoney (Physical Rev., 1929, [ii], **33**, 217—228).—The change of mobility with the age of the ion was investigated using a form of Erikson's apparatus modified to allow a better control of the purity of the gas, and to extend the measurements to mixtures of known constitution. No ageing effect was found in carefully and moderately dried air, and mobilities were normal. Ordinary and moist air showed an ageing effect. The effects of various percentages of added ammonia, hydrogen chloride, and acetylene were investigated. The results obtained are compared with those of Erikson, and theoretical explanations are suggested (cf. Erikson, A., 1926, 989; 1927, 1002).

N. M. Bligh.

Emission of electrons from metals. F. Rother and E. Münder (Physikal. Z., 1929, **30**, 65—68).—Millikan and Eyring (A., 1926, 219) found the pulling-out of electrons from a thoriated tungsten cathode by intense electric fields to be independent of temperature, and Gossling (A., 1926, 448) found the temperature effect up to 1700° Abs. on electron emission to be negligibly small. Gossling, in contrast to Millikan and Eyring, observed sudden changes in the characteristic curves for the discharge. According to Schottky's theory (Z. Physik, 1923, **14**, 80), the relation between log *i* (*i* being the current) and the root of the voltage gradient $(\text{volt/cm.})^{\frac{1}{2}}$ should be linear, but Millikan and Eyring did not obtain such results. Repetition of the work shows that log *i* is proportional to the square root of the field strength rather than to the reciprocal of the field strength (cf. Fowler and Nordheim, A., 1928, 681). The origin of the experimental discrepancies is discussed and the validity of Schottky's theory is accepted.

R. A. Morton.

Emission of electrons from a metallic surface by slow positive ions. O. Klemperer (Z. Physik, 1928, **52**, 650—656).—Difficulties of direct measurement render it necessary to calculate the probability of emission of an electron by a slow positive ion from a metallic surface from known data. This is done in two fundamentally different ways: (i) from known current potentials of the Townsend discharge; (ii) from the minimum spark potential and the energy associated with the formation of an ion pair.

G. E. Wentworth.

Isotope of oxygen, mass 18. W. F. Giauque and H. L. Johnston (Nature, 1929, **123**, 318).—The weak doublets of the atmospheric absorption bands of oxygen originate from a molecule consisting of an oxygen atom of mass 18 combined with one of mass 16. The average and maximum deviations of observed minus calculated separations of the isotopic doublets are, respectively, —0·05 and —0·13 cm.$^{-1}$ The data show that the normal state of the oxygen molecule has one half unit of vibration, in agreement with the wave-mechanics theory.

A. A. Eldridge.

Fundamental at. wts. VII. At. wt. of potassium. II. Analysis of potassium bromide. O. Hönigschmid and J. Goubeau (Z. anorg. Chem., 1928, **177**, 102—108).—The most probable value for the at. wt. of potassium, derived from the ratios potassium bromide : silver and potassium bromide : silver bromide is 39·104±0·0020, identical with that obtained by analysis of the chloride. The reason for the discrepancy between this value and that of Richards (39·095) has not been explained.

H. F. Gillbe.

Fundamental at. wts. VIII. At. wts. of silver and barium. Analysis of barium perchlorate. O. Hönigschmid and R. Sachtleben (Z. anorg. Chem., 1929, **178**, 1—32; cf. A., 1927, 806).—The ratio $Ba(ClO_4)_2 : BaCl_2$ has been determined by heating carefully purified and dried barium perchlorate in a current of hydrogen chloride at 550°. The barium chloride obtained was then titrated gravimetrically with silver nitrate and from the results the ratio Ag : 4O calculated. The mean of five determinations gave the value of 107·880±0·001 for the at. wt. of silver. The at. wt. of barium was calculated from the ratios $Ba(ClO_4)_2 : BaCl_2$, $Ba(ClO_4)_2 : 2Ag$, and $BaCl_2 : 2Ag$. The mean value found as the result of five determinations of each ratio was 137·355.

A. R. Powell.

At. wt. of copper from the Lake Superior region and from [Chuquicamata] Chile. T. W. Richards and A. W. Phillips (J. Amer. Chem. Soc., 1929, **51**, 400—410).—Cupric chloride was analysed, the copper being determined electrolytically and the chloride by nephelometric titration against pure silver (cf. Richards, Proc. Amer. Acad. Arts Sci., 1890, **25**, 195). The at. wt. of copper was found to be 63·557 (Ag = 107·880), independent of the geographical origin of the metal. S. K. Tweedy.

At. wt. of cerium. Analysis of cerium trichloride. O. Hönigschmid and H. Holch (Z. anorg. Chem., 1928, **177**, 91—101).—The most probable value of the at. wt. of cerium, derived from the ratios $CeCl_3 : 3Ag$ and $CeCl_3 : 3AgCl$, is 140·125±0·007, the at. wt. of silver and chlorine being taken as 107·880 and 35·457, respectively.

H. F. Gillbe.

Mass-spectrum of uranium-lead and the at. wt. of protoactinium. F. W. Aston (Nature, 1929, **123**, 313).—The mass-spectrum of lead tetramethyl prepared from uranium-lead (from bröggerite) includes lines corresponding with isotopes of at. wt. 206 (arbitrary intensity 100), 207 (intensity 10·7±3) and 208 (intensity 4·5±2). There is no indication of isotopes of at. wt. 203 or 205. These values correspond with the percentages 86·8, 9·3, and 3·9 which, with a packing fraction of $0·8 \times 10^{-4}$, give a mean at. wt. of 206·19. The line 207 is not due to ordinary lead, radium, or thorium; it is concluded that it is the end product of the disintegration of actinium. Extrapolation of the packing fraction curve then gives the value 231·08 for the at. wt. of protoactinium.

A. A. Eldridge.

Relative velocities of the α-particles emitted by certain radioactive elements. G. C. Lawrence (Proc. Roy. Soc., 1929, **A**, 122, 543—551).—A direct comparison has been made of the velocities of the α-particles emitted from thorium-*C* and -*C'* and radium-*F* with those from radium-*C'*. The apparatus employed is similar to that described by Briggs (A., 1927, 392; 1928, 569), a combined source, consisting of the two radioactive elements to be compared, being used. The ratio of the radii of curvature of the paths of the α-particles, measured in the usual way, is equal to the ratio of the velocities of the particles (after applying a small correction for the increase in mass at high velocities). In this way, the ratios are found to be Ra-*F* : Th-*C* : Ra-*C'* : Th-*C'* = 0·8277 : 0·8885 : 1·000 : 1·0679, with a probable error of 0·05%. Using Briggs' value of the velocity of radium-*C'* α-particles, $1·923 \times 10^9$ cm./sec. (*loc. cit.*), the others are calculated to be: thorium-*C*, 1·709, thorium-*C'*, 2·054, and radium-*F*, $1·592 \times 10^9$ cm./sec.

L. L. Bircumshaw.

Ranges of β-rays. B. W. Sargent (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 179—191).—The absolute ranges of β-rays have been obtained by using the data of various workers on the loss of energy of the rays on passing through metal foils. Curves are given from which the ranges of rays with energies from 25,000 to 1,363,000 equivalent volts can be readily obtained. The values derived are somewhat greater than the usually accepted effective ranges, but it is considered that they are correct to within 10%. In the determination of relative ranges the intensity of a β-ray beam is measured by ionisation, and in the theory it is assumed that the quantity of the rays is unaltered for all substances for the same depth of penetration. There is some doubt whether this assumption holds for the β-rays from radium-*E*. The rays appear to be hardened by their passage through substances. A true secondary β-radiation could not have this property. Since the β-rays from radium-*E* are thus modified it is necessary to revise previous estimates of the relative ranges in different substances. A repetition of the experiments shows that for the β-rays of radium-*E* the ratio of the stopping power of an atom to its atomic number *Z* decreases slowly with increasing *Z*. Previous results have shown that generally the mass range of β-rays in different elements is nearly proportional to A/Z, where *A* is the at. wt. Hence it follows that the stopping power of any atom for β-rays is proportional to its atomic number.

A. J. Mee.

Spatial distribution of the γ-radiation of radium in slightly dispersive media M. Bruzau (Ann. Physique, 1929, [x], 11, 5—140).—Compton's theory of scattering is reviewed and considered in relation to γ-radiation. A comparison of the absorption of scattered and primary γ-radiation by certain media was made, using methods of absolute and comparative absorption for the determination of the quality of the radiation. The intensity of the γ-radiation was determined experimentally through the ionisation effect. For this purpose an improved type of ionisation apparatus was designed, and adapted to the study of dispersive media. The intensity of the current in the ionisation chamber due to the radiation is proportional to the product of the intensity of the exciting radiation and the absorption coefficient of the chamber boundary. The sensitivity of such a chamber is a function of the atomic number of the element forming the boundary wall and of the wave-length. The energy emitted per sec. in the form of γ-rays by 1 g. of radium was calculated. The difference in the qualities of the two radiations was shown, and the effect produced at different depths on a mass of water was evaluated. The pseudo-transparency of the dispersive media is due to the selectivity of the ionisation chamber for primary and scattered radiation. The selectivity being a function of the atomic number, the difference between the ionisation currents due to the respective radiations increases with increase of atomic number. The methods employed are important for their adaptability to radio-therapy; they can be extended to the study of the spatial distribution of *X*-rays. The results obtained were applied to deduce certain modifications in Millikan's measurements on cosmic rays. N. M. BLIGH.

Long-range α-particles from radium-*C*. K. PHILIPP and K. DONAT (Z. Physik, 1929, **52**, 759—766).—The long-range α-particles from radium-*C* have been investigated by Wilson's cloud method, and new data concerning their range and the frequency of their appearance obtained. Wilson's apparatus was so adapted that stereoscopic photographs could be taken on a cinematographic film. Out of 3000 exposures, 221 long-range α-particles were observed; the ranges of these particles indicated two velocity groups with ranges of 9·2 and 11·0 cm., respectively. A few particles were observed with a path even longer than 11 cm. To every 10^6 normal α-particles there were 29 with a range of 9·2 cm., 4 of 11·0 cm., and 0·5 with a range greater than this. The data confirm the results of Rutherford and Chadwick (A., 1924, ii, 814). J. W. SMITH.

Ranges of the long-range α-particles from thorium-*C* and radium-*C*, using an expansion chamber. R. R. NIMMO and N. FEATHER (Proc. Roy. Soc., 1929, A, **122**, 668—687).—The relative advantages of the scintillation and expansion chamber methods for measuring the ranges of long-range particles are discussed, and a detailed description is given of experiments made to determine accurately the ranges of the long-range α-particles from thorium-*C* and radium-*C*, using a special form of Wilson expansion apparatus. Two different arrangements are used, specially designed to furnish as few protons as possible within the interval of range in which long-range particles were expected—*i.e.*, between 7 and 15 cm. for radium-*C'* and 8·6 and 15 cm. for thorium-*C'*. In one arrangement, the radioactive source was surrounded by a gas (carbon dioxide or oxygen) to avoid the production of disintegration protons. The results indicate that thorium-*C* gives out two groups of α-particles with extrapolated ionisation ranges of 11·70 and 9·90 cm., respectively. A few tracks were found, also thought to be due to α-particles emitted by the source, of which the range was greater than 12·5 cm. The ratio of the numbers of particles in the 9·9 and 11·7 cm. groups is found to be 1 : 5·1, which differs considerably from the value 1 : 2·8 obtained by Meitner and Freitag (A., 1926, 772). The conclusions for radium-*C* are less definite. There is certainly a group of α-particles having an extrapolated ionisation range of 9·16 cm. in standard air, but besides these particles there are others with ranges between 7·5 and 12·5 cm. No absolute decision can be made as to whether these particles are emitted in groups of constant velocity, but there is strong evidence for additional groups at 8·1 and 11·0 cm. with a doubtful group at about 10 cm. The results make it quite clear that radium-*C* does not emit only two groups of long-range α-particles of 9·3 and 11·3 cm. range, as has hitherto been supposed on the evidence of scintillation experiments (cf. Rutherford and Chadwick, A., 1924, ii, 814).

L. L. BIRCUMSHAW.

Separation and preparation of radium-*D*, radium-*E*, and polonium (radium-*F*). O. ERBACHER and K. PHILIPP (Z. Physik, 1928, **51**, 309—320).—Methods of determination of radium-*D* and -*E* and polonium are described, in which the milligram radium equivalent of a radium-*D* preparation is determined by means of a β-ray electroscope. This preparation is then compared with a mixture of radium-*D* and -*E*, which is itself compared with polonium in an α-ray apparatus depending on the ionisation produced by the α-rays between the plates of a condenser at 2000—4000 volts.

The preparation of pure radium-*D* and -*E* and polonium is described; the first is produced by the electrolysis of an acid solution of radium-*D* with a current of 3×10^{-4} amp., pure radium-*D* separating out at the anode under those conditions. Pure radium-*E* is deposited from an acid solution of the impure substance on to nickel foil on keeping, and pure polonium is similarly, but more slowly, deposited on silver foil. Tables of experimental results are given, showing that a degree of purity of 95% and upwards is readily obtained. D. W. BANDEY.

Behaviour of the radio-active deposit during the operations used for the removal of emanation from water. H. HERSZFINKIEL (Rocz. Chem., 1928, **8**, 519—526).—The shaking out from radioactive mineral waters of the radioactive deposit together with the emanation observed by Hammer and Vohsen (A., 1913, ii, 622) is only apparent; this phenomenon is due to the Lenard effect, as well as to adsorption of the deposit on the walls of the vessel in which the solution is shaken. A similar effect is obtained by boiling the solutions or by aërating them.

R. TRUSZKOWSKI.

Temperature coefficient of γ-ray absorption. L. BASTINGS (Phil. Mag., 1929, [vii], 7, 337—345).—Measurements have been made on the absorption of γ-rays by lead, tin (solid and liquid), iron, and aluminium at various temperatures. Within the limits of experimental error the temperature coefficient of the atomic absorption of γ-rays is in close numerical agreement with the coefficient of linear expansion of the metal. This suggests that the atomic absorption is probably a function of the distance between the atoms of the absorber and not of the atomic target, as might have been expected.

A. E. MITCHELL.

Two simple methods of purifying radium emanation. W. G. MORAN (Phil. Mag., 1929, [vii], 7, 399—404).—In the first method oxygen and hydrogen are ignited by means of a hot copper oxide filament which serves also to oxidise any excess of hydrogen. In the second method the oxygen and hydrogen are ignited by an electric spark and any excess of hydrogen is removed by diffusion through a heated palladium tube. In both methods potassium hydroxide solution is employed to remove carbon dioxide. The apparatus is described in detail. The methods are applicable particularly to the preparation of specimens for therapeutic purposes, and since concentrations of the order of 125 millicuries per mm.^{3} are obtained it is not considered necessary to remove water vapour. A. E. MITCHELL.

Waves associated with β-rays and the relation between free electrons and their waves. G. P. THOMSON (Phil. Mag., 1929, [vii], 7, 405—417).—A mathematical analysis, on the basis of de Broglie's theory of wave mechanics, of β-ray emission is made and it is shown that the variation in speed of the electrons in the continuous β-ray spectrum may be regarded as due to the dispersion of a short-wave group associated with each ray. The mean velocity is of the order of that to be expected if the group had the form of an error function of sufficient spread to give the observed velocity range. The velocity of an electron associated with a given wave is considered and is shown to be capable of variation even in force-free space, a result which offers an explanation of the results of Ellis and Wooster (A., 1927, 393) on the heat generated in the disintegration of radium-*E*.

A. E. MITCHELL.

Ultra-violet radiation of substances subjected to γ-rays. L. MALLET (Compt. rend., 1929, **188**, 445—447; cf. A., 1926, 885).—A new quartz spectrograph is described which has a high luminosity and may be used to analyse the very feeble ultra-violet radiations emitted by liquids subjected to γ-rays. In general, pure liquids (*e.g.*, water) emit such radiations when subjected to high-frequency γ-rays, and the continuous spectrum of the radiations may extend from the visible to the extreme ultra-violet region and is limited only by the absorptive power of the substance concerned. J. GRANT.

"Packing fractions" of the atoms and their interpretation. A. C. BURTON (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 379—395).—The work of Aston on "packing fractions," defined by him as the divergence of a given atom from the whole-number rule divided by its mass number, is discussed. To find the deviation, the actual mass found should be subtracted from (1·00778×mass number) instead of from the nearest whole number, 1·00778 being the mass of the hydrogen atom, *i.e.*, of one proton and one electron, the two being so far apart that there will be a negligible loss due to packing. It is enunciated that if it is found that in any two cases the addition of the same quantity to the nucleus in passing from one atom to the next produces the same extra loss in mass, it can be concluded that the addition has probably been made in the same way, and this is used in interpreting the results. It is believed that when more accurate data are available, the application of this method will give rise to a quantitative scheme of nucleus building. A graph is drawn of the total loss in mass due to packing against the mass number for the first twenty elements. The packing is not very different in the different elements, *i.e.*, the whole-number rule is not very far from accurate. Atoms of the type mass$=4n$ are at maxima in the curve, *i.e.*, packing is peculiarly close for these elements. If the nuclei are made up of assemblages of helium nuclei, the packing effect per α-particle can be calculated. The loss in mass due to packing of proton and electron in a single α-particle is 0·0290. The theory of packing developed gives evidence for the existence of neutrons (Rutherford), and the packing loss due to a loosely added neutron is calculated to be between 0·008 and 0·007. A graph of the packing per α-particle against the number of α-particles in the core is plotted. Starting at the packing loss of a single α-particle the loss at first increases, due to the packing effect of the α-particle on its neighbours in the core. The loss reaches a maximum in the region of mass 60 or 70, where there is a maximum stability of the nuclei of elements. The packing effect then decreases. The nuclei of the lighter elements where there is an extra proton or electron in the nucleus are more difficult to investigate, but some attempt is made to apply the above principles to them. A. J. MEE.

Significance of the "packing fraction." M. FRANÇON (J. Physical Chem., 1929, 33, 296—300).—Previous views of other authors are summarised and the possible significance of the packing fraction in determining the evolution and abundance of the elements is discussed. L. S. THEOBALD.

Absorption of penetrating radiation. L. H. GRAY (Proc. Roy. Soc., 1929, A, **122**, 647—668).—Assuming that penetrating radiation is an ultra-γ-radiation, its absorption in the atmosphere is investigated from the theoretical point of view, and an attempt is made to establish a quantitative correlation between the ionisation produced in an electroscope by penetrating radiation and the scattering absorption coefficient of the radiation. The extent to which the surrounding medium may influence directly the ionisation produced in an electroscope by changing the number and velocity distribution of the ionising particles is considered in detail. Assuming that a β-particle traversing a solid medium loses the same amount of energy in travelling a distance Δx short compared with its range as it would do in traversing $\rho\Delta x$ of air, where ρ is a proportionality factor independent of the velocity of the particle, it is calculated that, for a small air cavity in an extended solid medium traversed by penetrating radiation in any arbitrary manner, the variations in intensity of the radiation in distances comparable with the dimensions of the cavity being negligible, the energy lost per unit volume by β-particles in the cavity is $1/\rho$ times the energy lost by γ-rays per unit volume of the solid. The relative magnitudes of the ionisation produced by primary and scattered radiations at any point are calculated by approximate methods, and depth–ionisation curves are reproduced, computed both on the basis of the Compton scattering formulæ and on that of the new scattering formulæ proposed by Klein and Nishina (Nature, 1928, **122**, 398). The relation between the apparent absorption coefficient of a homogeneous isotropic radiation and the true scattering coefficient of the primary radiation is discussed in the light of the results obtained. The validity of the Klein–Nishina formulæ is considered.

The points of contact of theory and experiment are studied for the formulæ of Dirac, Compton, and Klein and Nishina, and conclusions are reached which are favourable to the new formulæ.
L. L. BIRCUMSHAW.

Velocity of cadmium atoms regularly reflected from a rock salt crystal. A. ELLETT and H. F. OLSON (Science, 1928, **68**, 89).—The velocities of cadmium atoms constituting a beam reflected (at an angle to the normal equal to that of the incident beam) from a cleavage face of rock salt are very nearly equal; between 200° and 500° the velocity is independent of the temperature of the crystal. The results obtained for various angles are shown to be in accord with de Broglie's equation $\lambda=h/MV$ for the wave-length of a phase wave associated with a particle of mass M and velocity V, and with Davisson and Germer's form of Bragg's law. A. A. ELDRIDGE.

Polarisation of Compton scattering according to Dirac's new relativistic dynamics. Y. NISHINA (Nature, 1929, **123**, 349).—A correction (cf. this vol., 5). A. A. ELDRIDGE.

Penetrating radiation. II. J. CLAY (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1091—1097; cf. A., 1928, 569).—An accurate determination of the capacity of the electrometers has shown that the values previously used were incorrect. A redetermination has been made of the residual ionisation and of the constants of the penetrating radiation. The origin of the latter is discussed, and its intensity is shown to decrease as the equator is approached.
N. M. BLIGH.

More elementary treatment of the hydrogen atom in wave mechanics generalised for the moving nucleus. J. K. L. MACDONALD (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 417—422).—Mathematical. The problem of the hydrogen atom is solved by wave mechanics in a more elementary and familiar way, the motion of the nucleus and of the atom as a whole being considered. A. J. MEE.

Chemical combination as an electrostatic phenomenon. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, **26**, 66—69).—A summary of the present conception of atomic structure is given. S. I. LEVY.

Sommerfeld's electronic theory of metals and the mean free path of electrons. L. BRILLOUIN (Compt. rend., 1929, **188**, 242—244).—It is shown that in the calculation of the mean free path of electrons from Sommerfeld's application of Fermi statistics to the case of free electrons in metals (A., 1928, 467), the results for light and electrons cannot be similar, since the former is subject to Bose–Einstein statistics. A modified calculation is suggested (cf. Houston, *loc. cit.*). J. GRANT.

Regularities in the table of the elements. D. STRÖMHOLM (Z. anorg. Chem., 1928, **177**, 303—312, and Phil. Mag., 1929 [vii], **7**, 691—705).—The percentage electron content of the atomic nucleus increases rapidly with increase of at. wt.; this increase occurs in five stages, of which the second commences at scandium, the third at gadolinium or germanium, the fourth at indium, and the fifth probably at hafnium. The significance of these stages is discussed, particularly as regards formation and disintegration of the elements. H. F. GILLBE.

Statistical periodic table. H. H. STEPHENSON (Chem. News, 1929, **138**, 129—130).—The author has arranged the elements in order of atomic number, calculated the percentage increase of at. wt. of each element over that of its predecessor, and arranged the resulting numbers in columns of six. The table is said to be "statistically periodic" and to exhibit chemical relationships. A. A. ELDRIDGE.

Relations between doublets of stripped atoms in five periods of the periodic table. R. C. GIBBS and H. E. WHITE (Physical Rev., 1929, [ii], **33**, 157—162).—The periods considered are Li—O, Na—Cl, K—Mn, Rb—Zr, and Cs—Pr. Combining the available data for the one-electron system, certain regularities between the successive elements in each period and between corresponding elements in successive periods are found by the application of the regular and irregular doublet laws. That the latter is closely followed for all five periods is shown by a graph giving the linear progression of frequency with atomic number for transitions involving no change in the total quantum number. The term values of any sequence when plotted on a Moseley diagram show very nearly a straight-line relation. Previous identifications of the principal doublet of cerium are corrected. Evidence indicates that the unexcited state of cerium involves a $5d$ rather than a $4f$ electron. New data are given for vanadium, chromium, and lanthanum. N. M. BLIGH.

Origin of actinium and the age of the earth. (SIR) E. RUTHERFORD (Nature, 1929, **123**, 313—314).—It is supposed that the new lead isotope "actino-uranium" (Aston, this vol., 370) is of mass 235, and that it undergoes first an α- and then a β-ray transformation into protoactinium. The β-ray substance is probably uranium-Y, whence the successive transformations follow the order αβαβ instead of αββα, as in the main uranium series. From the half-value period ($4{\cdot}5\times10^9$ years) of transformation of uranium it is computed that the period of actino-uranium is $4{\cdot}2\times10^8$ years. If it is supposed that the production of uranium in the earth ceased as soon as the earth separated from the sun, the earth cannot be older than $3{\cdot}4\times10^9$ years. If the age of the sun is of the order 7×10^{12} years, uranium and similar elements were being formed in the sun 4×10^9 years ago, and the process still continues.
A. A. ELDRIDGE.

Scattering of radiation by free electrons according to Dirac's new relativistic quantum mechanics. O. KLEIN and Y. NISHINA (Z. Physik, 1929, **52**, 853—868).—Mathematical. Using the principles of Dirac's theory the intensity of the Compton scattered radiation is calculated.
J. W. SMITH.

Stability of the silver atom. J. KAPLAN (Z. Physik, 1929, 52, 883; cf. Adams, this vol., 368).—It is suggested that although the shell of the $4d$-electrons in silver is quite stable in almost all chemical reactions, this may not be so stable with respect to electrical conductivity and that some of them may

enter into this process. It is suggested that the appearance of tervalent silver mentioned by Adams indicates that the 4*d*-electrons are not equally stable.
J. W. Smith.

Ionisation and chemical combination of gases. A. de Hemptinne (Bull. Acad. roy. Belg., 1928, [v], **14**, 450—454).—An experiment is described to investigate the relationship between ionisation and chemical reaction for mixtures of hydrogen and oxygen and of hydrogen and nitrogen. The ratio of the total number of ions formed to the number of combined molecules is calculated, and from the result it is shown that there is an intimate relationship between the amount of combination and the number of ions present. For the combination of hydrogen and nitrogen the ratio of ions to molecules combining varies only from 15 to 20, whilst the current through the gas is ten times as great in the second case as in the first.
A. J. Mee.

Quantum mechanics and radioactive disintegration. R. W. Gurney and E. U. Condon (Physical Rev., 1929, [ii], **33**, 127—140).—Theoretical. The statistical nature of the new quantum mechanics renders it very suitable for the treatment of radioactive decay. The method of wave mechanics is employed and a simple deduction of the disintegration constant is made. It is shown qualitatively that the nucleus can disintegrate without the absorption of energy, a result opposed to classical theory. The equivalent of the Geiger–Nuttall relation between the rate of disintegration and the energy of the emitted α-particle is deduced quantitatively. The law of force between the emitted α-particle and the rest of the nucleus is shown to be substantially the same in all atoms. The quantum mechanical assumption that particles can pass through regions where their total energy would classically be less than their total energy affords an explanation of the experiments of Rutherford and Chadwick (cf. A., 1925, ii, 1109).
N. M. Bligh.

Transmutation of elements. L. Thomassen (Physical Rev., 1929, [ii], **33**, 229—238).—If transmutation is possible it might take place in an *X*-ray tube, where it could be detected in the *X*-ray spectrum. No lines other than those due to tungsten were found before or after working an *X*-ray tube with a tungsten target for 80 hrs. No transmutation of lead to mercury could be detected when the experiments of Smits and Karssen (cf. A., 1926, 106) with the lead arc were duplicated. Their experiments on a high-potential discharge between platinum electrodes in carbon disulphide (cf. A., 1927, 87) were repeated, as a trace of mercury in the residue from the electrodes is regarded as an impurity.
N. M. Bligh.

Space required by atoms (ions) in crystals and the character of the lithosphere. V. M. Goldschmidt (Neues Jahrb. Min., 1928, **A**, 57, 1119—1130; Chem. Zentr., 1928, ii, 867—868).—A discussion. The influence of ionic size on molecular volume is examined; the density of space occupation of a compound AX of the sodium chloride type is greatest when $R_A : R_X = 0{\cdot}41$, and least when $R_A = R_X$. Oxygen is the only important anion of the lithosphere; the whole lithosphere is regarded as an oxygen-packing. The maximum density for spherical oxygen ions is 2·03, this value being modified by the cations.
A. A. Eldridge.

Low-voltage sparks as spectroscopic sources. A. Occhialini (Atti R. Accad. Lincei, 1928, [vi], 8, 389—393).—Low-voltage sparks suitable as spectroscopic sources may be obtained by using a cathode of incandescent carbon, forming part of an auxiliary arc, and a cold anode. A condenser of some microfarads capacity serves to store energy from the direct current source in the intervals of the sparks. Details are given of an electrolytic rectifier suitable for obtaining the necessary direct current.
F. G. Tryhorn.

Use of the under-water spark with the Hilger sector photometer in ultra-violet spectrophotometry. H. J. McNicholas (Bur. Stand. J. Res., 1928, **1**, 939—949).—Means for operating high-voltage under-water spark to produce a uniform continuous spectrum for quantitative spectrophotometric measurements are described. Spark terminals of tungsten are enclosed in an ebonite box, through which a stream of distilled water is circulated. External adjustments are provided for the length of the spark gap (about 16 mm.) and its position relative to the axis of the optical system. Methods of avoiding the wave-length dispersion in the Hilger sector photometer, and thus permitting the use of a shorter spark, are discussed.
C. J. Smithells.

Elimination of stray radiations in an infra-red spectrometer. J. Lecomte (Compt. rend., 1929, **188**, 622—625).—The proportion d ($d<1$) of stray radiation passing into the instrument at each point of the spectrum beyond 10 μ is determined by the transparent-shutter method, and the gross transmission of the substance is then determined by the usual opaque-shutter method. The true transmission of the radiation above 10 μ is given by the formula $T=(T'-d)/(1-d)$, where T' is the gross transmission of the radiation in the presence and absence of the absorbent. The true absorption is given by $1-T$. The variation of d with wave-length is usually a straight line.
R. Brightman.

Absorption vessel for variable thicknesses of liquid. C. Leiss (Z. Physik, 1928, **52**, 748—749).—A new form of absorption vessel is described, the distance between the windows of which can be set to within 0·05 mm. All possibility of contamination by metal, grease, etc. is avoided, the liquid coming into contact with glass only.
E. B. Robertson.

Vacuum spark-gap. C. Leiss (Z. Physik, 1928, **52**, 750—751).—A vacuum spark-gap is described which can be either attached to a vacuum spectrograph or placed on a stand directly in front of the slit.
E. B. Robertson.

Experimental test of the combination principle for band spectra. E. Bengtsson and E. Hulthén (Z. Physik, 1928, **52**, 275—279).—The AlH band spectrum has been examined with a large concave grating (dispersion 2·4 Å./mm.) and, in addition to the band systems $^1P \longrightarrow {}^1S$ and $^1S' \longrightarrow {}^1S$ already known, a new system given by $^1S' \longrightarrow {}^1P$ has been discovered and measured. This is therefore a case in which all three transitions between three electronic terms are realised, and the measurements confirm Kronig's combination principle (that transitions take place only between primed and unprimed terms).

E. B. ROBERTSON.

Spectrum of H_2: bands analogous to the orthohelium line spectrum. O. W. RICHARDSON and K. DAS (Proc. Roy. Soc., 1929, A, **122**, 688—718).—A summary is given of Richardson's previous work on the structure in the secondary hydrogen spectrum (A., 1926, 873; 1927, 1). An examination of the wave-length tables of Gale, Monk, and Lee (A., 1928, 1166) confirms the series of systems of Q branches recorded, and the combinations are found to be exact to the accuracy of the new data. This applies to the bands which involve the electron transitions $3\rightarrow2$ (α), $4\rightarrow2$ (β), and $5\rightarrow2$ (γ), but the weak bands involving the $6\rightarrow2$ (δ) and higher transitions require reconsideration. By using the more exact final vibration intervals thus obtained it has been possible to identify the P and R branches accompanying the Q branches previously studied. There are found to be only three branches, P', Q, and R', the initial levels for the P' and R' branches being different from those for the Q branches. There is a final level in the R' branches lower than any present in the Q branches. The lines of the P', Q, and R' branches of the H_α bands are tabulated, using the wave-numbers and intensities of Gale, Monk, and Lee. The bad agreement given by the older infra-red data for the Q branches has entirely disappeared. The existence of all the states, both initial and final, with vibration numbers between 0 and 7 is securely established, and there is some evidence for the occurrence of $n'=8$ and 9 and $n''=8$. The usual expression for the vibrational energy which includes only terms as high as n^2 is shown to be inadequate, but the function can be completely expressed by adding terms in n^3 and n^4. The Q branches of the H_β band system are also tabulated. The existence of the levels up to $n'=5$ and $n''=5$ is now certain. The P' and R' branches, extremely weak except for the $0\rightarrow0$ bands, have very similar properties to those of the corresponding H_α bands. There is the same alternation of intensity of the lines, and the maximum strength lies on or close to the diagonal sequence. The analysis has been extended to include the rotational structure of the band systems. The lines of the bands are single, and conclusive evidence is adduced that the bands are $2S-mP$. The system of bands ($2S-3S$) in the red and infra-red having the same final states as the $H_{\alpha,\,\beta,\,\text{etc.}}$ bands is also discussed, and the lines, with the final and initial vibration and rotational term differences, are tabulated. These bands are characterised by the presence of P and R branches of about equal intensity and by the absence of Q branches.

L. L. BIRCUMSHAW.

Fulcher bands of hydrogen. I. SANDEMAN (Nature, 1929, **123**, 410—411).—The terms of the bands fit the form $B\{j(j+1)-\sigma^2\}$, provided j is given integral values, but a correction term in the fourth power of j or j_k is present. The tentative formula $F(j)=\Sigma X_n\{j(j+1)-\sigma^2\}^n$, $n=1, 2 \ldots$, is adopted. For the hydrogen bands only the first two terms need be taken into account. The constants of the Fulcher null band $_0a_0$ are evaluated.

A. A. ELDRIDGE.

Existence of metastable molecules in active nitrogen. J. KAPLAN (Physical Rev., 1929, [ii], **33**, 189—194; cf. this vol., 365).—The only basis for the existence of metastable nitrogen molecules has been that they afforded an explanation of the nitrogen afterglow. Experimental evidence of their existence is found in the excitation of the fourth positive group of bands of the nitrogen molecule by a mild discharge simultaneously with the quenching of the afterglow. The main spectroscopic characteristics of a condensed discharge have been reproduced simply by introducing active nitrogen into a weak discharge. The relation of these phenomena to the structure of the nitrogen molecule is discussed. N M. BLIGH.

Band spectrum of chlorine or hydrogen chloride. E. B. LUDLAM (Nature, 1929, **123**, 414).—The bands previously recorded (this vol., 118) were caused by the presence of traces of sulphur.

A. A. ELDRIDGE.

Band absorption spectrum of iodine in an extreme ultra-violet region. M. KIMURA and M. MIYANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 33—42).—Oldenburg (A., 1923, ii, 708) has shown that iodine emits equally-spaced resonance lines in the region 1860—2173 Å. when exposed to monochromatic light in the region 1900 Å. The absorption thus disclosed has now been studied in detail, the iodine vapour being at 35—120° with vapour pressures corresponding with 35—60°. At 35°, the absorption extended from 1950 to 2064 Å., and as the temperature was slowly raised to 120°, the bands in the above region gradually disappeared and new bands with wider spacing progressively appeared until at 120° the spectrum extended from 2066 to 2145 Å. The bands were usually most intense in the middle of the spectrum. The interval 210 cm.$^{-1}$ appears in several series, and attention is directed to the agreement between this constant and the intervals between levels for iodine molecules in the normal state, and also the intervals of the resonance lines recorded by Oldenburg. The formula $\nu=52800+78n'-n'^2-210n$ cm.$^{-1}$ expresses approximately the wave numbers of the observed band edges.

R. A. MORTON.

Diffuse bands and predissociation of iodine monochloride. G. E. GIBSON and O. K. RICE (Nature, 1929, **123**, 347—348).—Evidence that the convergence limit of the group of bands (I*), of which Gibson and Ramsperger observed the members 17446 and 17570 cm.$^{-1}$, corresponds with dissociation of iodine monochloride into normal chlorine and excited iodine atoms has been obtained. A second continuum probably corresponds with the same process. The band 17446 cm.$^{-1}$ clearly shows fine structure, but the next following bands are diffuse. The effect is probably of the same nature as Henri's "predissociation." The diffuseness is probably due to interaction between the Cl* band group continuum and the discrete states of group I*. A. A. ELDRIDGE.

Spectra excited by active nitrogen. J. H. FINDLAY (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 341—352).—A comparison was made of the spectrum of the exciting discharge when the nitrogen afterglow was present and when it was absent. The differences between the two are, in the first place, the presence of the first positive nitrogen bands in the spectrum of the discharge with no afterglow and the absence of them from the glow-producing discharge, and, in the second place, a more intense spectrum in the latter case. The main problem attacked was the excitation of spark lines of elements with low ionisation potentials, *e.g.*, calcium, strontium, and barium, by means of active nitrogen. Although sodium and potassium lines were present in the afterglow spectrum no calcium lines were present. This is probably due to the formation of stable calcium nitride. The work of Ruark and of Okubo and Hamada on the excitation of the mercury spectrum by active nitrogen was repeated. The results agree with those of the latter authors, viz., the highest level of excitation was the 4^3D level, corresponding with an excitation potential of 9·51 volts. The temperature to which mercury had to be heated in order to produce the blue glow of mercury in the tube was found, and hence the vapour pressure of the mercury. The relative concentrations of mercury vapour and active nitrogen would not preclude the possibility of chemiluminescence being the origin of spectra excited by active nitrogen. It was not found possible to excite the spectrum of indium by active nitrogen in spite of its low ionisation potential (5·76 volts). This may be due to the fact that it does not combine with nitrogen. A. J. Mee.

Ultra-violet absorption spectrum of nitrogen peroxide. M. Lambrey (Compt. rend., 1929, **188**, 251—252).—The wave-lengths of the apparent absorption maxima of the NO_2 molecule and the intensities of the lines are tabulated for 2083—4009 Å., with an accuracy of 1 Å. Liquid nitrogen dioxide at −20° (1 mm. layer) shows a single spectrum with intense absorption for wave-lengths below 3975 Å., whilst the gas shows two spectra. That due to N_2O_4 has two large structureless bands at about 3400 and 2400 Å., whilst the bands due to NO_2 are complex in structure and extend from the yellow to 2900 Å., and from 2490 Å. to the limit of the spectrum. The absorption coefficient is a minimum at about 3020 Å., but is never zero. J. Grant.

Quantum analysis of the beryllium oxide bands. (Miss) J. E. Rosenthal and F. A. Jenkins (Physical Rev., 1929, [ii], **33**, 163—168).—New measurements of the lines in six bands of the visible BeO system are reported. Each band has *P* and *R* branches of almost equal intensity, and the agreement among the bands of the combination relations between the two branches is shown graphically. The rotational terms are investigated by the combination principle. An equation is deduced for the null lines. Some of the principal molecular constants are evaluated from rotational term-differences, using the new quantum mechanics. N. M. Bligh.

Ultra-violet spectrum of magnesium hydride. I. Band at 2430 Å. R. W. B. Pearse (Proc. Roy. Soc., 1929, **A**, **122**, 442—455; cf. Watson and Rudnick, A., 1926, 657; 1927, 395).—Besides the well-known visible (α) band system in the spectrum of MgH, two others (β and γ) are found in the ultra-violet. The β-system is represented by a strong band at 2430 Å., whilst the γ-system covers the range 5500—2430 Å. The 2430 Å. band has been measured and found to resemble the 0,0 band 5211 Å. of the α-system in possessing *P*, *Q*, and *R* branches, of which the *Q* are much the strongest. Each is composed of lines which are apparently single, but are probably double. The doubling appears to be similar to that of the 5211 Å. band in decreasing rapidly in separation with increasing *m*, but to be on a smaller scale. A curious feature of the band is the rapid decline of intensity in the *P* and *R* branches after passing the maximum value. A comparison of the combination differences relating to the final and initial states of the 2430 and 5211 Å. bands indicates that the final level of the 2430 Å. band is the same as that of the 5211 Å. band, and that the initial state is of the same type as that of the α-system, $2P$. The α-system is the MgH analogue of the "*D*" lines of Na, the "comparable atom," whilst the β-system corresponds with the second member of the $2P \longrightarrow S^2$ series of Na. The 2430 Å. band is the 0,0 band of the β-system. The *Q*-heads of three neighbouring bands of the same system have been detected and measured under low dispersion, and values of the initial and final vibrational quantum numbers n', n'' assigned. L. L. Bircumshaw.

Complexity of the $K\beta'$ line of *X*-ray spectra. V. Dolejšek and H. Filčáková (Nature, 1929, **123**, 412—413).—A study of various manganese compounds has not revealed any relationship between the state of chemical combination and the breadth or displacement of the line $K\beta'$. The intensity ratio $K\beta_1 : K\beta'$ is greater for oxides than for the free elements. For the elements of atomic number 24—27 the width of the line $K\beta'$ increases with decrease of atomic number; in the lower elements the line is composed of two unresolved doublet lines which in the higher elements are superimposed. The two lines cannot both be due to the transition $K \longrightarrow M_{II}$, $K \longrightarrow M_{III}$. A. A. Eldridge.

Absorption of *X*-rays from 0·63 to 2 Å. I. Backhurst (Phil. Mag., 1929, [vii], 7, 353—373).—An *X*-ray tube suitable for absorption measurements with homogeneous radiation in the region of 1 Å. is described. The results of absorption measurements on silver, aluminium, platinum, gold, and copper for wave-lengths 0·63—2 Å. are given. The relationship between absorption and wave-length was found to conform approximately to the law recently found by Jonsson (Uppsala Univ., Årsshrift, 1928). The *K*-absorption jump for copper and the *L*-absorption jumps for gold and platinum have been measured and the values are found to be in closer agreement with Jonsson's theory than with others. A. E. Mitchell.

Fluorescence of mercury vapour under low excitation. [Lord] Rayleigh (Nature, 1929, **123**, 127).—When the exciting source consists of radiation from which wave-lengths < 3360 Å. have been cut off, fine structure in the band at wave-length 3130—3650 Å. can still not be observed. A. A. Eldridge.

Absorption spectra and molecular structure of the dihalogen derivatives of benzene. J. Errera and V. Henri (J. Phys. Radium, 1928, [vii], 9, 205—224, 249—264).—The ultra-violet absorption spectra of some dihalogen derivatives of benzene, in the vapour state, have been investigated up to 400° and at pressures of from 10 to 100 mm. The source of illumination was a high-frequency condensed spark between electrodes of copper or aluminium under water and an iron spark was used for comparison. The minimum concentration of vapour necessary for the production of each band was found to within 5—10%, and the bands were thereby classified according to their intensities. The absorption spectra of dichloro- and dibromobenzene contain many bands and fine lines in the ultra-violet between 2850 and 2500 Å., whilst the three di-iodobenzenes give continuous spectra from about 3000 to 3100 Å., the absorption becoming more intense towards the ultra-violet. The dichloro- and dibromo-benzenes give spectra similar to all the mono- and di-derivatives of benzene, which are also characteristic of all aromatic substances, there being two regions, corresponding with two states of electronic activation. In the first of these regions are five or six groups of bands, at intervals of 80—60 Å. corresponding with atomic vibrations. Between the principal groups are secondary and tertiary groups. At very low pressures only the groups nearest to the red are obtained, more bands appearing as the pressure is raised. There is also a second region of continuous absorption beginning at about 2350 Å. From these bands the energies of dissociation of dichloro- and dibromo-benzene are deduced to be at least 124,000 g.-cal./mol., whilst for the di-iodo-derivative it is about 95,000 g.-cal./mol. The difference in moment of inertia between the activated and unactivated molecule has been calculated from the rotation spectra.

A formula is given showing the distribution of bands in the absorption spectrum of *p*-dichlorobenzene. The spectrum, like those of the *o*- and *m*-derivatives, is composed of doublets, but in this case the separation is more feeble, also the distribution of bands corresponds with three, not with two, intramolecular vibration frequencies. The formula for *p*-dibromobenzene is also given. Its absorption spectrum is very similar to that of the *p*-dichloro-derivative, but the vibration frequencies are less pronounced.

These spectra are discussed from the point of view of molecular structure. From the data obtained, the energies of activation and of dissociation of these molecules have been calculated. Both the dichloro- and dibromo-derivatives show two states of activation, the second state corresponding with dissociation of the molecule, whilst the di-iodo-derivative shows only one, its energy being less than for the others. This is due to the di-iodo-derivatives being more labile so that they dissociate at the first stage of activation. By comparison with benzene it is shown that the introduction of chlorine into this molecule progressively displaces the spectrum towards the red and lowers the energy of activation. By analogy with atomic spectra it is concluded that these derivatives possess an electron which is less firmly held than the others, and it is this electron which, under the influence of ultra-violet light, produces doublets by moving to an orbit of a higher energy level.

J. L. Buchan.

Theory of sensitised fluorescence. A. Carelli (Atti R. Accad. Lincei, 1928, [vi], 8, 495—500).—A mathematical treatment based on wave mechanics.

F. G. Tryhorn.

Fluorescence excited in oxygen and nitrogen by ultra-violet light of short wave-length. J. C. McLennan, R. Ruedy, and F. H. Clements (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 253—255).—The question whether ultra-violet light of short wave-length (1100 Å.) from a spark gives rise to any fluorescence in the surrounding air is studied experimentally. The light source was placed in the gas itself. Spectrograms were taken and it was found that the most intense bands of the first negative system and of the second positive system of nitrogen were present. Atomic oxygen lines also appeared, but no lines of molecular oxygen. This demonstrates the great stability of the nitrogen atom, and the fact that the oxygen molecule readily breaks down into atoms under the influence of light of short wave-length. There was no trace of the green auroral line of oxygen, λ 5577 Å., the absence of which is explained by the fact that at the comparatively high pressures used collisions of the second kind would be so numerous that atoms in the metastable state would lose their energy through these collisions instead of by the spontaneous emission of radiation. A method of obtaining light of the wave-length 5577 Å. (oxygen auroral green line) is suggested. The pressure used must make collisions of the second kind very infrequent, and the gas must be irradiated with light of wave-lengths slightly longer than those which would cause nitrogen molecules to emit any light of their second, and possibly of their first, positive band system. A. J. Mee.

Luminous discharge in gases at low pressure. H. Pettersson (Nature, 1929, 123, 346).—By the use of oscillations of frequency 10^8 cycles per sec., a luminous discharge was maintained in tubes only 5 mm. wide under extremely low pressure. The gas showed a faint blue luminosity; the silica tube showed a strong fluorescence in the blue or blue-green, although some tubes showed a brilliant fluorescence in the red. Thermo-luminescence and after-glow of the silica were also observed. Under the influence of the ultra-violet light of very short wave-length generated by the discharge, the silica appears to decompose, releasing oxygen. The spectrum from the white light of the self-generated gas represents the band spectrum of ozone, with some lines of elementary oxygen superimposed.

A. A. Eldridge.

Origin of the luminescent light of phosphorus. A. Petrikaln (Z. Physik, 1928, 51, 395—409; cf. A., 1924, ii, 289; Emeléus and Purcell, A., 1927, 497).—Investigations have been carried out on the emission and absorption spectra of phosphorus pentoxide and phosphorus trioxide. On electronic excitation of phosphorus pentoxide in the gaseous phase the spectrum of oxygen only is produced. The pentoxide vapour shows no absorption in the quartz ultra-violet region; its emission spectrum appears to lie in the Schumann region. On the other hand, phosphorus trioxide vapour on electronic excitation shows a band spectrum which is completely identical with the phosphorus luminescence spectrum. The trioxide gives a continuous spectrum in the visible region and a band spectrum built up of two band systems, *A* and *B*, of which the former, the longer-wave system, has been partly analysed and the latter completely analysed and classified. It is concluded that the continuous spectrum is to be attributed to solid phosphorus pentoxide. The conditions of excitation of the phosphorus trioxide in the oxidation of phosphorus are discussed. J. W. Smith.

Luminescence associated with electrolysis. R. T. Dufford (J. Opt. Soc. Amer., 1929, **18**, 17—28).—Investigations of the luminescence frequently found during electrolysis, its extent, brightness, efficiency, and the influence on the last two of voltage changes, concentration, nature of the solution and impurities, have been carried out. The brightness and efficiency at first increase with the applied voltage and subsequently decrease; the effects of differences in concentration are relatively small, and are comparable for chemically similar solutions. Impurities generally have a small effect on the brightness and efficiency. The chief solutions studied were sodium hydrogen carbonate and phosphates, and ethereal solutions of Grignard reagents.

N. M. Bligh.

Nitrogen afterglow. J. C. McLennan, R. Ruedy, and J. M. Anderson (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 303—321).—To discover how far chemiluminescence may contribute to the excitation of spectra by active nitrogen, the afterglow was allowed to act on an inert gas. If spectral lines are observed when these gases are mixed with activated nitrogen they must be due to direct excitation by the afterglow itself. If the available energy of active nitrogen is about 11·5 volts, as predicted from its spectrum, practically the whole spectrum of xenon should be excited in the afterglow, since the lowest excitation potential of xenon is 8·3 volts. Also several lower levels of krypton should be excited. It was found, however, that xenon when mixed with active nitrogen was not excited. The lines emitted by metallic vapours when acted on by active nitrogen are probably not due to the simple transfer to the metal atoms of the heat of recombination of nitrogen atoms produced by the discharge. Chemiluminescence probably plays a part when the spectra of foreign substances are excited. The result obtained with xenon is in agreement with evidence derived from a study of the decay of the nitrogen afterglow at different pressures. If it is assumed that a simple transfer of energy is responsible for the afterglow itself, the kinetics of the process do not agree with experiments. The effect of inert gases on the afterglow was studied and it was found that they all modify it in the same way, apart from minor details. The emission starts from the tenth, ninth, eighth, or seventh level, instead of from the eleventh level, as the amount of inert gas present is increased. The effect is probably due to pressure, since it is the same for all the gases. The bands observed can be accounted for on the theory of intensity distribution in a band system which is applied to the first positive bands. A. J. Mee.

Raman effect in quartz. M. Czerny (Z. Physik, 1929, **53**, 317—325).—A more detailed account of work already published (this vol., 240).

Secondary radiations in light diffused by quartz. J. Cabannes (Compt. rend., 1929, **188**, 249—250).—An attempt is made to verify the author's hypothesis that the action of light on a molecule depends on its orientation, by the study of the Daure diffusion spectra and the polarisation of the secondary radiations produced by quartz crystals in which the molecules are oriented in a small number of fixed directions. The Daure spectra always comprise the same radiations, whatever the orientation of the crystal. J. Grant.

Theory of light scattering in liquids. C. V. Raman (Phil. Mag., 1929, [vii], **7**, 160—161).—A reply to comments by Rocard on the work of Raman and Krishnan (A., 1928, 461).

A. E. Mitchell.

Raman spectra of scattered radiation. W. W. Coblentz (Phil. Mag., 1929, [vii], **7**, 203—204).—The calculated infra-red absorption bands of calcite and benzene (Wood, A., 1928, 1306) are shown to be in very good agreement with the observations of Coblentz and Nyswander and to afford a striking confirmation of Raman's discovery of the relation between infra-red bands and the frequency change of the scattered light. A. E. Mitchell.

Raman lines from gaseous hydrogen chloride. R. W. Wood (Nature, 1929, **123**, 166).—The modified lines of gaseous hydrogen chloride at atmospheric pressure corresponding with the vibration-rotation absorption band at 3·46 μ have been observed.

A. A. Eldridge.

Raman effect with liquid oxygen and with liquid nitrogen. J. C. McLennan and J. H. McLeod (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 413—416).—An attempt was made to see if the Raman effect could be obtained with liquid oxygen or nitrogen. At least six Raman lines were found. The primary vibration frequencies appear to be involved in the production of four of these lines, the other two being produced by absorptions corresponding with the frequencies of the second vibration states of the elements. These would appear to be the first examples of homopolar molecules having the power to absorb light having frequencies equal to those of fundamental vibrations of their nuclei. A. J. Mee.

Raman effect with liquid oxygen, nitrogen, and hydrogen. J. C. McLennan and J. H. McLeod (Nature, 1929, **123**, 160).—The spectrum of the scattered light contained the following lines not included in that of the irradiating light from a mercury arc: liquid oxygen, 4317·7, 4674·3, 5026·5 Å.; liquid nitrogen, 4468·9, 4849·3, 4980·3 Å.; liquid hydrogen, 4426·6, 4473·1, 4863·5 Å. Mean vibration frequencies involved in the Raman effect with oxygen and nitrogen, respectively, are 1551·5 cm.$^{-1}$ and 2328·5 cm.$^{-1}$, suggesting that primary vibration frequencies are involved in the production of four of the lines, the other two lines being produced by absorptions corresponding with the frequencies of the second vibration states of the two elements. The Raman effects with hydrogen are due to $0 \longrightarrow 2$ and $1 \longrightarrow 3$ rotational transitions and a $0 \longrightarrow 1$ vibrational transition for hydrogen molecules in the zero vibrational state. Thus it is shown that Raman effects can be obtained with homopolar molecules, that part of the energy of light quanta can be taken up directly as rotational energy, the balances appearing as quanta degraded in frequency, and that two-quantum rotational transitions can be demonstrated in connexion with light-scattering phenomena. In accord with Dennison's view, liquid hydrogen contains some molecules in the zero vibrational and zero rotational states, and others in the zero vibrational and first rotational states, the proportion being about 1 : 2.

A. A. Eldridge.

Raman and infra-red spectra of carbon dioxide. C. R. Bailey (Nature, 1929, **123**, 410).—A study of the concordance observed by Rasetti (this vol., 241) shows that there is a close connexion between the deduced values and the observed spectrum. The wave-number differences between the band centres in the double doublets and those in the "undoubled" bands are of the same order as the deduced frequencies, whilst with the double doublets themselves the agreement is exact; moreover, the frequency difference between the undoubled bands is a simple fraction of one of these frequencies. These facts are considered in relation to the results of Bailey and Lih (A., 1928, 687) for the emission spectrum, which can be represented in a simple manner.

A. A. Eldridge.

Incoherent scattering. R. M. Langer (Nature, 1929, **123**, 345).—The observations of Raman and Krishnan and others are accounted for much more successfully by the correspondence principle of Kramer and Heisenberg and by Schrödinger's wave mechanics than by Smekal's theory. A. A. Eldridge.

Apparent Mie effect and its possible rôle in atmospheric optics. G. I. Pokrovski (Z. Physik, 1929, **53**, 67—71).—The interference of light scattered from various centres is discussed. It is shown that under fixed conditions the greater portion of the light is only slightly deviated from the initial direction. The theoretical deductions are confirmed by comparison with the atmospheric light scattering and other observations. J. W. Smith.

Influence of temperature on the absorption [of light] by tourmaline. P. Le Roux (J. Phys. Radium, 1928, [vii], 9, 365—376; cf. A., 1928, 934).—By means of the apparatus previously described, measurements have been made on the absorption by tourmaline of the mercury arc lines 5790—3655 Å. at various temperatures. Two sections of tourmaline were cut from the same crystal, parallel and perpendicular, respectively, to the crystal axis. From the ordinary temperature up to about 250° the absorption is a linear function of the temperature and reversible. The slope of the straight lines obtained in this way decreases with increase in the wave-length, and depends also on the directions of vibration and propagation of the light. Measurements carried out up to 658° show that above a certain temperature (between 250° and 327°) the absorption ceases to be reversible. For these higher temperatures the tourmaline acquires a definite state depending on the temperature to which it has been heated. O. J. Walker.

Simultaneous energy transfers by collision and radiation. O. Oldenberg (Z. Physik, 1928, **51**, 605—612).—Arguments are advanced to show that evidence for the transfer of energy to a chemically inactive molecule by simultaneous collision and absorption of radiation in an atmosphere of excited molecules might be sought in the fluorescence of mercury vapour when mixed with helium. Experiment shows that under such conditions a continuum exists in the neighbourhood of the resonance line 2537 Å. extending in the direction of lower frequencies. This is regarded as affording the necessary evidence. R. W. Lunt.

Dissociation of hydrogen by collisions of the second kind. J. Kaplan (Nature, 1929, **123**, 162—163).—As an alternative interpretation of Cario and Franck's experiment on the dissociation of molecular hydrogen in a mixture of hydrogen and excited mercury atoms in the 2^3P_1 state, it is suggested that the result of a collision between an excited mercury atom and a normal hydrogen molecule is the excitation of the molecule from the 1^1S to the new 1^3S level, an unstable state, followed by immediate dissociation. The probability of such a transition is considered. A. A. Eldridge.

Change that a gaseous molecule may undergo between successive collisions. R. D. Kleeman (Phil. Mag., 1929, [vii], 7, 53—63).—It is shown that the function ξ in the equation $pv=\xi MRT$ (cf. A., 1928, 955) decreases as v increases. This is interpreted as signifying a decrease in the average velocity of translation of the molecules with an increase of v. It is concluded that the velocity of a molecule gradually decreases after a collision and that the subsequent collision increases it again to its initial value, whence the average velocity of the molecules will decrease with increase of volume. A. E. Mitchell.

Ionisation by slow electron impact of ammonia and hydrogen sulphide. J. H. Bartlett, jun. (Physical Rev., 1929, [ii], **33**, 169—174).—Positive-ray analysis showed the occurrence, in the case of ammonia, of three principal types of ion at $m/e=15$, 16, and 17, respectively, and interpreted as having the compositions $(NH)^+$, $(NH_2)^+$, and $(NH_3)^+$, with ionisation potentials of 11·2±1·5, 12·0±1·5, and 11·2±1·5 volts, respectively. In the case of hydrogen sulphide, three principal types of ions occurred at $m/e=32$, 33, and 34, and are interpreted as having the compositions $(S)^+$, $(HS)^+$, and $(H_2S)^+$, with ionisation potentials of approximately 10·4, 16·9, and 15·8 volts, respectively. The mechanism of ionisation is discussed for the two substances.

N. M. Bligh.

Dielectric anisotropy of liquid crystals in a magnetic field. M. Jezevski (Z. Physik, 1928,

52, 268—274).—Using an improved form of resonance method the dielectric constants of *p*-azoxyanisole and *p*-azoxyphenetole in the nematic phase have been determined with the substances in a magnetic field using condensers of different forms and different plate spacings. It was shown that a magnetic field parallel to the electric lines of force in the condenser caused a decrease in the dielectric constant and a magnetic field at right angles to them an increase. The negative results previously obtained with a perpendicular field are explained on the grounds that with the condenser plates close together the orientation action of the walls was considerable, whilst with more widely spaced plates the edge effect was quite large. J. W. Smith.

Dielectric properties of liquid crystals in simultaneous magnetic and electrostatic fields. M. Jezevski (Z. Physik, 1929, **52**, 878—881; cf. A., 1927, 92; this vol., 12).—The influence of the simultaneous application of magnetic and electrostatic fields on the capacity of a condenser filled with *p*-azoxyanisole and *p*-azoxyphenetole has been investigated, both with the fields parallel and at right angles. An electrostatic field of less than about 400 volts per cm. caused no appreciable change in the capacity of a condenser in a magnetic field of 4000 gauss, although such an electrostatic field alone produced a considerable diminution in the capacity. A stronger electrostatic field parallel to the magnetic field caused an increase in the dielectric constant, whereas when the fields were at right angles a diminution occurred. J. W. Smith.

Change of the dielectric constants of air and carbon dioxide with wave-length in the range 600—60 metres. (Frl.) M. Forró (Z. Physik, 1928, **51**, 374—377).—Both air and carbon dioxide show a slight increase in dielectric constant with increasing frequency over the wave-length range 600—60 metres. J. W. Smith.

Variation of dielectric constants of gases and vapours with temperature. II. Ethyl ether, methyl ether, ethylene oxide, and acetone. H. A. Stuart (Z. Physik, 1928, **51**, 490—510).—A description is given of the apparatus with which the temperature variation of the dielectric constant of methyl and ethyl ethers, ethylene oxide, and acetone in the temperature range 20—180° was measured in the gaseous state. The electrical measurements were carried out with the apparatus previously described (A., 1928, 460). A Spindler–Hoger standard air condenser calibrated at the P.T.R. was used as a capacity standard. Accurate values of the vapour densities of the compounds have been determined. The electric moments are: ethyl ether $1{\cdot}14\times10^{-18}$, methyl ether $1{\cdot}29\times10^{-18}$, ethylene oxide $1{\cdot}88\times10^{-18}$, acetone $2{\cdot}84\times10^{-18}$. The electric moment of the water molecule is calculated from the results of Zahn as $1{\cdot}79\times10^{-18}$. The results are compared with those of other authors and the molecular models of methyl and ethyl ethers discussed, together with the connexion between the electrical distribution of the charge of the molecules, association, and the van der Waals constant. G. E. Wentworth.

Dielectric constants of liquid hydrogen fluoride. K. Fredenhagen and J. Dahmlos (Z. anorg. Chem., 1929, **178**, 272—274).—The dielectric constant of hydrogen fluoride decreases from 174·8 at −73° to 83·6 at 0°. Hydrogen fluoride therefore belongs, like water and hydrogen cyanide, to the group of solvents which have an abnormally high dielectric constant. A. R. Powell.

Dielectric constants and absorption indices of several alcohols for short electric waves. S. Mizushima (Proc. Imp. Acad. Tokyo, 1929, **5**, 15—16).—Dielectric constants and absorption indices of methyl, propyl, *iso*butyl, and amyl alcohols are given together with those of glycerol for a wave-length of about 60 cm. over a range of temperatures. Comparison with earlier measurements (A., 1928, 934) indicates the existence of anomalous dispersion. Calculation of the molecular radii from the Debye theory gives the following values: methyl $1{\cdot}7\times10^{-8}$, propyl $2{\cdot}3\times10^{-8}$, *iso*butyl $2{\cdot}3\times10^{-8}$, and amyl alcohol $2{\cdot}5\times10^{-8}$ cm. These values accord well with those obtained from critical data. F. J. Wilkins.

Dielectric constants of some organic solvents. Y. Matsuike (Proc. Imp. Acad. Tokyo, 1929, **5**, 29—31).—The dielectric constants of benzene, toluene, carbon disulphide, carbon tetrachloride, ethyl ether, and chloroform have been measured at various temperatures between their b. p. and f. p. with a probable error of about 0·2%. F. J. Wilkins.

Electric moment of primary alcohols. P. N. Ghosh (Nature, 1929, **123**, 413—414).—Since the primary alcohols have practically the same dipole moment, it is inferred that the dipole moment is due to the polarisation of the oxygen atom by the hydrogen atom on one hand and by the carbon atom on the other. Hence the binding forces acting on the carbon atom reacting with the oxygen are the same whether the chain is long or short, open or closed. *iso*Alcohols give differing values. A. A. Eldridge.

Refraction of beams of molecules. I. I. Rabi (Nature, 1929, **123**, 163—164).—The refraction of beams of molecules in magnetic or electric fields is considered in analogy to optical refraction. A. A. Eldridge.

Refractivity of gaseous compounds. G. W. Brindley (Nature, 1929, **123**, 165).—If $(\mu-1)_R$ is the refractivity of the substance R in the gaseous state, under normal conditions as defined by Cuthbertson, where μ is the refractive index, then $(\mu-1)_{HCl}=\frac{4}{7}(\mu-1)_{Cl_2}$, $(\mu-1)_{HBr}=\frac{13}{25}(\mu-1)_{Br_2}$, $(\mu-1)_{CCl_4}=\frac{16}{7}(\mu-1)_{Cl_2}=4(\mu-1)_{HCl}$, $(\mu-1)_{CS_2}=\frac{4}{3}(\mu-1)_{S_2}$. The fractions are closely related to the number of loosely bound electrons. In general, such simple relations do not appear to hold. A. A. Eldridge.

Stability and molecular volume of organic groups in molecular compounds. E. Hertel [with E. Rissel and F. Riedel] (Z. anorg. Chem., 1929, **178**, 202—212).—Freshly-precipitated nickel cyanide reacts with ammonia, primary aliphatic amines, dimethylamine, and trimethylamine, yielding co-ordination complexes containing 1 mol. of ammonia or amine. Anhydrous nickel cyanide obtained by heating any of the above compounds to constant weight reacts with the evolution of heat with the anhydrous amines mentioned above and with aniline to form complexes containing 2 mols. of the amine. The mol. vol. of the primary amines in the complexes containing 1 mol. of amine is always greater than its zero volume (cf. Lorenz, A., 1916, ii, 311), the difference increasing with the length of the carbon chain; the zero volume increases by about 15 c.c. for every methylene group in the chain. The logarithm of the vapour pressure of these compounds is directly proportional to the reciprocal of the temperature and the stability of the primary amine complexes decreases with increasing mol. wt. of the amine. On the other hand, the benzylamine compound, $Ni(CN)_2,CH_2Ph\cdot NH_2$, is less stable than the ω-phenylethylamine compound, $Ni(CN)_2,CH_2Ph\cdot CH_2\cdot NH_2$. This may be explained on the assumption that in the latter case the nickel atom is co-ordinatively quadrivalent, the third co-ordination valency being attached to the amino-group and the fourth to the phenyl nucleus. The correctness of this view is borne out by the fact that a second group, *e.g.*, H_2O or NMe_3, may be introduced easily into the benzylamine compound, whereas this cannot be done in the case of the ω-phenylethylamine compound. A. R. Powell.

Molecular diameters in gas reactions. R. C. Tolman, D. M. Yost, and R. G. Dickinson (Science, 1928, 67, 241).—Previous conclusions (A., 1927, 604) are not greatly affected by the discovery of a numerical error. A. A. Eldridge.

Derivation of grating forces, grating energies, ionic dimensions, and compressibilities of simple salts by wave mechanics. H. Brück (Z. Physik, 1928, **51**, 707—727).—Mathematical. R. W. Lunt.

Liquid drops on the same liquid surface. J. Seth, C. Anand, and L. D. Mahajan (Phil. Mag., 1929, [vii], 7, 247—253).—Drops of liquid on the surface of the same liquid are divided into two classes. Primary drops arise from the introduction of liquid from an external source and represent the portions which do not mix immediately with the main body of the liquid. Secondary drops are those which arise from the splashing of liquid from the main body. Various methods for the production of such drops are described. The formation of primary drops appears to be easiest with a liquid having a surface tension 20—80 dynes/cm., a viscosity up to 0·25 c.g.s. unit, and a density about unity. For the production of secondary drops best results are obtained with different liquids, depending on the method of production. The best primary drop formation with a phenol solution was obtained with a concentration of 30% and with a Boys soap solution at a concentration of 15%. Both these solutions exhibit a sudden small rise in surface tension at the concentrations given. A. E. Mitchell.

Superficial properties of mercury. E. Perucca (Phil. Mag., 1929, [vii], 7, 418—419).—Previous work by the author (Atti Accad. Sci. Torino, 1921, **57**, 81, etc.) offered experimental support of the deductions of Oliphant and of Bircumshaw that in the surface of liquid mercury there is a superficial molecular or atomic orientation. A. E. Mitchell.

Surface tension of liquid sulphur dioxide. V. M. Stowe (J. Amer. Chem. Soc., 1929, **51**, 410—415).—The surface tensions (capillary-tube method) and densities of liquid sulphur dioxide are recorded for the range —79° to 50°. Between —20° and 50° the equation γ (dynes/cm.)$=0{\cdot}061534(157{\cdot}5-t)^{1{\cdot}2}$ holds to within 5%; the results indicate that the liquid is practically unassociated over this temperature range. Sulphur dioxide comes between chloroform and benzene in Hildebrand's solubility table. S. K. Tweedy.

Surface tension of insulating liquids under the influence of an electric field. M. J. Bickerman (J. Phys. Radium, 1928, [vii], 9, 386—389).—Theoretical. It has been calculated that the lowering of the surface tension of a liquid, produced by an electric field normal to its surface, is given by $-\Delta\gamma=\delta E^2/8\pi\varepsilon$, where $\Delta\gamma$ is the change in surface tension, δ the thickness of the surface layer, E the field strength (measured in the air), and ε the specific inductive capacity of the liquid. It is pointed out that even for high values of E, $\Delta\gamma$ will be very small. It is suggested that those authors who have failed to detect any alteration in the surface tension due to the influence of an electric field were not using sufficiently delicate methods. J. L. Buchan.

Interpretation of *X*-ray crystal photographs. I. Use of photographic grids. W. H. George (Phil. Mag., 1929, [vii], 7, 373—384).—The photographic plate or film is supported in the *X*-ray camera entirely by geometric constraints. A printing frame similarly fitted with geometric constraints is employed, with a light exposure, to obtain on the *X*-ray photograph an image of some network suitable for the interpretation of the particular type of *X*-ray photograph. A single calibration photograph serves to fix accurately the geometric constraints of the printing frame and any subsequent *X*-ray photograph contains both the photograph required and an accurately alined reference grid. Various applications to *X*-ray and other types of research are discussed. A. E. Mitchell.

Adsorption and crystal form. C. H. Saylor (Fifth Colloid Symposium Monograph, 1927, 49—54).—A general discussion of the effect on the crystal form of substances which crystallise in more than one modification or habit produced by adsorption of ions on certain faces or habits. Chemical Abstracts.

Spiral markings on carborundum crystals. A. W. C. Menzies and C. A. Sloat (Nature, 1929, **123**, 348—349).—A photograph and a description of spiral markings on the smooth hexagonal, basal pinakoid, surfaces of carborundum crystals are given. A. A. Eldridge.

Isomorphous mixtures in the calcite group. G. Bilibin (Mem. Soc. Russe Min., 1927, **56**, 3—36; Chem. Zentr., 1928, ii, 975).

Atomic spacing in gypsum crystals. J. Nagy (Z. Physik, 1928, **51**, 410—412).—The distances between corresponding planes in gypsum crystals from different sources are not quite constant, the greatest differences observed being about 2·5 per mille. J. W. Smith.

Systematic arrangement of neptunite and babingtonite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1928, **A**, 274—281; Chem. Zentr., 1928, ii, 1198).—Neptunite has *a* 16·54, *b* 12·64, *c* 10·04 Å., $\beta=115°$ 38′, with 8 mols. in the unit cell; the space-group may be C_{2h}^3 or C_{2h}^6; the formula $FeNa_2Si_2O_6,Si_2TiO_6$ is suggested. Babingtonite, the formula of which is preferably written $CaFeSi_2O_6,SiO_2$, has *a* 7·54, *b* 12·43, *c* 6·73 Å., α 93° 48′, β 86° 9′, γ 112° 22′; the axial ratio is computed to be $a:b:c=$ 0·607 : 1 : 0·541. A. A. ELDRIDGE.

Crystal structure of solid mercury. M. WOLF (Z. Physik, 1929, **53**, 72—79).—A thermostatic *X*-ray spectrograph is described, by means of which investigations of crystal structure may be carried out at various temperatures. With this apparatus the crystal structure of mercury at −80° has been investigated and a simple rhombohedral structure found, in agreement with the observations of McKeehan and Cioffi (A., 1923, ii, 864) and Terrey and Wright (this vol., 16). It was found that the preparation obtained from small drops of mercury (mean diameter 10 μ) persisted in a supercooled state even at −80° and was very difficult to crystallise out. J. W. SMITH.

Physical purity and powder-röntgenogram. N. H. KOLKMEIJER (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1028—1029).—Polemical against Levi (cf. A., 1928, 1079) concerning the crystallographic identity of the two forms of mercuric oxide. N. M. BLIGH.

***X*-Ray levels of the rare earths, and the deviations from Moseley's laws.** G. PICCARDI (Atti R. Accad. Lincei, 1928, [vi], 8, 414—418).—The regularities in the *X*-ray levels of the elements of the rare earths have been made the basis of a comparison of the corresponding levels of other elements of the periodic system. Using the values of the *X*-ray levels of the rare earths as the basis of the calculation of the constants in Moseley's law, the deviations of the levels for other atoms from the values obtained from this law have been plotted against atomic number. The irregular curves so obtained present certain regularities on analysis. The deviations for elements before the rare earths decrease (from positive to negative) on passing from the *K* level through the levels L_1, L_2, L_3, etc., to the *O* level. For elements after the rare earths the corresponding deviations are all positive, but do not exhibit the same regularities. Within a given set of *X*-ray levels a certain regularity is shown: for example, the deviations for the *L* series increase in the order L_3, L_2, L_1. But whereas the curves for different sets of *X*-ray levels for the earlier elements are separated, for the heavier elements considerable overlapping occurs among the curves for the different series. The deviations for all levels are of the same order of magnitude, reaching maximum values of about 4 in the case of the lighter elements, when the levels are expressed as $\sqrt{\nu/R}$, where ν is the frequency and *R* the Rydberg constant. F. G. TRYHORN.

Influence of *X*-rays on the structure of bismuth and tellurium. III. E. ADINOLFI (Atti R. Accad. Lincei, 1928, [vi], 8, 381—388).—The specific heat of bismuth is increased by about 14% and that of tellurium by about 8% by the exposure of these metals to *X*-rays. This result is attributed to a change of structure of the metals. Indications of this change were obtained in the case of bismuth by measuring the changes of resistance during solidification of spirals of bismuth before and after exposure to *X*-rays. F. G. TRYHORN.

Crystal structure of nickel. L. MAZZA and A. G. NASINI (Phil. Mag., 1929, [vii], 7, 301—311).—*X*-Ray examination of nickel produced by electrolytic deposition, separation from the carbonyl, and by reduction of the oxide has shown the metal to be crystallised in face-centred cubes, the mean value for the edge of the elementary cell being 3·514±0·002 Å., in close agreement with those of Wever (B., 1922, 359A), McKeehan (Physical Rev., 1923, **21**, 402), and of Lange (A., 1923, ii, 402). No confirmation of Hull's observation (Physical Rev., 1919, **14**, 540) of the existence of body-centred cubes was obtained. Annealed cold-drawn nickel shows no recrystallisation up to 940°. Characteristic recrystallisation structures are obtained by annealing at 1000° and above. Prolonged annealing at 1200° gives a recrystallisation into irregularly oriented coarse grains. Quenching produces no changes in the nickel lattice. A. E. MITCHELL.

Direct determination of Thomson coefficients in single-crystal zinc rods. L. A. WARE (Proc. Iowa Acad. Sci., 1927, **34**, 282).

CHEMICAL ABSTRACTS.

Crystal structure of rhenium. V. M. GOLDSCHMIDT (Naturwiss., 1929, **17**, 134—135).—Using the Debye–Scherrer method it was found that rhenium has a hexagonal close-packed structure, $a=2·752\pm0·001$, $c=4·448\pm0·002$ Å. The crystalline structure of rhenium resembles that of osmium, whilst tungsten, the element immediately preceding rhenium in the periodic table, has a body-centred cubic structure. The atomic radius of rhenium is calculated from the mean distance between the atoms in the crystal. It lies between those of tungsten and osmium, being 1·371 Å. From the lattice constants and the at. wt., the density of rhenium can be calculated. The specimen used, which contained 0·3% of molybdenum, gave 21·33. After making a small correction for the molybdenum the density of the pure element is found to be 21·40±0·06. This lies between the values for tungsten and osmium, and is in agreement with the value obtained by other methods. A. J. MEE.

Determination by *X*-rays of density and axial ratio of hexagonal silver iodide. N. H. KOLKMEIJER, W. J. D. VAN DOBBENBURGH, and H. A. BOEKENOOGEN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1014—1027).—*X*-Ray investigations were made of a specimen of silver iodide of *d* 5·68, supposed to be physically and chemically pure. Powder photographs were made of this specimen, and also of one of *d* 5·49, and evidence of cubic structure for the former and hexagonal structure for the latter specimen was obtained. By spectrographic means it is concluded that this evidence as to structure is correct, and the axial ratio is determined as 1·633(4). N. M. BLIGH.

Reflexion of soft X-rays. S. D. Gehman (Physical Rev., 1929, [ii], **33**, 141—144).—The relation between the wave-length of soft X-rays and the reflecting power of a metal mirror was investigated; the latter was measured by a photo-electric method, as a function of the voltage for a given angle of incidence and as a function of the angle for a given voltage. Mirrors of aluminium, carbon, and platinum were employed. The reflecting power–plate voltage curves for the light elements aluminium and carbon show a maximum related to a critical potential.

N. M. Bligh.

Soft X-rays from crystal faces. O. W. Richardson and U. Andrewes (Nature, 1929, **123**, 344).—An attempt to extend earlier experiments (A., 1928, 692) to diamond failed on account of the immeasurably high resistance of the material. With graphite, however, between 70 and 320 volts 17 discontinuities have been observed, each agreeing with a value, or with the mean of two values a few volts apart, previously found with carbon. Fifteen discontinuities observed with the carbon target were absent with the graphite target, *i.e.*, the number of discontinuities from a single crystal surface is smaller than from a polycrystalline surface. A. A. Eldridge.

Soft X-rays from a single-nickel crystal. S. R. Rao (Nature, 1929, **123**, 344—345).—The results (cf. preceding abstract) suggest that if an ideal crystal surface were employed inflexions would appear at 63·8, 72·2, 106·2, and 116·0 volts. The former two values can be associated with transitions from the $M_{\text{II,III}}$ level in the nickel atom, and the latter two with transitions from the M_{I} level. Surface alteration of the non-crystalline metallic target on electronic bombardment may account for the large number of inflexions which have been reported.

A. A. Eldridge.

X-Ray examination of some salts of the fatty acids. S. H. Piper (J.C.S., 1929, 234—239).—The spacing between the crystal planes in the potassium salts of the fatty acids from formic up to lignoceric acid has been measured. Since salts of long-chain compounds of this type crystallise with these planes separated by the lengths of two molecules placed end to end with like groups in contact, the spacing measured may be regarded as twice the effective length of the molecule. The spacing increases linearly with increase in the number of carbon atoms for the normal potassium salts. A similar linear increase in spacing, but with a lower rate of increase, is shown by the potassium hydrogen salts of these acids. The chain in this type of salt cannot be accounted for by a normal tetrahedral angle of 109° 28′ between the lines joining the centres of successive carbon atoms. A minimum angle of 111° 46′ is required.

F. G. Tryhorn.

X-Ray contributions to the problem of polymerisation. G. L. Clark (Ind. Eng. Chem., 1929, **21**, 128—133).—The X-ray method of investigating crystal structure is discussed and its application in the study of polymerised substances such as rubber, cellulose, proteins, and resins is explained in outline. The observation that the unit cell of these substances is very much smaller than would be anticipated on physico-chemical grounds and contains only a few simple chemical molecules is discussed.

H. Ingleson.

Deformation of fibrous materials. R. O. Herzog and W. Jancke (Z. Physik, 1929, **52**, 755—758).—By taking X-ray diagrams both parallel and at right angles to the direction of stress, it has been shown that both mercerised cellulose and natural silk on rolling or pressing yield a structure of the anisotropic class IV. J. W. Smith.

Supermolecular state of polymerised substances in relation to thin films and interfaces. S. E. Sheppard, A. H. Nietz, and R. L. Keenan (Ind. Eng. Chem., 1929, **21**, 126—127).—A discussion of the theories of the molecular constitution of rubber, cellulose, and proteins advanced by Hess and Pringsheim and by Staudinger. H. Ingleson.

Separation of the Faraday effect into two phenomena of different origin. Diamagnetic and paramagnetic rotatory polarisation. Law of magnetisation of a crystal. Bohr's magneton. J. Becquerel and W. J. de Haas (J. Phys. Radium, 1928, [vii], **9**, 346—356, and Z. Physik, 1928, **52**, 678—694).—In order to obtain evidence for the view that the large magnetic rotatory power of certain minerals which contain rare-earth elements is of paramagnetic origin, the variation of the rotatory power of tysonite with the intensity of the magnetic field has been investigated. At very low temperatures it is to be expected that the rotation will cease to be proportional to the field. Experiments made at the low temperatures obtainable by means of liquid helium show that this is the case. The following hyperbolic tangent relation is found to hold between the paramagnetic rotation ρ and the field H: $\rho=\rho_\infty\tanh(\Sigma_\infty H/RT)$. Σ_∞ is the saturation magnetisation per g.-mol. and has almost exactly the value of the Bohr magneton. This expression is derived from the theoretical views of Lenz and of Ehrenfest concerning the magnetisation of a crystal along its principal axis, on the assumption that the magnetic rotation is proportional to the magnetising effect producing it, which appears probable. The existence of paramagnetic rotatory polarisation is therefore proved. O. J. Walker.

Piezo-electric amorphous and crystalline substances in an electric field. A. V. Schubnikov and B. K. Brunovski (Bull. Acad. Sci. U.R.S.S., 1928, 367—374).—Experimental results are given which indicate that every dielectric, when placed in an electric field, owing to orientation of its molecules or other structural units, becomes more or less markedly piezo-electric. When such dielectric is subjected to shock, it assumes a state of vibration, that is, of periodic compression and expansion, the result being the establishment of an internal subsidiary electric field, which changes its direction during the vibration and so alternately strengthens and weakens the original electric field. T. H. Pope.

High-frequency hysteresis loss in steels. W. Neumann (Z. Physik, 1928, **51**, 355—373).—Data are given for the hysteresis loss and remanence of two varieties of Swedish bar steel and of an iron alloy containing 50% Ni at 500, 1500, and 2550 cycles per sec. R. W. Lunt.

Electrical conductivity in relation with mechanical stress in rock salt. Z. Gyulai and D. Hartly (Z. Physik, 1928, **51**, 378—387).—The conductivity of rock salt suddenly compressed between one pair of crystal faces increases and then, the compression remaining constant, decreases to the initial value in approximately 20 min. The crystal is then in a hardened state, and considerable increase in mechanical stress is required to produce a further increase in conductivity. Crystals of various thickness were examined in the stress range 20—200 kg./cm.^{2} R. W. Lunt.

Hall effect and other properties of the copper–antimony series of alloys. E. Stephens and E. J. Evans (Phil. Mag., 1929, [vii], 7, 161—176).—The temperature coefficient of resistance, thermo-electric power, Hall effect, specific heat, and density of fully annealed copper–antimony alloys have been measured. Singular points corresponding with both Cu_2Sb and Cu_3Sb were obtained in each of the curves showing the relation between all these constants and the concentration of one metal in the alloy. No evidence of the formation of Cu_2Sb and Cu_3Sb was obtained from the change of the temperature coefficient of the resistance with the antimony concentration. The electrical properties of Cu_3Sb were strongly modified by annealing, whilst those of Cu_2Sb remained practically unchanged. A. E. Mitchell.

Magnetic susceptibilities of some amalgams and binary alloys. W. G. Davies and E. S. Keeping (Phil. Mag., 1929, [vii], 7, 145—153).—The relative magnetic susceptibilities of dilute amalgams of gold, tin, indium, and gallium with respect to that of mercury have been determined. The diamagnetic susceptibility of the amalgams increases as the concentration of the solute metal increases. The atomic effect of the dissolved metal on the susceptibility of mercury is greatest in the case of indium. Similar measurements have been made with copper–magnesium and copper–antimony alloys. In the first series the susceptibility–composition curve shows maxima corresponding with eutectics and minima corresponding with compounds indicated by the equilibrium diagram. In the second series of alloys annealing increases the susceptibility, particularly over the region 20—60% Cu. Maxima on the susceptibility–composition curve again correspond with eutectics, but the only compound definitely indicated for the unannealed alloy is Cu_5Sb_2 and for the annealed alloy Cu_2Sb corresponding with the change of phase to be expected, from the equilibrium diagram, on annealing. A. E. Mitchell.

Conductivity and cold-working. M. Masima and G. Sachs (Z. Physik, 1928, **51**, 321—327).—Experiments are described dealing with the dependence of the electrical resistance of brass on the extension of the crystals, the degree of hardening of the metal, annealing, and temperature. Curves are given showing the relation between the resistance, the tensile strength, and compressibility. The temperature coefficient of the conductivity of the metal is shown to be independent of mechanical strains. D. W. Bandey.

Magnetostriction. L. W. McKeehan (Z. Physik, 1928, **52**, 752—754).—Polemical against Schulze (A., 1928, 1314). G. E. Wentworth.

Initial conductivity of gypsum and rock salt. N. A. Salessky (Z. Physik, 1928, **52**, 695—707).—The initial conductivities of gypsum and rock salt were observed at intervals of 0·01—0·06 sec. after the application of potential, and the impossibility of extrapolation was demonstrated. Ohm's law is obeyed by both substances. The applicability of the superposition principle, and the errors due to a previous passage of current, were confirmed. The temperature variation of the initial conductivity of gypsum is probably represented by an exponential function; that of rock salt, however, depends on the time period at which the measurements were made. G. E. Wentworth.

Initial current in quartz. A. D. Goldhammer (Z. Physik, 1928, **52**, 708—725).—A photographic method is used for the study of the initial current in two types of quartz. The dependence on time of the initial current in the first 4 to 17×10^{-2} sec. is given by $i = at^{-n}$, where the letters have their usual significance. The potential–current graph is not a straight line; it changes its sign with alteration in the time period. The superposition principle is inapplicable, the reason being that passage of current diminishes the conductivity in the direction of the current and increases it in the opposite direction. If the crystal is earthed for some time the unipolarity changes sign. G. E. Wentworth.

Recrystallisation of aluminium. II. A. E. van Arkel and M. G. van Bruggen (Z. Physik, 1928, **51**, 520—533).—Strong deformation of a crystalline body such as aluminium produces very small crystals which act as a nucleus for recrystallisation. These small nuclei are formed by the stresses acting within the lattice. The second crystallisation is not only proportional to the amount of cold working but, in contradistinction to the idea of recrystallisation by cold turning, is largely dependent on the initial state of the material. The surface recrystallisation of pure aluminium is much greater than in technical aluminium. Numerous etchings are shown and the results are compared with those of Smithells in the recrystallisation of pure tungsten. G. E. Wentworth.

Recrystallisation of single aluminium crystals. I. The orientation of crystals produced by cold turning, the deformation being small. W. G. Burgers and J. C. M. Basart (Z. Physik, 1928, **51**, 545—556).—An attempt is made to elucidate the problem of the orientation of crystals produced by the cold turning of aluminium when the deformation is relatively small (10—15% extension). These crystals appear to be connected on the average with the position of the mother crystal, but they are widely scattered, although the mother crystal must exert some influence. Experimental results show that the direction of deformation has a small influence, but the scattering is so large as to make any method of estimation difficult. G. E. Wentworth.

Measurements of ultrasonic velocities in liquids. R. W. Boyle, J. F. Lehmann, and S. C.

MORGAN (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 371—378).—The determination of the velocity of ultrasonic waves in liquids by modifications of the method of stationary waves is described. Methods are also given for use when a moderate quantity of liquid is available. The change of velocity in sodium chloride solution with small changes of concentration at a constant temperature of 17° was investigated. The velocity was found to increase slightly as the concentration is increased. Experiments were also carried out to measure the change in velocity with change in temperature from 0° to 20° in water and in sodium chloride solution. In both cases the velocity increases with rise of temperature.

A. J. MEE.

Electromotive potential and electrokinetic potential of graphite [and other elements]. N. THON (Compt. rend., 1929, **188**, 253—254).—A relation between the electromotive (ϕ) and electrokinetic (ζ) potentials analogous to that found for gold (A., 1928, 953) has been established for graphite, but in this case ϕ becomes more positive with an increase in the concentration of the electrolyte, whilst ζ, which is negative, decreases in value. This explains the action of graphite as a "borrowing electrode" and its electromotive behaviour as the metal of the ions in the solution. Platinum, silver, mercury, and copper behave similarly to gold.

J. GRANT.

Theory of electrical rectification. R. DE L. KRONIG (Nature, 1929, **123**, 314).

Superconductors. W. J. DE HAAS (Nature, 1929, **123**, 130—131).—Combinations of non-superconducting with superconducting metals (copper, silver, or antimony with tin; bismuth with thallium) have been studied. Combinations of antimony (but not copper) with tin and of bismuth with thallium become superconductors. Although neither gold nor bismuth is a superconductor at 1·5° Abs., their eutectic alloy is a superconductor. A. A. ELDRIDGE.

Measurement of the thermo-electric Thomson effect down to the temperature of liquid hydrogen. G. BORELIUS, W. H. KEESOM, and C. H. JOHANSSON (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1046—1058).—In view of its bearing on the electron theory of metals the temperature dependence of the Thomson effect below the temperature of liquid air was investigated, using wires of copper and silver alloyed with small quantities of gold, and also pure copper wire. The alloys were used for the lowest temperatures to minimise errors due to the variation of heat conductivity of pure metals with temperature; steps were also taken to avoid errors due to the Peltier effect. The specific heat-conductivity was measured and plotted against temperature. The measurements and calculations of the Thomson effect for a number of temperatures are tabulated and plotted. The thermo-electromotive forces of couples formed by the wires investigated and also with lead were measured for various temperatures, tabulated, and thence calculated per degree. N. M. BLIGH.

Theory of Heusler alloys. O. VON AUWERS and H. WEINNOLDT (Z. Physik, 1928, **51**, 754—756).—Polemical. R. W. LUNT.

Theory of Heusler alloys. A. KUSSMAN and B. SCHARNOW (Z. Physik, 1928, **51**, 757—758).—Polemical. R. W. LUNT.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. CAU (Compt. rend., 1929, **188**, 246—249).—The formulæ hitherto obtained by the author (this vol., 251) are valid only to a first approximation. Exact formulæ are deduced representing the effect on a rectilinear vibration of simultaneous rectilinear birefringence and dichroism having the same principal directions. Formulæ valid to a second approximation are then obtained, and a good agreement is shown to exist between the observed and calculated results.

J. GRANT.

Platinum thermometer temperature scale. F. E. HOARE (Phil. Mag., 1929, [vii], 7, 384—386).—A simplified method for finding the correction, to a platinum thermometer, for any value of the difference coefficient in the equation $X=(t-pt)=d(t-100)t$ is given. At temperatures as high as 1200° the correction is shown to give temperatures accurate to 0·1°.

A. E. MITCHELL.

Thermal conductivity of solid and liquid sulphur. G. W. C. KAYE and W. F. HIGGINS (Proc. Roy. Soc., 1929, **A**, **122**, 633—646).—An investigation has been made of the thermal conductivity of solid and liquid sulphur over the temperature range 20—210°, a region embracing the transition point from rhombic to monoclinic sulphur (95°), the "natural" m. p. of monoclinic sulphur (115°), and the change point of liquid sulphur (160°). In the case of solid sulphur, measurements were made on the rhombic and monoclinic varieties, each in the form of crystalline aggregates, and on the plastic modification. The progressive change in thermal conductivity was followed during the slow transition at the ordinary temperature from the unstable plastic to the stable rhombic form, and the influence of temperature on the rate of transformation was studied. The experiments demonstrate the effect of the previous thermal history on the velocities of the various transformations. The measurements were made by means of a "plate" method similar to that previously described (A., 1928, 114), using a small temperature drop, usually from 3° to 5°, across the test specimen. For the measurements on solid sulphur, it was necessary to employ glycerin films between the test layer and the surfaces of the hot and cold blocks. The following values were obtained: rhombic aggregate, 0·00065 (20°), 0·00061 (40°), 0·00058 (60°), 0·00055 (80°), 0·00054 (95°, change point); monoclinic aggregate, 0·00037—0·00040 (100°); liquid, 0·00031 (115°, m. p.), 0·00031 (120°), 0·00032 (140°), 0·00033 (160°), 0·00033 (165°), 0·00034 (170°, change-point region 160—170°), 0·00036 (190°), 0·00037 (210°); plastic, 0·0002 (20°).

L. L. BIRCUMSHAW.

Thermal conductivity of lead and of single- and poly-crystal zinc. C. C. BIDWELL and E. J. LEWIS (Physical Rev., 1929, [ii], **33**, 249—251).—Determinations were made over the range −250° to 100°, using an adaptation of the Forbes bar method (cf. Bidwell, A., 1926, 1087). The thermal conductivity increases as the temperature is lowered, but shows no great increase at very low temperatures as was found for lithium. Conductivity is about 18% better for single- than for poly-crystal zinc, and is about 7% poorer for a sample case in air than for one prepared in a vacuum. N. M. Bligh.

General formulæ for calculating the atomic or molecular heat and the specific heat of elements in the solid state. J. Maydel (Z. anorg. Chem., 1929, **178**, 113—145).—The true atomic heat (μ) of any element at any temperature (t) is given by the equation $\mu=\gamma-\alpha/(t+\beta)$, where β and γ are constant parameters for that element and α is a constant for all elements and equals 939·8. The values of β and γ for all the elements have been calculated and are shown to be periodic functions of the atomic number; when their values are plotted against one another for all the elements two intersecting curves are obtained, both of which are hyperbolas identical with the curve for μ given by the above equation. The elements may therefore be divided into two classes according to the line on which the point represented by their β and α values falls. For class I the equation to the curve is $\beta=B_1-\alpha(\gamma-G_1)$, and for class II $\gamma=G+\alpha/(\beta+B)$. Hence the constants G_1 and B_1 and G and B are the origins of a system of co-ordinate axes which are asymptotic to the curves for class II and class I, respectively. The calculated values for these constants are $G=6{\cdot}05$ kg.-cal., $B=0°$, $G_1=-0{\cdot}242$ kg.-cal., and $B_1=492{\cdot}3°$. Hence for elements of class II the atomic heat at 0° is 6·05 kg.-cal., which agrees with the value according to Dulong and Petit's law. To this class belong the elements of group 0, the four elements which succeed and the three elements which precede each of these in atomic number, but there are several exceptions; all the other elements belong to the first class except iodine and mercury, the β,γ points of which apparently do not fall on either curve. The atomic heat of elements of the first class may be calculated from the equation $\mu_{\mathrm{I}}=0{\cdot}242+\alpha(t+2\beta-492{\cdot}3)/(t+\beta)(492{\cdot}3-\beta)$. As every element has its own value for β, there is obviously no temperature at which the second expression on the right-hand side becomes zero or the same for all elements of this class, and hence these elements show more or less deviation from Dulong and Petit's law according as to whether their β,γ points lie remote from or near to the intersection of the two curves. Equations are given for calculating the true and mean specific heats of the elements of both classes, the mean atomic heat, and the heat required to raise 1 g.-atom from t_1 to t_2, and the effect of allotropic transformations on the atomic heat is discussed. Tables are given showing the values of β and γ for all the elements, and the atomic heats at various temperatures calculated from these values are compared with those obtained experimentally by various authors; in general, the agreement between calculated and observed values is very good. A. R. Powell.

Specific heat of tungsten between 90° and 2600° Abs. C. Zwikker (Z. Physik, 1928, **52**, 668—677).—The inconsistency in the published values of the specific heat of tungsten has led the author to a redetermination over a wide temperature range. A description of the experimental method is given for the high-temperature determinations, for which C_p increases linearly with rising temperature, whilst C_v falls, remaining below 8 g.-cal. per g.-atom. G. E. Wentworth.

Specific heat of molybdenum from 250° to —40°. D. Cooper and G. O. Langstroth (Physical Rev., 1929, [ii], **33**, 243—248).—Existing data for the specific heat of molybdenum being untrustworthy, experiments were made with a slightly modified Richards adiabatic calorimeter, by which values from high temperatures could be obtained. Values accurate to about 1% are given for the range —30° to 300° by the equation $C_p=0{\cdot}0593+0{\cdot}000013(T+40)-0{\cdot}0265/(T+40)^{1{\cdot}06}$. Stern's equation is linear (cf. A., 1928, 1083) and agrees with the values given between 50° and 300°. Below 50° the curve shows a decided bend. N. M. Bligh.

Specific heat of manganese phosphide. B. G. Whitmore (Phil. Mag., 1929, [vii], 7, 125—129).—The specific heat of manganese phosphide shows an increase at 16°. This is of the order required by the Weiss theory of ferromagnetism, but the temperature is just below the magnetic critical temperature at which, according to the theory, the phenomenon should occur. A. E. Mitchell.

Specific heats of acetone, methyl, ethyl, and *n*-propyl alcohols at low temperatures. S. Mitsukuri and K. Hara (Proc. Imp. Acad. Tokyo, 1929, **5**, 27—28).—The specific heats of acetone, methyl, ethyl, and *n*-propyl alcohols have been measured over the temperature range 170—270° Abs. F. J. Wilkins.

Heats of fusion and specific heats of calcium and magnesium. E. Zalesinski and R. Zulinski (Bull. Acad. Polonaise, 1928, A, 479—505).—The specific heats of calcium (99·13% Ca) and of magnesium (98·68% Mg) over a range of temperature have been determined in a silver-plated brass calorimeter furnished with a lid of iron, the only metal that does not react with calcium and magnesium at high temperatures. The mean specific heats found were: (*a*) Calcium, between 20° and 304°, 0·1610; 20—504°, 0·1764; 22—520°, 0·1768; 20—697°, 0·1887; 21—755°, 0·1927; 22—785°, 0·1901; 22—785°, 0·1724; 22—802°, 0·1724; 810—930° (liquid), 0·2670. The lower values were obtained when the specimen was first heated at about 800° and the specific heats determined on cooling and are due to the presence of two allotropic modifications of calcium. (*b*) Magnesium, between 22° and 625°, 0·2823; 650—775° (liquid), 0·2880. The heats of fusion were also determined in an electrically heated silica vacuum oven in an atmosphere of argon, the heat of fusion being calculated from the duration of crystallisation by Tammann's formula; the transition point of the two forms of calcium was about 800°. The results obtained were: (*a*) from duration of crystallisation; calcium, 74·0 g.-cal./g., heat of transition, 5·75 g.-cal./g.; magnesium, 46·0 g.-cal./g.; (*b*) calorimetrically: calcium 78·5 g.-cal./g., magnesium, 55·5 g.-cal./g. A. I. Vogel.

M.p.-pressure curves. F. Simon and G. Glatzel (Z. anorg. Chem., 1929, **178**, 309—316).—Tammann's equation ("Aggregatzustände," Leipzig,

1922) connecting the m. p. of a substance with the pressure is shown to give results for high pressures which are much too low; the p–T curve bends backwards. A much more accurate expression, derived from van der Waals' vapour-pressure equation, is the following: $\log (a+p)=c \log T+b$, where a, b, and c are constants, the values of which have been calculated for 19 substances. Using these constants, the deviations of the calculated values of the m. p. for pressures up to 12,000 atm. from the observed values are less than 5%. A. R. Powell.

Melting curve of hydrogen to 245 kg./cm.^{2} W. van Gulik and W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 1059—1060; cf. A., 1927, 301).—Continuing previous work, the curve is examined over the range of pressure 94—237 atm., corresponding with a temperature range 16·31—20·34° Abs., and gives results which combine with the previous ones for a smooth curve. N. M. Bligh.

Densities of *n*-propyl and *iso*butyl alcohols at low temperatures. S. Mitsukuri and Y. Kitano (Proc. Imp. Acad. Tokyo, 1929, 5, 21—22).—The densities of *n*-propyl and *iso*butyl alcohols have been measured over a range of about −10° to −110°. The results may be expressed by the formulæ, $D=0{\cdot}8193-0{\cdot}00006749t+0{\cdot}000001351t^2$ and $D=0{\cdot}8169-0{\cdot}0007055t+0{\cdot}000000684t^2$, respectively. F. J. Wilkins.

Vapour pressures at low temperatures. N. von Kolosovski (J. Russ. Phys. Chem. Soc., 1928, 60, 1403—1416).—It is shown that even at temperatures above the absolute zero the vapour pressure of a substance must be infinitesimally small and practically zero; also that at those temperatures any change in the temperature of the walls of the containing vessel will have no effect on the slight vapour pressure. Hence it is concluded that there can be no equation for the vapour-pressure curve, say, in the form $\log_e p=A-B/T-C \log_e T+DT$. The criticism by Golitschuch (this vol., 398) is answered. A. Freiman.

Lowering of the vapour pressure of liquid argon by active substances. G. F. Hüttig and R. Juza (Z. anorg. Chem., 1928, 177, 313—322).—Active calcium, nickel sulphide, and powdered cassiterite do not influence the vapour pressure of liquid argon. The depressions produced by various proportions of active carbon, active silica, antimony trioxide, and stannic acid have been measured at temperatures in the neighbourhood of 85° Abs. The system silica–argon closely resembles the systems silica–water–ethyl alcohol and -benzene; the other systems investigated exhibit more or less graded differences from that containing silica, but nevertheless the cause of the depression of vapour pressure by active carbon does not appear to be the same as in the case of silica. H. F. Gillbe.

Vapour density and pressure of ammonium iodide. R. H. Purcell and W. de Lange (J.C.S., 1929, 275—279).—A static method has been used for the redetermination of the vapour pressure and vapour density of ammonium iodide at temperatures between 299·1° and 426°. The results agree with those obtained by the isoteniscope method. Ammonium iodide is completely dissociated at all temperatures up to 400°. F. G. Tryhorn.

Vapour-pressure chart for hydrocarbons. H. B. Coats and G. G. Brown (Dept. Eng. Res. Univ. Michigan, 1928, No. 2, 1—17).—A new method of constructing vapour-pressure graphs is described, and curves are given for propane, *iso*butane, butane, dimethylbutane, pentane, di*iso*propyl, dimethylpentane, hexane, hexamethylene, benzene, dimethylhexane, and heptane from −150° to 280°. The accuracy claimed for the chart is ±0·5° in most cases. C. W. Gibby.

Interpretation of the linear isotherms derived from the Wiedemann–Franz–Lorenz law of conductivity. E. Grüneisen (Z. Physik, 1928, 51, 652—668).

Van der Waals' equation and thermodynamics. J. E. Verschaffelt (Compt. rend., 1929, 188, 312—313).—A criticism of Karpen's deductions (this vol., 138). J. Grant.

Equations of state and thermodynamics. V. Karpen (Compt. rend., 1929, 188, 496—498).—Polemical against Verschaffelt (preceding abstract). J. Grant.

Viscosities of ethyl, *n*-propyl, and *iso*butyl alcohols at low temperatures. S. Mitsukuri and T. Tonomura (Proc. Imp. Acad. Tokyo, 1929, 5, 23—26).—The viscosities of ethyl, *n*-propyl, and *iso*butyl alcohols have been measured over the temperature range of 0° to −100°. The results may be expressed by an equation of the form $\log \eta=-A+B/(T-C)$, where A, B, and C are constants. F. J. Wilkins.

Tube correction in measurements of the velocity of sound in gases. R. E. Cornish and E. D. Eastman (Physical Rev., 1929, [ii], 33, 258—259; cf. this vol., 253).—A reply to Shilling and Partington (this vol., 128). N. M. Bligh.

Thermal diffusion of rare constituents in gas mixtures. S. Chapman (Phil. Mag., 1929, [vii], 7, 1—16).—A mathematical examination of the effects and magnitude of the results of thermal diffusion in gases and the changes in concentration to be expected therefrom. A. E. Mitchell.

Molecular association. II. Relation between the viscosity of binary liquid mixtures and the polarity of the constituent molecules. J. Errera (Z. physikal. Chem., 1929, 140, 273—280; cf. A., 1928, 1316).—The viscosity–concentration curves are considered with reference to the polarity of the molecules. The curves are found to be concave to the concentration axis if the molecules of one or both components are non-polar and convex if the molecules of both components are dipolar. Gases dissolved in liquids also follow this rule. A theoretical interpretation of this regularity is given. R. N. Kerr.

Viscosity formula for binary mixtures. T. Ishikawa (Bull. Chem. Soc. Japan, 1929, 4, 5—15).—A formula is given for the viscosity η of a binary mixture $\eta=\eta_1+(\eta_2-\eta_1)k_2a_2Z_m/\{k_1a_1(1-Z_m)+k_2a_2Z_m\}$, where a_1 and a_2 are the degrees of association in the two liquids of viscosity η_1 and η_2, Z_m is the molar fraction of the second liquid, and k_1 and k_2 are constants. C. W. GIBBY.

Hardness and magnetic properties of iron–copper alloys and their relation to the equilibrium. A. KUSSMANN and B. SCHARNOV (Z. anorg. Chem., 1929, **178**, 317—324).—Alloys of iron with 0·5 and 1% Cu which is retained in solid solution show no change in the hardness or coercivity after quenching. Addition of more copper increases the hardness and decreases the coercivity after quenching from above the A3 point, showing that the solubility of copper in iron is greater at high temperatures than at the ordinary temperature. Quenching from above the A2 point but below the A3 point causes no sudden change in the hardness or coercivity, contrary to the results obtained by Ishihara (B., 1922, 941A). A. R. POWELL.

Influence of rate of cooling on the structure of eutectics. G. TAMMANN and A. A. BOTSCHWAR (Z. anorg. Chem., 1929, **178**, 325—328).—Very slow cooling of the lead–bismuth eutectic alloy from just above to just below the m. p. results in considerable segregation, the upper part of the alloy being enriched in bismuth, the excess of which beyond the eutectic composition crystallises in large cubes, and the lower part in lead, the excess of which crystallises in long dendrites in a ground mass of fine-grained eutectic. In the middle portion of the ingot both dendrites and cubes are found together in the eutectic ground mass. Similar results are obtained by slowly cooling eutectic alloys of bismuth–tin, bismuth–cadmium, and lead–antimony. On overheating the eutectic iron–carbon alloy and then cooling it slowly through the m. p. large graphite needles separate, especially at the top and round the sides of the ingot. A. R. POWELL.

Crystal form in the formation of solid solutions. III. Thermal analysis of the systems $MnCl_2$–$CoCl_2$, $CdCl_2$–$CoCl_2$ and $MgCl_2$–$CoCl_2$. A. FERRARI and A. INGANNI (Atti R. Accad. Lincei, 1928, [vi], 8, 238—243).—These three systems show complete series of solid solutions of which the m. p. are in all cases intermediate between those of the pure components and show neither maxima nor minima. F. G. TRYHORN.

Equilibrium between two liquid phases. V. System aniline–propionic acid–water. VI. System o-toluidine–propionic acid–water. E. ANGELESCU (Bul. Soc. Chim. România, 1928, **10**, 160—169, 183—191; cf. A., 1927, 1030).—V. Measurements of the solubility of aniline in aqueous solutions of propionic acid of various concentrations give no indication of the existence of lower critical points, so that the existence of such points in the system aniline–acetic acid–water (A., 1925, ii, 854) cannot be attributed solely to hydrolysis of the amine salt. The binodal curves for the ternary system at 0° and 20° have also been determined. The ratio of the concentration of acid in the aqueous phase to that in the other conjugate at 20° first decreases with increasing concentration, then passes through a minimum, and ultimately rises again, tending to the value 1 as the critical point is approached. The effect of lactic, acetic, and propionic acids in increasing the miscibility and depressing the critical solution temperature diminishes in this order, as does also the dissociation constant.

VI. Similar determinations have been made with the system *o*-toluidine–propionic acid–water. Here, however, there is evidence that at low temperatures closed solubility curves would be obtained, and it is therefore suggested that even the binary system possesses a lower critical point, and that the acid raises the critical solution temperature very considerably. The effect of propionic acid on the upper critical solution temperature is greater than that of acetic acid, the molecular depression increasing with increasing concentration in each case. R. CUTHILL.

Solubility of magnesium hydroxide at high temperatures. A. TRAVERS and NOUVEL (Compt. rend., 1929, **188**, 499—501; cf. Gjaldbaeck, A., 1925, ii, 653).—The solubility of magnesium hydroxide determined by electrometric or colorimetric titration (using phenol-red as indicator) in the absence of carbon dioxide decreases with time, and approximately linearly with temperature. It is not appreciable at 178° and is increased by salts such as sodium chloride or sulphate. Such determinations should be carried out in copper or paraffined glass vessels. J. GRANT.

Solubility of calcium hydroxide. L. B. MILLER and J. C. WITT (J. Physical Chem., 1929, **33**, 285—289).—The solubility of calcium hydroxide in water at 30° has been determined, the approach to equilibrium being followed by means of measurements of the conductance of the solutions. Mean values for calcium oxide prepared by ignition of Iceland spar and by ignition of the carbonate precipitated from solutions of the nitrate by ammonium carbonate are 1·199 and 1·197 g. of calcium oxide per 1000 c.c. of saturated solution, respectively. L. S. THEOBALD.

Solubility of calcium sulphate from 0° to 200°. E. P. PARTRIDGE and A. H. WHITE (J. Amer. Chem. Soc., 1929, **51**, 360—370).—The solubilities of anhydrite and hemihydrate are recorded for the range 100—200°. The values for anhydrite agree with those found by Melcher and the hemihydrate values agree with those previously recorded for "soluble anhydrite" (*e.g.*, Hall, Robb, and Coleman, B., 1926, 391). The "soluble anhydrite" curve above 100° is merely a continuation of the hemihydrate curve below 100°, thus supporting the view that the crystal structures of these two compounds are identical (cf. Jung, A., 1925, ii, 367). A provisional diagram is given for the calcium sulphate–water equilibrium which indicates that gypsum is converted into anhydrite at 38—39° and into hemihydrate at 98°. Hemihydrate is metastable in the approximate range 90—130°, showing decreasing stability with falling temperature below 90° and with rising temperature above 130°. S. K. TWEEDY.

Distribution law. I. Ideal distribution law expressed in molar fractions. II. Distribution law for condensed systems. R. LORENZ (Z. anorg. Chem., 1929, **178**, 346—352, 366—370).—I. If molar fractions are substituted for volume concentrations, the distribution law is readily established by the method of thermodynamic potential without any assumption other than the validity of an equation of state for "ideal" solutions.

II. Using the same method, an equation for the distribution ratio for "condensed" systems may be derived. R. CUTHILL.

Partition coefficient of infinitely soluble substances. S. G. MOKRUSCHIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 1633—1639).—Perschke (cf. A., 1926, 345) showed that for infinitely soluble substances the partition coefficient between two immiscible solvents should be unity. Partition coefficients calculated from the data of different workers prove them to vary between 0·5 and 2·1. These values are explained by the use of the kinetic theory, Langmuir's conception of molecules as "dipoles," Langmuir's "principle of independent surface action," and lastly Langmuir's idea of molecules reacting only when certain definite parts of their surfaces come close together. Deviations from the values of 0·5, 1, or 2 are explained by introducing a fresh conception of the reactivity of molecules being confined to strictly limited parts of their surface, a so-called "polypolar" structure for molecules; influences on the part of the solute molecules on the mutual miscibility of the two solvents are also assumed, and finally changes in the state of the solute molecule itself, *e.g.*, dissociation, association, solvation, etc. A. FREIMAN.

Adsorption of iodine, bromine, and some halogen salts by carbon from different organic liquids. J. TRIVIDIC (Rev. gén. Colloïd., 1929, **7**, 14—24).—A general introduction to the research. Contrary to the results of Davis (J.C.S., 1907, **91**, 1666), the adsorption of iodine by activated carbon from organic liquids is complete after 30 min.

R. N. KERR.

Adsorption. W. KÄLBERER and H. MARK (Z. physikal. Chem., 1928, **139**, 151—162).—The simplest formula deduced for the adsorption of a gas on a solid assumes that the phase concentration and the adsorption potential are independent of the surface density of film, and that the energy of polyatomic molecules which are adsorbed is represented by the same equations as in the gaseous state. The adsorption isotherms for argon on a given silicic acid were compared with those of the triatomic carbon dioxide on the same acid. Both gases give straight lines passing through the origin. There is no essential difference in behaviour. Other silicic acids show steep slopes for small increases in the film density, finally becoming straight lines. The heat of adsorption over the linear part of the curve is for argon 2500 g.-cal. and for carbon dioxide 6200 g.-cal. Similar relationships are found for the adsorption of carbon dioxide on aluminium and other foils: the adsorption isotherms for many temperatures are given and the thickness of the adsorbed layer appears to be of the order of magnitude $1{\cdot}5\times10^{-8}$ cm.

G. E. WENTWORTH.

Adsorption phenomena in solutions. XVII. Modifications of active carbon. M. DUBININ (Z. physikal. Chem., 1929, **140**, 81—88).—Sugar charcoal activated at 550° adsorbs inorganic acids from aqueous solution to an extent which increases with the basicity of the acid, whilst the adsorption of organic acids forms a series conforming to Traube's rule; activation of the charcoal at 800° results in the complete reversal of these series. The difference is ascribed to the formation of a surface layer of amorphous carbon on the one hand and of crystalline carbon on the other. In the absence of carbon dioxide neither modification is capable of adsorbing alkalis. By careful ignition of wood charcoal an active carbon is obtained which corresponds closely with the crystalline modification. H. F. GILLBE.

Adsorption of acetic and propionic acids in presence of salts with a common anion. E. ANGELESCU and V. N. COMANESCU (Bul. Soc. Chim. România, 1928, **10**, 170—182).—The amounts of acetic or propionic acid adsorbed by charcoal from aqueous solutions containing the corresponding sodium or potassium salt are somewhat less than when the salt is absent, but in both cases the Freundlich isotherm is applicable. It is also possible to represent the distribution of acetic acid between benzene and water by an equation of the same form as the adsorption isotherm, the result of adding potassium acetate being to displace the equilibrium in favour of the aqueous phase, whilst addition of sodium chloride has the opposite effect. Hence it may be concluded that the effect of the acetate on the adsorption is due to its increasing the tendency of the acid to dissolve in the water, whereas sodium chloride, acting in the reverse direction, promotes the adsorption (cf. Wiegner, Magasanik, and Virtanen, A., 1921, ii, 244).

R. CUTHILL.

Adsorption. XXII. Adsorption of alkali and of cupric salts in the precipitation of cupric hydroxide. M. R. MEHROTRA and N. R. DHAR (J. Physical Chem., 1929, **33**, 216—225).—The factors affecting the gravimetric determination of copper by precipitation with sodium and potassium hydroxides have been investigated. Both hydroxides are adsorbed to a marked extent by the copper oxide precipitated from solutions of copper chloride and sulphate. The amount adsorbed is greater with the chloride than with the sulphate, and sodium hydroxide is adsorbed in larger quantities than potassium hydroxide. Adsorption quickly reaches a saturation limit. Copper can be precipitated completely from cupric salts by an amount of alkali slightly less than the equivalent amount, and, in the case of copper sulphate, the weight of copper oxide obtained on ignition is too great owing to adsorption of copper sulphate. With excess of alkali, however, the weight of oxide obtained approaches the theoretical value. Cupric and sulphate ions are adsorbed by the hydroxide in equivalent quantities; cupric chloride is also adsorbed, but volatilises on ignition. The existence of the basic salt $3Cu(OH)_2,CuSO_4$ is supported.

L. S. THEOBALD.

Gas–solid equilibria. II. Pressure–concentration equilibria between benzene and (*a*) ferric oxide gel, (*b*) silica gel, directly determined under isothermal conditions. B. LAMBERT and A. M. CLARK (Proc. Roy. Soc., 1929, A, **122**, 497—512; cf. A., 1928, 131).—The equilibrium of the system ferric oxide gel–benzene has been examined at 40°, 50°, and 60° in a special form of apparatus and isothermals representing the pressure–concentration equilibria are given. Equilibrium pressures of benzene are plotted against concentration in grams of benzene per gram of gel. The adsorption and desorption isothermals are definitely coincident over the lower ranges of benzene concentration, but show great divergence, with the production of a hysteresis region, at intermediate concentrations, and become again coincident over the very steep portions of the curve obtained when the benzene concentrations approach the saturation value of the gel. The time taken for the establishment of equilibrium was about $\frac{1}{2}$ hr. over the coincidence ranges, but much longer (about 2 hrs.) over the intermediate range. Experiments were made at 40° to study the effect of interruptions in the "smooth" addition or withdrawal of benzene, and the effect on an established equilibrium of temporary alterations in the temperature of the system. It is shown that there are ranges of concentration—lower and higher—over which the pressure–concentration relations are reproducible and reversible, and also that intermediate ranges occur (the limits of which vary with the temperature) for which these relations are not reversible. In the latter circumstances results are reproducible only if the system is maintained at its constant temperature and the benzene "smoothly" added or withdrawn. The results obtained with the system silica gel–benzene at 15·25°, 40°, 50°, and 70° are, on the contrary, reproducible and reversible over the whole concentration range, from zero to saturation. Temporary cooling or heating of the system is without effect on the equilibrium pressure. Interruption of the "smooth" addition or withdrawal of benzene was also found to have no influence on the equilibrium state.

L. L. Bircumshaw.

Adsorption on the surface of binary liquid mixtures. R. S. Bradley (Phil. Mag., 1929, [vii], 7, 142—145).—Previous considerations of surface phenomena in liquids have paid undue attention to the adsorption of one constituent without considering at the same time changes in the surface concentration of the other. Schofield and Rideal's (A., 1925, ii, 960) expression for the surface concentration of alcohol in alcohol–water mixtures $d\sigma/(-RTd\log a_1)$, where σ is the surface tension of the mixtures and a_1 the activity of the alcohol, is in reality not a measure of the surface concentration of the alcohol, but $\Gamma_1-\Gamma_2 N_1/N_2$, where Γ_1 and Γ_2 are the Gibbs surface excesses and N_1 and N_2 the mol.-fractions of alcohol and water, respectively. Γ_1 and Γ_2 have been evaluated by means of Frumkin's potential at the surface (A., 1925, ii, 109) and each surface concentration is shown to exhibit a maximum. From these figures the sectional area of oriented alcohol is shown to be 25·6 Å.

A. E. Mitchell.

Adsorption at a water surface. I. B. W. Currie and T. Alty (Proc. Roy. Soc., 1929, **A**, **122**, 622—633; cf. Alty, A., 1926, 1096).—Measurements have been made of the velocity of air bubbles of various diameters in water and in sodium chloride solution, the bubble being introduced into a cylindrical silica cell with platinum end-pieces which served as electrodes. From the velocity under a known potential gradient, the total charge on the bubble, E, is derived from the formula $XE=6\pi\eta rv$. The results indicate that all bubbles, if they are not too small, have a charge which is independent of the radius and depends only on the rate of absorption; below a certain critical diameter, E ceases to be constant and decreases rapidly as the radius is still further decreased. The higher the rate of absorption the greater is E. The time taken for the surface to attain equilibrium is surprisingly long, being about 2000 sec. in the case of dilute sodium chloride solution. In very pure water ($\kappa=0{\cdot}7\times10^{-6}$ ohm^{-1}), however, there is no appreciable charging period. E is found to be $5{\cdot}4\times10^{-4}$ e.s.u., the critical radius in this case being 0·033 cm. The colour of the light used to illuminate the bubble appears to have no influence on the results.

L. L. Bircumshaw.

Adsorption of ions and the physical character of precipitates. H. B. Weiser and G. E. Cunningham (J. Physical Chem., 1929, 33, 301—316).—The influence of the adsorption of ions on the physical character of a precipitate has been investigated for the case of a sulphur sol coagulated by the addition of certain chlorides. The sulphur sol was prepared by passing hydrogen sulphide and sulphur dioxide simultaneously into a saturated aqueous solution of the latter, and approximate uniformity of particle size was obtained by coagulation with sodium chloride, re-peptisation with water, and dialysis through cellophane membranes. The physical character of the sol varies almost continuously from gelatinous and reversible to plastic and irreversible when coagulated by a lyotropic series of ions from lithium to cæsium and from magnesium to barium. Coagulation with a highly-hydrated, weakly-adsorbed ion, such as those of lithium and sodium, yields a reversible, gelatinous precipitate composed of individual micelles separated by a film of adsorbed water. Ions which are less hydrated and strongly adsorbed, *e.g.*, those of barium, potassium, and cæsium, yield plastic, irreversible precipitates. The rate of precipitation does not determine the character of the precipitate. Ultramicroscopic examination shows that replacement of a highly-hydrated ion from a gelatinous sulphur clump by one less hydrated and more strongly adsorbed is accompanied by a marked shrinkage due to loss of adsorbed water and coalescence of the particles, and ultramicroscopic convection currents become visible. When the sulphur sol is neutralised in the cell of a cardioid ultramicroscope so that the particles do not collide, the precipitation is reversible only when the adsorbed ion can be removed by washing. It is inferred that reversibility can be obtained in any sol when the conditions are such that coalescence is prevented by the intervention of a film of adsorbed solvent or by elimination of the opportunity to collide, provided that the adsorbed precipitating ion can be removed by washing. Further, the size and shape of a sulphur clump depend on the number and manner of chance collisions during the precipitation process. Von Weimarn's law of corresponding states for precipitation is discussed and shown to be often inapplicable and of little value in the prediction of the form of a precipitate.

L. S. Theobald.

Adsorption isotherms. A. Boutaric (Compt. rend., 1929, 188, 450—452).—The adsorption isotherms of J. Perrin and of Freundlich are compared after mathematical transformation with the symmetrical generalised form $dy/y^n=K\,.\,dc/c^n$, where y is the concentration of the adsorbed substance in the adsorbing material, c the concentration in the medium, K a constant, and n is 1 and 2, respectively.
J. Grant.

Equilibrium of heterogeneous systems including electrolytes. III. Effect of an electric field on the adsorption of organic molecules, and the interpretation of electrocapillary curves. J. A. V. Butler (Proc. Roy. Soc., 1929, A, 122, 399—416; cf. A., 1927, 112).—Starting with the electrostatic theorem, that the work done by an element of dielectric of volume ∂v, when it is moved from a place where the electric field is E to a place where it is 0, is $w=\partial v\int PdE$, where P is the polarisation per unit volume corresponding with the field strength E, an expression is derived for the variation of the amount of substance adsorbed from solution with the *P.D.* at the interface. This is given by $\Gamma=\Gamma_0e^{-aV^2+bV}$, where Γ is the excess amount of the substance adsorbed, Γ_0 is the amount adsorbed when $V=0$, V is the *P.D.* at the interface, and a and b are constants. It is also shown that $\Delta\gamma=\Delta\gamma_0\,.\,f(V)$, where $\Delta\gamma$ is the depression of the surface tension produced by the substance and $\Delta\gamma_0$ is the depression produced when $V=0$. The variation with the *P.D.* of the surface tension lowering produced by a number of organic substances at a mercury–aqueous solution interface has been determined. The values of the constants a and b, which have been calculated for numerous compounds, are discussed, and the main features of the electrocapillary curves of solutions containing organic substances, determined by Gouy, are interpreted. From a consideration of the effect of orientation at the interface, it is shown that the maximum of adsorption should occur when the *P.D.* between the mercury and the solution is zero. The maxima of the adsorption curves should all occur at the same value of V. It is found, however, that whilst in nearly all cases these curves are of the same general form, the maximum is often displaced, sometimes considerably, to the right or left of the maximum of the primitive solution. Reasons for this are adduced. L. L. Bircumshaw.

Effect of the addition of protein on the surface tension of a sodium glycocholate solution. R. Sugino (J. Biochem. Japan, 1928, 9, 353—381).—It is only at p_H values at which the protein exists as cation that it affects the surface activity of sodium glycocholate solutions, probably as a result of stoicheiometric combination. An explanation is offered for the fact that the addition of protein to a dilute glycocholate solution increases the surface tension, whilst that to a more concentrated solution diminishes it. Chemical Abstracts.

Orientation of organic compounds by cylindrical glass surfaces and superficial orientation of glass. Applications. J. J. Trillat (Compt. rend., 1929, 188, 555—556).—The author's *X*-ray spectrographic method (A., 1928, 938) is extended to deposits on a glass cylinder of layers of palmitic acid less than 0·01 mm. thick deposited from light petroleum solution. Anisotropic orientation was found in the direction of the radius of the cylinder, corresponding with reflexion from planes 35·6 Å. apart, containing two fatty acid molecules. In the other directions the orientation was isotropic. The surface of the glass itself also showed anisotropic orientation with an intermolecular spacing of 3·3 Å. J. Grant.

Floating mercury on water. N. K. Adam (Nature, 1929, 123, 413).—Finely-divided mercury may float on water, even when the surface tension is reduced to about 46 dynes per cm. by the addition of a drop of oleic acid. Since the tensions of clean mercury against air and against water differ by more than the surface tension of clean water, it would be impossible for clean mercury to float on clean water. Treatment of the mercury with sulphuric and chromic acids had apparently reduced the mercury–air tension by 100—200 dynes per cm. A. A. Eldridge.

Residual thermoelectricity of a mercury filament. T. Tsutsui (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 19—32).—Preliminary experiments on the effects of heating portions of capillary tubes containing filaments of mercury show that very small but measurable *E.M.F.* may thereby be set up which vary in magnitude with the nature of the glass–mercury interface. Although the cause of these thermoelectric effects could not be elucidated, it is suggested that they may be due to the production of a state of strain through the unequal expansion of the mercury and the glass surfaces.
H. T. S. Britton.

Velocity of dissolution of comminuted solids. I. W. Jacek (Rocz. Chem., 1929, 9, 19—40).—The process of dissolution is supposed to consists of two processes: one that of penetration of atoms, ions, or molecules of the solid into the solvent, and the other of deposition of solute on the surface of the solid. The velocity of the former process is, in the simplest case, constant, whilst that of the second is proportional to the concentration of solute at the given moment. An expression, $-dr/dt=(P/4\pi r^2)\,.\,(\rho/a_1^3)(a_1^3-a^3+r^3)$, is derived for the velocity of dissolution of solids, where a is the radius of a sphere the mass of which is the same as that of the solid at the beginning, r that of the undissolved solid after time t, a_1 that of a sphere corresponding with the mass of solute present in a saturated solution, ρ the thickness of a layer of solid dissolved in unit time, and P the total surface of the solid. In the case of crystalline solids, ρ is, as a result of their anisotropy, a variable quantity, and a mean value has to be taken. Values calculated from the above expression are in good agreement with those found experimentally for cubes of sodium chloride in water. R. Truszkowski.

Reciprocal action of ions in diffusion processes. W. S. Butkewitsch and W. W. Butkewitsch (Biochem. Z., 1929, 204, 303—321).—From consideration of Donnan's theory of membrane equilibrium, it is shown that the rate of diffusion of the ions of an electrolyte should be altered by changes in the amount of undissociated electrolyte present; experimental proof is given in support of this view.

The rate of diffusion of potassium nitrate through a collodion membrane increases with the initial concentration. The increase is in direct proportion to the increase in the relative quantity of undissociated molecules as determined by conductivity measurements. The rates of diffusion of nitric acid and potassium and sodium nitrates at equal concentrations differ considerably, but the ratio of the change of diffusibility with the concentration to the change in the number of undissociated molecules is the same for these three electrolytes. The value of the above ratio is much smaller for calcium nitrate, due probably to the presence of the bivalent cation. The effect of adding acid and alkali on the diffusion of ammonium nitrate has been investigated. The ions diffuse in equivalent quantities at p_H 3, but if the acidity falls below this value the rate of diffusion of the nitrate ion decreases and that of the ammonium ion increases. The rates of diffusion of the phosphate ion from solutions of the acid and of the three sodium salts have been determined. The highest value is obtained from the free acid and the lowest from the normal salt.

R. N. Kerr.

Osmosis of ternary liquids. VII—VIII. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 923—930; 1929, **32**, 23—31).—Theoretical. A discussion of the relations between the influence of the membrane and the composition of the liquids on the diffusion type in osmosis, and of the nature of the isotonic and isentonic W-curves in different species of osmotic equilibria.

F. G. Tryhorn.

Permeability of dry collodion membranes. II. J. H. Northrop (J. Gen. Physiol., 1929, **12**, 435—461; cf. A., 1928, 359).—The permeability of gases and dissolved solids with reference to dry collodion membranes indicates that the penetration is largely due to dissolution in the collodion, rather than to diffusion through the pores. The rate of penetration does not decrease regularly with increase in mol. wt.; hydrogen and carbon dioxide diffuse at the same rate whether the membrane is dry, wet, or immersed in water. At low concentrations, carbon dioxide, acetic acid, and phenol dissolve reversibly in collodion. Determination of the pore size from the rate of penetration of water gives a figure a hundred times as great as that determined by a vapour-pressure method.

E. Boyland.

Permeability of membranes. VII. Conductivity of electrolytes within the membrane. A. A. Green, A. A. Weech, and L. Michaelis. **VIII. Behaviour of dried collodion membrane towards bivalent cations.** A. A. Weech and L. Michaelis (J. Gen. Physiol., 1929, **12**, 473—485, 487—493; cf. this vol., 87).—VII. The electrical resistance of dried collodion membranes in concentrated electrolyte solutions varies with the concentration of electrolyte, but on dilution a limiting value is reached, which is probably due to the membrane itself rather than the electrolyte. Different electrolytes give markedly different values, hydrochloric acid conducting much better than potassium chloride, which in turn has a higher conductivity than sodium chloride. Lithium chloride has a still lower conductivity. These differences in conductivity of the alkali salts follow the electrolyte content of the membrane, but the high conductivity of hydrochloric acid is due to the high mobility of its ions within the membrane. Thus there are two factors concerned in the phenomenon.

VIII. The potential drop across a collodion membrane in calcium chloride solution is the same as that in a concentration chain. The resistance of this membrane is very high and the transport numbers of calcium and chloride ion are both about 0·5. These results are explained by the fact that very little calcium chloride penetrates into the membrane; the total electrolyte content of a membrane in equilibrium with a solution of calcium chloride was only 20% of that observed with a solution of lithium chloride.

E. Boyland.

Real concentration of solutions. M. Levalit-Ezerski (J. Russ. Phys. Chem. Soc., 1928, **60**, 1391—1398).—Raoult's simple relation is replaced by the expression $(p-p')/p=Kin/(N+in)$, where $i=\Delta_t$ obs./Δ_t calc. If E is the molecular depression of f. p. or elevation of b. p., then Δ_t calc. $=Em/M=En$. By substitution and transformation, expressions are obtained for the "real concentration" of a solution, and for Δ_t obs. Using Tammann's data, values for Δ_t and n are calculated and compared for sodium chloride, potassium chloride, bromide, iodide, nitrate, and chlorate, and for barium chloride.

A. Freiman.

Synthesis and properties of colloidal aluminium and magnesium hydroxides. I. A. Jakovlev (J. Russ. Phys. Chem. Soc., 1928, **60**, 1551—1555).—To carefully washed mercury protected from the action of carbon dioxide, air, and other gases was added a weighed quantity of aluminium or magnesium free from oxide and then distilled water (p_H 6·98). Sols were formed in the course of 6—12 hrs. A greater degree of dispersion of the aluminium sols is attained by peptisation with aluminium chloride. Experiments on the absorption of sodium d-tartrate from aqueous solution show that the aluminium sols have a smaller absorbing power than the sols prepared from aluminium chloride and ammonium carbonate.

A. Freiman.

Colloidal solutions of alumina and chromium oxide and their desiccation. P. Bary and J. V. Rubio (Compt. rend., 1929, **188**, 625—626).—The oxide obtained by drying colloidal aluminium oxide or chromium oxide at 60° is not homogeneous, and as in the case of the iron oxide (A., 1928, 1186) consists of two products, one more or less opaque tending to form more or less parallel with the liquid margin and the other a homogeneous gel. The differences observed in the three cases are probably due to differences in the relative amounts of the two products, and it is suggested that colloidal solutions of these oxides consist of a suspension of slightly hydrated oxide stabilised by a hydrate swelled with water, capable of giving gels on evaporation and behaving as a hydrophile.

R. Brightman.

Structure of colloids. A. Lumière (Rev. gén. Colloïd., 1929, **7**, 1—8).—Kruyt's theory of colloids is not applicable to lyophile sols. The latter cannot be regarded merely as hydrated lyophobe sols. The author's theory that colloids are divisible into two classes, in one of which the particles are molecular and in the other micellar, is more in accord with the facts. R. N. Kerr.

Colloidal structure in the solid state. J. Duclaux (Rev. gén. Colloïd., 1929, 7, 9—14).—The variation of the structure of cellulose nitrate obtained from different solvents and by addition of various substances has been studied. Evaporation from an anhydrous solvent gives a product of the well-known " compact " form; the density of the flakes obtained varies with the solvent employed. A very porous product is obtained by evaporation of ordinary collodion to which antipyrine has been added. A product of a new structure is obtained by evaporation of an alcohol–ether solution of cellulose nitrate to which cinnamic acid has been added. The name " cellular " is suggested for this new structure, which is characterised by slow desiccation in air and in this way resembles certain living tissues. The incompletely dried flakes are soft and plastic. Addition of carbamide or urethane also produces this structure, but to a less marked degree. R. N. Kerr.

Flocculation of gold hydrosols. Boutaric and (Mlle.) M. Dupin (Bull. Soc. chim., 1929, [iv], **45**, 28—29).—Flocculation of gold sols is accompanied by a change of colour. The opacity in the red attains a maximum and then diminishes. By addition of small quantities of electrolyte all the gold is not precipitated; the amount precipitated increases with the concentration of electrolyte used and a certain minimum amount of electrolyte is necessary for complete precipitation. Further examples of periodic precipitation (A., 1927, 309) have been obtained by treatment of gold sols with aluminium, ferric, and thorium chlorides. R. N. Kerr.

Coagulation by electrolytes of non-spherical colloidal particles. I. Rapid perikinetic coagulation. II. Slow perikinetic coagulation. G. Wiegner and C. E. Marshall (Z. physikal. Chem., 1929, **140**, 1—38, 39—63).—I. Ultramicroscopical study of the coagulation by electrolytes of vanadium pentoxide and of benzopurpurin sols, in which the particles are non-spherical, indicates that this type of sol coagulates more rapidly than do sols having spherical particles. Benzopurpurin sols with approximately spherical particles exhibit the normal rate of coagulation calculated by Smoluchowski. The abnormal rate of coagulation of the non-spherical sol particles is independent of the chemical natures of the colloid and of the coagulant, and increases as the ratio length/breadth of the particles increases; the initial velocity increases also with the initial number of particles present. Coagulation of the first aggregates produced proceeds more slowly than does that of the single particles, and the rate diminishes as the aggregates increase in size until, when the process is nearing completion, the rate becomes the same as that for spherical sol particles. The rate of coagulation of the aggregates is influenced to a considerable degree by shaking, and the same holds, to a smaller extent, for the single particles.

II. The slow coagulation of benzopurpurin sol, containing approximately spherical particles, follows Smoluchowski's law, and the rate is less influenced by shaking than in the case of rapid coagulation. The initial rate of the slow coagulation of sols having non-spherical particles, *e.g.*, vanadium pentoxide, may be greater than the rate of rapid coagulation of the spherical type, but the velocity decreases as the process approaches completion. The transition from rapid to slow coagulation at low concentrations of electrolyte is such that the retardation of the coagulation is greater for the non-spherical than for the spherical type. For a vanadium pentoxide sol having particles from 2 to 9 μ in length the relation between the number of particles remaining after a certain time and the concentration of coagulant is similar to that observed for lyophobic sols of the spherical type. A quantitative ultramicroscopical study has been made of the ageing and the slow and rapid coagulation of the non-spherical type of benzopurpurin sol in presence of various concentrations of electrolyte. The greater the aggregation velocity during the coagulation and the more nearly the particles approach the spherical form, the more nearly does the course of the coagulation agree with that calculated by Smoluchowski. H. F. Gillbe.

Effect of non-electrolytes on the coagulation of colloids. III. Copper ferrocyanide sol. S. G. Chaudhury and N. P. Chatterjee (J. Physical Chem., 1929, **33**, 244—249; cf. this vol., 135).—The effect of the addition of methyl or ethyl alcohol, carbamide, sucrose, gelatin, and acetic acid on the coagulating concentrations of hydrochloric, sulphuric, and citric acids, and of potassium, barium, and aluminium chloride for copper ferrocyanide sol, prepared from copper sulphate and potassium ferrocyanide, has been investigated. As in the case of ferric hydroxide sol (*loc. cit.*), but contrary to the finding of Mukherjee and others with arsenious oxide sol, methyl and ethyl alcohols have a uniform effect in sensitising the copper ferrocyanide sol against the electrolytes examined. Gelatin also has a similar effect except in the case of barium and aluminium chlorides, but with the other non-electrolytes examined the effects are specific, the valency of the coagulating ion giving no clue to the expected behaviour. This specific action is discussed, and it is emphasised that other changes, as well as changes in adsorbability and original charge, must be considered in the interpretation of coagulation phenomena.

L. S. Theobald.

Kinetics of the coagulation of gold sols. " Thermo-senescence effect " exhibited at elevated temperatures. (Miss) A. E. Davies (J. Physical Chem., 1929, **33**, 274—284).—The effect of maintaining a gold sol at a temperature of 80° for 4—6 hrs. has been investigated, using barium chloride as coagulant. The change in behaviour brought about by such treatment is termed " thermo-senescence." The sol was prepared by dialysis of the ruby-red sols obtained by boiling an aqueous solution containing gold chloride, potassum carbonate, and acetone, and the extent of coagulation for a coagulation time of 20 sec. was measured colorimetrically. The pronounced thermo-senescence at 80° is made up of (i) a primary effect which consists of a fall in the Smoluchowski coefficient β, with an increase in ageing period of the sol, to a minimum after 3 hrs., and (ii) a secondary effect, which shows itself by a subsequent rise in the value of β and practically disappears when evaporation is minimised. The primary effect is irreversible, and its nature is discussed. The ratio $\beta_{80^\circ}/\beta_{25^\circ}$ varies between 1·5 and 3·3 for different sols, but would be 2·9 if the temperature effect was due to viscosity alone; this discrepancy is discussed. It is pointed out that variability in behaviour due to thermo-senescence should be eliminated before investigating colloidal systems at the ordinary temperature, a desideratum which is made possible by the irreversibility of the primary effect mentioned above.

L. S. Theobald.

Protective action of silicic acid sols and of tin hydroxide on silver sols. A. V. Dumanski and P. A. Scherschnev (J. Russ. Phys. Chem. Soc., 1928, **60**, 1593—1600).—Alkaline solutions of the protecting sols were mixed with a few drops of 40% formaldehyde solution and the desired quantity of silver nitrate solution (dilution 1 : 5000) was then added. Differences in the colour of the protected and non-protected silver sols have been investigated by means of the spectral photometer. The curves obtained by plotting the percentage adsorption against the wavelength are very similar in character, both showing a maximum in the violet, although for the protected sol the maximum is farther in the violet, and both curves slope toward the red. A. Freiman.

Action of ionising radiations on colloids. J. A. Crowther (Phil. Mag., 1929, [vii], 7, 86—98).—Previous work of Crowther and Fairbrother has been extended by an investigation of the effects of *X*-rays and β-rays on ceric hydroxide sol and a Bredig copper sol. In both cases there is a constant ratio between the quantity of *X*-radiation and β-radiation required to produce a given amount of coagulation, an exposure of 1 hr. to β-rays being equivalent to a dose of 0·4 m.c. of *X*-radiation. Within the limits of the experimental error these two doses are found to represent the same relative energy. It is therefore suggested that the coagulation is due to the ionising effect which the two types of radiation possess in common, followed by the discharge of the colloidal particles as previously suggested by Crowther and Fairbrother. (Cf. A., 1921, 935; 1928, 1091.)

A. E. Mitchell.

Cellulose nitrate diffusion experiments. R. O. Herzog and D. Krüger (J. Physical Chem., 1929, **33**, 179—189).—Diffusion data for various commercial cellulose nitrates in acetone and in methyl ethyl ketone as solvents are recorded for solutions in which the heterodispersity of the solution may be disregarded. When referred to the diffusion coefficient in water at 20°, the values of these diffusion coefficients lie between 0·015 and 0·021. Other experiments show that the diffusion coefficient depends on the raw material employed and on the conditions of nitration, and in the majority of cases Fick's law is not followed. This is attributed to heterodispersity and to a disaggregation of the larger particles of cellulose nitrate during diffusion. L. S. Theobald.

Effect of temperature on viscosity and ease of precipitation of sols of cellulose acetate and rubber. G. S. Whitby and W. Gallay (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 1—6).—Experimental results are given for the relative viscosity (*i.e.*, the viscosity referred to the viscosity of the pure solvent at the same temperature) and the percentage volume occupied by the disperse phase (calculated from Hatschek's equation for the viscosity of emulsoids) of a rubber sol in benzene and of sols of cellulose acetate in phenylethyl alcohol, benzyl alcohol, acetone, and *cyclo*hexanone. The rubber sol showed only a small change in relative viscosity with change of temperature. The measurements with cellulose acetate were carried out on sols of different concentrations and it was found that, for sols with a relative viscosity of 4 or less, temperature had a comparatively small effect on the viscosity relative to the viscosity of the solvent at the same temperature. With sols of greater relative viscosity, the effect of temperature was more considerable. This conclusion is in accord with some data recorded by Mardles (J.C.S., 1923, **123**, 1951) for sols in triacetin and in benzyl alcohol. The viscosity of the sols is most markedly affected by temperature when the volume occupied by the disperse phase (cellulose acetate+bound solvent) is high, and especially when it is equal to or higher than the volume corresponding with close packing of the micelles. The ease of precipitation of sols of cellulose acetate by the addition of a non-solvent is affected by temperature to a much greater extent than is the relative viscosity, and the higher the concentration (and therefore the smaller the proportion of unbound solvent) the smaller is the volume of precipitant required to produce separation. It is concluded that precipitation by a non-swelling agent is not a trustworthy method of comparing the degree of solvation at different temperatures.

E. S. Hedges.

Influence of proteins on the solubility of sparingly soluble calcium salts. The carbonic acid compounds of proteins. W. Pauli and T. Stenzinger (Biochem. Z., 1929, **205**, 71—103).—The solubility of calcium sulphate increases in the presence of serum-albumin, pseudoglobulin, and hæmoglobin (the effect increases in this order). This depends on an equivalent inactivation of calcium and sulphate ions determinable by the decrease in conductivity, multivalent ions being formed with the protein. The absorption of calcium by the proteins on shaking with calcium carbonate as solid phase must be regarded as the result of the formation of calcium proteinate, calcium carbonate in saturated aqueous solution being 66% hydrolysed. The effect is accompanied by increased conductivity, strong anodic migration, and decreased coagulability by heat and alcohol. P. W. Clutterbuck.

Mutual influencing of the solubilities of proteins. G. Ettisch, W. Ewig, and H. Sachsse (Biochem. Z., 1928, **203**, 147—158).—Part of the protein precipitated by one third saturation of serum with ammonium sulphate goes again into solution by washing with the same medium. This effect depends only in part on changes of concentration of electrolytes. The protein remaining in solution must, therefore, by its presence cause a portion of protein to precipitate which in its absence redissolves. The redissolution may be avoided by washing with sulphate containing protein. This influence of protein increases with its concentration and depends on the nature of the protein, serum-albumin being especially active. P. W. CLUTTERBUCK.

Equilibrium of halogen ions. I. Combination of egg-albumin with halogen ions. K. ITO (J. Biochem. Japan, 1928, 9, 17—43).—The halogen-ion activity in potassium, sodium, or lithium chloride, and in sodium bromide or iodide, as measured with the silver halide electrode, diminishes on addition of egg-albumin. The effect is attributed to adsorption of the halogen ions. CHEMICAL ABSTRACTS.

Mechanism of the specific action of ions on proteins. Degree of activity of different myogen salts. P. RONA and H. H. WEBER (Biochem. Z., 1928, **203**, 429—451).—The distribution of diffusible ions between an inner protein-containing and an outer protein-free solution follows the Donnan law providing the "activity" of the ions is taken into account. It is possible therefore to measure the relative activity of different salts with the same protein. The activity of myogen salts decreases rapidly from myogen phosphate, chloride, bromide, nitrate, thiocyanate, to sulphate. The osmotic pressure runs parallel with the activity. The specific action of anions increases in the same order as the activity of their myogen salts decreases. The viscosity of the myogen in solution is smaller the smaller is the activity of the myogen salt. The specific action of anions with myogen depends on the activity of the salts which they form with this protein. P. W. CLUTTERBUCK.

Mutual influencing [of flocculation] of cholesterol and cholesteryl ester in colloidal solution. R. STERN (Biochem. Z., 1928, **203**, 313—322).—Further experiments (cf. A., 1926, 576; 1927, 1025) are described on the flocculation of cholesterol and cholesteryl ester sols in acetate and tartrate buffers with addition of serum- and egg-albumin at varying p_H. Cholesterol sol is much more sensitive to change of p_H than cholesteryl ester sol, flocculation occurring at p_H 4·7—5, whereas with the ester sol there is no flocculation at p_H 3 after 24 hrs. Small amounts of serum-albumin and of crystallised egg-albumin sensitise both sols. Cholesteryl ester sol is able to inhibit the flocculation of cholesterol sol, the protective action being readily shown by plotting the flocculation p_H (decreasing) against the quotient ester concentration ÷ cholesterol concentration, when a rapidly rising curve is obtained. P. W. CLUTTERBUCK.

Independence of protein hydration and protein ionisation. H. H. WEBER and D. NACHMANNSOHN (Biochem. Z., 1929, **204**, 215—252).—The non-solvent space of ionised and electro-neutral protein is found to be independent of the degree of ionisation, the value for albumin being 1 c.c. per g. and for globulin 1·3 c.c. per g. Measurements of osmotic pressure and viscosity show that these depend on the degree of ionisation. One g. of albumin has a viscosity volume increasing from 2·0 c.c. at isoelectric point to about 15 c.c. at the acid-swelling maximum.

The change in the total volume gives a measure of the dependence of the forces of hydration on protein ionisation. In the ionisation of various proteins and amino-acids there is no contraction but an increase in total volume. The value of the equivalent expansion when ionised by acids is 7—9 c.c. and by alkalis 16—22 c.c. according to the nature of the ampholyte. The difference between protein and amino-acid is scarcely greater than between individual proteins. Deionisation, whether by acid or alkali, leads to a total increase in volume of 22 c.c.

All the measurements point to virtual independence of protein hydration and protein ionisation.

J. H. BIRKINSHAW.

Reactions between colloids. I. Dyes and proteins. W. PAULI and E. WEISS (Biochem. Z., 1928, **203**, 103—141).—The preparation by electrodialysis of pure Congo-blue sol from Congo-red is described. This sol can be kept unchanged only in Jena glass vessels, and its p_H is determined by conductivity titration and not by use of the gas cell. The titratable hydrogen ions are completely dissociated only in dilute solution. The conductivity temperature coefficient of the blue sol is higher than for a typical electrolyte; at higher temperatures the colour becomes red, but returns to blue on cooling. Precipitation of the sol by a number of weak organic acids and by electrolytes is described. Filter-paper coloured blue by the sol becomes red on drying. Congorubin blue sol behaves similarly, but in aqueous solution there is always an equilibrium between red and blue phases, dilution favouring displacement to the blue. The precipitation of these sols with egg- and serum-albumin, glutin, pseudoglobulin, stannic acid, aluminium hydroxide sols, and a number of negative colloids, *e.g.*, neutral sodium caseinate, starch, silicic acid, colloidal gold, are quantitatively investigated. The concentration of protein just precipitated by Congo-blue sol decreases in the following order: egg-albumin, serum-albumin, glutin, pseudoglobulin. The presence of carbon dioxide in these experiments causes an increase of the free positive charges in the protein solution, and also an increase of sensitivity to precipitation. These reactions, therefore, permit the differentiation of the proteins, and the precipitation in presence of carbon dioxide is perhaps the most sensitive protein reaction. The highly sensitive colour change of the blue sol detects minute amounts of alkali, *e.g.*, of glass (except Jena), and filter paper, and after slight bacterial decomposition.

P. W. CLUTTERBUCK.

Hydrodynamics and the kinetic theory of gases. Y. ROCARD (Compt. rend., 1929, **188**, 553—554).—The limits of validity of classical hydrodynamics (*e.g.*, from the point of Stokes' law) are discussed. It is assumed that if a fluid is defined as obeying Maxwell's rule for the distribution of molecular velocities, then a gas or liquid is no longer a fluid in the neighbourhood of the walls of the containing vessel where its pressure is dependent on the orientation of the surface. J. GRANT.

Constant of mass action. R. F. GOLDSTEIN (Phil. Mag., 1929, [vii], 7, 205—206).—In his treatment of the constant of mass action Kleeman (A., 1928, 239) has not considered the decrease in free energy in the dissociation of his "sepro-stable" molecules, this being independent of the path chosen for a given initial and final state. When this is done the expression for the mass action constant reduces to the usual van 't Hoff form. Furthermore, the kinetic evidence adduced in support of Kleeman's new constant of mass action is substantially the deduction of the mass action law on the kinetic theory, and the correction factor introduced is not a correction to the velocity of reaction, but is the activity coefficient of the concentration term.

A. E. Mitchell.

Constant of mass action. R. D. Kleeman (Phil. Mag., 1929, [vii], 7, 206—208).—A reply to Goldstein (cf. preceding abstract). In the usual van 't Hoff cycle, it is generally supposed that no change in the partial pressure of the molecules in a reservoir takes place when a small fraction is removed and that this holds for the pressure in the cylinder used for removing them independently of dissociation. Hence the free energy remains constant and does not decrease, as claimed by Goldstein. A fresh deduction of the mass action constant is made by equating to zero the external work done during the cycle. It is shown that the factor introduced in the kinetic deduction of the new mass action constant is not the activity coefficient of the concentration term.

A. E. Mitchell.

Relation between stationary state and equilibrium. E. Baur (Z. physikal. Chem., 1929, **140**, 194—198).—Theoretical. The breaks in the Δ–k curves found in certain equilibrium reactions (see A., 1928, 1329) are not in disagreement with the equation connecting the equilibrium constant with the velocity coefficients.

R. N. Kerr.

Optical measurement of small degrees of dissociation of the vapours of metallic salts. I. Wyneken (Z. physikal. Chem., 1929, **140**, 78—80; cf. A., 1928, 1093).—An incorrect value for the heat of reaction was employed in the original paper; substitution of the correct figure causes the observed degree of dissociation to differ widely from the theoretical, but the discrepancy is attributed to traces of mercurous chloride in the mercuric chloride used.

H. F. Gillbe.

Calculation of the water-gas equilibrium by means of the exact form of Nernst's heat equation. E. Maurer and W. Bischof (Z. anorg. Chem., 1929, **178**, 371—380).—From existing specific heat data, the relation between the heat effect in the formation of water-gas and the temperature has been calculated. By application of the method of least squares to the resulting expression, the coefficients for the Nernst heat equation have then been derived. The values for K_p obtained from the equation are in good agreement with the published experimental figures.

R. Cuthill.

Thermal decomposition of water vapour into hydrogen and free hydroxyl. K. F. Bonhoeffer and H. Reichardt (Z. physikal. Chem., 1928, **139**, 75—97).—Spectroscopic evidence for the thermal dissociation of water vapour into hydrogen and free hydroxyl has been obtained at temperatures above 1300°. The dissociation constant of the reaction has been calculated in the following way. A consideration of the reaction $4OH=2H_2O+O_2+W_0$ shows that z_1/z_2 can be expressed as a simple function of v_1/v_2 provided that z is small, where z denotes p_{OH}, v denotes the ratio $(2p_{H_2O}+p_{OH})/(p_{H_2O}+2p_{O_2}+p_{OH})$, and the suffixes correspond with temperatures T_1 and T_2. The hydroxyl absorption of three oxygen-rich mixtures of water vapour and oxygen was determined at 1590° (T_1), and three corresponding temperatures, T_2, were then found at which the absorptions observed were respectively equal to that of a mixture weak in oxygen. Hence three values of z_1/z_2 are obtained; and, provided z is small, $k_1/k_2=z_1^4/z_2^4$, where k_1 and k_2 are the equilibrium constants of the reaction $4OH=2H_2O+O_2+W_0$ at T_1 and T_2, respectively. W_T may therefore be calculated from the equation: $W_T=(4\cdot571T_1T_2\log k_1/k_2)/(T_1-T_2)$. The mean of the three values for W_T is 146,000 g.-cal., corresponding with $W_0=142,000$ g.-cal. Hence it follows that $H_2+2OH=2H_2O+U_0$, where $U_0=128,000$ g.-cal. The dissociation constant of this reaction is then given by: $\log K_{OH}=-U_0/4\cdot571T+\Sigma Cp_0\log T/1\cdot986+(1/4\cdot571)\int_0^T(1/T^2)dT\int_0^T\Sigma Cp_T dT+\Sigma i$, where the symbols have their usual connotation. The chemical constants were calculated from the Sackur–Tetrode equation, the moments of inertia being derived from spectroscopic data: $\Sigma i=2i_{OH}-i_{H_2}-i_{O_2}=-0\cdot82+3\cdot36-0\cdot53=+2\cdot01$. Classical values for diatomic molecules were assumed for Cp_0 terms; and the Cp_T terms were calculated from $\phi(\nu/T)=R(h\nu/kT)^2e^{h\nu/kT}/(e^{h\nu/kT}-1)^2$, in which to ν the following values were assigned for hydrogen, oxygen, and hydroxyl, respectively: 5000, 3600, and 5100. The hydroxyl value was obtained by adopting that corresponding with the vibrational energy in the OH band spectrum, $\nu=3570$ cm.$^{-1}$ The values of K_{OH} so calculated differ but slightly from the accepted values of K for the reaction $2H_2+O_2=2H_2O$. The most intense absorption in the experiments recorded corresponds with a partial pressure of hydroxyl of 8 mm. at 1600°.

R. W. Lunt.

Ebullioscopic determination of equilibrium constants. W. Swientosławski, Z. Błaszkowska, and E. Józefowicz (Rocz. Chem., 1929, 9, 1—18).—Two mixtures are prepared containing ethyl alcohol, acetic acid, ethyl acetate, and water in such proportions that in one mixture the reaction is one of hydrolysis, whilst in the other it is one of esterification, and the mixtures are kept at boiling temperature in an atmosphere of nitrogen, until the b. p. of the two mixtures are identical (76·32°), indicating that equilibrium has been attained. Knowing the temperature coefficient of vapour pressure of such equimolecular systems (27·21), and the latent heat of vaporisation (8·76 kg.-cal./mol.), the equilibrium constant is derived from the b. p., and is found to be 3·76 for the above system.

R. Truskowski.

Ebullioscopic measurements on resorcinol in lithium chloride solutions. F. Bourion and E. Rouyer (Compt. rend., 1929, 188, 626—628; cf. A., 1928, 477).—In lithium chloride solutions resorcinol exists only as single or triple molecules; the equilibria observed in water or in potassium or sodium chloride solution between single and double molecules have not been observed in lithium chloride solutions even at low temperatures. The ebullioscopic constant increases with the concentration of the lithium chloride solution and, at constant alkali chloride concentration, decreases with the at. wt., whilst the equilibrium constant increases. In the series 1·225M-lithium chloride–water, for concentrations of resorcinol greater than 1·75M equilibrium appears to exist between single and quadruple molecules. These results are reconciled with earlier observations indicating that solutions of resorcinol in alkali chlorides have the properties of ideal solutions (A., 1927, 515) by assuming hydration of the alkali salt, the degree of hydration varying with the ionic activity of the salt. R. BRIGHTMAN.

Influence of sucrose on the dissociation constant of weak acids in aqueous solution. I. M. KOLTHOFF (Rec. trav. chim., 1929, **48**, 220—226).—The influence of sucrose on the p_H values of a series of buffer solutions has been determined, and has been found to be slight, confirming the inference that the addition of sucrose up to a concentration of 1·5M is practically without effect on the dissociation constants of acetic and citric acids. From measurements of the conductance of aqueous solutions of succinic, tartaric, acetic, and salicylic acids, and of similar solutions containing 20% of sucrose, it would seem that the dissociation constants of these acids may be regarded as unaltered by the presence of the sucrose if the concentration of the acid is expressed as the molal fraction with regard to the free water, and a hydration number of eight is accepted for sucrose in 20% solution. F. G. TRYHORN.

Dissociation constants of adenosinephosphoric acid of muscle and of inosinic acid. H. WASSERMEYER (Z. physiol. Chem., 1928, **179**, 238—242).—By electrometric titration the following dissociation constants were obtained: for adenosinephosphoric acid: $pK_1=3{\cdot}8$, $pK_2=6{\cdot}2$; for inosinic acid $pK_1=2{\cdot}4$, $pK_2=6{\cdot}3-6{\cdot}5$. J. H. BIRKINSHAW.

Dissociation constants of amino-acids. P. L. KIRK and C. L. A. SCHMIDT (J. Biol. Chem., 1929, **81**, 237—248).—Valine has K'_a $2{\cdot}40\times10^{-10}$, K'_b $2{\cdot}09\times10^{-12}$; *d*-*iso*leucine, K'_a $2{\cdot}09\times10^{-10}$, K'_b $2{\cdot}29\times10^{-12}$; *nor*leucine K'_a $1{\cdot}72\times10^{-10}$, K'_b $2{\cdot}46\times10^{-12}$; glutamic acid K'_a $5{\cdot}62\times10^{-5}$ and $2{\cdot}19\times10^{-10}$, K'_b $1{\cdot}55\times10^{-12}$; β-hydroxyglutamic acid K'_a $5{\cdot}82\times10^{-5}$ and $2{\cdot}76\times10^{-10}$, K'_b $2{\cdot}12\times10^{-12}$; serine K'_a $7{\cdot}08\times10^{-10}$, K'_b $1{\cdot}62\times10^{-12}$; oxyproline K'_a $1{\cdot}86\times10^{-10}$, K'_b $8{\cdot}32\times10^{-13}$. Introduction of a hydroxyl group into an amino-acid thus increases the acid dissociation constant. The isoelectric points of glutamic and β-hydroxyglutamic acids lie at p_H 3·22 and 3·28, respectively; the other amino-acids show an extended isoelectric zone. C. R. HARINGTON.

Dissociation constants of ornithine. W. SCHMIDT, P. L. KIRK, and C. L. A. SCHMIDT (J. Biol. Chem., 1929, **81**, 249—250).—Ornithine has K'_a $1{\cdot}74\times10^{-11}$, K'_{b_1} $4{\cdot}46\times10^{-6}$, K'_{b_2} $8{\cdot}70\times10^{-13}$; the isoelectric point is at p_H 9·7. C. R. HARINGTON.

Mutual displacement of benzoic acid and salicylic acid from their compounds with *m*-phenylenediamine. G. K. GLININ (J. Russ. Phys. Chem. Soc., 1928, **60**, 1641—1653).—The nature of the systems formed by benzoic acid with salicylic acid, by benzoic acid with the compound of salicylic acid with *m*-phenylenediamine, by salicylic acid with the compound of benzoic acid with *m*-phenylenediamine, and lastly by the two compounds with each other was investigated by the method of thermal analysis. The results of Kremann, Weber, and Zechner (A., 1926, 393) for the systems salicylic acid–*m*-phenylenediamine and benzoic acid–*m*-phenylenediamine have been recalculated so as to be expressed in the same terms as the author's other results and the thermal diagrams for these systems have been drawn. A rectangular diagram has been constructed, each corner of the diagram representing salicylic acid or benzoic acid or the compound of either acid with *m*-phenylenediamine. The fields occupied on the diagram by the four components differ both in size and character, that for the compound of salicylic acid with *m*-phenylenediamine is the largest and that for the other compound the smallest. One of the two diagonals represents a stable section and the other a metastable section. The stable section is represented by the section of the binary system benzoic acid–compound of salicylic acid with *m*-phenylenediamine. On this section there is practically no indication of any replacement of the salicylic acid by the benzoic acid from its compound with *m*-phenylenediamine. The section of the binary system salicylic acid–compound of benzoic acid with *m*-phenylenediamine represents the metastable section, and on it are clear indications of the salicylic acid displacing the benzoic acid from the compound of the latter with *m*-phenylenediamine to a large extent. A. FREIMAN.

Electrolytic solution forces and the condition of electrolytic ions. IV. Calculation and comparison of the energies of solution and solvation. Are electrolytic ions solvated gas ions? K. FREDENHAGEN (Z. physikal. Chem., 1929, **140**, 65—77).—The electrolytic solution energy and the solvation energy associated with the production of electrolytic ions from gaseous ions have been calculated for a number of uni- and bi-valent elements by regarding the solvation energy (solute ion ⟶ gaseous ion) as the sum of the solution energy (solute ion ⟶ gaseous atom) and the ionisation energy (gaseous atom ⟶ gaseous ion). The solution energy, which involves specific interaction between solvent and solute, is smaller than the energies of solvation and ionisation. The partition coefficients of the ions between the gaseous and liquid phases differ widely from the theoretical values based on the dielectric constants of the media; from this and other observations the conclusion is reached that electrolytic dissociation is not a simple process of electrostatic partition of charged particles between two media having different dielectric constants.

H. F. GILLBE.

Ionic radius and osmotic activity. G. B. BONINO and V. VAGLIO (Gazzetta, 1929, **59**, 49—56).—The conception of deformability of ions is applied to the Debye–Hückel theory, and the following expression is derived connecting the deformability, *d*, the

" osmotic " radius, a, and the effective radius, r, of an ion in $0{\cdot}1N$-solution: $a=0{\cdot}6z[(r/d)\times10^{16}+4{\cdot}67]\times10^{-8}$, where z is the valency of the ion. Using the ionic deformabilities given by Born (A., 1924, ii, 434) and the effective radii by Grimm and Wolff (A., 1926, 664), the values of a for the alkali and alkaline-earth metal ions in solutions of the chlorides have been calculated. These values can be used to calculate the depression of the f. p. in solutions of these chlorides, and the agreement with the experimental results recorded in the literature is good. It is therefore possible to calculate the osmotic properties of dilute solutions from physical constants of the ions without the introduction of an empirical constant depending on the nature of the ion.

O. J. Walker.

Generalisation of the third law of thermodynamics. J. G. Golitschuch (J. Russ. Phys. Chem. Soc., 1928, **60**, 1399—1401).—Polemical against Kolosovski (*ibid.*, 1927, **59**, 741). A. Freiman.

Equilibrium of a liquid with its vapour and the connexion with the thermodynamic potential. J. W. Dekker (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 973—977).—Boltzmann's condition $v_b e^{-\epsilon_{\text{mol.}}/kT}$ for the equilibrium between liquid and vapour requires that the value of $2\varepsilon_{pot}-RT\,.\log\,v_b$ shall be the same for the two phases. It is shown that the latter expression should be $\varepsilon_{pot}-(\partial\varepsilon_{pot}/\partial v)v-RT\,.\log\,v_b$, where v_b is per g.-mol. the space available for a last molecule centre among the molecules already present, ε the potential energy of one molecule in relation to the others, and kT is twice the mean kinetic energy per degree of freedom. F. G. Tryhorn.

Heat capacities in aqueous salt solutions. M. Randall and F. D. Rossini (J. Amer. Chem. Soc., 1929, **51**, 323—345).—The precision of the differential method of measuring apparent molal heat capacities of salts in solution previously recorded (A., 1927, 208) has been improved and the method used to carry out measurements at 25° on the chloride, bromide, iodide, nitrate, and sulphate of sodium and potassium in solutions up to 0·6, 1, 1·5, or 2·5 molal. The partial molal heat capacities of the solute (which rise to remarkably high values as the concentration of the solution increases), the partial molal heat capacities of the water, and the specific heats of the solutions are calculated from the results. The partial molal heat capacity of the potassium ion is more negative than that of sodium ion; the negativity increases for the anions in the order nitrate, chloride, bromide, iodide, sulphate. An equation is derived, on the basis of the Debye–Hückel theory, for the partial molal heat capacity of the solute, to which the experimental results for dilute solutions conform very well. A review of previously published data shows that in any given group of elements the partial molal heat capacity at infinite dilution becomes more negative as the atomic number increases, and becomes more negative in any given period of elements as the ion charge increases. The hydrogen ion does not fall in the regular order of the univalent positive ions, perhaps because of the formation of the oxonium ion, H_3O^+. The results are discussed with reference to hydration of ions and the temperature coefficient of the heat of dissolution of a strong electrolyte in a large amount of water. S. K. Tweedy.

Activities of molten alloys of thallium with tin and with lead. J. H. Hildebrand and J. N. Sharma (J. Amer. Chem. Soc., 1929, **51**, 462—471).—The *E.M.F.* of cells of the type Tl|fused mass containing 3 parts LiCl and 2 parts KCl|alloy were measured at 352°, 414°, and 478°. The activity coefficients, a_1, of thallium in the tin alloys are given by $\log a_1/N_1=(1{\cdot}0763-0{\cdot}00101T)N_2^2$, where N_1 is the mol.-fraction of thallium. Other thermodynamic quantities are calculated. The calculated heats of transfer of thallium from an ideal solution to a tin solution of the same mol.-fraction do not agree with the free energies calculated for the same process. The solution, therefore, is regular with respect to composition changes, but not with respect to temperature changes. The alloys exhibit a slight positive deviation from Raoult's law. Similar experiments were carried out on the thallium–lead system, which, although it does not deviate much from Raoult's law, exhibits complications attributable to the presence of $PbTl_2$. S. K. Tweedy.

Heat of combustion and dissolution of dihydroxyacetone. M. Kobel and W. A. Roth (Biochem. Z., 1928, **203**, 159—163).—The heat of combustion of freshly prepared dihydroxyacetone is 343·1 g.-cal. per mol., that of two molecules being 12·2—16·0 g.-cal. greater than that of the hexoses. The heat of dissolution is 3·98 g.-cal. per mol. P. W. Clutterbuck.

System magnesium–zinc. W. Hume-Rothery and E. O. Rounsefell (Inst. Metals, March, 1929, advance copy, 20 pp.).—The equilibrium diagram of the system magnesium–zinc has been investigated by thermal and microscopical methods in the range 0—70 at.-% magnesium. The solubility of magnesium in solid zinc increases from about 0·15 at.-% at 200° to 0·3 at.-% at 364°, which is the temperature of the Zn–$MgZn_5$ eutectic. The compound $MgZn_5$ discovered by Chadwick (B., 1928, 268) is confirmed, but the solid solution in this compound which was claimed by Chadwick is shown not to exist; the compound is formed at 381° by a peritectic reaction between $MgZn_2$ and liquid. The compound $MgZn_2$ melts at 590°, but does not form solid solutions. A new *compound*, MgZn, which is also of fixed composition, is formed at 354° by a peritectic reaction between $MgZn_2$ and liquid. The compounds MgZn and $MgZn_2$ are distinguished by etching with Benedicks' reagent, which stains MgZn brown. The equilibrium diagrams of the systems magnesium–cadmium and magnesium–zinc are compared, and the wide range of solid solutions in the former is shown to coincide with approximately equal atomic volumes. In elektron metal and similar alloys, any zinc which is present in excess of that in solid solution in magnesium exists as the new compound MgZn and not, as previously supposed, as $MgZn_2$.

W. Hume-Rothery.

Constitution of the cadmium-rich alloys of the system cadmium–gold. P. J. Durrant (Inst. Metals, March, 1929, advance copy, 33 pp.).—The system cadmium–gold has been investigated in the range 0—48 at.-% gold by thermal and microscopical

analysis. From pure cadmium the liquidus falls to a eutectic point at 7·95 at.-% (309°), rises to a flat maximum at 28·6 (500°), and then falls to a second eutectic at 30·0 (496°). From this point the liquidus continues to rise with a break at 540°, corresponding with a peritectic reaction at which a solid solution denoted III is formed. At 309° the solubility of gold in cadmium is 3·5 at.-%, but falls to 2·1 at 240°. The maximum at 500° corresponds with a solid solution denoted II, the solubility limits of which have been determined. The solid solution III was not detected by Saldau (J. Inst. Metals, 1923, 30, 351); it extends from 32·5 to 40 at.-% Au, and undergoes two transformations into forms denoted III′ and III″. The solubility limits diminish with falling temperature, until at 200° the range of solid solutions extends only from 37·5 to 38·5 at.-% Au. There is no evidence of the existence of a compound $AuCd_3$ at the liquidus, but there may be compounds Au_2Cd_5 and Au_2Cd_3, both being much dissociated at higher temperatures.
W. HUME-ROTHERY.

Silver–copper eutectic. J. A. A. LEROUX and E. RAUB (Z. anorg. Chem., 1929, 178, 257—271).—The formation of primary silver- and copper-rich mixed crystals simultaneously with eutectic in the cooling of silver–copper alloys containing 68—75% Ag is not always due to supercooling, nor is it caused by separation of two liquid phases in the molten alloy. The true explanation appears to lie in the greater rate of crystallisation of the copper-rich crystals as compared with the silver-rich crystals. This is especially marked in alloys which deviate by a few per cent. from the eutectic composition, the silver-rich alloys having a great tendency towards supercooling, whereas the copper-rich alloys have no such tendency. For these reasons the determination of the true eutectic composition is a matter of great difficulty and no trustworthy results have yet been obtained. The microstructure of eutectiferous alloys of this system has been studied both before and after homogenisation. In the cast alloys the eutectic colony is identical with the crystal grain, or several colonies may coalesce to form a grain the shape of which is therefore always dependent on the configuration of the colony; this in turn depends on the greater rate of growth of the copper-rich solution. The whole mechanism of the crystallisation of these alloys is therefore determined by the behaviour of this phase and is only relatively slightly affected by the properties of the silver-rich phase. A. R. POWELL.

Equilibria in the systems cobalt–sulphur–oxygen and nickel–sulphur–oxygen. R. SCHENCK and E. RAUB (Z. anorg. Chem., 1929, 178, 225—251).—Cobalt powder obtained by reduction of the formate with hydrogen reacts readily with sulphur dioxide yielding cobalt sulphide and oxide, and the reaction is irreversible, at least below 1050°. The reaction $CoSO_4+4Co=4CoO+CoS$ proceeds to completion at 525° and is also irreversible, but the reaction $3CoSO_4+CoS \rightleftharpoons 4CoO+4SO_2$ is reversible provided that the solid reactants are in an extremely fine state of subdivision. The decomposition of cobalt sulphate by heat first becomes appreciable at about 900° and is complete after prolonged heating at 970°. Nickel reacts rapidly with sulphur dioxide at 550°, but equilibrium is established only after many days, complete conversion into nickel oxide and monosulphide being effected. The equilibrium is univariant, as there are three solid phases, but by removing part of the sulphur dioxide one of these disappears and the equilibrium becomes bivariant. From a consideration of the equilibrium diagram and from measurements of the sulphur dioxide pressure the three phases appear to be nickel oxide, nickel sulphide, and the γ solid solution; with low pressures of sulphur dioxide the nickel sulphide phase disappears. The reverse reaction with the formation of nickel from nickel oxide and sulphide proceeds only as far as the solid solution phase below the m. p. (about 1400°); bundles of fine hair crystals of this phase, or possibly of Ni_3S_2, can be seen throughout the reacting mass in the early stages of this reaction. The sulphate reactions in the case of nickel are similar to those with cobalt, except that the temperature at which the gas pressure reaches 1 atm. is 475° instead of 525°. The heats of formation of cobalt and nickel sulphates have been calculated from the data obtained in this investigation as 228,800 and 232,000 g.-cal., respectively. A. R. POWELL.

Equilibria in the system calcium–sulphur–oxygen. I. R. SCHENCK and K. JORDAN (Z. anorg. Chem., 1929, 178, 389—399).—The reaction of calcium oxide with sulphur dioxide at high temperatures may be represented by the equations $4CaO+4SO_2=3CaSO_4+CaS$, and $CaSO_4+S_2 \rightleftharpoons CaS+2SO_2$. The gas pressures corresponding with the univariant equilibrium calcium oxide–calcium sulphate–calcium sulphide–gas (sulphur dioxide+sulphur vapour) are: 27 mm. at 850°, 34 mm. at 900°, and 46·5 mm. at 950°. R. CUTHILL.

Two correlated space models for representing the equilibria in the system iron–carbon–oxygen. E. JÄNECKE (Z. anorg. Chem., 1929, 178, 73—96).—The equilibria in the iron–carbon–oxygen system may be represented by two space models, one showing the relation between temperature and composition without reference to the gas pressure and the other the relation between the temperature and pressure with respect to the composition of the gas phase in equilibrium with the solid phase. The former model is a triangular prism and the latter a rectangular prism. In the construction of both models the invariant and univariant equilibria in the system are of considerable importance, especially the invariant point at which ferrous oxide first appears in the solid phase and the invariant equilibria at the temperatures at which martensite appears for the first time in the solid phase. In the first case the constituents present are iron, ferrous oxide, ferrosoferric oxide, and gas with carbon or cementite (metastable), and in the second case martensite, iron, ferrous oxide, and gas with carbon or cementite. With cementite the equilibrium is metastable and occurs at a relatively low temperature. The construction of the models is shown by diagrams and the equilibria in various sections are discussed fully. A. R. POWELL.

Two forms of crystalline beryllium hydroxide, and the system $BeO–Na_2O–H_2O$. R. FRICKE and

H. Humme (Z. anorg. Chem., 1929, **178**, 400—410).—If the crystalline variety of beryllium hydroxide which is obtained by heating the precipitated amorphous hydroxide with an aqueous solution of ammonia is left in contact with a 20—35% aqueous solution of sodium hydroxide at 30°, the crystalline form slowly changes, and ultimately becomes identical with that of the hydroxide prepared by slow hydrolysis of an alkali beryllate solution. The solubility of the stable form in the hydroxide solution increases with the sodium hydroxide concentration until the concentration of alkali hydroxide is about 35%; at this point the solubility curve shows a discontinuous maximum, owing to the solid phase undergoing transformation into monosodium beryllate, $BeO,NaOH,H_2O$. The solubility increases with rise in temperature.

R. Cuthill.

Ammonium sulphite and hydrogen sulphite. II. System ammonium sulphite–ammonium sulphate–water. F. Ishikawa and H. Murooka (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 75—88; cf. this vol., 141).—The solubility of ammonium sulphate in water (per 100 c.c. of solution) between the cryohydric point (−18·5°) and b. p. (108·5°) is given by the expression $(41{\cdot}22+0{\cdot}09t)$. The system ammonium sulphite–ammonium sulphate–water has been studied in detail at 15° and 30°. Between the cryohydric point (−21·5°) and 100° there is no evidence of the formation of compounds or solid solutions.

J. Grant.

Equilibrium between water, sodium nitrate, and sodium chloride. A. Chrétien and E. Cornec (Compt. rend., 1929, **188**, 628—631).—The equilibrium diagram is analogous to that for the system water–potassium chloride–sodium chloride. A warm saturated solution of the two salts deposits only the nitrate. The transition temperature, $NaCl+2H_2O \rightleftharpoons NaCl,2H_2O$, is lowered by successive additions of nitrate from 0·2° to −5·85°, at which point the saturated solution is in equilibrium with NaCl, $NaCl,2H_2O$, and $NaNO_3$. The ternary eutectic point, −24·3°, is in equilibrium with ice, $NaCl,2H_2O$, and $NaNO_3$.

R. Brightman.

System mercuric iodide–potassium iodide–acetone. (Mlle.) M. Pernot (Compt. rend., 1929, **188**, 635—637).—The compound $Me_2CO,4KI,4HgI_2$ is obtained by isothermal evaporation at 34°. When the crystallisation is effected by cooling, the compound $HgI_2,2KI$ and four supposedly isomeric compounds $Me_2CO,4KI,HgI_2$ are said to be formed (cf. A., 1926, 695). The compound, $2HgI,3KI$, found at 56°, is not obtained at 34°.

R. Brightman.

Equilibria between molten metals and salts. Displacement of the equilibrium in the reaction $Cd + PbCl_2 \rightleftharpoons Pb + CdCl_2$ by additions to (XIII) the salt phase and (XIV) both phases simultaneously. R. Lorenz and M. Hering (Z. anorg. Chem., 1929, **178**, 33—39, 40—48; cf. this vol., 266).—XIII. Addition of the eutectic sodium–potassium chloride mixture to the salt phase in the reaction $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ displaces the equilibrium from left to right, *i.e.*, lead becomes more noble with respect to cadmium.

XIV. Simultaneous addition of antimony to the metal phase in equimolecular proportion to the salt added to the salt phase first displaces the equilibrium from left to right, but larger additions have the reverse effect. At the same time the displaced isotherms approach more closely to those corresponding with the ideal mass action law.

A. R. Powell.

Equilibria between metals and salts in the molten state. XV. Displacement of the equivalence point in the equilibrium $Cd + PbCl_2 \rightleftharpoons Pb + CdCl_2$. R. Lorenz and M. Hering (Z. anorg. Chem., 1929, **178**, 337—345; cf. preceding abstract).—The effect of the simultaneous addition of an equimolecular mixture of sodium and potassium chlorides to the salt phase and antimony or bismuth to the metal phase has been investigated. With increase in the amount of substance added the displacement of the equilibrium tends to a limiting value. When both salts and a metal have been added, addition of more salts has a greater effect than the addition of an equimolecular amount of metal. From the data obtained, it is possible to calculate the amounts of metal and salts which must be added for the net displacement to be zero.

R. Cuthill.

Reduction of fused silicates by carbon monoxide. Copper silicates. B. Bogitch (Compt. rend., 1929, **188**, 633—635).—In presence of an atmosphere containing more than 2% of carbon monoxide at 1350—1400° fused blue copper silicate (stable in an oxidising atmosphere) is partly reduced to metallic copper, reduction being almost complete when the proportion of carbon monoxide exceeds 25%. Simultaneously with this reduction, the blue silicate is converted successively into other silicates as the proportion of carbon monoxide is increased: 2·5—4% green, 9% white, 10·5—12·5% opaque brick-red, 20—22·5% transparent blood-red.

R. Brightman.

Quaternary system lead acetate–lead chloride–acetic acid–water at 25°. K. Sandved (J.C.S., 1929, 337—344; cf. A., 1928, 131).—The systems lead acetate–lead chloride–water and lead chloride–acetic acid–water have been studied at 25°, and the former also at 35°. In combination with the data for the system lead acetate–acetic acid–water the results are applied to the quaternary system. In the first system two invariant points occur at 1·46% $PbCl_2$, 37·43% $Pb(OAc)_2$, and 4·48% $PbCl_2$, 21·25% $Pb(OAc)_2$, respectively. The solubility of lead acetate in pure water at 25° is 35·53%, and that of lead chloride 1·06%. At 35° the invariant points occur at 2·17% $PbCl_2$, 49·53% $Pb(OAc)_2$, and 7·72% $PbCl_2$, 31·90% $Pb(OAc)_2$, respectively. The solubilities of lead acetate and of lead chloride are 47·40 and 1·30%, respectively. The study of the quaternary system shows the existence of the compounds $PbCl{\cdot}OAc,Pb(OAc)_2,0{\cdot}5HOAc$ and $(PbCl{\cdot}OAc)_2,HOAc$.

F. G. Tryhorn.

System $NaNO_3$–Na_2SO_4–$MgCl_2$–H_2O in the neighbourhood of 0°, 10°, 25°, 75°, and 100°. G. Leimbach and A. Pfeiffenberger (Caliche, 1929, **10**, 447—468).—A detailed study has been made of the system at 0°, 10°, and 25°, and the results have been compared with those of other observers.

H. F. Gillbe.

Chemical equilibria between solid salts. C. Tubandt and H. Reinhold (Z. physikal. Chem., 1929, **140**, 291—308).—Interaction in pairs between the solid sulphides, selenides, tellurides, and halides of silver and of univalent copper leads to a definite state of equilibrium. The diffusion which takes place when the solids are brought into contact can be followed by the change in weight and the equilibrium composition derived. It is shown that the law of mass action is applicable to the reactions $Ag_2S+2CuI \rightleftharpoons Cu_2S+2AgI$ and $Ag_2S+Cu_2Se \rightleftharpoons Cu_2S+Ag_2Se$. The equilibrium constants have been determined at more than one temperature and the heats of reaction have been calculated. The values found, 12·7 and 8·77 kg.-cal., respectively, are in good agreement with values calculated by other methods. The difference in mechanism between these reactions and ordinary diffusion in solid salts is discussed.

R. N. Kerr.

Hydrocarbons as solvents. I. Conductivity of binary salts in ethylene chloride. P. Walden and G. Busch (Z. physikal. Chem., 1929, **140**, 89—123).—The conductivities of the following salts have been determined at 25° at dilutions up to 400,000 litres : tetraethylammonium chloride, perchlorate, and iodide, tetramethylammonium picrate, tetrapropylammonium picrate, perchlorate, and iodide, tetra*iso*amylammonium picrate and perchlorate, triethylammonium picrate and chloride, diethylammonium picrate and chloride, tripropylammonium picrate, dipropylammonium picrate, monopropylammonium picrate, and, at 0°, 25°, and 50°, tetraethylammonium picrate. The densities of the solvent and salts have also been determined. The Kohlrausch–Debye–Hückel square-root law is valid for ethylene chloride solutions at high dilutions. The nature of the salt has a well-defined influence on the value of the conductivity and on the classical degree of ionisation α. The tetra-alkylated ammonium salts behave as strong electrolytes, in contradistinction to the corresponding mono-, di-, and tri-alkylated compounds, the degree of ionisation of the strong electrolytes diminishing in the order $N(C_5H_{11})_4$, NPr_4, NEt_4, NMe_4. The causes of the difference of behaviour of the two classes are considered, and the relationships between the free bases in aqueous solution and their picrates in the fused state are discussed. Kohlrausch's law of the additivity of conductivities is completely valid for ethylene chloride solutions. The Walden constant $\lambda_\infty\eta$ has for tetraethylammonium picrate in ethylene chloride solution from 0° to 50° the value 0·563, in agreement with the value for water, methyl alcohol, ethyl alcohol, and acetone solutions. The individual ionic mobilities have been calculated.

H. F. Gillbe.

Conductivity of solutions of some aliphatic organic acids in water and ethyl alcohol. H. Hunt and H. T. Briscoe (J. Physical Chem., 1929, **33**, 190—199).—The specific conductances of the fatty acids from acetic to valeric acid and of their substituted derivatives, chiefly halogen, have been determined in water and in ethyl alcohol at 30°. In all cases the molecular conductance in alcohol is much less than that in water, and the rate of increase for successive dilutions is approximately twice as great in alcohol as in water. The order of conductance in the two solvents is not the same, *e.g.*, acetic acid is the 15th in the alcohol series and 8th in the water series, whilst β-bromopropionic acid is the poorest conductor in alcoholic solution, but stands above eight other acids in the water series. With the exception of *iso*valeric acid in water and hexoic acid in alcohol, the molecular conductance decreases with an increase in the number of carbon atoms for an homologous series. In alcohol, the *iso*-acids have a lower conductance than the corresponding normal acids, but in water the *iso*-acid may have a higher or lower conductance than the normal acid. The data do not show agreement in all cases with the Stark–Lewis theory of the effect of substituent groupings. The curves obtained by plotting the logarithm of the volume against conductance are in agreement with the mass action law at high dilutions.

L. S. Theobald.

High mobility of hydrogen and hydroxyl ions in aqueous solutions. M. S. Skanavi-Grigorieva (J. Russ. Phys. Chem. Soc., 1928, **60**, 1459—1475).—In order to ascertain the cause of the high mobility of the hydrogen and hydroxyl ions in aqueous solutions the molecular conductivities, viscosities, and densities of aqueous solutions of potassium chloride, hydrochloric acid, and sodium hydroxide containing different amounts (10, 20, 40, and 50%) of glycerol have been determined. The percentage changes in the molecular conductivities when compared with the changes in viscosity are found to be nearly the same for all three electrolytes. From this it is inferred that the high mobility of the hydrogen and hydroxyl ion is not due to the Grotthus–Danneel effect.

A. Freiman.

Influence of a high-potential direct current on the conductivity of an electrolyte. J. A. H. Leech-Porter and T. Alty (Phil. Mag., 1929, [vii], **7**, 153—159).—Direct-current potentials up to 600 volts have been applied to very dilute solutions of electrolytes in the measurement of their conductivities and have been shown to cause large variations in the conductivities in certain narrow ranges of concentrations. The effect is most marked in the case of hydrogen chloride solutions when the specific conductivity is about 2×10^{-4} ohm^{-1}, when the conductivity can vary as much as 600%. The results are explained on the view that the high potential causes a segregation of the ions towards the electrodes, where they remain until on reversing the potential each of the segregations moves across to the opposite electrode as a unit. Rough measurements of the velocity of this unit give a value of 74×10^{-5} cm./sec./volt/cm. for the mobility of the chlorine ion. This is in fair agreement with the accepted value of 68×10^{-5}, and indicates the possible application of the phenomenon in the determination of ionic mobilities.

A. E. Mitchell.

Voltage effect in electrolytic conductance with very high fields. M. Wien (Ann. Physik, 1929, [v], **1**, 400—416).—The limiting value for the voltage effect (A., 1928, 244 ; this vol., 32) for various electrolytes is in harmony with the concentration effect, and also shows close agreement with the values given by the

Debye–Onsager theory provided the valencies of the ions are small. With ions of higher valency, the theoretical values are lower than those obtained from the limiting voltage effect and the concentration effect. According to Debye and Falkenhagen, the influence of ionic forces should become vanishingly small with sufficiently strong fields. When association occurs, the limiting voltage effect should fall more markedly than the concentration effect. Inasmuch as the two phenomena run parallel, even with solutions containing ions of high valency, association can scarcely occur in the very dilute solutions of strong electrolytes which have been studied. R. A. Morton.

Potential of the nickel electrode. M. M. Haring and E. G. V. Bosche (J. Physical Chem., 1929, **33**, 161—178).—Measurements at 25±0·5° of the *E.M.F.* of cells of the type $Ni|NiSO_4|Hg_2SO_4|Hg$, using nickel and nickel sulphate prepared in various ways and from different sources, gave a mean value for E_0 equal to 0·852 volt, and using the value of Lewis and Randall for the electrode $Hg|Hg_2SO_4|SO_4''$, this gives for the standard potential of nickel at 25° the value —0·231±0·002 volt. Nickel prepared by electrolysis at high current densities is the most satisfactory for this type of work. Owing to hydrolysis of the nickel chloride, cells of the type $Ni|NiCl_2$(0·05 molal)$|Hg_2Cl_2|Hg$ could not be used. The necessity for excluding oxygen and hydrogen in such measurements is re-emphasised. Previous data are summarised and discussed. L. S. Theobald.

***P.D.* of dilute solutions. II.** M. Planck (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 9—11; cf. A., 1928, 481).—A formula applicable to simplified systems is deduced for the previously observed difference between the values found by Henderson and by the author for the diffusion potential between two dilute solutions of different electrolytes. An experimental arrangement is suggested which, according to this formula, is suitable for testing the two theoretical values for the potential. R. N. Kerr.

Dialuric acid–alloxan equilibrium. G. M. Richardson and R. K. Cannan (Biochem. J., 1929, **23**, 68—77).—Equilibrium potentials for the reversible oxidation–reduction system dialuric acid–alloxan have been determined for the p_H range 1—6 and related to the equilibrium potentials of alloxantin observed by Biilmann and Lund (A., 1923, ii, 605). Above p_H 6 approximate equilibrium potentials have been derived from the range p_H 6—12 on the assumption that over this range there is a slow isomeric change of alloxan to alloxanic acid. The first acidic constants of dialuric acid ($K'=1·48\times10^{-3}$) and of alloxan ($K'_1=6·31\times10^{-8}$) have been determined. A value has also been found for the second acidic constant of alloxan ($K'_2=1·0\times10^{-10}$). The association constant of alloxantin ($K=39$) has also been derived. Observations have also been made on the connexion between p_H and the rates of the isomeric change of alloxan and of the autoxidation of dialuric acid.

S. S. Zilva.

"Natural" *P.D.* at the boundary, cell–electrolyte. G. Ettisch (Z. physikal. Chem., 1928, **139**, 516—528).—Measurements made on *Amœba terricola* in a cell of the type Hg,HgCl,0·1*N*-KCl|buffer soln.|amœba|Hg,HgCl,0·1*N*-KCl show that such a cell assumes a state of minimum free energy. The *E.M.F.* measured is zero, but by altering the concentration of the buffer solution during the measurement, by introducing a small crystal of sodium chloride, a temporary *E.M.F.* is produced. In a very short time the reading recedes to the null-point again. At the boundary cell–electrolyte some phase boundary force must appear, the so-called "natural" *P.D.*, the living amœba setting up a state of equilibrium which is very quickly adjusted when disturbed by variation in concentration. G. E. Wentworth.

Nature of Kučera's electrocapillary curve anomalies. K. Teige (Chem. Listy, 1929, **23**, 54—58).—The maxima shown by Kučera (Ann. Phys., 1903, II, 568) to occur in electrocapillary curves are due to the displacement of non-electrolytes by electrolytes from the surface of the cathode, within certain limits of *E.M.F.* R. Truszkowski.

Hydrogen overvoltage of alloys. M. G. Raeder and D. Efjestad (Z. physikal. Chem., 1929, **140**, 124—132).—The hydrogen overvoltage of alloy cathodes has been studied by reference to potential–current density curves. Previous results (A., 1928, 597) have been confirmed. Mixed crystal formation sometimes has but little influence on the overvoltage curve (mercury–cadmium), but in other cases a peaked curve is produced (tin–lead, copper–tin, silver–zinc). A sharp drop in the overvoltage has not so far been observed. Formation of eutectics or of compounds has no marked influence on the curve.

H. F. Gillbe.

Theory of passivity. IV. Dependence of specific passivating time for iron on the concentration and nature of electrolytes. W. J. Müller and O. Löwy (Monatsh., 1929, **51**, 73—85).—The relation between initial current strength and passivation time has been studied with sulphuric acid over the range *N*/16—13*N*. The results confirm the validity of the formula $\log t_p=\log B+n\log(i_0/F_0)$ (cf., A., 1928, 714), where *B* is the specific passivation time when the current density is unity. Small acid concentrations give small specific passivating times. A maximum is reached at 2*N*, and above this concentration there is a fall in the time. In *N*-sulphuric acid the passivation time increases with rise of temperature over the range (20—60°) studied. With varying amounts of ferrous and ferric sulphates in *N*-sulphuric acid the values of *n* remain constant, but those of *B* decrease with increasing concentration of added salts. A rise of temperature is in this case associated with an increase in the value of *B*, but with saturated solutions of ferrous sulphate in *N*-sulphuric acid the values at 20° and 40° are the same. The results confirm the theory that the first stage of the passivation of iron consists in the deposition of a salt layer (cf. A., 1928, 247, 714). H. Burton.

Theory of physico-chemical periodicity. N. von Raschevsky (Z. Physik, 1928, **52**, 372—381).—Theoretical arguments are put forward indicating that when a sequence of reactions occurs which gives rise to a heterogeneous, cell-like structure it may occur in a periodic manner. J. W. Smith.

Velocity of combination of hydrogen atoms. Z. Bay and W. Steiner (Z. physikal. Chem., 1929, B, 2, 146—147).—Atomic hydrogen was obtained by the usual method, and the amount of combination determined by means of diffusion columns. It was found that if the concentration of atomic hydrogen were plotted against time, at low pressures a straight line was obtained, whilst at higher pressures curves were found. From the experiments at higher pressures (0·2 mm.), for a concentration of 35% of hydrogen atoms, the mean life (half-value period) was about 1 sec. This agrees with Bonhoeffer's value obtained by chemical methods. The half-value period obtained is the value expected on the assumption that there are triple collisions. A. J. Mee.

Mechanism of the homogeneous combination of hydrogen and oxygen. H. W. Thompson and C. N. Hinshelwood (Proc. Roy. Soc., 1929, A, 122, 610—621).—The chain theory of chemical reaction in gases is briefly reviewed, and it is shown that the velocity of a chain reaction can be expressed by the formula $v=F(c)/\{f(c,s)+A(1-\alpha)\}$, where $F(c)$ is a function of the concentrations of the reacting substances, to which the number chains starting in unit time is proportional; $f(c,s)$ is another function of the concentrations, governing the rate of breaking of the chains; A is a constant in reactions where only one kind of molecule is involved, but is a function of the concentration in reactions between two kinds of molecules; and α is a fraction measuring the average number of activated molecules produced in each act of transformation. Two types of chain reaction are possible, one leading to a "stationary" condition (identified with slow reaction) and the other where this condition is impossible (explosive reaction). The combination of hydrogen and oxygen between 500° and 600° has previously been shown to be a chain reaction, the rate increasing rapidly with the pressure (cf. A., 1928, 483, 960). It is now found that, as the pressure is decreased, the chains become "non-stationary" and the reaction explosive over a certain region of falling pressure, after which, with still further falling pressure, the reaction again becomes slow. A detailed investigation of the upper and lower pressure limits of the explosive region shows that, with regard to the upper critical pressure, (*a*) at a given temperature it is slightly lowered by an increase in the ratio of the H_2/O_2 mixture; (*b*) it is somewhat lowered by the presence of argon; (*c*) at any temperature over a wide range it is almost, if not quite, independent of the nature and extent of the surface of the reaction vessel; it diminishes rapidly as the temperature falls. The temperature at which ignition ceases completely will obviously be that at which the upper and lower pressure limits coincide. In an unpacked silica bulb this is about 450°, from which it is deduced that the lower limit will be approximately 8 mm. The theory of these phenomena is discussed, and a hypothesis of two simultaneously operating mechanisms is advanced. At high pressures the chains are initiated by the termolecular process $2H_2+O_2=2H_2O$, but at low pressures it is assumed that the termolecular process is to a large extent superseded by a chain of bimolecular process, $H_2+O_2=H_2O_2$, $H_2O_2+H_2=2H_2O$, etc. For a given condition of temperature and pressure there will be a small stationary concentration of hydrogen peroxide in the gas, regulated by the thermal equilibrium $H_2+O_2\rightleftharpoons H_2O_2$. This concentration will increase with pressure, and the upper and lower pressure limits will correspond with two limiting concentrations of hydrogen peroxide. This hypothesis accounts for the facts concerning the critical pressure limits, and also suggests an explanation of the influence of traces of nitrogen peroxide on the reaction.
L. L. Bircumshaw.

Spark ignition of hydrogen–air mixture. K. Yumoto (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 131—142).—Variations in the nature of the spark used for the ignition of a mixture of air and 5·5% of hydrogen indicate that the flame formed in a static electric field between parallel plate electrodes is attracted to the metallic cathode of the field, a considerable amount of heat then being lost by conduction so that the flame is eventually extinguished. Whether the flame is extinguished or further propagated, in the absence of a static field it is always propagated initially towards the cathode of the ignition spark gap. J. Grant.

Firedamp explosions within closed vessels; "pressure piling." C. S. W. Grice and R. V. Wheeler.—See B., 1929, 193.

Inflammation of mixtures of olefines and air in a closed spherical vessel. G. B. Maxwell and R. V. Wheeler (J.C.S., 1929, 245—251).—Experiments parallel to those already described (A., 1927, 1036) on the inflammation of mixtures of the paraffins and air have been made with ethylene, propylene, and butylene. The results for the olefines are similar to those obtained with the paraffins. There is a marked "displacement" of the observed maximum pressure mixture, from the theoretical for complete combustion, towards excess of hydrocarbon. This displacement is attributed to dissociation. The amounts of "lost pressure" are higher than with the paraffins. In accord with the results of the experiments with paraffins, a close correspondence between observed values for maximum speed mixtures and calculated values for the maximum temperature mixtures was found, indicating that flame temperature is the controlling factor in determining the mean rate of development of pressure. F. J. Wilkins.

Active nitrogen. V (amended). Decay of the nitrogen after-glow. E. J. B. Willey (J.C.S., 1929, 228—231; cf. A., 1928, 961).—An arithmetical error in an earlier paper is corrected and its influence on the theoretical discussion contained in it pointed out. It is now suggested that the decay process is of the third instead of the fifth order. The analysis is complicated by the existence of a surface action.
F. J. Wilkins.

Explosion regions of some gas and vapour mixtures in which carbon monoxide is the only or principal inflammable gas. J. H. A. P. Langen van der Valk (Rec. trav. chim., 1929, 48, 201—219; cf. A., 1925, ii, 874).—Under certain experimental conditions the upper and lower explosion limits of carbon monoxide in air were 72·75 and 15·35%, respectively. The effect of saturating the carbon monoxide at 14° with the vapours of various organic liquids has been determined. The explosion limits were brought closer together by trichloroethylene. For dichloroethylene and air the explosion limits were 3·25% and 15%. The lower limit decreases linearly with admixture of carbon monoxide, but the upper limit is little affected. Admixture of perchloroethylene, tetrachloroethane, or pentachloroethane brings closer together the explosion limits of carbon monoxide–air mixtures. The presence of little more than 1% of carbon tetrachloride vapour completely inhibits the explosion of carbon monoxide–air mixtures. For mixtures containing 3% and 2% of chloroform vapour the explosion limits were, respectively, 25·5—38·5%, and 22·5—45·5%. Of methylene dichloride 20% was necessary to inhibit explosion, the limits separating to 13·15 and 35·45% for mixtures containing 10% of this substance. Methyl chloride, of which the explosion limits in air are 16·3 and 24·4%, widens the limits of explosion of carbon monoxide–air mixtures. The investigation was extended to the quaternary system carbon monoxide–air–methane–chloroform, and an unsuccessful search was made for a closed explosion region in the system methylene dichloride–methylene dibromide–oxygen–nitrogen. F. G. Tryhorn.

Decomposition of nitrous oxide in the silent electric discharge. II. S. S. Joshi (Trans. Faraday Soc., 1929, **25**, 108—117; cf. A., 1927, 635).—In a previous paper (cf. A., 1927, 212) an equation was derived for the velocity of a chemical reaction in the silent electric discharge. In order to test the applicability of this equation to the initial stages of the decomposition of nitrous oxide the percentage decomposition of nitrous oxide (θ) has been determined under different conditions of gas pressure, applied potential, and duration of exposure. It is found that θ decreases with increase of initial pressure and increases with increase of potential applied to the ozoniser. The diminution of log θ with respect to the pressure is linear, as required by the velocity equation. From this equation the critical energy for the decomposition of nitrous oxide by an ionic collision is calculated, and the values from several experiments with different reaction vessels and applied voltage and a wide range of time intervals all lie between 0·7 and 1·0 volt. This value corresponds with the partial decomposition of nitrous oxide into the peroxide and nitrogen, and is smaller than the value of the critical energy of the reaction in which nitrous oxide changes completely into nitrogen and oxygen. O. J. Walker.

Decomposition of nitrous oxide in the silent electric discharge. III. Variation of the current and power during the reaction. S. S. Joshi (Trans. Faraday Soc., 1929, **25**, 118—128; cf. preceding abstract).—The decomposition of nitrous oxide has been examined with particular reference to the composition of the gaseous mixture at different stages of the reaction in order to determine to what extent the substances characteristic of the intermediate and final stages are responsible for the changes in the power and current, which were previously found to occur during the course of the reaction (cf. A., 1927, 635). These changes have been confirmed by more exact measurements of the power consumed in the ozoniser. The results are in good agreement with the mechanism of the reaction previously suggested. The first stage consists of the conversion of nitrous oxide into nitrogen peroxide and nitrogen. During this stage both the current and the power consumed in the ozoniser diminish from large initial values to a minimum at approximately the same time that the proportion of the peroxide reaches a maximum. The decomposition of the peroxide into nitrogen and oxygen is the main reaction in the intermediate and final stages. During the intermediate stage the values of the current, of the power consumed, and of the reaction rate are relatively low and practically constant. In the final stage, which is characterised by a sudden increase of pressure, the reaction becomes more rapid, and during this period the current and power increase appreciably up to a constant value corresponding with the completion of the decomposition. O. J. Walker.

Interference of characteristic vibrations as cause of energy fluctuations and chemical changes. M. Pólányi and E. Wigner (Z. physikal. Chem., 1928, **139**, 439—452).—The velocity coefficient of unimolecular reactions in solution and in the gaseous state contains in addition to an exponential term a quantity which is always of about the same order of magnitude, 10^{14}. In order to explain this, it is suggested that the atoms in molecules fluctuate about equilibrium positions and therefore give rise to characteristic vibrations. If, by interference, the amplitude for a certain band increases beyond a critical amount chemical change occurs. The expression for the velocity coefficient is $\nu e^{-Q/RT}$, where ν is the frequency of atomic vibrations. Calculations are given showing that this frequency is of approximately the required order of magnitude, 5×10^{12}—5×10^{13} sec.$^{-1}$ R. N. Kerr.

Oxidation by air of stannous chloride in sulphuric acid solution, and the dissolution velocity of oxygen in sulphuric acid solutions. S. Miyamoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 7—17, and Bull. Chem. Soc. Japan, 1929, **4**, 48—56).—The rate of oxidation of stannous chloride in sulphuric acid solutions by the passage through them of air at a definite speed at 20°, 30°, and 40°, when calculated as a zero-order reaction, increased slowly as the acid concentration was increased up to 0·8*N*, after which it assumed a constant rate. Calculations from the data obtained of the volumes of oxygen dissolved per min. revealed that they were nearly the same as those utilised in the oxidation in hydrochloric acid solutions under the same conditions. Temperature had a negligible effect when the concentration of sulphuric acid was greater than 0·8*N*. H. T. S. Britton.

Influence of the polarity of the solvent on the velocity of a reaction. R. N. Kerr (J.C.S., 1929, 239—242).—The reaction between allyl bromide and pyridine has been studied in a series of disubstituted benzene derivatives. The results for chlorobenzene and the dichlorobenzenes, anisole, and the tolyl methyl ethers may be interpreted on the basis of variations in the electric moments of the solvent molecules. In other cases, such as the nitrobenzenes, variations occur in the reaction velocities which cannot be explained only in terms of the influence of the dipole moment of the solvent molecules. F. J. WILKINS.

Kinetics of the hydrolysis of certain glucosides. II. Trehalose, α-methylglucoside, and tetramethyl-α-methylglucoside. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, **25**, 81—92; cf. A., 1928, 374).—The rates of hydrolysis of the above three substances by means of *N*-hydrochloric acid have been determined polarimetrically at two temperatures and the corresponding critical increments calculated. The critical increments furnish a more trustworthy guide in the comparison of structural stability than the velocity coefficients, which are only of qualitative value, since the ratio of velocity coefficients varies with the temperature except in particular cases. The lability of sucrose towards acids cannot be associated with the grouping –O·C·O·C·O– and is more probably due to the γ-fructose half. Evidence is advanced for the view that the process of mutarotation does not involve the rupture of the oxide ring. It is attempted to reconcile the data for glucoside hydrolysis with Hinshelwood's velocity equation (A., 1927, 26) based on a collision theory of unimolecular reactions. The idea that internal degrees of freedom of the "hydrolyst" molecule can contribute to the energy of activation can be used as a means of differentiating between enzymic and non-enzymic hydrolyses. It is suggested that the function of an enzyme is to allow a greater number of internal degrees of freedom to come into play in the process of activation than is possible in its absence. O. J. WALKER.

Atmospheric oxidation, or dealkylation, of aqueous solutions of methylene-blue. W. C. HOLMES and E. F. SNYDER (Stain Tech., 1929, **4**, 7—10).—At about 25° dilute solutions of methylene-blue are stable below p_H 9·5. Oxidation begins between p_H 9·5 and 9·8 and increases with increasing alkalinity. Below p_H 11 the rate is slow and the amount of oxidation limited, but at p_H 12 oxidation is rapid and complete in a few days.

Trimethylthionine is less stable than methylene-blue to atmospheric oxidation. H. W. DUDLEY.

Steric hindrance. S. C. J. OLIVIER (Rec. trav. chim., 1929, **48**, 227—236).—Hydrolysis velocity coefficients for a number of halogen-substituted benzoyl and benzyl chlorides were determined. The observed rates of hydrolysis of *o*-, *m*-, and *p*-bromo-, 2 : 6-, 2 : 4-, and 3 : 5-dibromo-benzoyl chlorides were (benzoyl chloride=1) 1·35, 1·69, 0·92, 0·0112, 2·19, 13·5, respectively, showing the considerable steric hindrance effect operative with the 2 : 6-compound. The author considers that in the case of hydrolysis of acid chlorides the reaction measured is addition of water: $ClR{\cdot}C{:}O+H_2O\longrightarrow ClR{\cdot}C(OH)_2$. No steric effects were observed in similar experiments with corresponding halogenated benzyl chlorides, for which the figures were (benzyl chloride=1) 0·280, 0·202, 0·51, 0·120, 0·207, 0·070, respectively. Reaction velocities were determined in 50 vol.-% acetone-water mixtures. R. J. W. LE FÈVRE.

Rate of oxidation of porcelain and ball clays. H. M. KRANER and E. H. FRITZ.—See B., 1929, 208.

Corrosion of steel at high temperatures. L. LOSANA and G. REGGIANI.—See B., 1929, 210.

Action of atomic hydrogen on hydrocarbons. H. VON WARTENBERG and G. SCHULTZE (Z. physikal. Chem., 1929, B, **2**, 1—9).—A method is described for measuring the heat evolved when methane, ethane, ethylene, and acetylene respectively are mixed with atomic hydrogen. The products of the reactions were also investigated. Methane remained practically unchanged, but brought about a little catalytic combination of the hydrogen atoms to form molecules. Acetylene and ethane were also unaffected, but brought about some catalytic combination of the atoms. Ethylene was converted into ethane and also catalysed the combination of hydrogen atoms, obviously through the action of the ethane formed. Some acetylene was also produced. An attempt is made to explain the catalytic activity of acetylene and ethane. Probably the reaction is represented by the equations: $C_2H_6+H=C_2H_5+H_2$; $C_2H_5+H=C_2H_6$. A. J. MEE.

[**Oxidative catalytic activity of iron.**] H. HANDOVSKY (Biochem. Z., 1928, **202**, 157—158).—The author's theory of the mechanism of the oxidative catalytic action of iron (A., 1928, 718) is maintained against Warburg's criticisms (*ibid.*, 1195). P. W. CLUTTERBUCK.

Action of carbon monoxide and hydrogen cyanide on catalysis by hæmatin. H. A. KREBS (Biochem. Z., 1929, **204**, 322—342).—Experiments on the catalytic oxidation of cysteine to cystine by hæmatin and by some of its derivatives show that the compound of hæmatin with pyridine is particularly active. At 20° an amount of this compound equivalent to 1 mg. of iron transfers 100,000 c.c. of oxygen per hr. to cysteine, the tervalent iron of the hæmatin compound being first reduced in the process to the bivalent iron of pyridine-hæmochromogen and then reoxidised by molecular oxygen. The tervalent iron of pyridine-hæmatin does not react with the thiol group of cysteine. Carbon monoxide and hydrocyanic acid (but not hydrogen sulphide) check the oxidation process. Carbon monoxide combines in the dark with the bivalent iron of the hæmochromogen and so interferes with the reaction between the iron and oxygen, but on illumination the carbon monoxide–hæmochromogen compound is dissociated and the catalytic process proceeds as before. Hydrocyanic acid, on the other hand, reacts with the tervalent iron of the pyridine-hæmatin compound. The reactions of the hæmin compounds are also the characteristic reactions of the respiratory enzyme. W. MCCARTNEY.

Biological oxidation–reduction systems. II. Reducing effect of cysteine induced by free metals. L. MICHAELIS and E. S. G. BARRON (J. Biol. Chem., 1929, **81**, 29—40).—Mercury, platinum, especially in the form of platinum-black, and gold deposited on platinum accelerate the uptake of oxygen by a solution of cysteine, the effect being maximal at p_H 12·8. Salts of the above metals have no such effect; cyanides have no influence in the case of mercury, but inhibit the effect of platinum. Mercury and platinum also accelerate the reduction of methylene-blue by cysteine. Silver has no effect on either reaction whether in the metallic state or as a salt. C. R. Harington.

Action of heavy metals on the autoxidation of alkali sulphides and of hydrogen sulphide. H. A. Krebs (Biochem. Z., 1929, **204**, 343—346).—The rate of oxidation of alkali sulphide is enormously increased by the presence of minute quantities of heavy metals. Manganese and nickel are the most active metals; the presence of the former in amounts of the order 10^{-9} g. or of the latter in amounts of the order 10^{-8} g. doubles the velocity of oxidation. Solutions of hydrogen sulphide require much greater amounts (10,000—100,000 times) of heavy metals to produce the same results. For aqueous solutions of hydrogen sulphide nickel is the most active catalyst; for solutions of hydrogen sulphide in *N*-hydrochloric acid a mixture of manganese and iron. The so-called autoxidation of solutions of sulphides is probably due to the presence of traces of heavy metals. W. McCartney.

Thermal decomposition of methane. T. Kusana and Y. Uno.—See B., 1929, 193.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. III. *X*-Ray examination of methyl alcohol catalysts composed of copper and zinc. P. K. Frolich, R. L. Davidson, and M. R. Fenske (Ind. Eng. Chem., 1929, **21**, 109—111; cf. A., 1928, 1112; this vol., 153).—Zinc oxide is partly reducible at 200—220° in a stream of methyl alcohol vapour particularly when in admixture with copper oxide. The exothermic reduction of the latter oxide may furnish the necessary energy for the partial reduction of the zinc oxide. An attempt has been made to ascertain by *X*-ray examination if the zinc oxide is reduced to the metallic state. It has not been possible to prove the presence of metallic zinc, although there are indications that it is present. The complete series of zinc oxide–copper catalysts studied (from pure zinc oxide to pure copper) all possess the characteristic crystal structure of the two components. The cell unit sizes of both copper and zinc oxide are markedly influenced by the presence of the other constituent. The selective activity of these catalysts appears to be related in some way to the distances separating the atoms of their constituents. H. Ingleson.

Catalysis by metals of the platinum group. G. R. Levi (Atti R. Accad. Lincei, 1928, [vi], 8, 409—414; cf. A., 1926, 365).—From measurements of the decomposition of hydrogen peroxide by preparations of pure platinum, and of platinum containing 10% respectively of palladium, osmium, ruthenium, iridium, and rhodium, supported in each case on an inert base, it has been found that the catalytic activity of the platinum is lowered by the presence of the other metals, except in the case of osmium. The inhibiting effects of these metals were in the order rhodium, palladium, and iridium. Ruthenium was almost without effect, whilst the presence of 10% of osmium roughly doubled the catalytic activity of the platinum. Except in this last case, the results are analogous to those obtained with the same catalysts in the formation of sulphur trioxide. F. G. Tryhorn.

Formation of hydrazine from ammonia by electrical discharges. G. Bredig, A. Koenig, and O. H. Wagner (Z. physikal. Chem., 1928, **139**, 211—223).—Ammonia is decomposed partly into hydrazine at pressures of the order of 100 mm. by an ozoniser discharge excited by alternating potentials of frequency 50, and by streaming the gas through a high-tension cooled arc excited by continuous or alternating potentials. By using streaming velocities of the order of 400 mg. per min. a yield of hydrazine corresponding with about 1 g. per kw.-hr. may be obtained. R. W. Lunt.

Quantitative electrolytic reduction. II. Reduction of nitric acid. E. Nietz (J. pr. chem., 1929, [ii], **121**, 27—55).—The various errors involved in the quantitative electrolytic reduction of a nitrate to ammonia have been studied in detail. With a spongy copper cathode, which is the most efficient for this reduction, the main causes of error are: (1) the evolution of a small amount of nitrogen, probably as oxides of nitrogen formed by anodic oxidation, a source of error which it was not found possible to remove either by cooling, by use of a gauze anode, or by using a soluble anode; (2) dissolution of traces of copper from the cathode during the reduction and subsequent washing. This source of error is almost eliminated by neutralising the reduced solution before stopping the current. Another important source of error, which, however, is negligible when the reduction proceeds normally, is the formation of hydroxylamine, since this is not reduced under the conditions of current density employed, but requires a much higher current density which causes a greater evolution of hydrogen, and is oxidised at the anode to nitrate. Incomplete reduction of the nitrate to ammonia from this cause arises if the cathode surface is not completely spongy, or if the path of the current is not symmetrical, since the cathode current density is then not uniform and a greater evolution of hydrogen occurs. Such is the case if the distance between the cell-wall and the cathode is too small. Rotation of the anode has no effect, since efficient mixing is brought about by the oxygen evolved at the anode. The degree of acidity is also unimportant, providing it is not reduced to a value approaching the theoretical quantity. Measurements of the electrode potentials show that the course of the reduction is conditioned by a large increase in the depolarisation of the spongy copper electrode due to the catalytic action of the copper surface. The depolarising effect of the nitrate ions occurs only above a certain minimal concentration, which is smaller for a spongy copper cathode than for one of polished copper. A considerable quantity of hydroxylamine is produced if the cathode potential goes beyond a certain negative value which varies with the other electrolysis conditions. J. W. Baker.

Quantitative electrolytic reduction. I. Reduction of tervalent to bivalent iron. E. Nietz

(J. pr. Chem., 1929, [ii], **121**, 1—26).—The various sources of error in the quantitative electrolytic reduction of tervalent iron have been studied. When either a porous pot or a collodion diaphragm is used a small quantity of iron always diffuses back against the current into the anode compartment, the quantity not being appreciably influenced by the period of electrolysis, the current strength, or the temperature. This back diffusion is not prevented by an increase in hydrostatic pressure in the anode compartment. If the same pot diaphragm is repeatedly used with only air drying intermediately, the quantity of iron in the anode compartment gradually decreases until finally no colour can be obtained with potassium thiocyanate, since a quantity of iron approximately proportional to the period of electrolysis and the original concentration of iron gets back through the cell-wall by an " interchange-absorption " mechanism. The reduction is never quite complete owing to the diffusion of persulphate ions through the diaphragm into the cathode department. The influence of various factors on the optimum period of reduction was investigated. When the quantity of iron is varied from 0·1 to 0·3 g. the optimum reduction period changes from 30—40 to 80—90 min., after which further electrolysis causes a small decrease in the amount of ferrous iron, due either to absorption by the diaphragm or to an increased amount of persulphate consequent on the increased concentration of sulphate ions in the anode compartment. The optimum concentration of acid is 5—10% of free sulphuric acid. Rise of temperature to 96° or use of a rotating anode shortens the period of reduction. The current strength must not fall below 1 amp. These results were tested in the quantitative electrolytic reduction of iron using a diaphragm and stationary platinum electrodes, by Hostetter's method (A., 1913, ii, 1078) and Allen's methods (A., 1914, ii, 581) using a closed cell with a soluble (amalgamated zinc) anode and a rotating copper cathode, and the errors of the various methods compared.

J. W. BAKER.

Electrolysis of cyanogen halides. R. H. CLARK and H. R. L. STREIGHT (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 323—329).—An attempt was made to isolate and identify the products of electrolysis of the cyanogen halides employing various solvents, in the hope of obtaining definite proof of the deposition of halogen on the cathode. In all cases, however, it was found that the halogen travels to the anode with the exception of iodine from iodocyanogen in pyridine, which goes to the cathode. It would appear that iodocyanogen acts as an electromeride $\overset{+}{\mathrm{I}}\cdot\overset{-}{\mathrm{CN}} \rightleftharpoons \overset{-}{\mathrm{I}}\cdot\overset{+}{\mathrm{CN}}$. The iodine reacts negatively in electrolysis in most solvents, but positively in pyridine solution.

A. J. MEE.

Effect of different electrolytes in the electrodeposition of copper. A. JULIARD and J. LEDRUT.—See B., 1929, 177.

Electrolysis of nickel. B. BOGITCH.—See B., 1929, 213.

Measurement of the strength of sunlight. H. H. BAGNALL (Analyst, 1929, **54**, 101—103).—Solutions of potassium iodide are acidified with sulphuric acid and exposed to the action of the light in presence of air. The amount of iodine liberated is a measure of the chemical activity of the light received. Tables illustrating the seasonal variations in the activity of the sunlight are given. J. S. CARTER.

***X*-Ray photolysis of hydrogen peroxide.** O. RISSE (Z. physikal. Chem., 1929, **140**, 133—157).—The conditions governing the X-ray photolysis of aqueous hydrogen peroxide solutions have been studied over the concentration range 0·001—0·25M. At very low concentrations the quantity decomposed bears a linear relationship to the product It, where I is the intensity of the incident rays and t the time of exposure; the decomposition velocity is practically independent of the concentration, whilst at the higher concentrations, and down to about 0·05M, the process conforms tolerably well to the law for unimolecular reactions. Since the observed values do not satisfy the equation for second- or third-order reactions a complex process is postulated. Investigation of the action of X-rays on conductivity water shows that dissolved oxygen is converted quantitatively into hydrogen peroxide and that even in absence of dissolved oxygen the conductivity and acidity increase. Irradiation of conductivity water by a quartz–mercury lamp results in a greater increase of acidity, but no hydrogen peroxide is produced unless a photocatalyst such as zinc oxide is present. Activation of the oxygen is thus a necessary condition for the production of hydrogen peroxide from water and oxygen. During the decomposition of hydrogen peroxide by X-rays an inflammable gas is produced in quantity equal to about 1·5—2% of the volume of oxygen liberated. The temperature coefficient of the reaction in about $M/600$-solution is unity at temperatures from 2° to 50°. Strong acids and alkalis retard the decomposition. From energy considerations it is demonstrated that the energy necessary for the complete decomposition of one molecule of hydrogen peroxide, which in $M/600$-solution is 70 kg.-cal., decreases with increase of the hydrogen peroxide concentration.

H. F. GILLBE.

Action of light and *X*-rays on ammonium thiocyanate. C. G. PATTEN and H. D. SMITH (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 221—224).—When a concentrated aqueous solution of ammonium thiocyanate is exposed to sunlight for 1 min. it turns bright red, but the colour disappears in the dark after 2 min. This is not due either to the formation of sub-microscopic particles of sulphur, or to the dissociation of the salt into ammonia and thiocyanic acid, as has been supposed, but to the fact that minute traces of iron in the salt are oxidised by a photo-reaction and then form the red ferric thiocyanate, the process being reversed in the dark. The wave-lengths effective in this reaction extend from the middle of the visible spectrum well into the ultra-violet. X-Rays are equally effective as sunlight. The importance of this photo-reaction with iron in the explanation of the coloration and change in optical transparency produced in many glasses by X-rays and intense sources of ultra-violet light is being investigated. A. J. MEE.

Action of X-rays on ferrous sulphate solutions. H. Fricke and S. Morse (Phil. Mag., 1929, [vii], 7, 129—141).—The action of different X-ray doses on 0·01—$4\times10^{-5}M$-solutions of ferrous sulphate in 0·8N-sulphuric acid saturated with air has been investigated. With 0·00878M-, 0·000337M-, and 0·001M-solutions the rate of decomposition is linear up to the same X-ray dosage. For increased dosages the decomposition is still linear, but the rate is halved. With a 0·0000406M-solution the rate of decomposition has a linear relationship to the X-ray dosage until decomposition is practically complete. With increased doses the concentration of ferrous sulphate is gradually restored to an equilibrium value about 50% of the initial one. In the first cases the change in the rate of decomposition is shown to take place at the point where all the dissolved oxygen in the solutions has been used up. It is concluded that in the later stages of the decomposition the transformation of the ferrous ions is a secondary effect due to activated water molecules produced by secondary X-ray electrons. The apparent reversal of the reaction in the last case is attributed to the presence in the solution of a reducing substance (perhaps hydrogen peroxide) which would interfere with the analysis, which was carried out by an oxidation–reduction potential method. A. E. Mitchell.

Production of colour in glass and in gems by X-rays and radium rays. M. C. Reinhard and B. F. Schreiner.—See B., 1929, 208.

Lattice energies and photochemical decomposition of the silver halides. S. E. Sheppard and W. Vanselow (J. Physical Chem., 1929, **33**, 250—273).—Theoretical. The energy changes accompanying the decomposition of the silver halides are discussed in relation to the lattice energies of the crystals concerned. The lattice energies of silver chloride, bromide, and iodide are first evaluated using the thermochemical cycle of Born (A., 1920, ii, 156) after a consideration from the results of previous investigators of the best values for the terms to be taken. By this method the lattice energies have the values 212, 205, and 201·5 kg.-cal., respectively, as compared with the values 184, 178, and 150 calculated from the electrostatic theory. It follows that the quantum required to overcome electron affinity is greater than that actually found by experiment to be necessary. The relation of lattice energy to photochemical change is discussed in the light of these results and of other evidence, and it appears that lattice loosening and electron liberation and transfer are closely connected with any photochemical change in solids. A discussion of lattice disorientation and of ionic deformation in the light of the work of von Hevesy and Fajans, respectively, leads to the conclusion that both photochemical and photo-electric effects take place primarily in such disoriented parts of the lattice that the initial work can be supplied by the quanta available, a view which receives support from the fact that photochemical decomposition commences locally on the surface of crystals. The preliminary overcoming of lattice energy which is necessary before absorbed radiation can loosen an electron is analogous to energy of activation in chemical reactions, and it is concluded that the photochemical decomposition of the silver halides can be regarded as a typical case of heterogeneous catalysis at an interface. Internal disorientation and photoconductance, photo-electric effects, and orientation at interfaces are also discussed. L. S. Theobald.

Intermediate regressions. Lüppo-Cramer (Z. wiss. Phot., 1929, 26, 295—299).—If a negative which has been treated with a sodium nitrite solution is exposed under the Eder–Hecht scale under conditions which would cause solarisation in an untreated plate, solarisation is hindered except under the red strip. Since the ordinary Herschel effect cannot be obtained with this red filter, it is suggested that the red rays exert a protective influence on the silver halide, preventing blackening when the silver nuclei are nascent, as in the present experiments, but not when, owing to previous exposure, they have become larger and less reactive. R. Cuthill.

Limiting short wave-length for the Herschel effect. E. Mauz (Z. wiss. Phot., 1929, **26**, 289—294).—On exposure to yellowish-orange light of "Satrox" paper which has previously been blackened by exposure to white light, the blackening at first diminishes, *i.e.*, the Herschel effect appears, but later increases again. In explanation it is suggested that one part of the orange light causes bleaching, and the other part blackening, and that when the time of exposure is increased beyond a certain point the blackening effect predominates. By photographing a spectrum on paper previously exposed to white light, it is found that light of wave-length shorter than about 600 mμ will not cause the Herschel effect. R. Cuthill.

Photo-decomposition of ethyl iodide. T. Iredale (J. Physical Chem., 1929, **33**, 290—295).—Measurements of the photo-decomposition of ethyl iodide at the ordinary temperature by light of the region 365 μμ from a quartz–mercury vapour lamp indicate that this is a simple process (cf. Job and Emschwiller, A., 1924, i, 929) in which one quantum effects the detachment of an atom of iodine from one molecule of the iodide. Preliminary experiments indicate that, contrary to Stobbe and Schmitt (A., 1921, ii, 76), oxygen is not necessary for the decomposition. L. S. Theobald.

Photosynthesis of naturally occurring compounds. IV. Temperature coefficient of the photosynthesis of carbohydrates from carbonic acid. E. C. C. Baly and N. R. Hood (Proc. Roy. Soc., 1929, **A**, **122**, 393—398; cf. A., 1927, 1040, 1041).—Nickel carbonate, free from every trace of adsorbed salts, may be prepared by the electrolysis of pure conductivity water, saturated with carbon dioxide, with nickel electrodes. The carbonate is dried at 100°, heated at 140° for 30 min., passed through a 100-mesh sieve, and activated by exposure to light. Nickel carbonate thus prepared gives very constant yields of carbohydrates if the temperature, light intensity, and relation between volume of water and weight of powder are kept constant. If the yield of carbohydrates (weight of photosynthesised organic matter soluble in absolute methyl alcohol) obtained with 50 g. of the carbonate suspended in

1500 c.c. of water is plotted against the temperature, the relation is found to be a linear one between 5° and 31° (maximum yield, 0·0783 g.), after which there is a rapid decrease in yield. The values of the temperature coefficient for 10° are in good agreement with those found by Warburg with the unicellular alga *Chlorella* under constant illumination (Biochem. Z., 1919, **100**, 258). The close analogy shown between the photosynthetic process *in vitro* and *in vivo* is discussed, with special reference to the work of Matthaei on the assimilation of carbon dioxide at various temperatures (Phil. Trans., 1905, **B**, **197**, 47), and to the fact that the process, both in the living leaf and in the laboratory, has an upper and a lower temperature limit. The results recorded support the view previously expressed (*loc. cit.*), that the complete activation of the carbonic acid takes place in two stages, *i.e.*, partial activation by adsorption on the surface of the catalyst and a further activation by the action of visible light on the adsorbed layer.

L. L. Bircumshaw.

Photochemical decomposition of benzaldehyde. A. de Hemptinne (Ann. Soc. Sci. Bruxelles, 1928, **48**, **B**, 98—100).—It is concluded that the photolysis of benzaldehyde by light of wave-lengths less than 2600 Å., which was previously observed (A., 1928, 720), takes place as follows : $C_6H_5\cdot CHO = C_6H_5 + H + CO$, the hydrogen then reacting with the phenyl group to form benzene. The energy necessary for this decomposition is calculated to be 115,780 g.-cal., corresponding with light of wave-length 2461 Å. This is the wave-length at which the total absorption band of the benzaldehyde spectrum begins. For benzaldehyde there is a complete parallelism between the appearance of total absorption and the possibility of photochemical decomposition.

O. J. Walker.

Photochemical decomposition of benzaldehyde vapour. A. de Hemptinne (J. Phys. Radium, 1928, [vi], **9**, 357—364; cf. preceding abstract).—The decomposition by ultra-violet light of benzaldehyde vapour at 0·2 mm. has been investigated. Only those wave-lengths corresponding with the " total absorption " portions of the benzaldehyde spectrum are effective in the photochemical decomposition. With rise of temperature the intensities of the bands gradually decrease until at 200° a continuous spectrum results, which in turn disappears at 400°. Below this temperature the photolysis is reversible. Between 400° and 500° benzaldehyde begins to decompose thermally and irreversibly. The decrease in the light energy necessary for decomposition at the higher temperatures is of the same order of magnitude as the increase in the vibration energy of the benzaldehyde molecule, as calculated from the variation of the specific heat with the temperature. The theory of absorption spectra and photochemical decomposition is discussed. O. J. Walker.

Relations between the photochemical reactivity and the fluorescence of organic compounds. Qualitative fundamental law. G. Kögel (Z. wiss. Phot., 1929, **26**, 311—319).—Theoretical. From the fact that by opening the rings of fluorescent closed-chain compounds and introducing unsaturated groups at the point of fission, if such groups are not already present there, compounds which are very sensitive to light are obtained, it is concluded that fluorescence is a criterion of photochemical activity. If, however, owing to structural or physical conditions reaction is not possible, the fluorescence represents only potential activity. The principal groups giving rise to photochemical sensitivity are : ·CH⁚CH·, ·CH⁚N·, >C⁚O, ·NO_2, ·NCl⁚N, and ⁚N⁚N. Substituents for the hydrogen atoms in the benzene ring will enhance the fluorescence or promote chemical action according as they oppose or facilitate, respectively, the opening of the ring. The groups Me and OMe and the halogens increase the reactivity of the sensitive groups, whilst the nitro-group has the opposite effect. R. Cuthill.

Physico-chemical investigations of irradiated proteins. V. Changes in serum-albumin produced by radium rays and their relation to coagulation by heat and light. A. Fernau and M. Spiegel-Adolf (Biochem. Z., 1929, **204**, 14—27).—Freshly electrodialysed serum-albumin kept under toluene loses its power of coagulation by exposure to radium owing to the formation of traces of ammonia. To prevent visible changes under radium irradiation, small amounts of acid or alkali are effective. Even when visible changes are prevented by hydrochloric acid there is almost complete denaturation. The period of coagulation is practically independent of the concentration of the serum-albumin. Coagulation is prevented by high concentrations of neutral salts. Radium coagulates are not rendered soluble by the action of alkali. Hydrogen peroxide coagulates show properties similar to those produced by radium.

J. H. Birkinshaw.

Reaction of monatomic hydrogen with hydrocarbons. K. F. Bonhoeffer and P. Harteck (Z. physikal. Chem., 1928, **139**, 64—74).—When hydrocarbon vapours, methane excepted, are allowed to mix with a stream of monatomic hydrogen a greenish-blue light, resembling that of the inner cone of a Bunsen flame, is emitted. The products of reaction have been examined for the following substances : ethane, pentane, ethylene, acetylene, and benzene. No change takes place in the case of methane, but the evidence indicates that this gas facilitates the recombination of monatomic hydrogen according to the equations : $CH_4 + H = CH_3 + H_2$, $CH_3 + H = CH_4$. Ethane gives small quantities of ethylene and acetylene and some methane, but is mostly unchanged. Pentane gives the same products as ethane with propane in addition. Ethylene yields acetylene, but acetylene, although giving a strong light emission, gives only traces of ethane and ethylene and remains practically unchanged. In the case of benzene the ring is broken, and methane, together with some ethylene and acetylene, is formed. The results therefore show that monatomic hydrogen may hydrogenate and dehydrogenate hydrocarbons, and may rupture very stable rings. R. W. Lunt.

Formation of acid lithium aluminate. D. Prociv (J. Czechoslov. Chem. Comm., 1929, **1**, 95—103).—The solution obtained by the dissolution of aluminium amalgam in aqueous lithium hydroxide which exhibits “ supersaturation ” (cf. Allen and Rogers, A., 1900, ii, 727) has been investigated by conductance and cryoscopic methods and it is concluded that the aluminium in the solution exists mainly as the normal aluminate, $Al(OH)_4'$, before spontaneous precipitation. The solubility of acid lithium aluminate, $Li[Al_2(OH)_7],2H_2O$ or $Li_2Al_4O_7,11H_2O$, deduced from the conductance measurements is $1{\cdot}2\times10^{-4}$ and $3{\cdot}3\times10^{-4}$ g.-equiv. per litre at 25° and 80°, respectively. The separation of the acid lithium aluminate takes place according to the equation, $2Al(OH)_4' \rightleftharpoons Al_2(OH)_7' \times OH'$, the mass action constant of which is about 1×10^4. A method for the determination of lithium based on its precipitation as the acid aluminate in sodium or potassium hydroxide solutions is described.

A. I. Vogel.

Combination of alkali metals with carbon. II. K. Fredenhagen and H. Suck (Z. anorg. Chem., 1929, **178**, 353—365).—The investigation previously described (A., 1927, 218) has been continued with improved apparatus. When heated at 400° in potassium vapour at a given pressure, both graphite and lampblack take up the same amount of metal, but with lampblack equilibrium is reached only after a considerable time. A curve constructed with the pressures of vapour as abscissæ and the amounts of metal taken up as ordinates consists of two almost vertical portions separated by a short flatter part; with further increase in pressure, the second and longer steep section is ultimately succeeded by a part which slopes much less. There is no evidence of the formation of K_2C_2, and the most satisfactory explanation of the form of the curve seems to be that adsorption occurs in two stages. Neither sodium nor potassium reacts with diamond at 500°.

R. Cuthill.

Displacement of copper from neutral and acidic copper sulphate solutions by hydrogen under pressure. V. Ipatiev and V. Ipatiev, jun. (Ber., 1929, **62**, [*B*], 386—390).—The experiments are performed in an Ipatiev high-pressure autoclave containing the solution in a glass tube. Under all conditions cuprous and cupric salt and metallic copper are present at the close of the experiment. Copper cannot be displaced without the simultaneous presence of cuprous and cupric ions in the solution, the latter frequently in very small amount. Precipitation of copper is never quantitative, a portion of the metal remaining ionised in solution no matter how long the experiment is continued. It appears that the following reactions proceed simultaneously: $2CuSO_4+H_2=Cu_2SO_4+H_2SO_4$; $Cu_2SO_4+H_2=2Cu+H_2SO_4$; $CuSO_4+Cu=Cu_2SO_4$. With increasing acidity of the solution, the conditions become more favourable for a high concentration of cuprous ions; in some cases, this increase is effected at the expense of the precipitated copper. At a constant pressure of hydrogen, the influence of added acid becomes less marked with increasing concentration of the copper sulphate solution.

H. Wren.

Reaction of cupric salts with thiosulphate. J. Hanuš and V. Hovorka (J. Czechoslov. Chem. Comm., 1929, **1**, 65—82).—A re-investigation of the reaction between cupric salts and sodium thiosulphate in aqueous solution over a wide variety of conditions has been made. The resultant precipitate was analysed as follows: sulphur, by extraction with nitrobenzene at 100°; cuprous sulphide, by treatment with silver sulphate solution which converts the cuprous sulphide into cupric sulphate, silver sulphate, and an equivalent quantity of silver (cf. Posnjak, A., 1915, ii, 24), the last-named being removed by dissolution in 6% ferric nitrate solution at about 80° and the silver determined by Volhard’s method. The precipitate consisted of a mixture of cuprous and cupric sulphides and free sulphur in varying proportions, the composition depending on the duration of boiling, the amount of thiosulphate, and the acidity of the solution. The maximum amount of cuprous sulphide in the precipitate was obtained from solutions in which the ratio was 1 g.-at. of copper to 2·5—3 mols. of thiosulphate. Further increase of the thiosulphate content resulted in a decrease of the amount of cuprous sulphide until with a very large excess (1 : 15—30) the precipitate consisted largely of cupric sulphide and free sulphur. The composition of the precipitate formed in acid solutions according to the analytical methods of Carnot (A., 1886, ii, 580) and Girard (Ann. Chim. anal., 1899, 4, 382) (copper : thiosulphate about 1 : 4—5) was 8% Cu_2S + 92% CuS.

A. I. Vogel.

Constitution of silver subfluoride. C. del Fresno (Anal. Fís. Quím., 1928, **26**, 407—416).—See A., 1928, 694.

Action of water on calcium aluminates. L. S. Wells.—See B., 1929, 173.

Carbon sulphidoselenide. H. V. A. Briscoe, J. B. Peel, and P. L. Robinson (J.C.S., 1929, 56—60).—Carbon sulphidoselenide (cf. Stock and Willfroth, A., 1914, ii, 200), a yellow oil, b. p. 83·90—83·95°/749·2 mm., has been prepared by treating ferrous selenide with carbon disulphide vapour at 650°, and repeatedly fractionating the product. The mol. wt., determined by vapour density and by cryoscopic measurement, is normal. The surface tension $\gamma=40{\cdot}44$ dynes/cm.^{2} at 20°, hence the molecular parachor is 156·4. If the constitution $S{=}C{=}Se$ be assumed for the sulphidoselenide, the atomic parachor of selenium is 58·7 (cf. Briscoe and Peel, A., 1928, 1021).

Carbon sulphidoselenide is reduced by zinc and hydrochloric acid to hydrogen sulphide and hydrogen selenide. It reacts with ammonia, but the products are ill-defined. With phenylhydrazine in alcoholic solution it yields the *compound* $(NHPh{\cdot}NH_2)_2,CSSe$, m. p. 98°, which is unstable and decomposes when kept; under similar conditions aniline yields a *compound*, $(NHPh)_4CSSe$, m. p. 164°, which is somewhat more stable in air.

C. W. Shoppee.

[Silicic acids.] H. Staudinger (Ber., 1929, **62**, [*B*], 442).—The conception of the relationship between fibrous structure and molecular size, attributed by Dilthey and Hölterhoff (this vol., 280) to Meyer, has been enunciated previously by the author.

H. Wren.

Reactions between colloidal silica and lime. P. Jolibois and L. Chassevent (Compt. rend., 1929, 188, 452—454).—It is concluded from electrometric determinations of the amounts of lime present in the precipitate produced in solutions containing various concentrations of lime and silica mixed at 30° that the reactions are due to (1) coagulation of silica by lime, (2) fixation of lime by silica to form a hydrated calcium silicate, and (3) adsorption of lime which may continue for several months in concentrated solutions. J. GRANT.

Action of silica, alumina, and kaolin on barium sulphate. (MLLE.) G. MARCHAL (Compt. rend., 1928, **188**, 399—402).—Earlier experiments (this vol., 266) have been extended to various mixtures of barium sulphate and silica, alumina, or dehydrated kaolin heated at 1300°, and have resulted in each case in a reaction which is rapid at first and then very slow. They indicate an advantage in replacing barium carbonate by the sulphate in certain manufactures, *e.g.*, of glass. J. GRANT.

Dissolution of metals in fused salts. II. W. EITEL and B. LANGE (Z. anorg. Chem., 1929, **178**, 108—112; cf. A., 1928, 700).—From thermodynamical considerations based on the work of Lorenz and Adler (A., 1928, 945), and from their own experiments, the authors show that the dissolution of lead and cadmium in their respective fused chlorides is a chemical process involving the formation of a lower chloride. The reaction is reversible, the metal being precipitated in a highly dispersed, colloidal form when the fused mass solidifies. A. R. POWELL.

Acid phosphates of thorium. J. D'ANS and W. DAWIHL (Z. anorg. Chem., 1929, **178**, 252—256).—Addition of thorium phosphate to a 40% solution of phosphoric acid results in the slow crystallisation of the *compound* $Th(HPO_4)(H_2PO_4)_2,2H_2O$. From solutions of thorium hydrogen phosphate in sulphuric and phosphoric acids crystalline *compounds* having the composition $Th(SO_4)(HPO_4),4H_2O$ and $Th_2SO_4,(H_2PO_4)_6,8H_2O$ have been obtained. A. R. POWELL.

Reaction mechanism in the sulphuric acid contact process and the action of promoters. B. NEUMANN.—See B., 1929, 205.

Nitrosylsulphuric acid. II. C. W. H. JONES, W. J. PRICE, and H. W. WEBB (J.C.S., 1929, 312—315; cf. A., 1926, 811).—Attempts to synthesise dinitrosyl sulphate, $SO_2(O{\cdot}NO)_2$, have been unsuccessful. The methods of preparation of nitrosylsulphuric anhydride suggest that it has the structure $O{\cdot}NO{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO$. When heated it suffers partial decomposition to form the *substance* $2(2SO_3,N_2O_3),SO_3$. F. J. WILKINS.

Metallic chromates. S. H. C. BRIGGS (J.C.S., 1929, 242—245; cf. Britton, A., 1926, 247).—The author has confirmed the existence of a normal zinc chromate (cf. Schulze, A., 1896, ii, 24; Briggs, A., 1908, ii, 113), and has isolated the following *compounds*: $9ZrO_2,5CrO_3,12H_2O$; $3Al_2O_3,2CrO_3,6H_2O$; $2Fe_2O_3,4CrO_3,H_2O$; $3SbO_2,2CrO_3$; $2Sb_2O_3,Cr_2O_3$; $3Bi_2O_3,2Cr_2O_3$. Sodium chromate with a large excess of a very concentrated solution of the corresponding dichromate gives the normal chromates of copper, cobalt, and cadmium in the hydrated forms $CuCrO_4,2H_2O$, $CoCrO_4,2H_2O$, and $CdCrO_4,H_2O$. Corresponding zinc and nickel compounds could not be prepared. F. J. WILKINS.

Preparation and electrical conductivity of pure hydrogen fluoride. K. FREDENHAGEN and G. CADENBACH (Z. anorg. Chem., 1929, **178**, 289—299).—When potassium hydrogen fluoride is heated, one third of its content of hydrogen fluoride is evolved slowly with rising temperature up to 504°, at which the remainder is steadily evolved. For the preparation of pure hydrogen fluoride not only must the salt used be perfectly anhydrous but all traces of moisture must be rigorously excluded from the apparatus and the first distillate should be redistilled very slowly. Working in this way hydrogen fluoride with a specific electrical conductivity of only 14×10^{-6} has been obtained. Although this value is about 0·0005 of that usually accepted it is believed still to be much too high owing to the presence of minute traces of water. A. R. POWELL.

Bromine chloride. S. BARRATT and C. P. STEIN (Proc. Roy. Soc., 1929, **A**, **122**, 582—588).—The fact, first observed by Balard (Ann. Chim. Phys., 1826, **32**, 371), that a marked diminution takes place in the colour of bromine on mixing with chlorine, is a strong argument in favour of the formation of a compound between the halogens, more transparent than bromine in the visible region of the spectrum. The results of spectrophotometric observations on the colour charges on mixing carbon tetrachloride solutions of bromine and chlorine can be accounted for quantitatively on the basis of the formation of a compound BrCl, and that in equimolecular mixtures this compound is formed to the extent of approximately 50%. The conclusions are based on the assumption that the intensity of the bromine absorption band in the visible forms a measure, in the mixtures, of the amount of bromine left uncombined with the chlorine. It was found to be impossible to measure the chlorine left in the free state by similar observations on the ultra-violet bands, owing to the overlapping of the various spectra concerned. The formation of a chemical compound is further indicated by the appearance of a new ultra-violet absorption band, with the maximum at 3700 Å., peculiar to the mixtures, and by the fact that in carbon tetrachloride solutions an appreciable time-lag is detected in the colour charge. The formula suggested agrees with the observation that the volume change on mixing chlorine and bromine in the gaseous state, if existent, is very small. L. L. BIRCUMSHAW.

Action of bromine on phosphorus trichloride. T. MIŁOBĘDZKI and S. KRAKOWIECKI (Rocz. Chem., 1928, **8**, 563—567).—Crystalline phosphorus tetrachlorobromide is produced by the action of bromine on phosphorus trichloride, or of bromine with phosphorus pentabromide on phosphorus pentachloride. The compound PCl_3Br_2 could not be prepared. A number of crystalline products of the general type PCl_3Br_n and PCl_3Br_n, where *n* is 2—10, are obtained by the action of bromine vapour on phosphorus trichloride vapour. R. TRUSZKOWSKI.

Oxygen compounds of rhenium. I. NODDACK and W. NODDACK (Naturwiss., 1929, **17**, 93—94).—

White rhenium peroxide, Re_2O_8, is obtained as a "snow" by heating the metal or lower oxides in a stream of oxygen below 150°. It melts near 150° and is rapidly converted into a yellow oxide. The peroxide is readily soluble, the aqueous solution being very weakly acid. Hitherto the oxide has been regarded as Re_2O_7, but this view is mistaken, not only because the analysis corresponds with $Re/O=1/4$, but also because the substance reacts as a peroxide.

The yellow oxide obtained in hexagonal plates as a result of the interaction of rhenium and oxygen above 150° melts to a yellow liquid at 200° and boils at 450°, distilling without decomposition in an atmosphere of oxygen or nitrogen. The oxide is Re_2O_7 and not ReO_3 as was thought earlier; it deliquesces in air and the aqueous solution is colourless and strongly acid. The following *salts* have been prepared as white crystals and their solubilities determined: NH_4ReO_4, $NaReO_4$, and $Ba(ReO_4)_2$. By heating the two salts first named in a current of hydrogen at 400°, rhenium dioxide is formed as a black solid. When the dioxide is dissolved in dilute nitric acid, the solution is at first bright orange, but when heated or kept becomes colourless. If the yellow solution is treated with sodium hydroxide the colour persists and by adding calcium or barium hydroxide a yellow precipitate is formed which is stable only for a brief period even in alkaline media. The barium salt analyses to $BaReO_4$ (rhenate). The yellow solution first obtained therefore contains ReO_3, which is oxidised to Re_2O_7 by keeping or heating. By the action of sulphur dioxide on dry Re_2O_7 or Re_2O_8, blue and violet oxides of variable composition are formed. When sulphur dioxide is led into a sulphuric acid solution of the heptoxide, a deep violet colour appears. The blue oxide corresponds approximately with Re_3O_8, and the violet and blue oxides are compounds of ReO_2 with ReO_3 or Re_2O_7. The black oxide, ReO_2, results after sodium per-rhenate has been fused in hydrogen. It is readily reduced to the metal at 800°. R. A. MORTON.

Oxidation of iron in water by the action of oxygen and carbon dioxide. N. M. GAVRILOV, S. K. MEL, and P. K. MEL.—See B., 1929, 210.

Corroding action of solutions of various chlorides on cast iron and lead. B. K. PERSHKE and G. I. CHUFAROV.—See B., 1929, 210.

[Iron carbonyls containing pyridine.] W. HIEBER and F. SONNEKALB (Ber., 1929, 62, [*B*], 422; cf. A., 1928, 511; this vol., 41).—The method described for the preparation of iron carbonyls containing pyridine should be deleted from the literature. Further investigation of the system iron carbonyl–pyridine has shown that oxidised products are formed which, when treated with acid, evolve carbon dioxide in addition to carbon monoxide and hydrogen.

H. WREN.

Action of mercury salts on iron pentacarbonyl. II. H. HOCK and H. STUHLMANN (Ber., 1929, 62, [*B*], 431—437, cf. A., 1928, 1344).—Iron pentacarbonyl reacts with a solution of 1 mol. of mercuric sulphate in about 10% sulphuric acid, giving carbon dioxide, sulphuric acid, and a *compound*, $Fe(CO)_4Hg$, designated "*mercury iron tetracarbonyl.*" When heated at about 150°, it decomposes quantitatively into mercury, iron, and carbon monoxide. The compound is also derived from iron pentacarbonyl and mercurous sulphate, metallic mercury being precipitated. It does not give a precipitate of mercury sulphide when its solution in dilute sulphuric acid is treated with hydrogen sulphide. When treated with iodine in ether, pyridine, or carbon disulphide, it gives mercuric iodide and the compound $Fe(CO)_4I_2$. A similar change is effected by bromine in light petroleum, but is accompanied by partial decomposition of the compound $Fe(CO)_4Br_2$. The analogous change with chlorine is best effected by passing the dry gas over the substance. Iron tetracarbonyl does not appear to be produced by the interaction of mercury iron tetracarbonyl and the substance $Fe(CO)_4I_2$. Hydrogen peroxide and potassium permanganate in acetone readily attack mercury iron tetracarbonyl, whereas it is indifferent towards boiling pyridine. Iron pentacarbonyl and cupric chloride in acetone give a transitory reddish-yellow precipitate and, ultimately, cuprous chloride, ferrous chloride, and carbon monoxide; a precisely analogous change occurs with mercury iron tetracarbonyl. When mercury iron tetracarbonyl is shaken with a feebly acid, aqueous solution of mercuric sulphate or when the pentacarbonyl is treated with an excess of mercuric sulphate, the *compound* $Fe(CO)_4Hg,HgSO_4$ separates in rhombic crystals. It is rapidly decomposed by boiling water into ferrous sulphate, mercury, and carbon monoxide and transformed by iron pentacarbonyl into mercury iron tetracarbonyl. Prolonged agitation of mercury iron tetracarbonyl with a solution of mercuric bromide in methyl alcohol gives the *compound* $Fe(CO)_4Hg,HgBr_2$; the *substance* $Fe(CO)_4Hg,HgI_2$ is analogously prepared, whereas mercuric chloride in aqueous solution yields the compound $Fe(CO)_4Hg,HgCl_2$. In contrast with the substance $Fe(CO)_4Hg,HgSO_4$, these compounds, when suspended in water, do not react with hydrogen sulphide. Iron pentacarbonyl and mercuric acetate afford mercury iron tetracarbonyl and the additive *compound* $Fe(CO)_4Hg,Hg(OAc)_2$. H. WREN.

Univalent iron, cobalt, and nickel, and nitrososulpho-salts. L. CAMBI (Gazzetta, 1929, 59, 56—59).—A reply to Manchot's criticism (A., 1928, 1344) of the author's previous work. The formation of hyponitrite in the decomposition of Roussin salts by silver nitrate cannot be due to the reduction of the silver salt, since a similar reaction occurs with silver salts in general. The largest yields of hyponitrite are obtained using silver perchlorate. The reactions between metallic mercaptides and nitric oxide are discussed. O. J. WALKER.

Quantitative analysis with the spectrograph. C. C. NITCKIE (Ind. Eng. Chem. [Anal.], 1929, 1, 1—7).—The spectrum of the sample is compared with a graded series of standards photographed under similar conditions. Determinations usually agree within 10%. The choice of lines for comparison depends only on the concentration, the weakest lines that are clearly defined being selected. Magnesium and some other metals can be detected at a concentration of less than 1 in 10^6, but arsenic at

1 in 10^4. It is essential that the standards shall have nearly the same composition as the sample, so that a considerable number of standards is needed. An arc between carbon electrodes is preferred as a source of light, but the impurities in the carbon must be known. The sample should be obtained from a solution, as 20—50 mg. only are required and uniformity cannot be certain if it is prepared direct from the solid. A drop of solution is placed in a cavity of the lower arc carbon. C. IRWIN.

Quantitative emission spectrum analysis. I. Principles of quantitative spectrum analysis. H. THURNWALD and G. F. HÜTTIG (Z. anal. Chem., 1929, 76, 260—272).—A lecture. A. R. POWELL.

Micro-electroanalysis. R. KELLER (Naturwiss., 1929, 17, 100—103).—A general account is given of the application of micro-electrical methods to physiological problems with inhomogeneous materials, special reference being made to the transport of sugar in the organism. R. A. MORTON.

Derivation of reference values for the calomel electrode used in p_H determinations. D. H. CAMERON (J. Amer. Leather Chem. Assoc., 1929, 24, 80—87).—Assuming that a hypothetical normal hydrogen electrode has zero potential at 25°, that 0·1N-hydrochloric acid at 25° contains 0·0816 g.-mol. per litre of free hydrogen ions, and that for the temperature range 15—30° the hydrogen-ion concentration of 0·1N-hydrochloric acid remains constant, the author has derived a series of reference values for the saturated potassium chloride–calomel half cell for each degree from 15° to 30°. The reference value of the calomel electrode is equal to its true value at a particular temperature minus the true value of a hypothetical normal hydrogen electrode at that temperature. The true temperature coefficient of the saturated potassium chloride–calomel electrode is less than that of the 0·1N-potassium chloride–calomel electrode, but the change in reference value of the latter is less than for the saturated.

D. WOODROFFE.

Simplified methods of potentiometric and conductometric analysis and their industrial application. T. CALLAN and S. HORROBIN.—See B., 1929, 154.

Simple reference electrode for potentiometric titrations. H. H. WILLARD and A. W. BOLDYREFF (J. Amer. Chem. Soc., 1929, 51, 471—474).—A platinum wire is sealed in the lengthened tip of the burette. Such an electrode exhibits constant potential in oxidation–reduction, neutralisation, and precipitation reactions. S. K. TWEEDY.

[Colorimetric] determination of hydrogen-ion concentration of salt solutions. A. NEUMANN (Pharm.-Ztg., 1929, 74, 278—280).

Universal indicator giving spectrum colours for the p_H range 2—12. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 157—162; cf. this vol., 162).—A modified indicator mixture, giving sharper colour changes than that formerly proposed, is suggested.

S. I. LEVY.

Possible indicators to determine the p_H of alkaline solutions. F. R. MCCRUMB and W. R. KENNY (Ind. Eng. Chem. [Anal.], 1929, 1, 44—46).—Most of the dyes sold for the purpose of p_H studies over the range 10·0—14·0 are unsatisfactory. About five can be used for hydrogen-ion work: α-naphtholbenzein, which is, however, low in tinctorial power; Clayton-yellow, alizarin-yellow GR and R (the last gives misleading lemon-yellow shades in solutions containing lime); tropæolin O, which gives quite marked readings but has been reputed to have rather a large salt error; and azo-blue, which gives good colour changes in the p_H range 10·0—11·0 but is not entirely satisfactory above or below. None of these, however, is as satisfactory in this range as the sulphonphthaleins of Clark and Lubs, and of Cohen at lower ranges. D. G. HEWER.

Colorimetric hydrogen-ion determination. D. H. CAMERON (J. Amer. Leather Chem. Assoc., 1929, 24, 76—80).—To 25 c.c. of the solution in a 50 c.c. Nessler tube 1·6 cm. in diam. 1 c.c. of a suitable indicator solution (0·004% or 0·008%) followed by distilled water to 50 c.c. is added. 25 c.c. of a solution containing 0·1M-potassium hydrogen phthalate, potassium dihydrogen phosphate, or boric acid for p_H values 4—6, 6—8, or 8—10, respectively, are pipetted into a similar Nessler glass, 1 c.c. of the same indicator solution is added, and 0·2N-sodium hydroxide added from a burette until the colour produced matches that in the first glass. The volume of buffer solution is made up to 50 c.c. before the final comparison of the colour is made. The p_H value is obtained from the composition of the buffer mixture in the second tube (cf. W. M. Clark, "Determination of Hydrogen Ions," 1922).

D. WOODROFFE.

Oxidation–reduction indicators. J. GILLIS (Natuurwetensch. Tijds., 1929, 11, 15—20).—A short account of the commoner oxidation–reduction indicators, with special reference to the transition range potentials. Curves are given for electrometric titration of ferrous chloride in acid buffered solution by means of potassium dichromate, and of zinc by potassium ferrocyanide containing a trace of ferricyanide. S. I. LEVY.

Detection of bromide and iodide. E. MURMANN (Oesterr. Chem.-Ztg., 1929, 32, 36—37).—The solution is treated with 0·1 g. of ammonium persulphate or potassium permanganate and a current of air is passed through the liquid, the issuing gases passing along a narrow-bore delivery tube. To test for bromine a piece of cotton wool soaked in fluorescein is placed at the end of this tube; a red colour appears with as little as 1×10^{-6} g. of bromine. Iodine is tested for in a similar manner using cotton wool soaked in a solution of starch in 50% glycerol; the sensitivity is the same as that of the bromine test.

A. R. POWELL.

Determination of traces of iodine. II. Iodine in vegetables. J. F. MCCLENDON and R. E. REMINGTON (J. Amer. Chem. Soc., 1929, 51, 394—399).—A modification of the method previously described (A., 1928, 607). The vegetables are moulded into rods, which are fed into a strongly heated silica tube through which oxygen is passing, the feeding being regulated so that combustion

proceeds without the separation of carbon and tarry matter. After washing, the oxygen is passed to a Cottrell precipitator. The ashing may also be carried out in boats, or by prolonged heating below 450° in an open dish. The ash must not be allowed to fuse and calcium lactate and sodium carbonate must be added if the vegetable yields an acid ash.
S. K. TWEEDY.

Micro-determination of iodine in organic materials. J. F. REITH (Rec. trav. chim., 1929, **48**, 254—262).—Details are given of a simplified combustion method for the determination of minute amounts of iodine in organic substances. The apparatus is much simpler than that hitherto employed, and the accuracy of the determination is increased by the adoption of a colorimetric method which renders possible the use of less material than is usually necessary. F. G. TRYHORN.

Critical examination of the determination of nitrous oxide by gasometric methods. H. MENZEL and W. KRETZSCHMAR (Z. angew. Chem., 1929, **42**, 148—156).—Nitrous oxide from the thermal decomposition of ammonium nitrate was carefully purified by chemical means, then by fractional distillation after liquefaction, and four methods of determining it in gas mixtures were thoroughly tested. In Winkler's method involving thermal decomposition on the surface of a glowing platinum spiral results correct to ±0·2 c.c. were obtained for nitrous oxide in gas mixtures containing less than 10% N_2O; with higher percentages nitrogen peroxide is formed and reacts with the mercury in the gas apparatus. Explosion with hydrogen–oxygen mixtures gives fair results when the gas mixture contains less than 5% N_2O. Explosion with a limited supply of moist hydrogen (Bunsen) or reduction by hydrogen in a heated quartz capillary tube containing a platinum spiral gives results accurate to ±0·1 c.c. with mixtures containing 0·4—100% N_2O. Oxygen can be determined in mixtures containing nitrous oxide by absorption with slightly damp phosphorus over mercury, and nitrous oxide in the residual gas is then determined by either of the last-named methods.
A. R. POWELL.

Dimethyl-α-naphthylamine for determination of nitrite ion. F. G. GERMUTH (Ind. Eng. Chem. [Anal.], 1929, **1**, 28—29).—Dimethyl-α-naphthylamine can be advantageously used in place of α-naphthylamine in nitrite determinations. Whilst with the latter the colour begins to fade in about 30 min., with the former it is unchanged for 60 days. Permanent standards can be prepared, obviating the use of fuchsin. The dimethyl derivative is also less affected by hydrogen sulphide. C. IRWIN.

Acidimetry of phosphorous acid in presence of indicators. T. MIŁOBĘDZKI and K. BORATYŃSKI (Rocz. Chem., 1928, **8**, 554—562).—Pure phosphorous acid is prepared by the action of concentrated hydrochloric acid on phosphorus trichloride; the product, 480 g. of which can be dissolved at 20° in 100 g. of water, is obtained free from hydrogen chloride after five recrystallisations. The neutralisation of the first hydrogen atom using sodium hydroxide solution is best indicated using bromophenol-blue, whilst α-naphtholphthalein is most suitable for the second hydrogen atom.
R. TRUSZKOWSKI.

Sensitive test for silicic acid. F. OBERHAUSER and J. SCHORMÜLLER (Z. anorg. Chem., 1929, **178**, 381—388).—As little as 1 part in 10^6 of silicon in a solution of a silicate may be detected by the blue colour produced by adding an excess of a neutral 10% solution of ammonium molybdate, acidifying slightly, and then adding in the cold a stannite solution, freshly prepared by adding a large excess of sodium hydroxide to stannous chloride solution. The silicon forms with the molybdic acid a heteropoly-acid (cf. Parmentier, A., 1882, 702), which is reduced by the stannite to a blue lower oxide of molybdenum. Silicon as fluosilicic acid also gives the reaction. Arsenates and phosphates, if present in large amount, interfere. R. CUTHILL.

Apparatus for the determination of silica in steel and iron by the chlorine method. P. DICKENS.—See B., 1929, 210.

Determination of cyanides and basic cyanides of mercury. A. IONESCO-MATIU and (MLLE.) A. CARALE (Bul. Soc. Chim. România, 1928, **10**, 127—130).—See A., 1928, 1230.

Colorimetric determination of carbon disulphide in gas. G. G. DÉSY.—See B., 1929, 194.

Determination and separation of rare metals from other metals. XII. Separation of lithium from potassium, sodium, and magnesium. L. MOSER and K. SCHUTT (Monatsh., 1929, **51**, 23—42).—A detailed investigation of the various methods for the quantitative separation of lithium from sodium, potassium, and magnesium is described. Two main sources of error are (1) the hygroscopic nature of lithium chloride, (2) the small amounts of organic solvents which remain adhering to the walls of the vessels. The first is avoided by drying the lithium chloride at 120—150° and storing over concentrated sulphuric acid (Winkler's contention [A., 1913, ii, 877] that lithium chloride is unaltered by heating at 180° is confirmed) and the second by the use of mechanical filtration and washing in a specially designed apparatus which is described. The following methods for the quantitative separation of lithium from sodium and potassium are found to be untrustworthy; Gintl (Polyt. J., 1881, **240**, 83), Richard (A., 1905, ii, 653; this method is completely worthless), Murmann (A., 1911, ii, 334), Kahlenberg and Krauskopf (A., 1908, ii, 777), and Smith and Ross (A., 1925, ii, 601). Very satisfactory results are obtained by slight modification of Winkler's method (*loc. cit.*). By improved drying of the *iso*butyl alcohol by repeated refluxing with barium oxide the correction for the solubility of sodium and potassium chlorides, when three 10 c.c. extractions with this solvent are used, is reduced to −0·5 mg. of mixed sulphates, and by use of mechanical filtration extremely accurate results both for lithium and sodium+potassium are obtained. Berzelius' method (Jahresber., 1842, **21**, 142) for the separation of lithium from magnesium is vitiated by the fact that magnesium chloride cannot be completely converted into the oxide by heating with yellow mercuric oxide. Even less complete conversion occurs with the sulphate, bromide, or iodide. In Gooch and Eddy's method (A., 1908, ii, 632), although magnesium is quantitatively precipitated by addition of an alcoholic ammonium carbonate solution, some lithium is always adsorbed by the precipitated magnesium ammonium carbonate. Satisfactory results are obtained by Berg's method (A., 1927, 639), the precipitated $Mg(C_9H_6ON)_2,2H_2O$ being almost free from lithium by spectroscopic examination. On the basis of the above results lithium is quantitatively separated from sodium, potassium, and magnesium by first precipitating the magnesium with 8-hydroxyquinoline, and separation of the lithium from sodium and potassium in the filtrate by means of *iso*butyl alcohol. J. W. Baker.

Spectroscopic determination of small quantities of strontium, barium, and cæsium in minerals, rocks, mineral waters, etc. F. Zambonini and V. Caglioti (Atti R. Accad. Lincei, 1928, [vi], 8, 268—273).—A spectroscopic method is described by which small traces of elements (strontium, barium, cæsium) in minerals and waters may be determined with a degree of accuracy much higher than is usually obtained. Absolute originality is not claimed, but the method has been used with considerable success by the authors, results from this and other methods agreeing well. Dealing separately with solutions of the alkaline earths, the effect of dilution and addition of comparatively large quantities of the other alkaline-earth salts on the intensity of characteristic lines is shown, with considerable data. For the determination of barium and strontium the solution must contain no free acid. G. E. Wentworth.

Decomposition of barium sulphate by solutions of sodium carbonate. E. Wolesensky (Ind. Eng. Chem. [Anal.], 1929, **1**, 29—31).—If precipitated barium sulphate is boiled for 1 hr. with fourteen times its equivalent of sodium carbonate solution, at least 99% of the sulphate is brought into solution. Natural barium sulphate requires boiling for 2 hrs. The procedure can therefore be substituted for alkali fusion in the determination of sulphur in rubber compounds in conjunction with the acid oxidation method.

C. Irwin.

New metallic complexes [co-ordination compounds] of nitrosophenylhydroxylamine and their application in microchemical analysis. A. Martini (Anal. Asoc. Quím. Argentina, 1928, **16**, 117—124).—See this vol., 164.

Determination and separation of rare metals from other metals. XIII. Gravimetric analysis of vanadium and two new methods for its determination. L. Moser and O. Brandl. **XIV. Separation of beryllium from the alkaline-earth metals and the metals of the ammonium sulphide and arsenic groups.** L. Moser and F. List (Monatsh., 1929, **51**, 169—180, 181—189).—XIII. Previous methods for the detection and determination of vanadium are reviewed. The error in the determination as silver pyrovanadate is large. When alkali vanadates are treated with sodium acetate and a small amount of ammonia (to neutralise the liberated acetic acid), and then with silver nitrate, silver orthovanadate is precipitated quantitatively. When an alkali vanadate is treated with lead nitrate solution the salt $Pb_2V_6O_{17}$ is first formed. This is converted by lead nitrate into lead pyrovanadate provided the hydrogen-ion concentration of the solution is lowered by the addition of potassium bromide and bromate. The method is useful, but not so accurate as the silver orthovanadate precipitation. The method for the determination of vanadium with mercurous nitrate is improved by precipitating in presence of hydrogen peroxide. This gives a mixture of insoluble mercurous pyro- and ortho-vanadates, whilst in its absence the essential product is the soluble mercurous hexavanadate, $Hg_4V_6O_{17}$.

XIV. Beryllium is separated from calcium, strontium, or magnesium by precipitation as hydroxide with ammonium nitrite (A., 1928, 146). Since the nitrite invariably contains sulphate it is impracticable to use the same method for separating beryllium from barium. The barium is first precipitated as sulphate and the beryllium obtained from the filtrate by the action of tannic acid (*loc. cit.*). Separation from zinc is effected by precipitating the zinc as sulphide in presence of sulphosalicylic acid and subsequent nitrite treatment. Cadmium is removed as sulphide in sulphuric acid solution, and the beryllium obtained with tannin. The nitrite method can be used in the first place, with subsequent determination of cadmium. Nickel is separated with dimethylglyoxime from an ammoniacal solution in presence of either tartaric or sulphosalicylic acid. After removal of this last acid as tribromophenol, precipitation with tannin is employed. It is more convenient to separate the beryllium by the nitrite method and determine the nickel in the filtrate with dimethylglyoxime. Separation from cobalt and manganese can be accomplished by the nitrite method, or manganese is precipitated as the dioxide with ammonium persulphate and sulphuric acid, and the beryllium subsequently with tannin. The nitrite method is also used to separate beryllium from thallium (which is then determined as chromate [cf. A., 1927, 436] provided neutralisation is effected with sodium carbonate). Arsenic is removed either as sulphide or volatile chloride (cf. A., 1922, ii, 315); antimony as sulphide. The beryllium is then precipitated with tannin. To separate beryllium and tin, the latter is precipitated from a hot solution in concentrated hydrochloric acid by treatment with 10% tannin solution, solid ammonium acetate, and solid ammonium nitrate. The resulting tin–tannic acid complex is incinerated and the tin weighed as oxide. After neutralisation of the filtrate with ammonia the beryllium is precipitated with tannin. The precipitation of tungsten with tannin in presence of acetic acid (A., 1928, 145) is incomplete; if the filtrate is warmed with a 15% antipyrine solution the remainder of the tungsten is precipitated with the tannin.

H. Burton.

Applications of recent analytical methods. J. J. Fox (J. Oil and Col. Chem. Assoc., 1929, **12**, 38—45).—The use of 8-hydroxyquinoline as an analytical reagent is illustrated by its application to the determination of magnesium and its separation from aluminium, and to the titration of the acid radical of salts of aluminiun, zinc, etc. The determination of metals, *e.g.*, cobalt, copper, zinc, etc., by forming their pyridine–thiocyanate complexes, according to Spacu's method, is discussed. The potentiometric titration method is briefly described and the results of four typical titrations are tabulated.

S. S. WOOLF.

Titration of thallous salts with permanganate in hydrochloric acid solutions. A. JÍLEK and J. LUKAS (J. Czechoslov. Chem. Comm., 1929, **1**, 82—94).—The empirical nature of the volumetric determination of thallium in hydrochloric acid solutions by titration with potassium permanganate, which is due largely to the hydrolysis of the thallic chloride produced, has been overcome by the addition of potassium chloride, when a double salt, probably $3KCl,TlCl_3$, is formed, The latter is not hydrolysed in strongly acid (hydrochloric) solutions.

A. I. VOGEL.

Detection and determination of mercury as the complex ammonium iodide compound. E. H. VOGELENZANG (Pharm. Weekblad, 1929, **66**, 65—67).—A colorimetric method is based on the Nessler reaction, by interaction between the mercury salt, an iodide, and ammonium chloride in alkaline solution. The molecular concentration of iodide must be between 3 and 16 times that of the mercury salt; preliminary determination of the amount of iodide required is therefore necessary. The solution must be at least 0·02*N* in respect of alkali hydroxide; the proportion of ammonium salt added has no influence. The test will detect about 2·2 mg. of mercury per litre, and is suitable for concentrations up to 50 mg. per litre.

S. I. LEVY.

Rapid determination of mercury. G. SPACU and J. DICK (Z. anal. Chem., 1929, **76**, 273—277).—The solution (150 c.c.) containing not more than 0·3 g. of mercury is treated with 2 g. of powdered ammonium dichromate and, when that has dissolved, with 1 c.c. of pyridine. After stirring for 10 min. the mercury is completely precipitated as the compound $HgCr_2O_7,2C_5H_5N$, a coarsely crystalline, orange precipitate which filters readily on a porous porcelain crucible; it is washed first with water containing dichromate and pyridine, then with 80% alcohol, and finally with absolute alcohol containing a trace of pyridine, dried in a vacuum desiccator, and weighed. It contains 34·90% Hg. Ammonium chloride must be removed by evaporation with nitric acid.

A. R. POWELL.

Potentiometric titration of gallium. S. ATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 1—5).—The formula, $Ga_4[Fe(CN)_6]_3$, assigned by Kirschman and Ramsey (A., 1928, 861) to the precipitate obtained in the potentiometric titration of gallium in slightly acid solutions with potassium ferrocyanide has been confirmed when the concentration of hydrochloric acid in 1% gallium chloride solution was between 0·005*N* and 0·0025*N*. For other acid concentrations the gallium contents of the precipitates were slightly lower than that demanded by the formula. The concentration of acid had, moreover, a marked effect on the change in potential at the end-point; in concentrations lower than 0·0005*N* the end-point could not be accurately detected. Concentrations of hydrochloric acid between 0·05*N* and 0·0025*N* enabled satisfactory titrations to be made.

H. T. S. BRITTON.

Comparative colorimetric investigations. R. WASMUHT (Z. angew. Chem., 1929, **42**, 133—134).—Determination of iron as ferrocyanide with a dipping colorimeter gave results in good agreement with the titration method of Zimmermann and Reinhardt. For the colorimetric determination of manganese using potassium permanganate as standard, lead peroxide is more satisfactory as the oxidising agent than ammonium persulphate, since the colour given by the latter inclines to a rose shade and can be matched with the purplish tint of the permanganate only by the use of a compensating colorimeter.

F. R. ENNOS.

Volumetric determination of sodium and potassium ferrocyanides, using zinc sulphate solution. AZOT CHEMICAL FACTORY, JAWORZNO (Przemysł Chem., 1929, **13**, 65—66).—Ferrocyanide solutions are titrated with 0·2*N*-zinc sulphate solution, the end-point being ascertained by observing when drops of the solution fail to give a blue coloration on ash-free filter-paper wetted with ferrous ammonium sulphate. The equivalent value of the zinc sulphate solution has previously to be determined separately for sodium and for potassium ferrocyanides.

R. TRUSZKOWSKI.

Diphenylamine as oxidation–reduction indicator for indirect titration of cobalt. J. GILLIS and V. CUVELIER (Natuurwetensch. Tijds., 1929, **11**, 20—24).—The method of Willard and Hall (A., 1922, ii, 875) has been modified, after examination by potentiometric methods, to permit of the use of diphenylamine as internal indicator. The alkaline solution, after oxidation by means of sodium perborate, and removal of the excess by boiling, is reduced by a known excess of stannous chloride, and this excess, together with the ferrous salt formed from any iron present, is determined by means of potassium dichromate in presence of the indicator. The parallel potentiometric titrations show that the minimum quantity of indicator must be used, and must be added only towards the end of the titration, and a small correction must be made. With these precautions, accurate results are obtained in the presence of nickel, and of considerable proportions of iron.

S. I. LEVY.

Volumetric determination of cobalt. G. A. BARBIERI (Atti R. Accad. Lincei, 1928, [vi], 8, 405—408).—In the green liquids which result from the decomposition of cobaltinitrites by means of hot sodium hydrogen carbonate (A., 1928, 973), all the nitro-groups of the original cobaltinitroso-complex are present as alkali nitrite, whilst the tervalent cobalt exists as cobalticarbonate, to which the green colour is due. When the green liquid is added to permanganate solution acidified with sulphuric acid, the nitrous acid is oxidised quantitatively in the cold to nitric acid and the tervalent cobalt is reduced to the bivalent form, eleven equivalents of the permanganate oxygen being consumed for each molecule of the cobaltinitrite. This reaction forms the basis of volumetric determinations of potassium (Ind. saccarifera ital., 1928, **21**, 387) and of cobalt, the details of the procedure in the latter case being now described. T. H. POPE.

Reactions of molybdates, nitrophosphomolybdates, tungstates, and phosphotungstates. T. GASPAR Y ARNAL (Anal. Fís. Quím., 1928, **26**, 435—445).—The precipitation reactions are given in tabular form of solutions of sodium molybdate, ammonium molybdate, sodium nitrophosphomolybdate, sodium tungstate, and sodium phosphotungstate with lithium, sodium, ammonium, potassium, cupric, rubidium, silver, cæsium, beryllium, magnesium, calcium, zinc, strontium, cadmium, barium, mercurous, mercuric, aluminium, thallium, lead, thorium, bismuth, uranyl, manganous, ferric, nickel, and cobalt salts in aqueous solution and, in some cases, in aqueous-alcoholic solution. The results are discussed, particularly from the point of view of the possibility of separation of metals by the use of these reagents. R. K. CALLOW.

Gravimetric micro-determination of molybdenum. J. B. NIEDERL and (MISS) E. P. SILBERT (J. Amer. Chem. Soc., 1929, **51**, 376—377).—Pregl's method for the micro-determination of metals in organic substances may be used in principle for the gravimetric micro-determination of molybdenum as trioxide in substances containing no other non-combustible or non-volatile constituents. S. K. TWEEDY.

Potentiometric determination of titanium in the presence of other metals, especially iron. H. BRINTZINGER and W. SCHIEFERDECKER (Z. anal. Chem., 1929, **76**, 277—280).—The solution is treated with 20 g. of calcium chloride crystals (or 12 g. of sodium chloride) and 10—20 c.c. of concentrated hydrochloric acid, diluted to 100 c.c., and titrated in an atmosphere of carbon dioxide at 90° with chromous chloride. Ferric chloride is reduced first, then cupric to cuprous chloride, and finally titanic to titanous chloride, the end-point being marked in all cases by an appreciable potential fall. A. R. POWELL.

Determination of traces of antimony in copper and its alloys. S. G. CLARKE and B. S. EVANS.—See B., 1929, 175.

Solubility of Reinsch antimony films in water. S. G. CLARKE (Analyst, 1929, **54**, 99—101).—If washing of the film with water is unduly prolonged appreciable amounts of antimony are removed, the solubility being due to the presence of dissolved oxygen. Ordinary distilled water may safely be used provided the washing occupies a few seconds only. J. S. CARTER.

Determination of the platinum metals in ores and concentrates. H. R. ADAM.—See B., 1929, 212.

Methods and apparatus used in the cryogenic laboratory. XX. High-vacuum pump. W. GAEDE and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 985—988).—Details are given of a mercury diffusion pump with an exhausting capacity at 0·15 mm. pressure of 130 litres/sec. for air, and 420 litres/sec. for helium. F. G. TRYHORN.

Gas density balance. A. STOCK (Z. physikal. Chem., 1928, **139**, 47—52).—An improved form of density balance is described in which the beam containing a small piece of soft iron is controlled by means of an external electromagnet. An ammeter may then be conveniently calibrated to read gas densities. R. W. LUNT.

Determination of refractive indices of materials, especially of fused mixtures, used in the Becke immersion method. A. GOOSSENS (Natuurwetensch. Tijds., 1929, **11**, 1—5).—The method of the Duke of Chaulnes, in which the apparent depth of a layer of liquid of known refractive index, and that of a layer of the liquid to be examined, of the same thickness, are determined by means of a vertically moving microscope, is modified for measurements with transparent solids. S. I. LEVY.

Extraction apparatus. S. J. GAŠPERÍK (Chem. Listy, 1929, **23**, 58—59).—A modification of Soxhlet's extraction apparatus is described. R. TRUSZKOWSKI.

Continuous laboratory extractor for liquids. A. W. FRANCIS (Ind. Eng. Chem. [Anal.], 1929, **1**, 15).—The sample is drawn into a pipette bulb packed with glass beads and the condensed vapour of the extracting liquid allowed to bubble up or down according as it is lighter or heavier than the sample. C. IRWIN.

Extraction apparatus for liquids. II. J. FRIEDRICHS (Chem. Fabr., 1929, 90—91; cf. A., 1928, 389).—The comparative rates of extraction of 0·01N-aqueous benzoic acid by chloroform, carbon disulphide, and carbon tetrachloride in various types of extractor were determined. A glass spiral to prevent the extracting liquid taking the shortest path, or a condenser with serrated edges, was less efficient than a distributor consisting of fine hollow points dipping into the solution, and this in turn less than the porous glass frits designed by the author. C. IRWIN.

Micro-extraction method. J. B. NIEDERL (J. Amer. Chem. Soc., 1929, **51**, 474—475).—One drop of the liquid and one drop of extraction medium are repeatedly centrifuged in a sealed capillary tube so that the layer of higher density is forced through the layer of lower density. The tube is then separated under a microscope at the boundary of the two liquids. S. K. TWEEDY.

Haughton–Hanson thermostat. Method of fine adjustment. P. J. DURRANT (Inst. Metals, March, 1929, advance copy, 4 pp.).—In a method by which the temperature of the Haughton–Hanson thermostat can be adjusted to within 0·1° over a range of 5°, the "cold bulb" is placed in a small toluene thermostat, and the temperature of this is controlled by a movable wire in a mercury U-tube. The temperature of the thermostat depends on that of the "cold bulb," which in turn depends on the level of the wire. Preliminary experiments enable a scale to be drawn by the side of the wire. W. HUME-ROTHERY.

Apparatus for vapour-pressure determinations. O. A. PICKETT (Ind. Eng. Chem. [Anal.], 1929, **1**, 36—38).—Ramsay and Young's vapour-pressure apparatus is modified by the insertion of a reflux condenser after the boiling tube. A mercury thermometer is used for approximate readings and a platinum resistance thermometer for precision, each being fitted with a cotton wick. By the use of different bath-liquids data over the temperature range 10—220° can be obtained in 2—4 hrs. with an accuracy of 0·5%. C. IRWIN.

Pressure regulator for vacuum distillations. H. L. COX (Ind. Eng. Chem. [Anal.], 1929, **1**, 7—8).—A closed-arm mercury manometer contains an adjustable contact in the open side and a fixed contact in the top of the same side. These are connected in series to a battery and a relay operating the motor vacuum pump. Any desired pressure between 2 mm. and atmosphere can be maintained to within 0·1 mm. C. IRWIN.

Sublimation mercury still. K. HICKMAN (J. Opt. Soc. Amer., 1929, **18**, 62—68).—An improved type of electrically heated glass still is described. A number of units can be worked in series, condensed mercury which ordinarily falls back into the mother-liquor being passed on to the next still. The still works automatically, and an advantage claimed is that the need for frequent chemical treatment of the mercury before distillation is avoided. N. M. BLIGH.

Automatic mercury still. F. L. ROBESON (J. Opt. Soc. Amer., 1929, **18**, 72—74).—An easily constructed glass still is described employing two barometric columns to maintain the vacuum. The still starts and stops automatically, and needs little attention. The power required is 90 watts for an output of 100 g./hr. of mercury. N. M. BLIGH.

Still for liquids of high b. p. K. HICKMAN (J. Opt. Soc. Amer., 1929, **18**, 69—71).—The apparatus is in the form of an alembic, and works on the principle that distillation can take place rapidly under very low pressures if the evaporating and condensing surfaces are large and close together. It is intended for liquids that oxidise or decompose when distilled in air. N. M. BLIGH.

Distilling apparatus for the chemical engineering laboratory. W. L. BEUSCHLEIN (Ind. Eng. Chem. [Anal.], 1929, **1**, 43—44).—An apparatus which combines the batch and continuous-type fractionating equipment, and gives constant conditions, consists of a 30-gallon still, plate column, and condenser of the usual type, with thermometers in the hand-hole covers of each plate, and in the vapour of the kettle. Piping from condenser to kettle converts into a continuous process, and the condensate passes through two Venturi meters (one for the reflux and one for the net output), of the two-liquid multiplying type. The reflux ratio is obtained and regulated by a valve, an open vent eliminating siphoning. In operation the condensate composition is built up by returning all as reflux to the kettle, after which a portion is allowed to flow continuously through the sight gravity jar into the kettle, and readings of the Venturi manometers, kettle thermometer, and condensate hydrometer are taken. By directing a fraction of the condensate through a cock to the storage vessel, concentration may be changed and a new set of conditions established. D. H. HEWER.

Application of the vacuum tube in the falling-ball method [of determining viscosity] for dark-coloured solutions. E. M. SYMMES and E. A. LANTZ (Ind. Eng. Chem. [Anal.], 1929, **1**, 35—36).—A steel ball is used and the coils of an oscillating circuit are wound in two slots corresponding with the graduation marks of the viscosity tube. The change in note due to the change in frequency of the oscillations marks the passage of the ball through the coils. C. IRWIN.

Brine circulator for cooling condensers. H. T. GERRY (J. Amer. Chem. Soc., 1929, **51**, 475).—An easily constructed laboratory adaptation of the air-lift pumps used in sulphuric plants is described. S. K. TWEEDY.

Colorimeter for determination of hydrogen-ion concentration. J. J. BEAVER (J. Opt. Soc. Amer., 1929, **18**, 41—49).—The apparatus described avoids the use of standardised buffer solutions. It has an additional cup and plunger and the total depth of liquid in the light path is kept constant irrespective of what this depth or the ratio of the depths of liquid in the two cups may be. The method is rapid and accurate, and it can be used for coloured or turbid solutions if the colour is not too deep. The apparatus can easily be adapted for use as an ordinary colorimeter. N. M. BLIGH.

Suction as a filtering aid. G. L. HOCKENYOS (Chemist Analyst, 1928, **17**, No. 4, 18).—A pressure regulator, consisting of a tube containing a variable amount of water, and fitted with a stopper carrying a tube to the suction flask and another tube from the water upwards into the air, is recommended. CHEMICAL ABSTRACTS.

Porous filter crucibles. S. GERICKE (Chem.-Ztg., 1929, **53**, 119).—Porous filter crucibles have a limited application only. Untrustworthy results are obtained when such crucibles are used in the determination of phosphoric acid as magnesium pyrophosphate or as phosphomolybdate, and the determination of nickel as the dimethylglyoxime compound. Calcium oxalate and barium sulphate pass through most porous crucibles and filtration of gelatinous precipitates is slow. J. S. CARTER.

Ebullioscopic apparatus for high-pressure researches. W. SWIENTOSLAWSKI (Compt. rend., 1929, **188**, 392—395).—The author's differential ebullioscope (this vol., 255) may be adapted for work at pressures up to 25 atm. by the use of compressed nitrogen, the apparatus being placed in gas-tight, steel protecting vessels. Electrical heating and temperature-measuring devices are used, and the pressure is determined from the b. p. of water, which is used as a control, or from the amount of nitrogen in a tube attached to the source of pressure and maintained at a constant temperature (cf. following abstract). J. GRANT.

Modification of [Swientoslawski's] ebullioscope for high pressures. A. ZMACZYNSKI (Compt. rend., 1929, **188**, 395—396; cf. preceding abstract).—A reservoir supplied with a siphon is connected to the portion of the apparatus containing the boiling liquid and serves to maintain a constant liquid level over wide ranges of pressure, and to compensate for the effect of thermal dilatation. J. GRANT.

Stirrer from [motor-car] windscreen wiper. A. V. MOTSINGER (Ind. Eng. Chem., 1929, 21, 192).—A suction-operated windscreen wiper with a piece of wire attached is used as a stirrer. C. IRWIN.

Collapsing temperatures of various kinds of laboratory glass tubing. A. W. LAUBENGAYER (Ind. Eng. Chem., 1929, 21, 174).—The collapsing temperatures of glass tubing with a diameter of 13 mm. were found to range from 700° for soft soda-lime glass to 860° for Jena or Bohemian combustion tubing. Evacuated tubes collapse at temperatures 50—150° lower. C. IRWIN.

Geochemistry.

Influence of temperature on the composition of the upper layers of the atmosphere. HELGE-PETERSEN (Physikal. Z., 1928, 29, 879—884).—The hypothesis of a stationary streaming state as against that of a static diffusional equilibrium provides a plausible explanation of the absence of helium at great heights, *e.g.*, at 200 km., as evidenced by the lack of helium lines in the northern light spectrum. R. A. MORTON.

Amount of ozone in the earth's atmosphere and its relation to other geophysical conditions. III. G. M. B. DOBSON, D. N. HARRISON, and J. LAWRENCE (Proc. Roy. Soc., 1929, A, 122, 456—486; cf. A., 1926, 493; 1927, 439).—Observations have been made at seven stations in N.-W. Europe and the accuracy of the measurements is discussed. A study of the monthly means of the ozone values shows that the autumn minimum value is roughly the same for all stations, whereas the spring maximum is much greater at the northern stations. The results suggest that in the Arctic the ozone values are high in spring, but relatively low in the late summer. The tendency for days with much ozone to be associated with magnetically disturbed conditions is again indicated. The distribution of ozone in typical cyclones and anticyclones is discussed at length, and a series of maps is constructed to show the changes in the ozone distribution for typical pressure distributions. The 1927 observations entirely confirm the close connexion between the amount of ozone and the pressure distribution observed previously. The measurements give evidence that the great polar and tropical air currents extend to a great height and bring their own stratosphere with them. The amount of ozone appears to be uninfluenced by pressure surges or Föhn conditions. The results of the present observations make it almost certain that the chief cause of the formation of atmospheric ozone is not the action of the sun's ultra-violet radiation of wave-length about 1600 Å., as hitherto supposed, but that, on the contrary, the effect of sunlight is mainly to decompose the ozone already present. L. L. BIRCUMSHAW.

Altitude of the ozone layer. J. C. MCLENNAN, R. RUEDY, and V. KROTKOV (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 293—301).—An account of attempts to determine the height of the ozone layer over Toronto is given. A series of spectrograms of the zenith of a clear sky were taken, and the intensities of the Huggins bands (absorption bands in the ultra-violet due to ozone) were determined by means of a photomicrometer. The observations are employed to determine the height of the ozone layer. Values varying from 47·55 to 57 km. are obtained for different days and times. The average of the results is slightly higher than that of those previously obtained by Cabannes and Dufay. The thickness of the ozone layer is only 3 mm. on the average. A. J. MEE.

Measurements of ozone in the higher atmosphere in 1928. H. BUISSON (Compt. rend., 1929, 188, 647—648).—Diurnal determinations of ozone in the higher atmosphere during 1928 by the method previously described (A., 1928, 611) have confirmed the observations made in 1927, the maximum (spring), 3·75 mm., and minimum (autumn), 2·25 mm., being slightly less pronounced. The irregular variations are strongest at the beginning and end of the year and disappear in summer. The measurements are in agreement with those made at Arosa (Switzerland) at 1800 m. and for the period January to October the figures at each station are 0·16 mm. lower than those of 1927. R. BRIGHTMAN.

γ-Rays of potassium. A. SALMONY (Chem.-Ztg., 1929, 53, 137).—Radiations from potassium are believed to be responsible for the radioactivity of certain mineral deposits and to play an essential part in the re-activation, under the influence of radiation from radioactive substances, of hearts removed from the body. J. S. CARTER.

Dolomitisation of Palæozoic limestones in Manitoba. D. J. BIRSE (Trans. Roy. Soc. Canada, 1928, [iii], 22, IV, 215—221).—The fossiliferous limestone presents a mottled appearance with darker dendritic forms in a lighter ground. It has been thought that these forms are of fucoidal origin. They can be etched out with dilute acids, and analyses of the dark and light portions show that the former are richer in magnesium carbonate. The forms are therefore due to a selective dolomitisation of the limestone. L. J. SPENCER.

Keweenawan sill-rocks of Sudbury and Cobalt, Ontario. T. C. PHEMISTER (Trans. Roy. Soc. Canada, 1928, [iii], 22, IV, 121—197).—Detailed petrographical descriptions are given of the quartz-diabase occurring as large intrusive sills in rocks of Keweenawan age in these two mining areas. The quartz forms a micrographic intergrowth with an acid plagioclase, and as this increases in amount the rock grades into a micropegmatite. Analyses are given of the rocks and of the constituent pyroxenes. L. J. SPENCER.

Cyanite as found in Western North Carolina. A. H. FESSLER and W. J. MCCAUGHEY.—See B., 1929, 209.

Approximate gallium content of green kaolin from Tanokami. Existence of gallium in the solar chromosphere. S. IIMORI (Suppl. to Sci. Papers Inst. Phys. Chem. Res., 1929, **10**, No. 8, 1—4; cf. A., 1928, 42).—Spectrographical examination suggests that the gallium content of the green kaolin from Tanokami is of the order 0·0004—0·004%. It is suggested that certain of the solar lines are those of gallium. J. S. CARTER.

Pink kaolin, and ruthenium as a minor constituent of the Tanokami kaolins. S. IIMORI and J. YOSHIMURA (Bull. Chem. Soc. Japan., 1929, 4, 1—5).—An analysis is given of a pink kaolin from Tanokami. From measurements of the X-ray absorption spectrum it is considered that the pink colour is due to the presence of rhodium or ruthenium as a minor constituent. C. W. GIBBY.

Prochlorite from Monte Rosso di Verra (Monte Rosa group). T. CARPANESE (Atti R. Accad. Lincei, 1929, [vi], 9, 77—83).—Analysis of this mineral gave: H_2O 13·13; SiO_2 29·20; Al_2O_3 21·32; Fe_2O_3 1·55; FeO 3·41; MgO 31·89; total 100·50%. Dehydration on heating follows a course closely resembling that observed with pennine from Zermatt and with clinochlore from Val Devero, the existence of a hydrate containing about 5% of water and stable at about 550—700° being indicated. Re-absorption of atmospheric moisture by the anhydrous mineral proceeds rapidly at first and then gradually ceases. Optical transformation occurs when the prochlorite is heated, the optic axial angle diminishing to zero and then becoming negative; later, the crystals become biaxial, still remaining negative but with the plane of the optic axis perpendicular to its original position. Comparison of the dehydration and re-absorption curves for the "noble" variety of serpentine and for antigorite indicates a sharp chemico-physical distinction between these two minerals. T. H. POPE.

Baryta in the jurassic and cretaceous deposits of the Tschuvaschki Republic. L. M. MIROPOLSKI (Bull. Acad. Sci. U.R.S.S., 1928, 425—441).—the different forms of baryta, which appears in these deposits both as concretion and as separate crystals of varying habit, are described. T. H. POPE.

Structure of leucite and of complex kaolinates. M. DOMINIKIEWICZ (Rocz. Chem., 1928, 8, 542—553).—Structural formulæ derived for leucite, andalusite, sillimanite, topaz, and beryl are shown to be in accordance with many of the observed properties of these minerals. R. TRUSZKOWSKI.

Chemical and mineralogical composition of red and green eocene schistous clay of the Eastern Carpathians. A. GAWEL (Bull. Acad. Polanaise, 1928, A, 523—537).—Chemical analyses are recorded of the portion of slate clay soluble in hydrochloric acid and these are expressed by the general formula

$$4SiO_2,(Al_2O_3+Fe_2O_3),(FeO,MgO,CaO,K_2O,Na_2O).$$

The red clay is characterised by the absence of combined ferric oxide but contains free ferric oxide, to which the colour is due, whilst in the green clay the iron oxide is combined with silica. A. I. VOGEL.

Relation between the increase in the magnetic susceptibility of certain rocks when heated and the modifications induced in certain of their mineral constituents. A. MICHEL-LÉVY and G. GRENET (Compt. rend., 1929, **188**, 640—642).—The increase in magnetic susceptibility of five specimens of rhyolite, containing varying amounts of biotite, chlorite, and titanite, a specimen of dacite and one of andesilabradorite produced by heating at 700° is connected with the dehydration of the chlorite surrounding titanite crystals and the formation of magnetite or titanomagnetite. R. BRIGHTMAN.

Calcareous soils of Bavaria. H. NIKLAS, R. PÜRCHKAUER, and H. POSCHENRIEDER (Z. Pflanz. Düng., 1929, **13A**, 39—53).—The general classification of these calcareous soils is discussed from the point of view of chalk content and p_H value. Generally, poverty in phosphate is characteristic, but easily-soluble potash is present in satisfactory amounts. The growth of *Azotobacter* is not as satisfactory as the reaction and nutritive value would indicate. The catalytic power of these soils is also described. A. G. POLLARD.

Weathering of sandstone, limestone, and basalt in red-earth areas. A. REIFENBERG (Z. Pflanz. Düng., 1929, **13A**, 53—66).—The chemical and physical processes involved in the formation of some Palestine soils are examined and discussed. The soils are classified and their characteristic properties enumerated. A. G. POLLARD.

Etna and its lavas. A. RITTMANN (Naturwiss., 1929, **17**, 94—100).—A general account of volcanic eruptions from Mt. Etna is given, together with chemical analyses of the lava of different periods of activity. The composition varies within fairly narrow limits. The geological interpretation of the changes is discussed. R. A. MORTON.

Constitution and classification of coal. A. C. FIELDNER.—See B., 1929, 155.

Organic Chemistry.

Purification of methyl fluoride. Quantitative gas analysis by high-dispersion infra-red spectroscopy. W. H. BENNETT (J. Amer. Chem. Soc., 1929, **51**, 377—381).—Pure methyl fluoride may be prepared by heating 2 parts of anhydrous potassium fluoride with 5 parts of potassium methyl sulphate at 140—200°, passing the gas successively through concentrated sulphuric acid (to remove methyl ether), concentrated potassium hydroxide solution, soda-lime, and calcium chloride, and finally condensing in liquid air. This gas is free from methyl ether and ethylene. The quantitative analysis of methyl fluoride for these two impurities by high-dispersion measurements of the infra-red spectra of the gas is described. S. K. Tweedy.

Catalytic activity of aluminium chloride. G. Dougherty (J. Amer. Chem. Soc., 1929, **51**, 576—580).—The author's view that the catalytic activity of aluminium chloride is due to the formation of ionogenic additive products is confirmed by the observation that the halogens in mixtures of halogenoparaffins are readily interchangeable in presence of a little aluminium chloride (cf. Walker, J.C.S., 1904, **105**, 1082). Thus, in equimolecular proportions, methyl iodide and ethyl bromide give methyl bromide and ethyl iodide, ethylene bromide and ethyl iodide give ethyl bromide (70% of theory), ethyl bromide and chloroform at the ordinary temperature give 35% of dichlorobromomethane, and ethylene chloride and bromide give an equilibrium mixture containing 50% of ethylene chlorobromide. The same mixture is obtained from ethylene chlorobromide

H. E. F. Notton.

Reactivity of carbinols. Walden inversion. P. A. Levene and A. Rothen (J. Biol. Chem., 1929, **81**, 359—368).—The velocity of substitution of Br for OH on heating a number of carbinols under standard conditions with hydrogen bromide was observed. The greatest difference was found between the rapidly reacting mixed aliphatic–aromatic carbinols and the slowly reacting aliphatic compounds. In the aliphatic series, the normal primary alcohols reacted more rapidly than those with branched chains, and the primary alcohols as a whole more rapidly than the secondary; methyl*cyclo*hexylcarbinol reacted much more slowly than any other compound studied. The unexpected fact that Walden inversion takes place principally in the mixed aliphatic–aromatic series in spite of the high speed of substitution may be accounted for by the great mobility of the groups in these compounds.

C. R. Harington.

Synthesis of methyl alcohol. E. Audibert.—See B., 1929, 162.

Derivatives of aliphatic glycols. G. M. Bennett and F. Heathcoat (J.C.S., 1929, 268—274).—Treatment of glycol monomethyl ether, in dimethylaniline solution, with thionyl chloride conveniently gave methyl β-chloroethyl ether, b. p. 90·5°/747 mm., d_4^{20} 1·031. An attempt to repeat Foran's preparation of bromodiethyl ether gave vinyl bromide as the only isolable product.

The reaction of sulphur monochloride on tri-, tetra-, and penta-methylene glycols has been examined. γ-*Chloropropyl* 3 : 5-*dinitrobenzoate* has m. p. 77°. Trimethylene glycol, by the successive interaction of acetic anhydride and sulphur chloride, gives γ-chloropropyl acetate, b. p. 66°/14 mm., in good yield. Treatment of the last substance with propyl mercaptan and aqueous-alcoholic sodium hydroxide leads to γ-*hydroxydipropyl sulphide*, b. p. 112°/16 mm., d_4^{20} (vac.) 0·9794, n_α^{20} 1·47789 (*phenylurethane*, m. p. 36°). β-Hydroxyethyl butyl sulphide yields the isomeric *phenylurethane*, m. p. 44·5°.

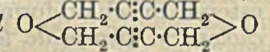
Tetramethylene glycol (corresponding *di-α-naphthylurethane* has m. p. 198°) gave, by treatment with sulphur chloride, crude δ-*chlorobutyl alcohol*, b. p. 86°/15 mm. (decomp.), from which the α-*naphthylurethane*, m. p. 66°, was isolated. δ-*Chlorobutyl acetate*, b. p. 87°/17 mm., d_4^{20} (vac.) 1·0803, n_α^{20} 1·43811, was obtained either by heating tetramethylene glycol with sulphur chloride and acetylating the product or by the interaction of the glycol and acetyl chloride under pressure. δ-Chlorobutyl acetate reacted with ethyl mercaptan in methyl-alcoholic–aqueous solution, giving *ethyl* δ-*hydroxybutyl sulphide*, b. p. 120°/19 mm., d_4^{20} (vac.) 0·9794, n_α^{20} 1·48118 (*phenylurethane*, m. p. 37°); similar use of thiophenol led to *phenyl* δ-*hydroxybutyl sulphide*, m. p. 24° (*phenylurethane*, m. p. 68·5°).

Pentamethylene glycol (corresponding *diphenylurethane* and *di-α-naphthylurethane*, m. p. 174° and 147°, respectively) interacted with sulphur chloride to give crude ε-*chloroamyl alcohol*, b. p. 114°/16 mm. (α-*naphthylurethane*, m. p. 92°). ε-*Chloroamyl acetate*, b. p. 103°/18 mm., d_4^{20} (vac.) 1·0648, n_α^{20} 1·43791, was converted by methyl mercaptan and methyl-alcoholic–aqueous potassium hydroxide into *methyl* ε-*hydroxyamyl sulphide*, b. p. 121°/16 mm., d_4^{20} (vac.) 0·9846, n_α^{20} 1·488185 (*phenylurethane*, m. p. 43·5°). *Phenyl* ε-*hydroxyamyl sulphide* has m. p. 31·5° (*phenylurethane*, m. p. 59°).

Attention is directed to the general fact that an alternation of m. p. occurs in the diurethanes when the lengthening chain is terminated by large polar groups, whilst the m. p. fall with but slight alternation if the highly polar group is at one end only.

R. J. W. Le Fèvre.

Action between copper salts and glycerol. B. K. Vaidya (Nature, 1929, **123**, 414).—When copper salts, except cupric chloride, are heated with glycerol at 150—200°, metallic copper and free acid (which may undergo further decomposition) are produced, together with ethyl alcohol, acraldehyde, carbon dioxide, methane, and small quantities of carbon monoxide and hydrogen. Cupric chloride yields cuprous chloride quantitatively. Glycol, erythritol, and mannitol give analogous results. Probably the decomposition is catalysed by the copper, which is pure and finely divided. A. A. Eldridge.

Diacetylenic heterocyclic compound. Lespieau (Compt. rend., 1929, **188**, 502—503).—By condensation of dichloromethyl ether with magnesium acetylide the *compound*  $O{<}^{CH_2\cdot C⋮C\cdot CH_2}_{CH_2\cdot C⋮C\cdot CH_2}{>}O$ is formed, m. p. (with deflagration) 180°. When heated slowly, it turns yellow, shrinks, and does not melt or deflagrate below 200°. It forms a precipitate with mercuric chloride, and absorbs 4 atoms of bromine from an ethereal solution.

B. W. Anderson.

Cyclic acetals. I. R. Dworzak and T. M. Lasch (Monatsh., 1929, **51**, 59—72).—The formation of cyclic acetals by the interaction of a series of glycols with various aliphatic aldehydes is investigated. Contrary to experience in the case of cyclic benzylidene derivatives, the yields obtained are approximately the same whether the mixture is heated with concentrated hydrochloric acid in a sealed tube or condensed at 0° by the action of anhydrous hydrogen chloride. Contrary to Hibbert and Timm's experience (A., 1924, i, 710), the yield of cyclic acetal increases with increasing mol. wt. of the aldehyde used. Acetals could be obtained only with αβ- and αγ-glycols (yielding five- and six-membered rings) (cf. Franke and Gigerl, A., 1928, 759) and no definitely characterised, halogen-free compound could be isolated from the product of the action of *iso*butaldehyde with pentane-αδ-, octane-αθ-, nonane-αι-, and decane-ακ-diols. By the above methods from the appropriate glycol and aldehyde are obtained the cyclic *methylene* derivatives of β-methyl-β-ethylpropane-αγ-diol, b. p. 150—152° (yield 30%); ββ-dimethylpropane-αγ-diol (30%) (cf. Apel and Tollens, A., 1896, i, 115): the cyclic *ethylidene* derivatives of β-methyl-β-ethylpropane-αγ-diol, b. p. 156—160° (30%): the cyclic iso*butylidene* derivatives of ββ-dimethylpropane-αγ-diol, b. p. 159—161° (67%); β-methylpentane-αγ-diol, b. p. 69—70°/12 mm. (69%); butane-αγ-diol, b. p. 42·5—43°/10 mm. (63%); βδ-dimethylpentane-βδ-diol, b. p. 67—73°/21 mm. (25%); βγ-dimethylbutane-βγ-diol (pinacol), b. p. 59°/13 mm. (68%); and γδ-dimethylhexane-γδ-diol, b. p. 81—83°/10 mm. (66%): and the cyclic *heptylidene* derivative of ββ-dimethylpropane-αγ-diol, b. p. 234—239° (78%).

J. W. Baker.

Esters of phosphoric acid. I. Phosphates of cetyl alcohol, cholesterol, chloroethyl alcohol, and ethylene glycol. II. Action of ethyl metaphosphate on alcohols, ammonia, and some amino-compounds. R. H. A. Plimmer and W. J. N. Burch (J.C.S., 1929, 279—291, 292—300).—I. The interaction of phosphoryl chloride and cetyl alcohol in chloroform gave *barium monocetyl phosphate monohydrate* (from which monocetyl dihydrogen phosphate was isolated), *calcium monocetyl phosphate*, and *dicetylphosphoryl chloride* (hydrolysis of which yielded *barium dicetyl phosphate* and dicetyl hydrogen phosphate, softening at 46°). The action of 1 mol. of phosphoryl chloride on 1 mol. of cetyl alcohol at 100° gave cetene as the only isolable product. Tricetyl phosphate was obtained by the interaction of cetyl alcohol and phosphorus pentachloride and by boiling excess of cetyl alcohol with phosphoric oxide in presence of ether. It gave sodium dicetyl phosphate when boiled with aqueous sodium hydroxide.

The interaction of phosphoryl chloride and cholesterol in chloroform solution gave *barium monocholesteryl phosphate tetrahydrate* (from which *monocholesteryl dihydrogen phosphate* and its *lead*, *silver*, *copper*, and *sodium* salts were obtained) and *barium dicholesteryl phosphate* (whence *dicholesteryl hydrogen phosphate* was prepared). *Tricholesteryl phosphate* was obtained by treatment of cholesterol with phosphorus pentachloride.

Analogous reactions with phosphoryl chloride and ethylene chlorohydrin led to *tri*-β-*chloroethyl phosphate*, b. p. 140°/40 mm., *d* 1·39, barium β-hydroxyethyl phosphate, and *barium di*-β-*hydroxyethyl phosphate dihydrate*. The interaction of ethylene chlorohydrin and phosphoryl chloride in cold pyridine resulted in good yields of *barium chloroethyl phosphate monohydrate*; the corresponding *brucine* salt $[C_{23}H_{26}O_4N_2,(C_2H_4Cl)H_2PO_4,4H_2O]$ was converted into barium β-hydroxyethyl phosphate. Barium chloroethyl phosphate was also obtained by the action of ethyl metaphosphate on ethylene chlorohydrin. Treatment of a saturated aqueous solution of trisodium phosphate with ethylene chlorohydrin resulted in the isolation of *disodium* β-*hydroxyethyl phosphate hexahydrate*, m. p. 61°. A very soluble salt, probably *sodium ethylene phosphate*, $C_2H_4O_2{:}PO{\cdot}ONa$, was formed by the action of phosphoryl chloride on the disodium derivative of ethylene glycol.

The various esters of phosphoric acid were completely hydrolysed by dilute acids. The mono- and di-esters of the aliphatic alcohols with phosphoric acid were not hydrolysed, and the triester was hydrolysed to the diester, by dilute alkali. The mono-, di-, and tri-phenyl phosphates were completely hydrolysed by dilute alkali. *Sodium dicetyl phosphate* is also described.

II. Ethyl metaphosphate and absolute ethyl alcohol interacted in chloroform solution to give *barium ethyl phosphate monohydrate* and *barium diethyl phosphate*. *n*-Propyl alcohol and ethyl metaphosphate similarly gave barium ethyl phosphate, *barium di*-n-*propyl phosphate*, and *barium dipropyl pyrophosphate* (whence *barium propyl phosphate* was obtained). Cetyl alcohol and ethyl metaphosphate yielded barium mono- and di-cetyl phosphates with barium mono- and di-ethyl phosphates. Phenol and ethyl metaphosphate formed barium ethyl phosphate, *barium phenyl phosphate*, barium diethyl phosphate, and *barium diphenyl phosphate tetrahydrate*. Similar treatment of cholesterol with ethyl metaphosphate gave barium ethyl phosphate and *barium cholesteryl phosphate tetrahydrate*, *cholesteryl ethyl ether*, b. p. 237°/20 mm., being also formed. Passage of anhydrous ammonia through a chloroform solution of ethyl metaphosphate gave ammonium ethyl hydrogen phosphate identical with the product obtained directly from ethyl alcohol and phosphoric oxide. *Diammonium ethyl phosphate* and *ammonium diethyl phosphate* were prepared by the action of ammonium sulphate on barium ethyl phosphate and barium diethyl phosphate, respectively.

The product of the interaction of ethyl metaphosphate and hydrazine (Strecker and Heuser, Ber., 1924, **57**, 1364) is *hydrazine ethyl dihydrogen phosphate*, which reacted with copper sulphate to give *hydrazine copper sulphate* and copper ethyl phosphate. Similarly, ethyl metaphosphate formed with phenylhydrazine, alanine, and guanidine, respectively, phenylhydrazine ethyl dihydrogen phosphate, alanine ethyl pyrophosphate (which formed alanine ethyl dihydrogen phosphate on treatment with water), and *guanidine diethyl pyrophosphate*; in no case were any compounds isolated in which nitrogen is directly linked to phosphorus.

The use of ethyl metaphosphate for the preparation of phosphoric esters has no advantage over the alcohol–phosphoric oxide reaction.

R. J. W. Le Fèvre.

Silver salts of esters of hexosemonophosphoric acids. F. Weinmann (Biochem. Z., 1929, 204, 493—494).—The silver salt of Neuberg's hexosemonophosphoric ester, obtained in 81% yield from the barium salt, is a faintly yellow powder easily soluble in cold water and, when prepared from satisfactory material, stable towards light. Its solution soon gives a silver mirror when heated. The silver salt of Robison's ester is, in solution, more sensitive than, but otherwise very similar to, the salt of the isomeric ester. W. McCartney.

Hexosemonophosphate (Robison). P. A. Levene and A. L. Raymond (J. Biol. Chem., 1929, **81**, 279—283).—The rate of hydrolysis by 0·1*N*-hydrochloric acid of the methyl glucoside of the hexosemonophosphate of Robison (A., 1923, i, 86) indicates that the latter has the structure of a γ-lactone; the phosphoric acid residue must therefore be attached to the ϵ-carbon atom. C. R. Harington.

β-Hydroxyethyl allyl sulphide and its derivatives. S. M. Scherlin and V. V. Vasilevski (J. pr. Chem., 1929, [ii], **121**, 173—176).—See this vol., 293.

Refractometric determination of formic acid in the presence of acetic acid. J. Bulíř (Chem. Listy, 1929, **23**, 25—26; cf. *ibid.*, 1920, **14**, 6, 45).—Objections raised against this method by Šťastny are shown to be unfounded, fairly accurate results (0·2 g. of formic acid per 100 c.c.) being attained provided that no substances other than the above acids and water are present in the solution. R. Truszkowski.

Thorium formates. H. Reihlen and M. Debus (Z. anorg. Chem., 1929, **178**, 157—176).—The compound $[Th_3(HCO_2)_6(OH)_5]SCN,7H_2O$ obtained by Weinland and Stark (A., 1926, 498) by the action of potassium thiocyanate on thorium formate is now shown to be *potassium hexaformiato-oxytetrahydroxythiocyanatotrithoriate*, $K[SCN(OH)_4O(HCO_2)_6Th_3],7H_2O$. In a vacuum it loses $7H_2O$ rapidly and a further $2H_2O$ after being heated for 24 hrs. at 61°, being converted into the *trioxy*-compound, $[Th_3(HCO_2)_6O_3SCN]K$. When thorium formate is added to a half-saturated solution of potassium thiocyanate until it ceases to dissolve, the *compound*

$$3K[SCN(OH)_4O(HCO_2)_6Th_3],2K_2[(SCN)_2(OH)_2O_2(HCO_2)_6Th_3],30H_2O$$

crystallises on cooling to 0°. The following *compounds* have been obtained in a similar manner from thorium formate and solutions of alkali nitrate, chlorate, or perchlorate:

$$Na[Th_3(HCO_2)_6O(OH)_4NO_3],10{\cdot}5H_2O;$$
$$Na[ClO_3(OH)_4O(HCO_2)_6Th_3],13H_2O;$$
$$Na[Th_3(HCO_2)_6O(OH)_4ClO_4],9H_2O;$$
$$Na[NO_3(OH)_4O(HCO_2)_6Th_3],[NO_3(OH)_5(HCO_2)_6Th_3],21H_2O;$$
$$2K[NO_3(OH)_4O(HCO_2)_6Th_3],[NO_3(OH)_5(HCO_2)_6Th_3],30H_2O;$$
$$K[ClO_3(OH)_4O(HCO_2)_6Th_3],2[(OH)_2O(HCO_2)_6Th_3],29{\cdot}5H_2O.$$

Dissolution of thorium hydroxide in formic acid yields crystals of thorium formate; as this compound is not an electrolyte it should be formulated as $[Th_3(HCO_2)_{12}],9H_2O$; when treated with pure formic acid on the water-bath the hydrate with $3{\cdot}5H_2O$ is obtained, but with water under the same conditions hydrolysis ensues with separation of the complex $[Th_3(HCO_2)_6(OH)_6],4H_2O$. Interaction of aqueous solutions of thorium nitrate and sodium formate affords two *basic formates* which are most satisfactorily formulated as $[Th_3(HCO_2)_{10}(OH)_2],7H_2O$ and $[Th_3(HCO_2)_9(OH)_3],10H_2O$. Electrical conductivity measurements of solutions of the neutral formate $[Th_3(HCO_2)_{12}],9H_2O$ show that the conductivity increases very rapidly with rise of temperature; this is ascribed to decomposition of the complex with the formation of the complex formate

$$[(H_2O)_3Th(HCO_2)_3Th(HCO_2)_3Th(H_2O)_3](HCO_2)_6.$$

A. R. Powell.

Products of partial hydrogenation of higher monoethylenic esters. T. P. Hilditch and N. L. Vidyarthi (Proc. Roy. Soc., 1929, **A**, **122**, 552—563).—Methyl oleate, palmitoleate, and erucate were treated with hydrogen at 114—220° in the presence of nickel mounted on kieselguhr (15% Ni), the concentration of metallic nickel present with respect to the ester being about 0·5%, until their iodine values were reduced by about 30%. The products of hydrogenation were examined by oxidation with potassium permanganate in hot acetone solution, with formation of free monocarboxylic acids and monomethyl ethers of dicarboxylic acids, together with neutral (non-oxidised) material of negligible iodine value. The evidence afforded by the identification of the dicarboxylic acids (and to a smaller extent of the monocarboxylic acids) indicates that the isomeric acids produced during hydrogenation consist in each case of a mixture of acids in which the ethylenic linking is adjacent to the position occupied in the original compound, and that these acids, together with the original position isomeride, are almost certainly present in both *cis*- and *trans*-forms in the hydrogenated products. The proportion of *iso*-acids formed appears to vary with the length of the carbon chain. The present results are in full accord with the view previously expressed by Armstrong and Hilditch (A., 1925, i, 355). L. L. Bircumshaw.

Products of partial hydrogenation of some higher polyethylenic esters. T. P. Hilditch and N. L. Vidyarthi (Proc. Roy. Soc., 1929, **A**, **122**, 563—570; cf. preceding abstract).—In the case of higher polyethylenic esters the conclusions to be reached from the acids isolated as scission products from the oxidised esters are complicated by the facts that (*a*) the hydrogenation process is selective, not only as regards the degree of unsaturation present, but also to a considerable extent in that each ethylenic linking is not equally attacked, and (*b*) isomerisation occurs, as previously described (*loc. cit.*), although to a smaller degree. The utility and limitations of the procedure are illustrated by a description of experiments with methyl linoleate (from soya-bean and cotton-seed oil) and ethyl linolenate (from linseed oil). It can be deduced with certainty that the unsaturation in linoleic acid is in the Δ^{ι}- and Δ^{μ}-positions, whilst in linolenic acid the positions of the Δ^{ι} and Δ^{μ} linkings can be fixed, but it can only be indicated that the third double linking lies beyond the fourteenth carbon atom of the chain. L. L. Bircumshaw.

ω-Hydroxyaliphatic acids; synthesis of sabinic acid. W. H. Lycan and R. Adams (J. Amer. Chem. Soc., 1929, **51**, 625—629).—ω-Hydroxyaliphatic acids are conveniently prepared through their methyl esters, which are formed quantitatively by hydrogenating ω-aldehydo-esters (cf. A., 1926, 712) in presence of platinum and ferrous sulphate. The following are described: θ-*hydroxynonoic acid*, m. p. 53—54° (*methyl* ester, b. p. 137—139°/3 mm., d^{20} 0·9588, n_D 1·4438, and its *phenylurethane*, m. p. 53—54°), which gives at 220—230° a (?) dimeric intermolecular *ester*, m. p. 64—66°; ι-*hydroxydecoic acid*, m. p. 75—76° (*methyl* ester, b. p. 145—147°/3 mm., d^{20} 0·9618, n_D 1·4471, and its *phenylurethane*, m. p. 54—55°); κ-*hydroxyundecoic acid*, m. p. 65·5—66° (*methyl* ester, b. p. 156—159°/3 mm., d^{20} 0·9542, n_D 1·4493, and its *phenylurethane*, m. p. 64·5—65·5°); λ-hydroxydodecoic acid, m. p. 83—84° (*methyl* ester, b. p. 164—166°/3 mm., m. p. 34—35°, and its *phenylurethane*, m. p. 64—65°), which is identical with naturally occurring sabinic acid (Bougault, A., 1909, i, 82; cf. Simonsen and others, A., 1928, 1355), and μ-hydroxytridecoic acid, m. p. 77—78° (*methyl* ester, b. p. 170—173°, m. p. 40·5—41·5°, and its *phenylurethane*, m. p. 73·5—74°) (cf. Ruzicka and Stoll, this vol., 68). *Methyl hydrogen decane-ακ-dicarboxylate*, m. p. 51·5—52°, is a by-product in the preparation of methyl κ-aldehydoundecoate (*semicarbazone*, m. p. 90—92°). H. E. F. NOTTON.

Hydrogen peroxide as an oxidising agent in acid solution. IX. Oxidation of keto-acids. W. H. HATCHER and A. C. HILL (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 211—220).—The methods of analysis of pyruvic acid are studied and compared. Oxidation by means of alkaline hydrogen peroxide or acid permanganate is preferred. The oxidation of pyruvic and mesoxalic acids by acid permanganate was investigated with special reference to the effect of concentration of mineral acid. The oxidation of these acids with aqueous hydrogen peroxide was also investigated, the effects of temperature, concentration, alkali, and added mineral acid being given. In the case of pyruvic acid, the formation of a complex $CH_3\cdot CO\cdot CO_2H,H_2O_2$ is assumed. This breaks down rapidly to give acetic and carbonic acids. With mesoxalic acid there is formed a complex, $CO(CO_2H)_2.2H_2O_2$, which decomposes into carbonic acid. Mesoxalic acid is about one fifth as reactive towards hydrogen peroxide as pyruvic acid.

A. J. MÉE.

Configurative relationship of β-hydroxy- and β-chlorobutyric acids, and of β-hydroxybutyric acid with methylpropylcarbinol. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 425—433).—l-Δ^α-*Penten-δ-ol*, $[\alpha]_D^{20}$ −6·1° in ether (*hydrogen phthalate*, $[\alpha]_D^{24}$ −4° in ether; α-*naphthylcarbamate*, m. p. 47—49°, $[\alpha]_D^{20}$ +1·37° in alcohol), gave with phosphorus pentachloride d-δ-*chloro*-Δ^α-*pentene*, b. p. 95—97°, $[\alpha]_D^{20}$ +11·1° in ether; with ozone the latter yielded d-β-*chlorobutyric acid*, b. p. 67—70°/0·35 mm., $[\alpha]_D^{23}$ +11·5° in ether, $[\alpha]_D^{23}$ +21·5° in water (*sodium* salt, $[\alpha]_D^{23}$ +15·7° in water). When reduced with hydrogen and palladium, *l*-Δ^α-penten-β-ol gave *l*-pentan-δ-ol, and when oxidised with ozone it yielded *l*-β-hydroxybutyric acid; the configurative relationship of the two last-mentioned compounds is thus confirmed (cf. A., 1927, 591) and *l*-β-hydroxybutyric acid is configuratively related to *d*-β-chlorobutyric acid.

C. R. HARINGTON.

Hydrates of calcium oxalate. W. F. JAKÓB and E. ŁUCZAK (Rocz. Chem., 1929, 9, 41—48).—γ-Calcium oxalate, $CaC_2O_4,3H_2O$, is precipitated in rhombic plates or prisms on the gradual addition at 0° of 1% ammonium oxalate to 0·007*M*-calcium nitrate or chloride solutions containing 0·061*M*-normal sodium citrate. This modification is unstable at the ordinary temperature, and is rapidly converted into the monohydrate at 40°. The β-oxalate, erroneously supposed by Souchay and Lenfsen (Annalen, 1856, 100, 308) to possess 3 mols. of water of crystallisation, has in reality only $2\cdot25H_2O$. It is prepared by the addition at 40—50° of 1% ammonium oxalate to a 0·024*M*-solution of calcium salt containing normal sodium citrate (0·061*M*). The crystals thus obtained are flattened octahedra, which lose $0\cdot25H_2O$ at 80°, but regain this when kept at the ordinary temperature. Above 100° a further molecule of water is irreversibly lost, the stable monohydrate being obtained.

R. TRUSZKOWSKI.

Ferric oxalate and ferric oxalate perchlorate. R. WEINLAND and K. REIN (Z. anorg. Chem., 1929, 178, 219—224).—On keeping a solution of ferric nitrate enneahydrate and oxalic acid in concentrated nitric acid in a desiccator over concentrated sulphuric acid a canary-yellow powder, $Fe_2(C_2O_4)_3,5H_2O$, is obtained. The compound dissolves slowly in water, but the solution gives no reaction for oxalic acid; it therefore appears to be a ferric salt of a ferrioxalic acid. When a solution of ferric chloride and oxalic acid in perchloric acid is evaporated on the water-bath a light green, microcrystalline, hygroscopic *compound*, $Fe_3C_2O_4(C_2O_4H_2)_2(ClO_4)_5,14H_2O$, separates. A solution of the compound in water gives reactions for perchloric but not for oxalic acid.

A. R. POWELL.

Mixed oxalato-fluoro- etc. -anions of tervalent chromium, iron, antimony, and bismuth. R. WEINLAND and W. HÜBNER (Z. anorg. Chem., 1929, 178, 275—288).—Evaporation of a solution of chromic nitrate, oxalic acid, and pyridine over sulphuric acid yields dark reddish-violet leaflets of *pyridine trioxalatotrinitratodichromiate*, $[Cr_2(C_2O_4)_3(NO_3)_3(H_2O)_3]H_3,(C_5H_5N)_4$. Under the same conditions quinoline yields *quinoline trioxalatonitratodichromiate*, $[Cr_2(C_2O_4)_3NO_3(H_2O)_4]H,(C_9H_7N)_4$. From a solution of chromic acid, oxalic acid, and pyridine hydrofluoride on evaporation minute satin-green crystals of *pyridine dioxalatotrifluorodichromiate*, $[Cr_2(C_2O_4)_2F_3]H,(C_5H_5N)_2,7H_2O$, are obtained, whereas from a solution of chromic fluoride, oxalic acid, and pyridine *pyridine dioxalatopentafluorodichromiate*, $[Cr_2(C_2O_4)_2F_5]H_3,(C_5H_5N),5H_2O$, crystallises as a light green, microcrystalline powder. Addition of pyridine to a solution of ferric hydroxide in hydrofluoric and oxalic acids yields *pyridine oxalatodifluorodiaquoferriate*, $[Fe(C_2O_4)F_2(H_2O)_2]H,C_5H_5N$, as a white, crystalline powder. Under the same conditions antimony oxide affords *pyridine oxalatodifluoroantimoniate*, $[Sb(C_2O_4)F_2]H,C_5H_5N$, in large, rectangular columns. Antimony and bismuth trichlorides yield with oxalic acid and pyridine large well-defined crystals of the complex *compounds* $Sb_4(C_2O_4)_5Cl_{12}H_{10}(C_5H_5N)_8$ and $Bi_3(C_2O_4)_4Cl_{10}H_9(C_5H_5N)_4,10H_2O$. A. R. POWELL.

Autoracemisation. R. Kuhn and T. Wagner-Jauregg (Naturwiss., 1929, **17**, 103—104).—The autoracemisation of ethyl bromosuccinate is due to traces of hydrogen bromide which can be eliminated almost completely by repeated distillation in a high vacuum. The pure ester is very stable and the racemisation constants in different solvents do not apply. Not only does hydrobromic acid catalyse the racemisation in aqueous solution, but other bromides act similarly. The efficiency of a given catalyst varies enormously with the solvent, the merest trace of potassium bromide exerting a marked effect in acetone solutions, whereas in methyl alcohol the same effect is obtainable only when the bromide concentration is 0·5—1·0*N*. Animal charcoal, silver and lead bromides, lead oxide, and anhydrous copper sulphate strongly inhibit the racemisation, possibly through adsorption or combination with the catalyst. Chlorides and iodides in general catalyse the racemisation in acetone, but zinc bromide is exceptional in that it strongly inhibits the action of other bromides.

The racemisation of (+)-nitrodiphenic acid in *cyclo*hexanone is much more rapid in glass than in quartz vessels, indicating apparently the catalytic activity of traces of alkali. R. A. Morton.

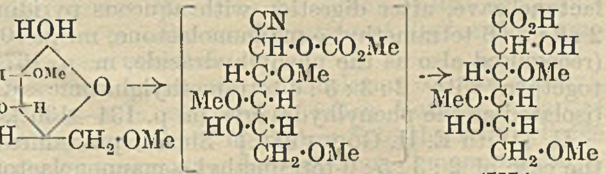
Cleavage of ethyl αδ-dibromoadipate by secondary amines. R. C. Fuson and R. L. Bradley (J. Amer. Chem. Soc., 1929, **51**, 599—602).—Further evidence for the mechanism previously proposed for this reaction (A., 1928, 738) is afforded by the observation that, contrary to the results of von Braun (A., 1926, 1128; cf. A., 1928, 1115), ethyl *meso*-dibromoadipate yields with di-*n*-propylamine ethyl β-dipropylaminopropionate and with piperidine 75% of the theoretical of *ethyl β-piperidinopropionate*, b. p. 114—116°/22 mm., d^{20} 0·927 (*methiodide*, m. p. 100—102°), and only a little ethyl αδ-dipiperidinoadipate. H. E. F. Notton.

Transformations of propino-αγ-dicarboxylic acid. F. Makulec, R. Małachowski, and L. Manitius (Rocz. Chem., 1928, **8**, 576—582).—*Methyl glutinate*, b. p. 101°/6 mm., is prepared by the action of methyl sulphate on glutinic acid. Glutinic acid reacts with acetic anhydride to form 4-acetyl-4 : 6-dihydroxypyrone; with hydrogen bromide it yields cis-*β-bromoglutaconic acid*, m. p. 140·5°, the *anhydride*, m. p. 148—149°, of which is prepared by the action of acetic anhydride. Direct bromination of glutinic acid yields cis-*βγ-dibromoglutaconic acid*, m. p. 132° (*anhydride*, m. p. 93—96°), and cis-*αβγ-tribromoglutaconic acid*, m. p. 151°. R. Truszkowski.

Conjugated unsaturated compounds. VII. Determination of side-chains [methyl groups] in bixin and crocetin. R. Kuhn, A. Winterstein, and L. Karlovitz (Helv. Chim. Acta, 1929, **12**, 64—71).—The oxidation number (number of atoms of oxygen necessary to oxidise an unsaturated acid to carbon dioxide and any stable acid, such as acetic) has been determined for crotonic and sorbic acids, by oxidation with alkaline potassium permanganate. The best values, 4·91 for crotonic, 9·75 for sorbic (theory 5 and 10, respectively), are obtained by treating the acid with 0·4*N*-permanganate acidified with phosphoric acid on the water-bath, cooling, making alkaline with 2*N*-sodium carbonate solution, and then heating for 30 min. at 90°. Application of the method to bixin and crocetin gives values of approximately 45 and 33, respectively, which are in agreement with those necessary for γηλο-tetramethyloctadecanonaene-ασ-dicarboxylic acid and γηλ-trimethyltetradecaheptaene-αξ-dicarboxylic acid, respectively (Kuhn and others, Karrer and Salomon, A., 1928, 869). Determination of the acetic acid produced during the oxidation shows that 4 mols. are obtained from bixin and 3 mols. from crocetin, thus affording further confirmation of the above formulæ. The paper also contains an analysis of Rinkes' results (A., 1917, i, 660; 1928, 1377) on the oxidation of methylbixin. H. Burton.

Ultra-violet spectroscopic investigation of β-ketogluconic acid. P. Niederhoff (Z. physiol. Chem., 1929, **181**, 83—87).—The ultra-violet absorption spectrum of β-ketogluconic acid, m. p. 152°, $[\alpha]_D^{20}$ −70°, shows no selective absorption and hence favours the oxy-ring form (Ohle and Berend, A., 1927, 647) rather than the open-chain keto-form which contains two adjacent chromophoric groups. In alkaline solution, however, selective absorption occurs, a maximum at 2750 Å. (ε 60·2) being observed, the intensity of which depends on the concentration of the solution, temperature, and the proportion of alkali, and is assumed to be due to the βγ-dienol form. After a time the alkaline solution becomes yellow, this colour being destroyed by addition of acids and reappearing on shaking. The absorption spectrum of the potassium salt in 0·2*N*-hydrochloric acid does not differ appreciably from that of the free acid in aqueous solution. J. W. Baker.

Synthesis of *l*-2 : 3 : 4 : 6-tetramethyl-δ-gluconolactone and of *l*-2 : 3 : 4 : 6-tetramethyl-δ-mannonolactone from *l*-2 : 3 : 5-trimethylarabofuranose. W. N. Haworth and S. Peat (J.C.S., 1929, 350—357).—An improved method of ascent from pentose to hexose is described; *e.g.*, 2 : 3 : 4-trimethylarabopyranose, dissolved in aqueous potassium cyanide, was treated with methyl chloroformate; the product contained both trimethylcarbomethoxymannono- and -glucono-nitriles. Similar treatment of *l*-2 : 3 : 5-trimethylarabofuranose led to the two lactones (see title) of trimethylhexonic acid (III).



(I.) (II.) (III.)

Hydrolysis of the mixture (II) of *l*-3 : 4 : 6-trimethyl-2-carbomethoxy-glucono- and -mannono-nitriles was effected by the action of ethereal hydrogen chloride and gave l-2-*carbomethoxy*-3 : 4 : 6-*trimethylmannonic acid* (III), m. p. 155°, a syrup. Treatment of the latter after removal of the carbomethoxy-residue by digestion with aqueous barium hydroxide and with phenylhydrazine gave a mixture of *phenylhydrazides*, m. p. 111—127°, resolved into the *phenylhydrazide*,

m. p. 137—139°, of trimethylmannonic acid, and the phenylhydrazide, m. p. 125°, of trimethylgluconic acid. Acid hydrolysis of the former phenylhydrazide afforded l-3 : 4 : 6-*trimethyl-δ-mannonolactone*, m. p. 96—97° (constant), $[\alpha]_D$ —112·8°, whilst hydrolysis of the latter gave *l*-3 : 4 : 6-trimethyl-δ-gluconolactone. A fourth methyl group was introduced into this pair of lactones by Purdie's method; the products yielded the *phenylhydrazides* of l-2 : 3 : 4 : 6-*tetramethyl-mannonic* and *-gluconic acids*, m. p. 183—184°, $[\alpha]_D^{16}$ +22° (in chloroform), and m. p. 115°, $[\alpha]_{5780}^{19}$ —50° (in ethyl alcohol), respectively, identical in all properties except optical rotation with the enantiomorphous compounds. Further, l-2 : 3 : 4 : 6-*tetramethyl-δ-mannonolactone* (from the corresponding phenylhydrazide) had $[\alpha]_D^{18}$ —150° (initially) $\longrightarrow$ —58° (150 hrs.), whilst a specimen of the *d*-lactone from *d*-2 : 3 : 4 : 6-tetramethyl-*d*-mannose gave $[\alpha]_D^{18}$ +150° $\longrightarrow$ +63° (150 hrs.).

The constitution of trimethylarabofuranose, I, having been definitely settled previously, these syntheses confirm the conclusions previously stated in the constitutional studies of γ- and normal sugars inasmuch as it is shown that these stand in relation to one another as five-atom ring compounds to six-atom ring compounds. The furanose type has thus been transformed into the pyranose type by a procedure which admits only of the formation of a six-membered ring. R. J. W. Le Fèvre.

Conversion of tetramethyl-γ- and -δ-gluconolactones into corresponding mannonolactones and of trimethyl-γ- and -δ-xylonolactones into corresponding lyxonolactones. W. N. Haworth and C. W. Long (J.C.S., 1929, 345—350).—Supplementary evidence to that previously adduced for the existence of two types of ring structure among sugars is given together with a correlation of a number of methylated lactones which have already been studied in their relation to the constitution of sugars. Epimerisation was accomplished in all cases by heating with dilute aqueous pyridine. It is suggested that epimerisation might proceed through an enolic lactone intermediate form rather than through an enolic acid (or salt), since the lactone which is less easily hydrolysed by water is found to be the one which predominates in the epimeric mixture.

I. Crystalline 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone gave, after digestion with aqueous pyridine, 2 : 3 : 5 : 6-tetramethyl-γ-mannonolactone, m. p. 109° (recognised also as the phenylhydrazide, m. p. 167°), together with 2 : 3 : 5 : 6-tetramethylgluconic acid (isolated as the phenylhydrazide, m. p. 134—136°).

II. [With E. H. Goodyear.] Similar procedure in the case of 2 : 3 : 5 : 6-tetramethyl-γ-mannonolactone led to a 30% formation of 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone.

III. 2 : 3 : 4 : 6-Tetramethyl-δ-gluconolactone epimerised to give, after treatment with phenylhydrazine, the phenylhydrazide of 2 : 3 : 4 : 6-tetramethylmannonic acid (90% conversion), m. p. 184—185°, together with the phenylhydrazide of 2 : 3 : 4 : 6-tetramethylgluconic acid, m. p. 115°.

IV. 2 : 3 : 4 : 6 - Tetramethyl - δ - mannonolactone yielded the phenylhydrazides of 2 : 3 : 4 : 6-tetramethylmannonic and 2 : 3 : 4 : 6-tetramethylgluconic acids (conversion 8%).

V. The conversion of 2 : 3 : 4-trimethyl-δ-xylonolactone led abnormally to a 63% yield of furancarboxylic acid together with the phenylhydrazide of 2 : 3 : 4-trimethyl-lyxonic acid (which was not identical with the *phenylhydrazide* of 2 : 3 : 4-trimethyl-δ-xylonic acid, m. p. 137—138·5°).

VI. 2 : 3 : 5-Trimethyl-γ-xylonolactone and hot aqueous pyridine led to the *phenylhydrazide*, m. p. 142°, of 2 : 3 : 5-trimethyl-γ-lyxonolactone (conversion 60%). R. J. W. Le Fèvre.

Selenocyanopropionic acid. I. A. Fredga (J. pr. Chem., 1929, [ii], 121, 56—69).—Potassium selenocyanate reacts smoothly with potassium α-bromopropionate in aqueous solution at the ordinary temperature to give a 50—60% yield of the potassium salt, from which α-selenocyanopropionic acid, m. p. 69—70°, *k* $2{\cdot}31\times10^{-3}$, is obtained (cf. Simon, A., 1905, i, 866). By fractional crystallisation of the *strychnine* salt is obtained an active acid, $[\alpha]_D$ +19°, but the acid regenerated from the *quinine* salt is inactive. Starting with *d*-α-bromopropionic acid was obtained *potassium* d-*selenocyanopropionate*, $[\alpha]_D$ +65°, which is probably pure. When the inactive acid (which need not be isolated) is heated with concentrated hydrochloric acid at 80—90° it is converted into *diselenodi-α-propionic acid* (I), which is isolated in two interconvertible forms, m. p. 70·5—72·5° (? meso), and m. p. 107—108° (? racemic). α-Selenocyanopropionic acid is stable in neutral solution, but with concentrated alkalis it is decomposed with separation of selenium, the main product being I. In acid solution it is smoothly decomposed in accordance with the scheme $2RSeCN=RSe^-+(CN)^-$, $2RSe^-=RSe{\cdot}SeR$, $2(CN)^-=(CN)_2$ ($R=CHMe{\cdot}CO_2H$). The reaction is followed polarimetrically and with *N*-hydrochloric acid gives a constant unimolecular velocity coefficient ($9{\cdot}37\times10^{-5}$ min.$^{-1}$), only the first of the above reactions proceeding with a measurable velocity. β-*Selenocyanopropionic acid*, m. p. 58°, *k* $1{\cdot}40\times10^{-4}$ (*potassium* salt), is similarly prepared from β-chloropropionic acid. A method for the accurate determination of selenium is described. J. W. Baker.

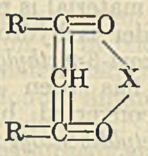
Carbohydrates and polysaccharides. XXI. Tendencies of saturated and unsaturated aldehydes towards acetal formation. H. Hibbert, E. O. Houghton, and K. A. Taylor (J. Amer. Chem. Soc., 1929, 51, 611—614).—Δ^{α}-Unsaturated aldehydes show very little tendency to form cyclic acetals with ethylene glycol in presence of a trace of dilute sulphuric or phosphoric acid. Thus, cinnamaldehyde and crotonaldehyde give negligible yields of the corresponding acetals and α-methyl-β-ethylacraldehyde gives 10% of the theoretical yield of impure *ethylene α-methyl-β-ethylacrylidene ether*, b. p. 170—174°/12 mm. α-Chlorocinnamaldehyde, however, gives 22% of *ethylene α-chlorocinnamylidene ether*, m. p. 69—70°, and α-chlorocrotonaldehyde, 22% of *ethylene α-chlorocrotonylidene ether*, b. p. 76—80°/14 mm. βγ-Dichloro-γ-phenylpropaldehyde gives 37% of *ethylene βγ-dichloro-γ-phenylpropylidene ether*, b. p. 164—166°/8 mm., and βγ-dichlorobutaldehyde, 50% of *ethylene* βγ-*dichlorobutylidene ether*, b. p. 100—105°/13—15 mm. H. E. F. Notton.

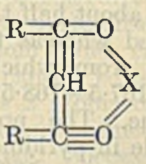
Structure of the higher carbohydrates. M. Bergmann (Z. physikal. Chem., 1928, **139**, 692—694).—The mechanism of the reduction of β-hydroxypropaldehyde and its acetyl derivative in relation to the structure of carbohydrates is discussed.

L. S. Theobald.

Parachor and chemical constitution. X. Singlet linkings in chelated co-ordination compounds. S. Sugden (J.C.S., 1929, 316—330).—Of the two possible formulæ (I and II) for chelated metallic derivatives of β-diketones I is preferred from a consideration of atomic neutralities. Measurements of the parachors of these substances support

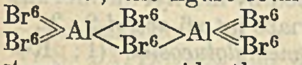
(I.)





(II.)

this preference, since in every case the parachor anomaly associated with the presence in a compound of a singlet linking or linkings is found. Surface tensions were determined by the method of maximum bubble pressure. Parachors for six-membered chelate ring compounds were as follows: ethyl thalloacetoacetate, [P]=332·2; dimethylthallium benzoylacetonate, [P]=523·7; beryllium acetylacetonate, [P]=470·4; beryllium propionylacetonate, [P]=539·0; aluminium acetylacetonate [P]=680·5; aluminium propionylacetonate, [P]=788·0. From the values obtained in the cases of thallous ethoxide, formate, acetate, and nitrate, mercury diphenyl, lead tetraethyl, basic beryllium propionate, and boron acetylacetone difluoride (177·3, 150·3, 183·5, 177·3, 448·7, 456·6, 985·4, and 300·6, respectively) new atomic parachors (viz., thallium, 65·5; mercury, 68·7; lead, 76·2; beryllium, 38; aluminium, 39) have been extracted. Metallic mercury had [P]=69·4. In the cases of beryllium and aluminium duplet formulation of chelate derivatives leads to an inadmissable negative parachor. The formula $Al^{\cdots}[AlBr_6]'''$ is excluded for aluminium bromide; the figure found, 457·6, agrees better with



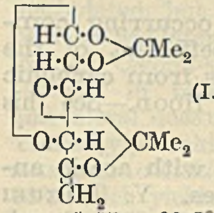
$$\begin{matrix}Br^6\\Br^6\end{matrix}\!\gg\!Al\!<\!\begin{matrix}Br^6\\Br^6\end{matrix}\!>\!Al\!\ll\!\begin{matrix}Br^6\\Br^6\end{matrix}$$

(III). The following substances are evidently open-chain and not chelate rings: acetylacetone, [P]=245·4; propionylacetone, [P]=279·7; benzoylacetone, [P]=382·4; and stannic bisacetylacetone dichloride, $(C_5H_7O_2)_2SnCl_2$, [P]=617·2. R. J. W. Le Fèvre.

Degradation of *l*-arabinose. V. Deulofeu and R. J. Selva (J.C.S., 1929, 225—227).—Tetra-acetylarabononitrile, m. p. 119—120°, by treatment with a solution of sodium in methyl alcohol, gives a syrup containing erythrose and inorganic salts. A purer, nearly ashless, and dextrorotatory product is obtained by the action of barium hydroxide and silver carbonate on arabononitrile. Oxidation of the syrup isolated in the former experiment leads to a mixture of calcium oxalate and mesotartrate.

R. J. W. Le Fèvre.

Acetone [*iso*propylidene] sugars. XVI. *l*-Altromethylose, chinovose, and digitoxose. System of the methylpentoses K. Freudenberg and K. Raschig (Ber., 1929, **62**, [*B*], 373—383; cf. A., 1927, 858).—Di*iso*propylidenegalactose-ξ-iodohydrin is converted by sodium methoxide in methyl alcohol at 125—130° into the unsaturated *compound* (I), b. p. 133°/15 mm., m. p. 86°, [α]$_D^{20}$ —128° in *s*-tetrachloroethane, which is hydrogenated in presence of spongy platinum to a mixture of di*iso*propylidenemethylpentoses, b. p. 128°/13 mm., [α]$_D^{20}$ —60·6° in substance, from which *d*-fucose is isolated after hydrolysis. The separation of the mixed methylpentoses is best effected by removal of the greater part of the *d*-fucose as the sparingly soluble p-*toluenesulphonylhydrazone*, m. p. 175°, [α]$_D^{15}$ +17·1° in pyridine (l-*fucose*-p-*toluenesulphonylhydrazone*, m. p. 174°, [α]$_D^{19}$ —17·0° in pyridine, is described), after which *l*-altromethylose is isolated as the p-*bromophenylhydrazone*, m. p. 178° (converted in boiling amyl alcohol into an *isomeride*, m. p. 155°). The new sugar is lævorotatory, but has not been obtained crystalline. It gives a *phenylosazone*, m. p. 185°, [α]$_D$ about +75° in pyridine–alcohol (2 : 3 vols.), a p-*bromophenylosazone*, m. p. 203°, and a freely-soluble *phenylhydrazone*, m. p. 132°, [α]$_D$ about —1° in pyridine.



(I.)

Chinovose, the sugar component of α- and β-chinovin, has been considered identical with allo- or altro-methylose, but this view is irreconcilable with the m. p. of the respective phenylosazones. β-Chinovin has therefore been converted into "ethylchinovoside," b. p. 136°/1 mm., [α]$_D^{20}$ +106° in alcohol, which on hydrolysis is found to give exclusively *d*-epirhamnose, identified by mixed m. p. and mutarotation as osazone and *p*-bromophenylosazone. The name "chinovose" should therefore be deleted from the literature.

Windaus and Schwarte (Nachr. Ges. Wiss. Göttingen, 1926) have obtained from the anhydride of digitoxose a methylpentose to which they assign the structure of *l*-altromethylose. The crystalline sugar does not induce solidification in the syrupy *l*-altromethylose and the compounds differ in optical activity. The *p*-bromophenylosazones are closely similar to one another in m. p. (and mixed m. p.), but their specific rotations are of opposite sign. The sugar cannot therefore be either *l*-altro- or *l*-allomethylose and the configuration of digitoxose is rendered quite uncertain.

For the systematic nomenclature of the methylpentoses, it is proposed to follow Votoček's plan of suffixing the term "methylose" to the root syllable of the corresponding hexose, thus "manno-methylose," whilst retaining the terms "rhamnose, fucose, epirhamnose, epifucose." The expression "*iso*-rhamnose" should be abandoned in favour of epirhamnose. The name "rhodeose" for the antipode of natural *l*-fucose is superfluous, as are all names dependent on it.

Three of the natural methylpentoses may be derived by disproportionation in the plant of two natural hexitols: sorbitol (*d*-epirhamnose) and dulcitol (*d*-fucose and *l*-fucose). For natural *l*-rhamnose an explanation from natural mannitol is insufficient. A common explanation for the conversion of dextrose into the methylpentoses may be found in the fission of inositol and, possibly, quercitol. H. Wren.

Photosynthesis of naturally occurring compounds. IV. Temperature coefficient of the photosynthesis of carbohydrates from carbonic acid. E. C. C. Baly and N. R. Hood.—See this vol., 408.

Acetylation of carbohydrates with acetic anhydride and alkali thiocyanates. Y. Tsuzuki (Bull. Chem. Soc. Japan, 1929, 4, 21—23).—Starch is readily acetylated by acetic anhydride in presence of lithium, sodium, or calcium thiocyanate, and lithium or sodium iodide, but the product differs from that previously described (this vol., 175) since it disperses only slowly in organic media, forming highly viscous solutions. Hydrolysis of the acetyl derivative regenerates a product similar to the original starch. Acetylation of dextrose and galactose with acetic anhydride and dry sodium thiocyanate yields β-penta-acetylglucose, $[\alpha]^{14}_{D}$ +4·4° in acetic acid, and β-penta-acetylgalactose, $[\alpha]^{13}_{D}$ +25·5° in chloroform, respectively. Similar results are obtained using potassium thiocyanate.

H. Burton.

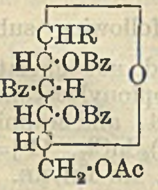
Influence of hydrogen sulphite solutions on sugars at higher temperatures. E. Hägglund (Ber., 1929, 62, [*B*], 437—440; cf. this vol., 297).—The possibility that dextrose is converted by sodium hydrogen sulphite solutions into non- or fully-reducing polymeric sugars is excluded, since the solutions when heated with hydrochloric acid directly or after fermentation do not exhibit an increase in reducing power. The presence of sorbitol in the solutions could not be established, but *d*-gluconic acid is produced. The hydrogen sulphite ion thus oxidises the sugar to the aldonic acid, whereby the thiosulphate ion is produced. The rate of reaction therefore increases with the concentration of hydrogen sulphite ion and sugar as previously established (*loc. cit.*). H. Wren.

Quantitative determination of acetone groups. A. Grün (Ber., 1929, 62, [*B*], 473—474).—The application of the method described by Elsner (this vol., 50) to *iso*propylidene sugars has been indicated previously by the author (Grün and Limpächer, A., 1926, 632). H. Wren.

Constitution of *l*-glucosan [β-glucosan]. K. Josephson (Ber., 1929, 62, [*B*], 313—316; cf. Pictet, A., 1920, i, 819; Irvine and Oldham, J.C.S., 1921, 119, 1744; Karrer and Smirnov, A., 1921, i, 766).—6-Triphenylmethyl-β-methylglucoside, m. p. about 105—110°, or, after solidification, m. p. about 148° (corr.) (cf. Helferich, A., 1924, i, 500), is converted by benzoyl chloride in cold pyridine into 2 : 3 : 4-*tribenzoyl*-6-*triphenylmethyl*-β-*methylglucoside* (+1MeOH), m. p. 99—101°. The product is very rapidly transformed by hydrogen bromide in glacial acetic acid in the presence of chloroform at 0° into 2 : 3 : 4-*tribenzoyl*-β-*methylglucoside*, transformed by acetic anhydride in pyridine at the atmospheric temperature into 6-acetyl-2 : 3 : 4-tribenzoyl-β-methylglucoside, m. p. 150° (corr.), $[\alpha]^{20}_{\mathrm{Hg\,yellow}}$ −6·9° in chloroform, identical with the product obtained by Bergmann and Koch (see below) from β-glucosan. Provided that an unknown change in the position of groups does not occur when β-glucosan is used as initial material, the presence of a 1 : 6-oxygen bridge is confirmed. H. Wren.

Acyl derivatives of glucose and β-methylglucoside from *l*-glucosan [β-glucosan]. K. Josephson (Ber., 1929, 62, [*B*], 317—321; cf. preceding abstract).—Attempts to remove only the 6-acyl group of 6-acetyl-2 : 3 : 4-tribenzoyl-β-methylglucoside (cf. Bergmann and Koch, following abstract) by means of 1 mol. or a slight excess of alkali show that the process cannot be carried out in this sense but that about half the original material is recovered unchanged whereas the remainder is hydrolysed to products from which a *dibenzoyl*-β-*methylglucoside*, m. p. 167·5—168·5° (corr.), has been obtained crystalline. The product is converted by acetic anhydride in pyridine into *diacetyldibenzoyl*-β-*methylglucoside*, m. p. 166°, and by benzoyl chloride in pyridine into tetrabenzoyl-β-methylglucoside, m. p. 160—161° (cf. Fischer and Helferich, A., 1911, i, 802). Tribenzoyl-β-glucosan is converted by successive treatment with hydrogen bromide in glacial acetic acid and silver benzoate into 6-*acetyl*-1 : 2 : 3 : 4-*tetrabenzoylglucose*, m. p. 183—184° (corr.), hydrolysed by mild treatment with aqueous sulphuric acid in the presence of acetone to a substance regarded as 2 : 3 : 4-*tribenzoylglucose*, m. p. 189—191° (corr.), on the assumption that acyl migration has not taken place during the change. It is converted by acetic anhydride and pyridine into *diacetyltribenzoylglucose*, m. p. 178—183° after softening at about 167°, which does not appear uniform. H. Wren.

Preparation of mixed acetylated sugars. M. Bergmann and F. K. V. Koch (Ber., 1929, 62, [*B*], 311—313; cf. Ohle and Spencker, A., 1926, 1126).—Tribenzoyl-β-glucosan, m. p. 201—202° (corr.), dissolved in chloroform, is converted by a saturated solution of hydrogen bromide in glacial acetic acid into acetyltribenzoylglucose bromohydrin (I; R=Br), converted by methyl alcohol and silver carbonate into 6-*acetyl*-2 : 3 : 4-*tribenzoyl*-β-*methylglucoside* (I; R=OMe), m. p. 150—151° (corr.), $[\alpha]^{17}_{D}$ −5·15° in *s*-tetrachloroethane, $[\alpha]^{20}_{D}$ −6·5° in chloroform. With silver acetate the bromohydrin affords 1 : 6-*diacetyl*-2 : 3 : 4-*tribenzoylglucose* (I; R=OAc), m. p. 172—173° (corr.), $[\alpha]^{20}_{D}$ +24·75° in *s*-tetrachloroethane.

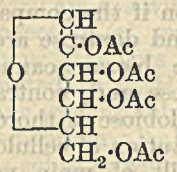

(I.)

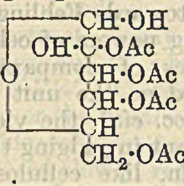
H. Wren.

New, unsaturated anhydro-sugars. II. K. Maurer (Ber., 1929, 62, [*B*], 332—338; cf. A., 1927, 751).—The action of diethylamine on acetobromoglucose in the presence of benzene under somewhat modified conditions affords *tetra-acetylglucoseen* (I), m. p. 65—66°, $[\alpha]^{20}_{D}$ −20·71° in ethyl alcohol, in 51% yield (for nomenclature cf. Helferich and Himmen, A., 1928, 1221). The constitution of the compound is established by its conversion into glucosazone by the restricted action of phenylhydrazine in boiling

50% acetic acid (whereby the loosening effect of the double linking on the acetyl groups is remarkable)

(I.)





(II.)

and by its oxidation by potassium permanganate to *potassium triacetylarabonate*, m. p. 214—215°, hydrolysed to potassium *d*-arabonate, which yields the phenylhydrazide of *d*-arabonic acid, m. p. 214°. The products obtained by hydrolysis of the tetra-acetylanhydro-sugar with methyl-alcoholic ammonia and sodium methoxide contain, respectively, nitrogen and sodium; 1 mol. of the sugar neutralises 5 mols. of sodium hydroxide. The compound cannot be hydrogenated catalytically or caused to add water at the double linking. It adds 2 atoms of halogen without giving crystalline products, since halogen hydride is subsequently eliminated. Successive treatment of the compound in anhydrous ether with chlorine until the colour of the gas just persists followed by silver carbonate and water gives a partly acetylated *hydrate* (II), m. p. 116—118°, $[\alpha]_D^{21}$ +14·2° to +54·45° in 5 days in water, and a strongly halogenated syrup which retains chlorine very firmly. The hydrate reduces cold Fehling's solution and decolorises permanganate, but not bromine water. It does not react with phenylhydrazine in acetic acid, but, after pre-treatment with alkali, it affords glucosazone. Acetylation of the hydrate gives a crystalline substance of unknown constitution in the production of which acetyl groups are removed. Protracted chlorination of the anhydro-sugar gives a crystalline product apparently containing 3 atoms of halogen per sugar complex; these are so firmly retained that their removal or exchange with the usual reagents has not been found possible. If the tetra-acetylanhydro-sugar is warmed with aqueous sodium pyrophosphate solution, the amount of inorganic phosphate remaining in the solution diminishes with increasing amount of the sugar. Dextrose and tetra-acetylglucose do not produce this effect. H. WREN.

Preparation of α- and β-methylglucoside. T. S. PATTERSON and J. ROBERTSON (J.C.S., 1929, 300—302).—When a solution of pure anhydrous dextrose in twice its weight of dry methyl alcohol containing 3% of hydrogen chloride is boiled for 4·5 hrs. or longer at the ordinary pressure, α- (42·6%) and β-methylglucoside (2·5%) are obtained. If, after removal of α-methylglucoside, boiling be continued with further addition of hydrogen chloride, α-methylglucoside is produced at the expense of β-methylglucoside; a total yield of 75% may be obtained.

R. J. W. LE FÈVRE.

Structure of β-(para)glucochloralose. H. W. COLES, L. D. GOODHUE, and R. M. HIXON (J. Amer. Chem. Soc., 1929, **51**, 519—524).—The constitution of this compound is discussed, a formula of the cyclic acetal type being preferred to those proposed by Pictet and Reichel (A., 1923, i, 755) and by Hanriot and Kling (A., 1913, i, 593). Its conversion into two dichloralglucoses and its reduction and subsequent hydrolysis to dextrose and dichloroacetaldehyde are confirmed. With methyl sulphate and solid sodium hydroxide at 60° it yields *trimethylparachloralose*, m. p. 109—110° (optically inactive), which cannot be further methylated, but yields a monoacetyl derivative (to be described later) and reacts with magnesium methyl iodide. *Chloral-γεζ-trimethylglucose*, m. p. 120°, $[\alpha]_D^{25}$ −29·01° in chloroform, from γεζ-trimethylglucose and chloral, does not contain an active hydrogen atom. Trimethylparachloralose is reduced by aluminium amalgam to *dichloroacetaldehydetrimethylglucose*, m. p. 68°, which yields dichloroacetaldehyde when hydrolysed with *N*-hydrochloric acid, and by sodium amalgam and water to *chloroacetaldehydetrimethylglucose*, b. p. 155—160°/4 mm., which, like the preceding compound, requires such concentrated acid for its hydrolysis that the methylated sugar obtained is rendered unidentifiable. H. E. F. NOTTON.

Carbohydrates. VI. Derivatives of 1-aminoglucose. P. BRIGL and H. KEPPLER (Z. physiol. Chem., 1929, **180**, 38—63).—Acetylation of 1-aminoglucose (Ling and Nanji, J.C.S., 1922, **121**, 1682) with pyridine and acetic anhydride yields a mixture of *penta-acetyl*-1-*aminoglucose*, m. p. 159—160° (decomp.), [α] +16° (converted by the action of methyl-alcoholic ammonia at the ordinary temperature into α-N-*acetylglucosidylamine*, decomp. 257°, [α] −23·0°), and *octa-acetyl-α-diglucosidylamine*, m. p. 216—217° (decomp.), [α] +87° (also obtained by acetylation, without isolation, of α-diglucosidylamine, which is obtained by the action of anhydrous dextrose on 1-aminoglucose in pyridine at 75—80°). Deacetylation of the latter product with methyl-alcoholic ammonia yields *α-diglucosidylamine*, decomp. 167—168°, initial [α] +85·1°, not identical with the compound obtained by Sjollema (A., 1899, i, 732), the latter being *β-diglucosidylamine*, decomp. 122—123° (*loc. cit.*, m. p. 132—134°), initial [α] −20°, which by acetylation yields *β-octa-acetyldiglucosidylamine*, sintering at 135—140°, clearing at 190—192°, partial conversion into the α-form taking place, [α] +7·6°. Under appropriate experimental conditions either the α- or β-octa-acetate can be obtained from both forms of the parent amine (which exhibits mutarotation) and they exhibit mutarotation, especially in the presence of acids (equilibrium 66% α-octa-acetate). Acetylation of either the α- or β-octa-acetate or of penta-acetyl-1-aminoglucose with acetic anhydride and zinc chloride yields N-*acetylocta-acetyldiglucosidylamine*, m. p. 192°, [α] −9·2°. By the action of nitrous gases on an ethereal solution of the α-octa-acetate is obtained the *nitrosoamine*, m. p. 204—205° (decomp.), [α] +80·4°, which is reconverted into its parent by hot alcohol, and by hydrolysis with methyl-alcoholic ammonia at the ordinary temperature yields *α-diglucosidylnitrosoamine*, which could not be obtained crystalline but was reacetylated to the octa-acetylnitrosoamine, or converted by the Schotten–Baumann reaction into *α-octabenzoyldiglucosidylnitrosoamine*, m. p. 202—203° (decomp.), [α] +81·1°. By heating with acetic anhydride and zinc chloride this yields 1-acetyl-2 : 3 : 4 : 6-*tetrabenzoylglucose*, m. p. 159—160°, [α] +78·9°, whilst the corresponding octa-acetyl derivative yields penta-acetylglucose.

The corresponding β-*octa-acetyldiglucosidylnitrosoamine*, m. p. 218—220° (decomp.), [α] +12·5°, is obtained similarly from the β-octa-acetate, or by the action of sodium nitrite on an acetic acid solution of the α-octa-acetate, which is partly converted into the β-form during the reaction. The supposed heptabenzoyl derivative of 1-aminoglucose, m. p. 91°, obtained by Schmuck (A., 1923, i, 1062) is shown to be a mixture from which a *substance*, m. p. 180—182°, [α] +16·7°, not a heptabenzoate, can be isolated.

J. W. Baker.

Constitution of nodakenin, a new glucoside from *Peucedanum decursivum*, Maxim. I. J. Arima (Bull. Chem. Soc. Japan, 1929, 4, 16—20).—Mainly an account of work already reviewed (A., 1927, 599). The following appears to be new. Nitration of nodakenetin (*loc. cit.*) with warm nitric acid (*d* 1·2) gives a *nitro*-derivative, m. p. 206—207°, whilst fusion with potassium hydroxide and a small amount of water at 190—200° affords resorcinol, acetic acid, and a phenolic *substance*, $C_8H_8O_4$, m. p. 258—260°. When nodakenetin is heated with aqueous-alcoholic potassium hydroxide iso*nodakenetic acid*, $C_{14}H_{16}O_5$, m. p. 205—206° (decomp.) (*silver* salt), is obtained. This is methylated by diazomethane, forming *dimethyl*iso*nodakenetic acid*, m. p. 65—67°. It is concluded that nodakenetin contains a $\cdot O\cdot C_6H_4\cdot O\cdot CO\cdot$ (1 : 3) grouping.

H. Burton.

Constitution of carthamin. I. (Miss) C. Kuroda (Proc. Imp. Acad. Tokyo, 1929, 5, 32—33; cf. J.C.S., 1910, 97, 1415).—When crude carthamin is treated with cold dilute hydrochloric acid, dried, and crystallised from dilute methyl alcohol, iso*carthamin*, $C_{21}H_{20}O_{10}$, is obtained as the *dihydrate*, yellow needles, m. p. 228°, losing $1H_2O$ at 60° in a vacuum and $2H_2O$ at 100° in a vacuum. It is unstable and when exposed to air passes into a red, amorphous powder. *iso*Carthamin is isomeric with, and is converted into, carthamin (red needles) when treated with pyridine; carthamin and *iso*carthamin are glucosides; hydrolysis with dilute mineral acid yields 1 mol. of dextrose.

C. W. Shoppee.

Lignin and cellulose. IX. Cellulose. K. Freudenberg (Ber., 1929, 62, [*B*], 383—386; cf. A., 1928, 1227).—The synthesis of trimethylglucose anhydride (Freudenberg and Braun, A., 1928, 399) is disproof of the hypothesis of Hess that cellulose is composed of monomeric glucose anhydride units, since the compound should be identical with the trimethylcellulose of his conception, whereas it shows completely different properties. It is considered that cellulose can be represented by a formula based on cellobiose linkings and that the usual doctrine of valency is adequate. Hess' more recent conception of cellobiosan as unit of cellulose (cf. A., 1928, 1225) is based mainly on the isolation of a biosan hexa-acetate by the cautious acetolysis of cellulose. Preparations which have been precipitated with methyl alcohol give analytical values generally according with those required by a biosan hexa-acetate. After dissolution in acetone, precipitation with water, and careful desiccation, the percentage of acetyl is uniformly greater (45·8 instead of 44·8%) than that expected. The product is therefore not a biosan but a polysaccharide with a mean chain length of 10—16 members. This view is confirmed by its reducing power towards Fehling's solution if the comparative reducing powers of cellobiose and dextrose are used as bases of comparison. The biosan cannot be regarded as the unit of cellulose and, contrary to Hess (*loc. cit.*), the yield of cellobiose is thoroughly significant in judging the constitution of cellulose.

Lignin, like cellulose, is built of main valency chains.

H. Wren.

Allylcelluloses. I. Sakurada (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 114—117).—By the action of allyl bromide on cotton cellulose suspended in 40—50% sodium hydroxide, di- and tri-allylcelluloses were prepared. The addition of bromine showed that the double linking remained intact. Diallylcellulose tetrabromide was obtained practically pure. Highly alkylated products were partly soluble in organic solvents. The purified ether was unchanged when heated at 210°.

R. K. Callow.

Celluloseglycollic acid. I. Sakurada (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 96—102).—It was found that celluloseglycollic acid was best prepared by soaking cellulose in 20% sodium hydroxide solution and then treating with concentrated cold sodium monochloroacetate solution. In this way a sodium salt was obtained which was soluble in water but precipitated by alcohol or acetone. Mineral acids precipitated the free acid in a finely-divided form which was flocculated by alcohol. The analysis of the products by electrometric and conductometric titration, titration of the acid with sodium hydroxide, and determination of ash indicated that no more than one glycollic acid residue per $C_6H_{10}O_5$ unit could be introduced. The celluloseglycollic acid was not hydrolysed by heating with acid or alkali. *Barium*, *zinc*, *silver*, and *copper* salts were prepared. The acid was readily dyed by basic dyes. The sodium salt was miscible with viscose.

R. K. Callow.

Cellulosexanthoacetic acid. T. Nakashima (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 103—108; cf. Lilienfeld, B., 1925, 913).—When viscose, after purification by treatment with acetic acid, was treated with sodium chloroacetate, sodium cellulosexanthoacetate separated slowly as a jelly and was precipitated by alcohol or salt solution. Addition of dilute sulphuric acid to the aqueous solution precipitated cellulosexanthoacetic acid, which was stable at 105°, but decomposed slowly in alkaline solution. In contrast to cellulose xanthate, brief boiling with dilute sulphuric acid caused no decomposition. Analysis of the products obtained by the action of varying amounts of sodium chloroacetate was based on the determination of sulphur in the portions decomposable and non-decomposable in this way, total sulphur, and sodium, and the proportion of xanthoacetic acid formed was found to increase with the amount of sodium chloroacetate used. A product the composition of which approximated to $C_{12}H_{19}O_9\cdot O\cdot CS\cdot S\cdot CH_2\cdot CO_2Na$ was obtained when 2 mols. of chloroacetate were used.

R. K. Callow.

Cellulosexanthamides [thiourethanes]. T. Nakashima (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 109—113; cf. Lilienfeld, B., 1925, 913, 955, 985).—The reaction of ammonia or primary or secondary amines with solutions of sodium cellulosexanthoacetate (cf. preceding abstract) slowly yielded gelatinous products the composition of which approximated to $C_{12}H_{19}O_9$·O·CS·NRR′. Cellulosethiourethane was insoluble in water or the usual solvents. It dissolved in alkali hydroxide solution to give a viscous solution which decomposed slowly, regenerating cellulose. It was stable to dilute mineral acids and was unchanged by heating at 105° (cf. this vol., 300). R. K. Callow.

Primary amines from Grignard reagents and chloroamine. II. G. H. Coleman and C. B. Yager (J. Amer. Chem. Soc., 1929, **51**, 567—569).—The yields of primary amines and ammonia obtained as previously described (A., 1928, 622) from chloroamine and a slight excess of the Grignard reagents from *iso*propyl, *sec.*-butyl, diethylmethyl, *tert.*-butyl, and *tert.*-amyl chlorides, bromides, and iodides are tabulated. They are similar to those obtained with primary alkyl halides. *Benz*-tert.*-amylamide* has m. p. 93—94°. H. E. F. Notton.

Complex-chemical behaviour of lithium. I. System lithium halide–mono-, di-, and trimethylamine. A. Simon and R. Glauner (Z. anorg. Chem., 1929, **178**, 177—201).—Lithium halides, dehydrated at 170° in a vacuum and loosened by treatment with liquid ammonia at −80° followed by removal of the ammonia in a vacuum, react with mono-, di-, and tri-methylamine to form series of additive compounds. Thermal analysis of the various systems shows the existence of the following *compounds* (decomposition temperature in parentheses): lithium chloride with 1 (16°), 2 (0°), 3 (−19°), and 4 (−47°) mols. of monomethylamine, 1 (3°), 2 (−15°), and 3 (−36°) mols. of dimethylamine and 1 (−15°) and 2 (−41°) mols. of trimethylamine; lithium bromide with 1 (63°), 2 (35°), 3 (28°), 4 (−32°), and 5 (−57°) mols. of monomethylamine, 0·5 (59°), 1 (44°), 2 (30°), 3 (−18°), 4 (−30°), and 5 (−57°) of dimethylamine, and 1 (23°) and 2 (−15°) mols. of trimethylamine; lithium iodide with 0·25 (200°), 0·5 (180°), 1 (100°), 2 (40°), 3 (−3°), and 3·5 (−55°) mols. of monomethylamine, 0·5 (140°), 1 (90°), 1·5 (51°), 2 (20°), 3 (5°), and 5 (−72°) of dimethylamine and 1 (67°), 1·5 (30°), and 2 (−16°) of trimethylamine. The valency isobars and thermochemistry of the various systems are discussed. A. R. Powell.

Catalytic racemisation of amino-acids and peptides. M. Bergmann and L. Zervas (Biochem. Z., 1928, **203**, 280—292).—When optically active amino-acids are treated in an anhydrous medium (acetic acid) with 1 mol. of acetic anhydride, an almost quantitative yield of an optically active monoacetyl derivative is obtained, whereas with a small excess of anhydride the acetyl derivative is completely racemised, the anhydride acting catalytically, and with a large excess of anhydride it is also dehydrated, yielding an azlactone. Monoacetyl-*d*-arginine may be heated at 100° in acetic acid solution for an hour without decrease of rotation, but if a little acetic anhydride is added to the cold solution, complete racemisation rapidly occurs. The derivatives of *l*-tyrosine, *d*-glutamic acid, and *l*-histidine behave similarly. Racemisation is similarly obtained if the acetyl group is replaced by the benzoyl group. If, however, the acetyl derivative is esterified, the anhydride is no longer able to racemise. Diketopiperazine compounds of optically active amino-acids also are not racemised by acetic anhydride. *d*-*iso*Valine is not racemised. Glycyl-*l*-leucine and *d*-phenylalanyl-*l*-tyrosine are readily racemised. A slower racemisation occurs when benzoic anhydride replaces acetic anhydride. P. W. Clutterbuck.

Separation of hexone bases by electrolysis. T. Noguchi (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 152—155).—By electrolysis in a three-compartment cell with suitable membranes under certain conditions (cf. Bull. Agric. Chem. Soc. Japan, 1926, **2**, 60), arginine, lysine, and histidine were isolated in the cathode compartment from the hydrolytic products of casein and ox-blood without the adjustment of the reaction of the centre compartment found necessary by Foster and Schmidt (A., 1923, i, 963). R. K. Callow.

Ultra-violet absorption spectra of certain aromatic amino-acids, and of the serum-proteins. F. C. Smith (Proc. Roy. Soc., 1929, B, **104**, 198—205).—Spectrophotometric examination of the ultra-violet absorption of tyrosine shows the presence of new bands at λλ 2240·0 and 1940 Å. as well as the known one at λ 2750·0 Å. In the case of tryptophan the known bands at λλ 2790·0 and 2180·0 Å. were observed, whilst in the case of phenylalanine only a single simple absorption band was detected. The absorption of highly-purified serum-globulin and serum-albumin from horse and human sera has also been examined without disclosing any differences. W. O. Kermack.

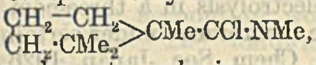
Synthesis of [calcium] cyanamide by combination of carbon and calcium nitride. Kadlec-Fleck (Compt. rend., 1929, **188**, 561—563).—When 1 part of calcium cyanide finely powdered and well mixed with 5 parts of Acheson graphite was heated in soft steel tubes at 800—1100° the amount of nitrogen transformed according to the equation $Ca_3N_2+5C=CaCN_2+2CaC_2$ was found to increase from 33 to 91% with rise in temperature for a heating period of 3 hrs. Above 1000° small amounts of calcium cyanide were formed. J. Grant.

Mechanism of the reaction between organomagnesium compounds and *NN*-disubstituted crotonamides. N. Maxim (Bul. Soc. Chim. România, 1928, **10**, 97—115).—*Crotondiethylamide*, b. p. 113°/23 mm., 224—225°/756 mm., is obtained in 95% yield by treatment of crotonyl chloride, b. p. 124—125°, with diethylamine in benzene. With magnesium ethyl bromide it yields quantitatively β-*methylvalerdiethylamide*, b. p. 123°/28 mm., 224°/760 mm.; with magnesium phenyl bromide are formed diphenyl and β-*phenylbutyrdiethylamide*, b. p. 184°/23 mm., also obtained from β-phenylbutyryl chloride and diethylamine. Neither amide could be hydrolysed to the corresponding acid. *Crotondiphenylamide*, m. p. 113—114°, prepared from crotonyl chloride and diphenylamine, when treated with magnesium ethyl bromide yields exclusively β-*methylvalerdiphenylamide*,

m. p. 55—56°, b. p. 270—280°/78 mm., hydrolysed by alcoholic potassium hydroxide to β-methylvaleric acid. With magnesium phenyl bromide the diphenylamide gives quantitatively β-*phenylbutyrdiphenylamide*, m. p. 76°, b. p. 267°/18 mm., also obtained from diphenylamine and β-phenylbutyryl chloride; hydrolysis with alcoholic potassium hydroxide regenerates β-phenylbutyric acid. These results are considered to exemplify 1 : 4-addition in agreement with the Thiele theory.

C. W. Shoppee.

Imide and amide chlorides of non-aromatic acids. III. J. von Braun and A. Heymons (Ber., 1929, 62, [*B*], 409—413; cf. A., 1927, 231, 547).—Campholmethylimide chloride,



$\left.\begin{array}{l}CH_2-CH_2\\ CH_2\cdot CMe_2\end{array}\right>CMe\cdot CCl\cdot NMe$, is converted by distillation under atmospheric pressure into campholonitrile, m. p. 70°; a similar behaviour is shown by the corresponding *ethylimide chloride* (obtained from *campholethylamide*, b. p. 160°/20 mm., m. p. 88°) and iso*amylimide chloride* (derived from *campholisoamylamide*, b. p. about 150°/1 mm., m. p. 42—43°). The gradual transition in behaviour by transition from the non-aromatic to the aromatic series is thus established.

Somewhat unexpectedly, *trichloroacetdiethylamide*, b. p. 108—112°/12 mm., and *campholdiethylamide*, b. p. 140—145°/12 mm., m. p. 29—30°, are unaffected by phosphorus pentachloride in the presence of benzene or chloroform. *Chloroacetdiethylamide*, b. p. 112—113°/10 mm., with phosphorus pentachloride gives products which decompose when distilled. n-*Butyrdiethylamide*, b. p. 92°/12 mm., is transformed when similarly treated into the amidochloride, which loses hydrogen chloride when distilled, yielding the *compound* (?) $CHEt:CCl\cdot NEt_2$, b. p. 100—107°/13 mm. α-*Methylbutyrdiethylamide*, b. p. 84—86°/11 mm., is converted by the action of phosphorus pentachloride followed by distillation of the product into a mixture of the *compound* $CMeEt:CCl\cdot NEt_2$, b. p. 76—85°/13 mm. (slowly decomposed by water), and α-*methylbutyrdiethylamide chloride*, instantaneously hydrolysed by water to the original amide and transformed by aniline in chloroform into the *amidine*, $CHMeEt\cdot C(:NPh)\cdot NEt_2$ (non-crystalline *picrate* and *hydrochloride*; *chloroplatinate*, decomp. 124—127%).

Aliphatic and fatty-aromatic imide chlorides (or bromides), in the form arising by displacement of hydrogen, add chlorine or bromine: $R\cdot CH_2\cdot CCl:NR' \longrightarrow R\cdot CH:CCl\cdot NHR' \longrightarrow R\cdot CHBr\cdot CCl(Br)\cdot NHR' \longrightarrow R\cdot CHBr\cdot CCl:NR'(+R\cdot CHBr\cdot CBr:NR')+HBr(+HCl)$. Iodine does not behave similarly, so that α-iodo-acids cannot be prepared in this manner. If the acid residue contains an unsaturated linking, this can also be saturated; by using a suitable proportion of phosphorus pentachloride it is possible to achieve the production of the imide chloride, the exhaustive chlorination of the α-carbon atom, and the addition of chlorine to the double linking in a single operation. Thus Δ^{ι}-*undecenoethylamide*, $CH_2:CH\cdot[CH_2]_8\cdot CO\cdot NHEt$, m. p. 35°, is transformed by 5·2 mols. of phosphorus pentachloride and subsequent treatment with water into ααικ-*tetrachloroundecoethylamide*, b. p. about 180°/0·2 mm.

H. Wren.

Organic catalysts. III. Formation of oxamide from dicyanogen in presence of aldehydes. W. Langenbeck (Annalen, 1929, 469, 16—25).—The production of oxamide from cyanogen by the action of water in presence of acetaldehyde and propaldehyde at the ordinary temperature, followed by heating, is due to the aldehyde reacting in its enolic form. Acetaldehyde in presence of dilute acetic acid, formaldehyde, benzaldehyde, chloral hydrate, and dextrose does not promote the change. When a mixture of acetaldehyde, cyanogen, and water is allowed to remain at 15° for some days, and then evaporated at 30°/15—17 mm., the intermediate product, $NH_2\cdot CO\cdot C(:NH)\cdot O\cdot CH:CH_2,H_2O$, m. p. 150° (decomp.) on rapid heating, is produced. This is decomposed by warming with dilute acid into oxamide, oxalic acid, and acetaldehyde, whilst decomposition with a few drops of 0·1*N*-sodium hydroxide causes immediate production of acetaldehyde and oxamide. When heated at 150° in a vacuum the above intermediate yields oxamide.

H. Burton.

Hydrazide of ικ-dihydroxystearic acid; *s*-bisdihydroxyheptadecylcarbamide. C. Bernstein and F. Ulzer (Wiss. Mitt. Österr. Heilsmittelstelle, 1928, xi—xiv; Chem. Zentr., 1928, ii, 1317).—ικ-*Dihydroxystearic hydrazide* has m. p. 164° [*hydrochloride*, m. p. 194—195° (decomp.); *benzylidene* derivative, m. p. 143—144°; *piperonylidene* derivative, m. p. 153·5—154·5°]. s-*Bis*-ικ-*dihydroxystearic hydrazide*, from the monohydrazide and iodine in alcohol, has m. p. 202—204°. ικ-*Dihydroxystearic azide*, from the hydrazine hydrochloride and nitrogen trioxide, m. p. 168—173°, when boiled with water affords s-*bis*-ικ-*dihydroxyheptadecylcarbamide*, m. p. 187°.

A. A. Eldridge.

Complex metallic cyanides. II. H. Reihlen and U. von Kummer (Annalen, 1929, 469, 30—44).—Further support is deduced in favour of the polynuclear structure of complex metallic cyanides (cf. Reihlen and Zimmermann, A., 1927, 233). The complex *salts*, $[Fe(CN)_6Pb(H_2O)_2]Tl(Cs)$ and $[Co(CN)_6Pb(H_2O)_2]Tl(Cs)$, are obtained by the action of 1 mol. of thallium and cæsium nitrates on 1 mol. of the complexes $FePb_2(CN)_6NO_3,5\cdot 5H_2O$ (I) and $CoPb_2(CN)_6NO_3,5H_2O$ (II). These salts have relatively high solubilities and at $v = 100$ litres per mol. the molecular conductivity is only about 60% of that of potassium ferricyanide. Further dilution causes an anomalous increase in the conductivity, presumably because of further dissociation of the complex ion into $[Fe(CN)_6]^{---}$ and Pb^{++}. The compounds I and II are formulated with homopolar linkings in the complex. The salt $[(NO_3)_2Pb_2Fe(CN)_6]K$ could not be obtained in the solid form, but the solubilities of potassium nitrate and I in presence of one another are much greater than for each salt alone. The *salts* $FePbK(CN)_6,3H_2O$ and $Fe_2(CN)_6,2H_2O$ are also described.

H. Burton.

Electrolysis of organometallic compounds. W. H. Rodebush and J. M. Peterson (J. Amer. Chem. Soc., 1929, 51, 638—639).—Electrolysis of magnesium ethyl bromide in ether with platinum electrodes (cf. Gaddum and French, A., 1927, 756) gives a crystalline adherent deposit of magnesium at the cathode. Pure zinc diethyl is non-conducting, but in ether it is electrolysed and zinc is deposited at the cathode. H. E. F. NOTTON.

Thermal decomposition of sodium ethyl. W. H. CAROTHERS and D. D. COFFMAN (J. Amer. Chem. Soc., 1929, 51, 588—593).—Sodium ethyl is quantitatively formed from mercury diethyl and sodium in a vacuum at the ordinary temperature. The product, containing sodium and mercury, decomposes rapidly at 90—100° into sodium hydride and a mixture of ethylene (85%) and ethane (15%), and slowly at the ordinary temperature, yielding ethylene (about 30%) and ethane (70%). The quantitative results indicate that the ethane is formed during the decomposition of the sodium ethyl through $C_2H_4Na_2$ and $C_2H_2Na_4$ into sodium carbide. No indication of a preliminary dissociation into sodium and the ethyl radical was found (cf. Schorigin, A., 1910, i, 547). H. E. F. NOTTON.

Organomagnesium halides. H. GILMAN and J. M. PETERSON (Rec. trav. chim., 1929, 48, 247—250).—Magnesium ethyl bromide underwent no decomposition at 100° or 150°. At 200° the average percentage decomposition was 6·7, at 300°, 14·3 (times of heating 1 hr.). Heating at 300° for 2 hrs. caused 17·8% decomposition. A boiling cymene solution underwent no change during 45 min. It was stable to sunlight and to rays from a mercury arc lamp.

The interactions of the following substances with magnesium ethyl bromide were examined: boiling diphenylmethane (no reaction), boiling triphenylmethane (2% reaction), triphenylchloromethane (100% reaction), sodium hydrogen carbonate (no reaction), di-α-hydroxybenzyl-*p*-tolylarsine (no reaction), triphenylphosphine oxide (10% reaction), phenyl allyl ether (5% reaction), nitrous oxide (no reaction), *as*-diphenylethylene (no reaction).

R. J. W. LE FÈVRE.

Zinc alkyls; preparation and use in synthesis of hydrocarbons. C. R. NOLLER (J. Amer. Chem. Soc., 1929, 51, 594—599).—Zinc diethyl, di-*n*-propyl, *di*-n-*butyl*, b. p. 81—82°/9 mm., and di*iso*amyl have been prepared in high yield (cf. Lachman, A., 1900, i, 542) (*a*) by using an alloy of zinc with 5—8% of copper, (*b*) by using a suitable mixture of alkyl bromide and iodide instead of pure iodide, and (*c*) by vacuum-distilling the product. *sec.*-Alkyl halides, *cyclo*hexyl bromide, and ethyl sulphate yield mainly hydrocarbons. In hydrocarbon solvents the zinc alkyls do not inflame spontaneously and, when warmed with *tert.*-butyl and -amyl chlorides yield 24—51% of theory of tetra-alkylmethanes. In this way ββ-dimethylbutane, ββ-dimethylpentane, *ββ-dimethylhexane*, b. p. 106—107°, d_4^{20} 0·6967, n_D^{20} 1·3931; ββε-trimethylhexane, γγ-dimethylpentane, γγ-dimethylhexane, and *γγ-dimethylheptane*, b. p. 137—138°, d_4^{20} 0·7304, n_D^{20} 1·4095, are prepared.

H. E. F. NOTTON.

β-Substituted alkylarsinic acids and their derivatives. I. β-Substituted ethylarsinic acids. S M. SCHERLIN and G. I. EPSTEIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1487—1492).—See A., 1928, 1231. A. FREIMAN.

Alkylation of octacyanotungstic acid. F. HÖLZL (Monatsh., 1929, 51, 1—22; cf. A., 1928, 279).—When potassium octacyanotungstate (Olsson, A., 1914, i, 944) is treated in dilute sulphuric acid solution with silver nitrate it yields, in addition to the normal salt $Ag_4[W(CN)_8]$, the acid products $Ag_2H_2[W(CN)_8]$ and $Ag_3H[W(CN)_8]$. Methylation of these yields a series of complex salts of quadri- and quinque-valent tungsten by replacement of silver by a methyl group, some of the carbylamino-groups co-ordinating a molecule of water or alcohol to form the grouping C(OH)·NHMe. Alkylation of all eight cyano-groups is not possible, only acidic or neutral complexes being obtained and never a salt containing tungsten in a complex cation. When the precipitated silver octacyanotungstate is treated with methyl iodide in the dark for 8 days and the ether-washed and dried solid residue is extracted with anhydrous methyl alcohol, the solution by evaporation yields a *compound* $[W(CN)_6\{C(OMe)\cdot NHMe\}_2]H_2$ (I), which reacts acidic in aqueous solution, neutral in alcoholic solution, yields carbylamine by treatment with alkali, and with methyl-alcoholic silver nitrate gives a yellow precipitate. This latter *compound* is also obtained by the action of methyl-alcoholic silver nitrate on the methyl-alcoholic solution of the product obtained when the original action of methyl iodide is extended for 28 days, and is assigned the structure $[(CN)_4(CNMe)\{C(OMe)\cdot NHMe\}W(CN)_2W\{C(OMe)\cdot NHMe\}(CNMe)(CN)_4]Ag_2$, formed by elimination of a molecule of alcohol from I and the union of two complexes by a doubly co-ordinated cyano-bridge. The residue, insoluble in methyl alcohol, after extraction of I is extracted with water and evaporation of the golden-yellow solution in a vacuum yields a brown, hygroscopic powder which after drying over phosphoric oxide has a composition corresponding with the *compound* $[(CN)_4(CNMe)_2\{C(OH)\cdot NHMe\}W(CN)W\{C(OH)\cdot NHMe\}(CNMe)_2(CN)_4]OH$ (II), and in agreement with this it is found to titrate as a monobasic acid. When dried over sulphuric acid one additional molecule of water remains. The residue, insoluble in methyl alcohol and water, from the extraction of I and II dissolves in dilute hydrochloric acid with separation of silver iodide. Complete evaporation of this solution in a vacuum and extraction of the crystalline residue with methyl alcohol yields the *compound* $[(CN)_5\{C(NHMe)\cdot O'\}_2W(CN)W\{C(NHMe)\cdot O'\}_3(CN)_4]H_5$ (III) (*silver* salt). The residue from the extraction of III is almost completely soluble in water. Concentration of the aqueous solution, which has an acid reaction and yields carbylamine with alkalis, yields the *compound* $[(CN)_4\{C(OH)\cdot NHMe\}_2W(CN)_2W\{C(OH)\cdot NHMe\}_2(CN)_4]$ containing a double co-ordinated cyano-bridge. The evidence on which these structures are based is discussed. J. W. BAKER.

New type of complex platinum compounds. Ter- and quinque-valent platinum. P. C. RÂY and K. C. B. RÂY (Z. anorg. Chem., 1929, 178, 329—336).—Prolonged heating on the water-bath of a mixture of chloroplatinic acid and dibenzyl sulphide affords the *compound* $PtCl(CH_2Ph\cdot S)_2$ as a chocolate-coloured powder soluble in chloroform and benzene. Ebullioscopic determination of the mol. wt. in the former gives a value corresponding with five times and cryoscopic determination in the latter a value corresponding with seven times the above formula. Treatment of the chloromercaptide $Et_2S_2{\cdot}PtCl$ (Rây, J.C.S., 1923, **123**, 134) with ammonia at 0° yields the orange-yellow *compound* $Pt_3Cl{\cdot}2Et_2S_2,2NH_3,6H_2O$, with piperidine the *compound* $Pt_3Cl{\cdot}2Et_2S_2,C_5H_{11}N$, with boiling anhydrous diethylamine the *compound* $Pt_5Cl{\cdot}4Et_2S_2,2NHEt_2$, with boiling benzylamine the *compound* $Pt_5Cl{\cdot}4Et_2S_2,CH_2Ph{\cdot}NH_2$, with aniline at 100° the *compound* $Pt_5Cl{\cdot}4Et_2S_2,PhNH_2$, with hot ethylenediamine the *compound* $Pt_5Cl{\cdot}4Et_2S_2$,2 en, with alcoholic methylamine the *compound* $Pt_5Cl{\cdot}4Et_2S_2,2NH_2Me$, with cold toluidine the *compound* $Pt_5Cl{\cdot}4Et_2S_2,C_7H_7{\cdot}NH_2$, with warm hydrazine hydrate the *compound* $Pt_5Cl{\cdot}4Et_2S_2,4N_2H_4$, with propylamine the *compound* $Pt_7Cl{\cdot}5Et_2S_2,2NH_2Pr$, with phenylhydrazine the *compound* $Pt_9Cl{\cdot}7Et_2S_2,2NHPh{\cdot}NH_2$, and with 50% ethylamine the *compound* $Pt_{13}Cl{\cdot}10Et_2S_2,2NH_2Et,8H_2O$. A second piperidine *compound*, $Pt_5Cl{\cdot}4Et_2S_2,C_5H_{11}N$, has also been prepared. The constitution of these compounds is discussed on the assumption that the quinquevalent platinum atom in the chloromercaptide becomes tervalent and that the diethyl sulphide radical behaves like an unsaturated compound with four latent valencies. A. R. POWELL.

***p*-Bromoethylenic benzenes and their magnesium organo-derivatives. I.** R. QUELET (Bull. Soc. chim., 1929, [iv], 45, 75—97; cf. A., 1927, 452).—The mono- and di-magnesium derivative of *p*-dibromobenzene (A., 1927, 890) with allyl bromide gives a mixture, b. p. 95—96°/12 mm., of p-*bromoallylbenzene*, b. p. 96°/12 mm., 222—223°/730 mm., d_4^{15} 1·324, n_D^{15} 1·559, *p*-diallylbenzene, and unchanged *p*-dibromobenzene. The first-named is isolated by treating the mixture with bromine, distilling off the p-*bromo-βγ-dibromopropylbenzene* (yield 60%), b. p. 178—180°/11 mm., d_4^{17} 1·950, n_D^{17} 1·622, and treating this with zinc dust and acetic acid (yield 60%). Potassium hydroxide in amyl alcohol isomerises *p*-bromoallylbenzene to *p*-bromopropenylbenzene (yield 75%), m. p. 35°, b. p. 110°/12 mm., d_4^{36} 1·332, n_D^{36} 1·590 (p-*bromobenzene-αβ-propylene oxide*, yield 80%, has b. p. 123—124°/11 mm., d_4^{11} 1·426, n_D^{11} 1·570), and perbenzoic acid in chloroform affords α-p-*bromophenyl-βγ-propylene oxide*, b. p. 132°/10 mm., d_4^{10} 1·430, n_D^{10} 1·570. Similarly from magnesium, *p*-bromobenzyl chloride and allyl bromide there are derived p-*bromo-γδ-dibromobutylbenzene*, b. p. 190—191°/12 mm., d_4^{9} 1·859, n_D^{9} 1·610, p-*bromo-Δ^δ-butenylbenzene*, b. p. 113°/14 mm., d_4^{13} 1·275, n_D^{13} 1·553, and the corresponding *oxide*, b. p. 140—141°/10 mm. *p*-Bromophenylmethylcarbinol, b. p. 130°/12 mm., d_4^{18} 1·464, n_D^{18} 1·574 (*phenylurethane*, m. p. 103—104°), yield 95% from *p*-bromobenzaldehyde, 45—50% from acetaldehyde and magnesium *p*-dibromobenzene bromide, with phosphoric acid gives improved yields of *p*-bromostyrene, b. p. 87—88°/12 mm., d_4^{18} 1·401, n_D^{18} 1·599 (cf. Ziegler and Tiemann, A., 1923, i, 30). Similarly, *p*-bromophenylethylcarbinol, b. p. 140—141°/13 mm., d_4^{18} 1·405, n_D^{18} 1·561 (*phenylurethane*, m. p. 102°), yield 90% from *p*-bromobenzaldehyde, with phosphoric oxide gives 80% and with potassium hydrogen sulphate only 60% of *p*-bromopropenylbenzene. p-*Bromophenylpropylcarbinol*, b. p. 147°/11 mm., d_4^{11} 1·339, n_D^{11} 1·558 (*phenylurethane*, m. p. 83°), yield, 48% from *p*-dibromobenzene and 90% from *p*-bromobenzaldehyde, with potassium hydrogen sulphate gives 85% of p-*bromo-Δ^α-butenylbenzene*, m. p. 30°, b. p. 126—127°/14 mm., d_4^{31} 1·282, n_D^{31} 1·580, phosphoric oxide giving unsatisfactory results, apparently due to isomerisation to a product of lower b. p. p-*Bromo-αβ-dibromobutylbenzene* has m. p. 78°, α-p-*bromophenyl-αβ-butylene oxide*, b. p. 138°/12 mm., d_4^{15} 1·362, n_D^{15} 1·557. *p*-Bromo-Δ^α-butenylbenzene gives a magnesium derivative which is decomposed normally into Δ^α-*butenylbenzene*, b. p. 80°/12 mm. (αβ-dibromobutylbenzene has m. p. 70°). The ethylenic derivatives with an αβ-double linking are characterised by a higher m. p. and b. p. than the corresponding βγ-derivatives, and by greater density and refractivity for light. *p*-Bromobenzaldehyde is obtained in 50% yield from *p*-bromobenzyl alcohol by Sommelet's reaction.

R. BRIGHTMAN.

Highly polymerised compounds. XVI. Polymerisation of α-methylstyrene. H. STAUDINGER and F. BREUSCH (Ber., 1929, 62, [*B*], 442—456; cf. this vol., 305, 306).—α-Methylstyrene is very violently polymerised by tin tetrachloride, yielding, in addition to Tiffeneau's dimeride, more complex, saturated compounds in small amount. Attempts to moderate the violence of the reaction by use of solvents cause essentially the formation of only the dimeride. Since the tendency towards polymerisation of α-methylstyrene is much less than that of styrene (*loc. cit.*) shorter chains are produced and ring closure takes place when only a few molecules have become attached to one another. A polymeric homologous series of polymethylstyrenes therefore results, extending from dimeric to octameric members. The presence of rings is established by the saturated nature of the products and the absence of other residues as terminal groups. The differences in properties between the individual members are sufficient to enable the separation of the simpler members by distillation in a vacuum and of the more complex substances by fractional dissolution and precipitation. As expected, the b. p. rises with increasing mol. wt., whereas the solubility diminishes greatly. The viscosity in benzene solution increases more rapidly than required by proportionality of mol. wt., so that it appears that with polymeric homologous compounds evidence as to the degree of polymerisation may be obtained by comparison of the viscosities of equally concentrated solutions (with respect to the unit molecule). Density and refractive index increase with degree of polymerisation. The molecular refraction of all polymerides agrees with that calculated for the saturated rings, showing that the mode of union of the unit molecule is the same. The dimeride and tetrameride have been obtained crystalline, whereas the other polymethylstyrenes are amorphous. The pentameride to octameride are white powders resembling externally the hemi-colloidal polystyrenes. Their temperature of liquefaction increases with the degree of polymerisation and is a criterion of the latter. With individual compounds mixtures of different polymerides soften far below the softening point of their components. The m. p. of the dimeride and tetrameride are far above the softening interval of the (undercooled) materials; the molecules in the crystalline product are more firmly united by lattice forces than in the amorphous substance. Consequently, the density is greater.

It is remarkable that dimeric methylstyrene is a homogeneous compound, since four modifications are theoretically possible. Polymerisation proceeds therefore only in one direction, as observed with *cyclo*pentadiene. Whether the more complex polymethylstyrenes are uniform or mixtures of isomerides cannot be established.

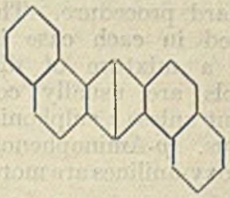
The presence of poly-membered rings in the polymethylstyrenes is firmly established, since the dimeride is already known and the similar constitution of the higher members is based on refractometric evidence. It is probable that eucolloidal polystyrene and caoutchouc are formed of extraordinarily large rings. This has a great effect on physical properties, since substances composed of thread molecules, such as guttapercha and cellulose, behave quite differently. Colloidal properties are not shown by the simpler members of the styrene series and appear only when their degree of polymerisation is great. Pummerer's conception of caoutchouc as an octameride of isoprene appears incorrect.

Dehydration of phenyldimethylcarbinol to α-methylstyrene is most conveniently effected by boiling acetic anhydride. The following polymerides are described: dimeride (1 : 3-diphenyl-1 : 3-dimethyl*cyclo*butane), b. p. 118—120°/0·1 mm., m. p. 52°, softening temperature −32° to −24°, d^{20} (undercooled) 1·1183, n_D^{20} 1·5633; *trimeride* [1 : 3 : 5-*trimethyl*-1 : 3 : 5-*triphenyl*-cyclo*hexane*], b. p. 172—178°/0·1 mm., softening temperature, −3° to +9°, d^{20} 1·0455, n_D^{20} 1·58429; *tetrameride* [1 : 3 : 5 : 7-*tetraphenyl*-1 : 3 : 5 : 7-*tetramethyl*cyclo*octane*], b. p. 208—212°/0·1 mm., m. p. 127—129°, softening temperature, 38—48°, d^{20} (amorphous) 1·0594; d^{20} (crystalline) 1·1452; n_D^{20} 1·5934; *pentameride* [1 : 3 : 5 : 7 : 9-*pentaphenyl*-1 : 3 : 5 : 7 : 9-*pentamethyl*cyclo*decane*], b. p. 240—244° (slight decomp.)/0·1 mm., softening temperature, 60—68°, d^{20} 1·0624, n_D^{20} 1·5960; *hexameride*, [1 : 3 : 5 : 7 : 9 : 11-*hexaphenyl*-1 : 3 : 5 : 7 : 9 : 11-*hexamethyl*cyclo*dodecane*], b. p. 275—285° (partial decomp.)/0·1 mm., softening temperature, 98—108°, d^{20} 1·0657; n_D^{20} 1·6050; *heptameride* [1 : 3 : 5 : 7 : 9 : 11 : 13-*heptaphenyl*-1 : 3 : 5 : 7 : 9 : 11 : 13-*heptamethyl*cyclo*tetradecane*], b. p. 312—316° (partial decomp.)/0·1 mm., softening temperature, 125—133°, d^{20} 1·0671, n_D^{20} 1·6010; *octameride* [1 : 3 : 5 : 7 : 9 : 11 : 13 : 15-*octaphenyl*-1 : 3 : 5 : 7 : 9 : 11 : 13 : 15-*octamethyl*cyclo*hexadecane*], b. p. 345—360° (decomp.)/0·1 mm., softening temperature, 165—172°, d^{20} 1·0684, n_D^{20} 1·6120.

The polymerisation of α-methylstyrene by undiluted boron trichloride and titanium tetrachloride, by Florida earth, and by heating in an atmosphere of nitrogen at 250° is described; polymerisation does not occur at 180° or under the influence of ultra-violet light. All the polymerides are unsaturated. The following are described: *unsaturated dimeric α-methylstyrene*, b. p. 117—120°/1·0 mm., d^{20} 0·9889, n_D^{20} 1·5677 (non-crystalline *dibromide*); the *trimeride*, a viscous resin probably not homogeneous. H. Wren.

Polynuclear, aromatic hydrocarbons and their derivatives. I. Dibenzanthracene and its quinones. E. Clar (Ber., 1929, **62**, [*B*], 350—359).—The action of α-naphthoyl chloride on β-methylnaphthalene in the presence of aluminium chloride and carbon disulphide affords 2-*methyl*-1 : 1′-*dinaphthyl ketone*, m. p. 140—141°, in about 90% yield. When heated at its b. p., the ketone loses water and gives 1 : 2 : 7 : 8-*dibenzanthracene* (I), m. p. 260—261° (*picrate*, m. p. 212°), oxidised by chromic acid in boiling glacial acetic acid to 1 : 2 : 7 : 8-*dibenzanthraquinone*, m. p. 243—244°. Similarly, β-naphthoyl chloride and β-methylnaphthalene afford successively 2-*methyl*-1 : 2′-*dinaphthyl ketone*, m. p. 170—171°, 1 : 2 : 5 : 6-dibenzanthracene (II), m. p. 262° (picrate, m. p. 214°), and 1 : 2 : 5 : 6-dibenzanthraquinone, m. p. 244—245° (cf. Weitzenböck and Klingler, A., 1918, i, 494). The hydrocarbons and their derivatives show unusually close resemblance to one another in their physical properties, but are differentiated by their behaviour towards ultra-violet light. The 1 : 2 : 7 : 8-dibenzanthracene prepared by Homer (J.C.S., 1910, 97, 1148) from naphthalene and *s*-tetrabromoethane differs widely from that described by the author. Re-examination of the product obtained by Hönig by the action of concentrated sulphuric and anhydrous oxalic acid on α-naphthol and regarded as 1 : 2 : 7 : 8-dibenzanthraquinone discloses the presence of only one carbonyl group; although it does not appear identical with the compound so described in the literature, it is considered to be 1 : 2 : 7 : 8-dibenzxanthone, m. p. 297° (decomp.), and to be converted by magnesium phenyl bromide into 9-*phenyl*-1 : 2 : 7 : 8-*dibenzxanthol* (+1C_5H_5N), m. p. 195° after incipient decomp. 175°.

(I.)



(II.)

The product prepared by the action of *o*-toluyl chloride on phenanthrene in presence of aluminium chloride is not homogeneous, containing mainly *o*-tolyl 9-phenanthryl ketone mixed with isomerides. If the mixture of ketones is heated, the main and most soluble product is 1 : 2 : 3 : 4-*dibenzanthracene*, m. p. 196—197° (*picrate*, m. p. 207°), the structure of which appears confirmed by its oxidation (even with an excess of reagent) to 1 : 2 : 3 : 4-*dibenzanthraquinone* (9 : 10-*phthaloylphenanthrene*), m. p. 179°, whereas the isomerides of higher m. p. yield diquinones under like conditions. The phthaloylphenanthrene obtained by the action of phosphoric oxide on *o*-phenanthroylbenzoic acid is a mixture of isomerides in which the 9 : 10-derivative probably predominates. H. Wren.

Decahydroquinoline and its derivatives. V. Synthesis of *trans-o*-dimethylaminopropyl*cyclo*hexane. S. Fujise (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 2).—By reduction of 2-propyl*cyclo*hexanoneoxime, followed by methylation, *trans*-2-dimethylaminopropyl*cyclo*hexane is obtained. Dehydration of 2-propyl*cyclo*hexanol yields Δ^1-*n*-propyl*cyclo*hexene. B. W. Anderson.

Nitration of substituted anilines. E. R. Riegel, H. W. Post, and E. E. Reid (J. Amer. Chem. Soc., 1929, **51**, 505—508).—In order to compare the protective action of substituents, 14 derivatives of aniline containing hydroxyl, carboxyl, sulphonic acid, and nitro-groups have been nitrated at about 0° with sulphuric and nitric acids, using a standard procedure. The percentage of nitroamine isolated in each case is tabulated. Aniline itself gives a mixture of dinitro-derivatives. *o*-Aminophenols are usually completely oxidised by the reagent unless a sulphonic group is also present in the nucleus. *p*-Aminophenols and *m*- or *p*-sulpho- or -carboxy-anilines are more stable. H. E. F. Notton.

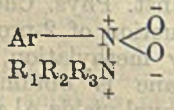
Introduction of the thiocyano-group into organic compounds. H. P. Kaufmann (Ber., 1929, 62, [*B*], 390—391; cf. A., 1926, 392).—Acetic or formic acid, as solvent, may be replaced by methyl alcohol, acetone, methyl or ethyl acetate. Methyl alcohol, saturated with the corresponding alkali halide as a protection against halogenation, is particularly suitable. Thus *p*-thiocyanoaniline, m. p. 97°, is prepared in 97% yield by the addition of bromine in methyl alcohol saturated with sodium bromide to a methyl-alcoholic solution of aniline and sodium thiocyanate. H. Wren.

Monoarylguanidines. I. α-Phenylguanidine. G. B. L. Smith (J. Amer. Chem. Soc., 1929, **51**, 476—479).—The sulphate of methyl*iso*thiocarbamide (cf. Phillips and Clarke, A., 1923, i, 903) yields with aniline a mixture of aniline and α-phenylguanidine sulphates, from which the latter may be precipitated as *carbonate*, m. p. 138—140°, after liberating the bases in aqueous solution. The optical properties of α-phenylguanidine and of its *sulphate*, m. p. 205°, *hydrochloride*, nitrate, picrate, and chloroplatinate (cf. Kämpf, A., 1904, i, 534) are described.

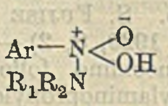
H. E. F. Notton.

Structure of organic molecular compounds. G. M. Bennett and G. H. Willis (J.C.S., 1929, 256—268).—The theory of the union of organic molecules by residual valency of a whole molecule or group is examined and rejected in favour of union through definite localised covalent linkings (cf. Lowry, Chem. and Ind., 1924, 218). The existence of organic molecular compounds in solution, often with occurrence of visible colour, supports the authors' theory, which also accounts for the general occurrence of a simple molecular ratio between the components of a complex. It is shown that the formation of the equimolecular compound of trinitrobenzene and quinoline (Sudborough and Beard, J.C.S., 1910, **97**, 773) rather than a complex $[3C_6H_3(NO_2)_3,C_{10}H_7N]$ is to be anticipated. Union of polynitro-compounds and bases is considered to occur through a nitro-group (acceptor) and the basic nitrogen atom (donor) to yield complexes of type I, which if R_3=H may pass into form II (cf. Brewin and Turner, A., 1928, 402).

(I.)



$$Ar-\overset{+}{N}\!\lessdot^{\bar{O}}_{O}\;\;|\;\;R_1R_2R_3\overset{-}{\underset{+}{N}}$$



$$Ar-\overset{+}{N}\!\lessdot^{\bar{O}}_{OH}\;\;|\;\;R_1R_2N$$

(II.)

Examination of the *o*-, *m*-, and *p*-nitrobenzyldialkylamines supports the mode of formulation I proposed; the *o*-nitro-isomerides should exhibit intramolecular co-ordination and should therefore possess lower b. p. than, and differ in solubility from, their respective *m*- and *p*-isomerides in which any co-ordination must be intermolecular (cf. Sidgwick and Callow, A., 1924, i, 506). The o-, m-, and p-*nitrobenzyldimethylamines* were prepared from the respective nitrobenzyl chlorides in 50—60% yield, using hexamethylenetetramine (cf. A., 1926, 1132), and also by means of dimethylamine hydrochloride and alkali in alcoholic solution; their b. p. determined (*a*) in the ordinary way, and (*b*) by the method of Smith and Menzies (A., 1910, ii, 687), are as follows (order *o*-, *m*-, *p*-): (*a*) 133°/16 mm., 144°/16 mm., 146°/16 mm.; (*b*) 116—117°/11 mm., 130—132°/10 mm., 131—133°/10 mm.; *o*-nitrobenzyldimethylamine (*hydrochloride*, m. p. 215°; *picrate*, m. p. 143°) possesses a more intense yellow colour than either the *m*-isomeride (*picrate*, m. p. 217°) or the *p*-isomeride (*picrate*, m. p. 149°). The *o*-, *m*-, and *p*-nitrobenzyldiethylamines were prepared by the action of excess of diethylamine on the appropriate nitrobenzyl chlorides in 70—85% yield. The b. p. of the isomerides are: (*a*) 144°/13 mm., 158°/13 mm., 160°/13 mm.; (*b*) 124—127°/10 mm., 139—142°/10 mm., 146—148°/10 mm.; the *o*-isomeride is distinguished by its more intense yellow colour, and the *p*-isomeride yields a picrate, m. p. 151° (lit. m. p. 161°). The solubility of naphthalene in the nitrobenzyldiethylamines, and of the three nitroamines in trimethylene glycol were determined and in each case the *o*-isomeride differs to a small but definite extent from the *m*- and *p*-isomerides, which afford almost identical results.

Complexes between polynitro-compounds and hydrocarbons result from an ethylenic linking, which in the polarised form $-\overset{|\,-}{C}H-\overset{+}{C}H-$, provides one covalency; the benzene nucleus provides one covalency only. Increased stability occurs when several nitro-groups are present, and it is shown that any group attracting electrons should stabilise these complexes. Thus methyl 5-nitro*iso*phthalate forms with α-naphthylamine the *compound* $[C_6H_3(NO_2)(CO_2Me)_2,C_{10}H_7{\cdot}NH_2]$, m. p. 82°, and 5-nitrobenzene-1 : 3-disulphonyl chloride, m. p. 97—98°, forms *compounds* with mesitylene, m. p. 68—70°, anisole, m. p. 55—60°, and naphthalene, m. p. 102—103°, in the molecular ratio 1 : 1.

Compounds of picric acid with bases and hydrocarbons are discussed, and an explanation of the red and yellow forms of various picrates is suggested; s-*trichloroaniline picrate*, m. p. 80—83°, forms deep red needles (cf. 2 : 4-dichloroaniline picrate, which is yellow).

Two compounds of benzoquinone with bases are described: a green *compound* with *pp'*-tetramethyldiaminodiphenylcarbinol $[C_6H_4O_2,2C_{17}H_{22}ON_2]$, m. p. 169—170°, and with *pp'*-tetramethyldiaminodiphenylmethane a purple *compound* $[C_6H_4O_2,2C_{17}H_{22}N_2]$, m. p. 71°. The halochromic effects displayed by quinones in the presence of sulphuric acid are due to complexes in which the quinone functions as the donor-molecule. Evidence in support of Pfeiffer's suggestion (A., 1925, i, 262) that the development of colour is connected with the appearance of positive unsaturation on a carbon atom owing to co-ordination has been obtained by a study of the halochromic effects produced by sulphuric acid with a series of substituted styrylquinoxalines. The preparation of 3-*styryl*-2-*methylquinoxaline*, m. p. 137°, is described.

Other types of complex formation are discussed, and many illustrative examples are given.

C. W. SHOPPEE.

Modified Curtius reaction. II. C. NAEGELI (Helv. Chim. Acta, 1929, **12**, 205—207; cf. A., 1928, 881).—A reply to Lindemann (this vol., 78).

H. BURTON.

Action of methyl *p*-toluenesulphonate on α-naphthylamine. V. M. RODIONOV and W. E. VVEDENSKIJ (Bull. Soc. chim., 1929, [iv], **45**, 121—124; cf. A., 1926, 532).—When α-naphthylamine (1 mol.) is heated with 1 mol. of methyl *p*-toluenesulphonate at 155—160° for 5 hrs., 42% of dimethyl-α-naphthylamine is obtained, together with 5% of αα-dinaphthylamine, 24% of α-naphthylamine, recovered as sulphate, and 23% of methyl-α-naphthylamine, separated as its acetyl derivative; with 2 mols. of ester a 90—97% yield of dimethyl-α-naphthylamine, b. p. 268—274°, is obtained. α-*Naphthylmethylammonium* p-*toluenesulphonate*, m. p. 163—164°, is obtained by heating methyl α-naphthylamine with *p*-toluenesulphonic acid in alcohol at 50°. α-*Naphthyltrimethylammonium* p-*toluenesulphonate*, m. p. 82—83°, obtained by heating dimethyl-α-naphthylamine with the ester at 153—160°, with potassium iodide yields the corresponding iodide, m. p. 163—164°, and is an excellent alkylating agent for phenols, especially aminophenols, at higher temperatures than are possible with phenyltrimethylammonium *p*-toluenesulphonate. R. BRIGHTMAN.

Methylated nitronaphthylamines. V. VESELY and A. VOJTECH (J. Czechoslov. Chem. Comm., 1929, **1**, 104—118).—Methylation of 3-nitro-α-naphthylamine with methyl sulphate at 160° affords 3-*nitro*-α-*naphthyldimethylamine*, m. p. 64—65° (*picrate*, m. p. 188—189°), and 4-nitro-β-naphthylamine under similar conditions gives 4-*nitro*-β-*naphthyldimethylamine*, m. p. 65° (*picrate*, m. p. 194—196°). 4-Nitro-α-naphthylamine and methyl sulphate at 118° yield a mixture of 4-*nitro*-α-*naphthylmethylamine*, m. p. 184—185°, and 4-*nitro*-α-*naphthyldimethylamine*, m. p. 65—66°, the latter in poor yield. 2-Nitro-α-naphthylamine cannot be methylated with methyl sulphate; treatment of 1 : 2-dinitronaphthalene with dimethylamine and alcohol gives 2-*nitro*-α-*naphthyldimethylamine*, b. p. 182—184°/14 mm. (oriented by conversion into 2-nitro-α-naphthol, m. p. 127—128°, with alkali). Methyl sulphate with 5-nitro-α-naphthylamine gives 5-*nitro*-α-*naphthyldimethylamine*, b. p. 194—196°/14 mm. (*picrate*, m. p. 165—166°), at 145°; with 8-nitro-α-naphthylamine, 8-*nitro*-α-*naphthylmethylamine*, m. p. 81°, at 140°; with 5-nitro-β-naphthylamine, 5-*nitro*-β-*naphthyldimethylamine*, m. p. 74° (*picrate*, m. p. 176—177°), at 160°; with 8-nitro-β-naphthylamine, 8-*nitro*-β-*naphthyldimethylamine*, m. p. 77° (*picrate*, m. p. 174—176°), at 135°; with 6-nitro-β-naphthylamine, a mixture of 6-*nitro*-β-*naphthylmethylamine*, m. p. 185—186° (*picrate*, m. p. 138—140°; *acetyl* derivative, m. p. 186—187°), and 6-*nitro*-β-*naphthyldimethylamine*, m. p. 164° (*picrate*, m. p. 158—160°) at 150°. Nitration of β-naphthyldimethylamine with 86% nitric acid in glacial acetic acid solution gives a *dinitro*-compound, m. p. 157—158°, whilst nitration with fuming nitric acid and concentrated sulphuric acid yields a eutectic mixture, m. p. 52°, of two mononitro-compounds. Further nitration of the eutectic mixture with 86% nitric acid in glacial acetic acid solution affords an easily separable mixture of a dinitro-compound, m. p. 110°, identical with the product obtained by the nitration of 5-nitro-β-naphthyldimethylamine, *i.e.*, 1 : 5-dinitro-β-naphthyldimethylamine, together with an isomeric dinitro-compound, m. p. 176—177°, identical with the compound obtained by nitration of 8-nitro-β-naphthyldimethylamine, *i.e.*, 1 : 8-dinitro-β-naphthyldimethylamine. Nitration of α-naphthyldimethylamine with nitric acid (*d* 1·525) in glacial acetic acid solution gives 2 : 4-dinitro-β-naphthyldimethylamine, m. p. 88°, and a *substance*, m. p. 127—128°; nitration with fuming nitric acid and concentrated sulphuric acid yields a *dinitronaphthyldimethylamine*, m. p. 137—138°, 5-nitro-α-naphthyldimethylamine, b. p. 192—195°/14 mm. (*picrate*, m. p. 162—164°), and a small quantity of a mononitro-compound (*picrate*, m. p. 73°).

A. I. VOGEL.

Stereoisomerism of diphenyl compounds. II. Resolution of 3 : 3′-diaminodimesityl. W. W. MOYER and R. ADAMS (J. Amer. Chem. Soc., 1929, **51**, 630—639).—Further evidence for the mechanical theory of the stereoisomerism of diphenyl compounds (cf. A., 1928, 1234) is afforded by the resolution of a derivative in which the 2-, 6-, 2′-, and 6′-substituents are identical. Dimesityl is more conveniently prepared from magnesium mesityl bromide and cupric chloride (cf. Sakellarios and Kyrimis, A., 1924, i, 381) than by Ullmann's method (A., 1904, i, 725). It is converted by nitric acid (*d* 1·50) into *tetranitrodimesityl*, m. p. 270—271°, which is reduced by alcoholic ammonium sulphide to a mixture of nitro-amines and by zinc with hydrochloric and acetic acids to *tetra-aminodimesityl*, m. p. above 360° (*hydrochloride*). Dimesityl gives with bromine in carbon tetrachloride 3 : 3′-*dibromodimesityl*, m. p. 112—113°, and with acetyl nitrate a *dinitro*-derivative, m. p. 162·5—163·5°, which is not further nitrated by this reagent and is, therefore, probably the 3 : 3′-derivative. It is reduced by zinc and acid to dl-3 : 3′-*diaminodimesityl*, m. p. 206—207° (*diacetyl* derivative, m. p. 303—304°), which is readily separated through the d-*camphorsulphonate*, m. p. 186—188° (indef.) (also $+H_2O$, m. p. 175—187°), $[\alpha]_D^{20}$ +16·3°, into d-3 : 3′-*diaminodimesityl*, m. p. 203·5—204·5°, $[\alpha]_D^{20}$ +42·3° (*diacetyl* derivative, m. p. 312—313°, shrinking from 307°, $[\alpha]_D^{20}$ +30·8°), and the l-*form*, m. p. 203—204°, $[\alpha]_D^{20}$ −41·5° (*diacetyl* derivative, m. p. 311—313°, $[\alpha]_D^{20}$ −30·4°). The active amine is only slightly racemised by boiling with hydrochloric acid or alcoholic potassium hydroxide. The diazonium salt from nitroaminomesitylene (Küster and Stallberg, A., 1894, i, 278) yields with potassium iodide *iodonitromesitylene*, m. p. 96—97°, which does not give 3 : 3′-dinitrodimesityl when heated with copper powder.

H. E. F. NOTTON.

Nitrophenylfluorenylamines. C. ANASTASI and L. GUGLIALMELLI (Anal. Asoc. Quím. Argentina, 1928, **16**, 125—133).—2 : 4-*Dinitrophenyl-2-fluorenylamine*, m. p. 217°, is obtained in 56% yield by boiling a solution of 2 : 4-dinitrochlorobenzene and 2-fluorenylamine in absolute alcohol with anhydrous sodium acetate for 10 hrs. A preliminary account is given of the reduction of this compound by iron and acetic acid and by ammonium sulphide to the (?)*diamino*- and (?)*nitroamino*-derivatives, respectively, and its nitration to the (?)*tetranitro*-compound, m. p. 230° (decomp.), which has the properties of a ψ-acid.

R. K. Callow.

Manufacture of [new] substituted guanidines. I. G. Farbenind. A.-G.—See B., 1929, 163.

Hexa-aminobenzene. B. Flürscheim and E. L. Holmes (J.C.S., 1929, 330—337).—*Hexa-aminobenzene* has been prepared by reduction of 2 : 4 : 6-trinitro-1 : 3 : 5-triaminobenzene with phenylhydrazine (cf. Walther, A., 1896, i, 542); an attempt to employ stannous chloride in dry pyridine was unsuccessful. The base, m. p. 247—248° in hydrogen, forms light brown octahedra, the colour being due to surface oxidation, and is completely soluble in cold water; it may be crystallised from phenylhydrazine but is insoluble in all other media. Both the solid and the aqueous solution yield black oxidation products when kept in the air. The *hexa-acetyl* derivative, m. p. 356—357°, *tripicrate*, no m. p., and the *tetrahydrochloride*, no m. p., are described; the last when treated with cold 50% aqueous potassium hydroxide yields a *base* (*acetyl* derivative, m. p. above 385°).

An attempt to reduce 2 : 4 : 6-*trinitro*-1-*amino*-3 : 5-*dianilinobenzene*, m. p. 264° (decomp.) (obtained from pentanitroaniline and aniline in acetone solution), with phenylhydrazine failed, but from 2 : 4 : 6-trinitro-1 : 3-diaminobenzene was obtained *penta-aminobenzene*, m. p. 228° in hydrogen, soluble in water with instantaneous decomposition and insoluble in organic solvents.

The stability of all known polyamino-derivatives of benzene, its homologues, and of anisole is discussed and it appears that (*a*) vicinally substituted compounds are more stable than their isomerides, and (*b*) vicinal as well as non-vicinal compounds become less stable as the number of amino-groups increases. The superior stability of hexa-aminobenzene as compared with penta-aminobenzene is accounted for on the theory of affinity demand. C. W. Shoppee.

Double salts of benzenediazonium iodide with mercuric iodide and the formation of diphenyliodonium salts by their decomposition. A. N. Nesmejanov (Z. anorg. Chem., 1929, **178**, 300—308).—A methyl-alcoholic solution of benzenediazonium chloride at −10° yields a yellow, crystalline precipitate of *benzenediazonium tri-iodomercuriate*, $C_6H_5N_2HgI_3$, m. p. 63—64° (decomp.), on addition of the requisite potassium and mercuric iodides in methyl-alcoholic solution. With a further quantity of potassium iodide in aqueous solution this compound yields the corresponding *tetraiodomercuriate*, $(C_6H_5N_2)_2HgI_4$, m. p. 59·5—60° (decomp.), as a canary-yellow powder. Both salts decompose when kept at the ordinary temperature chiefly with the production of iodobenzene and mercuric iodide, but the first gives also a 10% and the second a 3% yield of *diphenyliodonium tri-iodomercuriate*, $[(C_6H_5)_2I]HgI_3$, light yellow crystals, m. p. 171·5°. The same substance is obtained by heating diphenyliodonium iodide, mercuric iodide, and acetone in a sealed tube at 100°. A. R. Powell.

Manufacture of new azo-dyes and intermediate products [2-anilino-8-hydroxy-6-naphthoic arylamides]. I. G. Farbenind. A.-G.—See B., 1929, 165.

Manufacture of *N*-ω-aminoalkylaminonaphthoic acids. I. G. Farbenind. A.-G.—See B., 1929, 200.

Influence of colloids on precipitation of salts. R. Dickinson (J.C.S., 1929, 358—359).—The solubility of *lead sozoiodolate* (2 : 6-*di-iodophenol*-4-*sulphonate*) in water is 0·512 g. per 100 c.c. of solution. When the compound is prepared from lead acetate and sodium sozoiodolate in presence of 2% of gum acacia precipitation of more than half of the expected amount of lead salt is prevented: the solubility of lead sozoiodolate in 2% gum acacia solution is 1·116 g. per 100 c.c. of solution. Gelatin gives a white rubber-like precipitate with sodium sozoiodolate.

A. I. Vogel.

3 : 5-Dichlorophenetidine. G. Bargellini and P. Leone (Atti R. Accad. Lincei, 1928, [vi], **8**, 399—404).—The compound, m. p. 46°, b. p. about 275°, obtained by Jaeger (A., 1875, 1260) by passing hydrogen chloride into an alcoholic solution of nitrosophenol may be either 3 : 5- or 2 : 6-dichlorophenetidine, but the latter has been prepared in another way (following abstract) and is found different. Treatment of 3 : 5-dichlorophenetidine with hydriodic acid gives the dichloroaminophenol obtained by passing hydrogen chloride through an ethereal solution of nitrosophenol (Jaeger, *loc. cit.*), so that this is 3 : 5-dichloro-4-aminophenol. Oxidation of the latter with dichromate and sulphuric acid yields 3 : 5-dichlorobenzoquinone (cf. Weselsky, Ber., 1870, **3**, 646). 3 : 5-Dichlorophenetidine does not condense with aromatic aldehydes, carbon disulphide, phenylthiocarbimide, potassium thiocyanate, etc., but forms an *acetyl* derivative (3 : 5-*dichlorophenacetin*), m. p. 129—131°, a *diacetyl* derivative, m. p. 86—88°, and a *benzoyl* compound, m. p. 188°, and condenses with phthalic anhydride to give the *compound*, $C_{16}H_{11}O_3NCl_2$, m. p. 193—194°, and with succinic anhydride to give a *compound*, m. p. 137°. On diazotisation and treatment with alkaline β-naphthol solution, it gives the *azo*-compound, $C_{18}H_{14}O_2N_2Cl_2$, m. p. 120°.

T. H. Pope.

2 : 6-Dichlorophenetidine. G. Bargellini (Atti R. Accad. Lincei, 1928, [vi], **8**, 505—511; cf. preceding abstract).—2 : 6-Dichloro-4-aminophenol condenses with carbon disulphide to give 3 : 5 : 3′ : 5′-*tetrachloro* - 4 : 4′ - *dihydroxydiphenylthiocarbamide*, softening at 200°, m. p. 210° (decomp.); with phenylthiocarbimide, s-3 : 5-*dichloro*-4-*hydroxydiphenylthiocarbamide*, m. p. 138—140°; with 1-chloro-2 : 4-dinitrobenzene, 3 : 5-dichloro-2′ : 4′-dinitro-4-hydroxydiphenylamine, m. p. 208—210°; it also gives a *piperonylidene*, m. p. 151—153°, and a *benzylidene* derivative, m. p. 99—101°. Treatment of the last-named compound with alcoholic potassium hydroxide and ethyl iodide yields 2 : 6-*dichlorophenetidine*, m. p. 105—107°, which forms an *acetyl*, m. p. 176—178°, a β-*naphtholazo*-, m. p. 171—173°, and a *piperonylidene* derivative, m. p. 133—135°, and condenses with 1-chloro-2 : 4-dinitrobenzene to give 3 : 5-*dichloro*-2′ : 4′-*dinitro*-4-*ethoxydiphenylamine*, m. p. 160—162°.

T. H. Pope.

Condensation products of dextrose and *p*-phenetidine. II. M. Amadori (Atti R. Accad. Lincei, 1929, [vi], 9, 68—73).—The compound, m. p. 118° (A., 1926, 60), has $[\alpha]_D^{20}$ −84° in fresh aqueous solution, this value gradually diminishing and the compound decomposing; in alcoholic solution $[\alpha]_D^{20}$ also falls from −88° to −91° to the constant value −35°. For the more stable compound m. p. 155° (now given as 115°) the value of $[\alpha]_D^{20}$ in methyl alcohol is initially −50° and falls slowly to −25°. Evidently α- and β-forms of these compounds exist and the presence of alkali in the solutions hastens the attainment of equilibrium. The conclusion is reached that the condensation of a primary aromatic amine with dextrose gives rise to (1) a glucosidic compound, resulting from the reaction of one of the aminic hydrogen atoms with the glucosidic hydroxyl of the dextrose, and (2) a basic compound, formed by the reaction of two aminic hydrogen atoms with the ketonic oxygen of the aldehyde group or of the lactonic linking of the dextrose.

T. H. Pope.

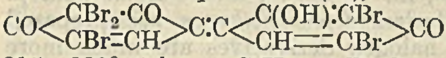
Replaceability of methoxy-group in 4 : 6-dinitro-*m*-tolyl methyl ether. J. G. Kerkhof (Rec. trav. chim., 1929, 48, 251—253).—In support of de Capeller's (A., 1928, 631) claim that the dinitromethoxytoluene isolated in the nitration of 5-methyl-2-*tert*.-butylanisole (Barbier, A., 1928, 280) is 4 : 6-dinitro-*m*-tolyl methyl ether its interactions with the following reagents are described: boiling alcoholic ammonia, which gave 4 : 6-dinitro-*m*-toluidine, m. p. 195°; alcoholic methylamine under pressure, which furnished 4 : 6-dinitro-*N*-methyl-*m*-toluidine; boiling alcoholic hydrazine hydrate, giving 4 : 6-dinitro-*m*-tolylhydrazine.

R. J. W. Le Fèvre.

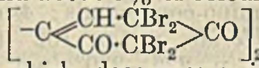
2-Substituted derivatives of *p*-cresol. M. Copisarow (J.C.S., 1929, 251—253).—An improved preparation of 2-nitro-*p*-cresol, m. p. 76—77° (yield 79%), by nitration of *p*-tolyl carbonate is described (cf. Holleman and Hoeflake, A., 1917, i, 133); methylation with methyl sulphate and anhydrous sodium carbonate in toluene at 110° gives a 77% yield of 2-nitro-*p*-tolyl methyl ether (cf. Knecht, A., 1882, 968), also obtained directly from 2-nitro-*p*-tolyl carbonate (yield 60%); the ethyl ether may be prepared similarly. 2-Amino-*p*-cresol, m. p. 157—159°, is obtained in 79% yield by simultaneous reduction and hydrolysis of 2-nitro-*p*-tolyl carbonate with iron filings and acid, or preferably with sodium sulphide (cf. Knecht, A., 1882, 728; Wallach, A., 1883, 329; Maasen, A., 1884, 1145); 2-nitro-*p*-tolyl methyl ether on reduction with iron filings and acetic acid at 95—98° gives a 78—82% yield of 2-amino-*p*-tolyl methyl ether (cf. Knecht, *loc. cit.*). The preparation of *p*-tolyl chloroformate in 78—80% yield is also described.

C. W. Shoppee.

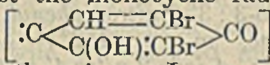
Oxidation of tribromoresorcinol. T. L. Davies and J. W. Hill (J. Amer. Chem. Soc., 1929, 51, 493—504).—Tribromoresorcinol (cf. Benedikt, A., 1883, 984), quantitatively prepared from resorcinol and bromine in chloroform, has been oxidised in benzene with aqueous chromic acid. In addition to bromine and carbon dioxide, a product (I) (33—37% yield) is obtained which contains about 60% of "*rhodobromoresoquinone*" (II),



$CO<\begin{matrix}CBr_2\cdot CO\\CBr{=}CH\end{matrix}>C{:}C<\begin{matrix}C(OH){:}CBr\\CH{=\!=}CBr\end{matrix}>CO$, red, m. p. 215—220° (also $+C_6H_6$, $+Et_2O$, and +0·25 mol. CS_2). This is identified by reduction with sulphur dioxide in aqueous alcohol to tetrabromodiresorcinol (III), by bromination in glacial acetic acid to tribromoresoquinone (IV) (cf. Zincke and Schwabe, A., 1909, i, 241), and by iodometric determination of its oxidising power. Rhodobromoresoquinone is formed from IV and a mixture of bromine and benzene, reduction being brought about by hydrogen bromide. Its benzene additive product slowly decomposes at 120° into a colourless *polymeride* or *isomeride* of II, m. p. 228—229°, which cannot be brominated and has only half the oxidising power of II. The product I also contains a trace of IV and about 9% of colourless *tetrabromoresoquinone*,



$\left[-C\ll\begin{matrix}CH\cdot CBr_2\\CO\cdot CBr_2\end{matrix}>CO\right]_2$, m. p. 227—228° (decomp.), which decomposes in boiling glacial acetic acid into bromine and IV, and is quantitatively reduced to III by hydriodic acid. It is formed by brominating either II or IV. These results show that the oxidation of tribromoresorcinol probably yields first the monocyclic radical of dibromoresoquinone,



$\left[{:}C<\begin{matrix}CH{=\!=}CBr\\C(OH){:}CBr\end{matrix}>CO\right]_2$, which is then brominated to the mixture I.

H. E. F. Notton.

Orientation in the benzene ring. Bromination of 2-aminoresorcinol dimethyl ether. A. A. Levine and H. Linford (J. Amer. Chem. Soc., 1929, 51, 524—527).—Attempts to brominate the free amine were unsuccessful. It is readily acetylated by acetic anhydride in glacial acetic acid at the ordinary temperature. The acetyl derivative gives in this solvent with 1 mol. of bromine 4-*bromo*-2-*acetamidoresorcinol dimethyl ether* (I), m. p. 161—162°, with 2 mols. at the ordinary temperature, *dibromo*-2-*acetamidoresorcinol dimethyl ether*, m. p. 213—214°, and at 100°, an isomeric *dibromo*-derivative, m. p. 187—188°. Hydrolysis of I with 2*N*-alcoholic potassium hydroxide gives 4-*bromo*-2-*aminoresorcinol dimethyl ether*, m. p. 67—68°, which is also formed by reducing 4-bromo-2-nitroresorcinol dimethyl ether (Kauffmann and Franck, A., 1907, i, 1092) with tin and hydrochloric acid.

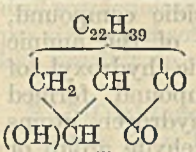
H. E. F. Notton.

Chloro- and bromo-derivatives of 2 : 4-dihydroxydiphenylmethane and their germicidal action. E. Klarmann and J. von Wowern (J. Amer. Chem. Soc., 1929, 51, 605—610).—4′-*Chloro*-2 : 4-*dihydroxybenzophenone*, m. p. 155°, from *p*-chlorobenzonitrile and resorcinol in presence of zinc chloride, is reduced by amalgamated zinc and hydrochloric acid to 4′-*chloro*-2 : 4-*dihydroxydiphenylmethane*, b. p. 200—225°/5 mm., m. p. 80·4°, which is also formed from *p*-chlorobenzyl chloride and resorcinol in nitrobenzene in presence of aluminium chloride. 4′-*Bromo*-2 : 4-*dihydroxybenzophenone*, m. p. 169°, and 4′-*bromo*-2 : 4-*dihydroxydiphenylmethane*, m. p. 96°, are prepared similarly. 5-*Chloro*-, m. p. 122°, and 5-*bromo*-, m. p. 122·4°, derivatives are obtained by cautious addition of sulphuryl chloride and bromine (1 mol.), respectively, to 2 : 4-dihydroxydiphenylmethane in ether. 5-*Chloro*-, m. p. 136·7°, and 5-*bromo*-, m. p. 152·1°, -2 : 4-*dihydroxydiphenylethanes* are prepared similarly. The halogen derivatives are much more strongly bactericidal than the parent phenols, but the former undergo a proportionately greater reduction in efficiency in presence of gelatin and peptone. The 4′-halogenophenols are more active than the corresponding 5-derivatives. H. E. F. Notton.

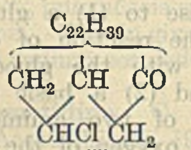
Molecular compounds from aromatic iodo-compounds. P. Pfeiffer, H. Schmitz, and T. Inoue (J. pr. Chem., 1929, [ii], **121**, 70—84).—Several iodo-derivatives of diphenyl and stilbene have been prepared and the possibility of compound formation with metallic salts, aromatic bases, and ketones has been investigated. By the usual methods the following are prepared from the corresponding amino-compounds : 4-iododiphenyl, m. p. 112° [*iodochloride*, m. p. 102° (decomp.); *iodoso*-compound, m. p. 225—230° (not pure)]; 4 : 4′-di-iodo-, m. p. 109—110°, 4 : 4′-dichloro-, m. p. 58—58·5°, and 4 : 4′-dibromo-, m. p. 71°, -3 : 3′-ditolyl (lit. gives m. p. 99—100°, 51°, and 58—59°, respectively); 4 : 4′-*di-iodo*-3 : 3′-*dimethoxydiphenyl*, m. p. 181·5—183° [*iodochloride*, m. p. 109—110° (decomp.)]; 4 : 4′-*di-iodo*-3 : 3′-*dinitrodiphenyl*, m. p. 246—247°; 4-*iodostilbene*, m. p. 152°; 4-*iodo*-2-*nitrostilbene*, m. p. 110°; 4-*iodo*-2-*nitro*-4′-*methoxystilbene*, m. p. 100—100·5°. By thermal analysis it is shown that no compounds are formed by these iodine derivatives with mercuric chloride or iodide, silver nitrate, piperonylideneacetophenone, dipiperonylideneacetone, sarcosine anhydride, α-naphthol, menthol, α-naphthylamine, or *s*-trinitrobenzene. Only in the case of dianisylideneacetone (2 mols.) and 4-iododiphenyl (1 mol.) is a compound formed. J. W. Baker.

Action of aromatic aldehydes on phenols. O. Hinsberg (Ber., 1929, **62**, [*B*], 418—421).—Compounds provisionally regarded as derivatives of 9 : 10-diphenyl-9 : 10-dihydroanthracene are obtained when equivalent quantities of an aromatic aldehyde and phenol are heated with glacial acetic and concentrated hydrochloric acids under pressure. Thus benzaldehyde and phenol at 100° afford, after treatment of the product with acetic anhydride and a little zinc dust, 2 : 7(+2 : 6)-diacetoxy-9 : 10-diphenyl-9 : 10-dihydroanthracene, m. p. above 202°, hydrolysed to 2 : 7(+2 : 6)-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene, which darkens and softens at about 250°. Oxidation of the diacetoxydihydro-compound with potassium dichromate and glacial acetic acid yields 2 : 7(+2 : 6)-diacetoxy-9 : 10-diphenylanthracene, m. p. 215—235°, which is hydrolysed by alkali hydroxide to 2 : 7(+2 : 6)-dihydroxy-9 : 10-diphenylanthracene hydrate, $C_{26}H_{20}O_3$, derived from benzaurin. The hydrate crystallises with 1 mol. of water, which is removed at 120°, but the removal of a second molecule of water, which should lead to dihydroxydiphenylanthracene, could not be effected. *p*-Cresol and *p*-nitrobenzaldehyde yield 4 : 5(+4 : 8)-dihydroxy-9 : 10-di-*p*-nitrophenyl-1 : 8(+1 : 5)-dimethyl-9 : 10-dihydroanthracene, m. p. above 270°. H. Wren.

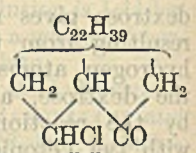
Oxidation of cholesterol with chromic acid. S. Minovici and M. Vanghelovici (Bull. Soc. Chim. România, 1928, **10**, 91—96).—The substance obtained by Mauthner and Suida (A., 1896, i, 425) by hydrolysis of the product of oxidation of cholesteryl acetate with chromic acid has now been obtained from cholesterol by oxidation with chromic acid in glacial acetic acid; it has m. p. 216—217° (decomp.), empirical formula $C_{27}H_{44}O_3$. The structure I is suggested. Cholesteryl chloride, similarly oxidised, yielded a neutral ketonic *substance*, $C_{27}H_{45}OCl$, m. p. 137° (p-*nitrophenylhydrazone*, m. p. 200°), isomeric with that obtained by Windaus (A., 1904, i, 1010) and that obtained by Mauthner (*ibid.*, 49). The *cis*- and *trans*-forms of II and III are possible structures for these isomerides.



(I.)



(II.)



(III.)

C. W. Shoppee.

Cholesterol and its relations with the terpenes. E. Montignie (Bull. Soc. chim., 1929, [iv], **45**, 97—100).—The terpenic structure for cholesterol suggested by Steinle and Kahlenberg (A., 1926, 633) rests on inconclusive evidence, since certain unsaturated fatty acids give similar colour reactions with antimony pentachloride and the terpenes themselves do not give Liebermann's reaction. Cholesterol is converted by sulphuric and acetic acids into β-cholesterylene; terpenes yield an isomerisation or a hydration product with this reagent. Formic acid, which converts cholesterol into its formate, produces isomerisation with certain terpenes, and similarly with phthalic anhydride at 220°, which converts sesquiterpene alcohols into the hydrocarbons, cholesterol affords its phthalate, m. p. 157°. The sterols are accordingly regarded as constituting a distinct type of compound and not as belonging to the terpene group. The formation of chrysene and homologous hydrocarbons by distilling cholesterol is attributed to the condensation of the indene rings from two molecules of cholesterol. R. Brightman.

Reactions of cholesterol. E. Bahl (Biochem. Z., 1929, **204**, 474).—Cholesterol gives a yellowish-brown coloration with a solution of benzidine in glacial acetic acid and an intensely red coloration with a faintly pink solution of rosaniline in chloroform. Both tests are parallel to those of Salkowski and Liebermann. W. McCartney.

Preparation of styrene (with a note on the detection and identification of β-phenylethyl alcohol). S. Sabetay (Bull. Soc. chim., 1929, [iv], **46**, 69—75).—β-Phenylethyl alcohol when distilled with dry potassium hydroxide is converted quantitatively into styrene, b. p. 52—53°/28 mm., 143°/760 mm., n_D^{23} 1·5440, d^{20} 0·9038. β-*p*-Tolylethyl alcohol is similarly converted into *p*-methylstyrene, b. p. 170—173° (dibromide, m. p. 45°). β-2-Naphthylethyl alcohol behaves similarly, but γ-phenylpropyl alcohol and phenylethylcarbinol are not dehydrated under these conditions. Phenylmethylcarbinol is partly decomposed but affords no styrene. The reaction is regarded as characteristic of the group $\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$ and is attributed to the influence of the phenyl group on the mobility of the neighbouring hydrogen atom. The reaction can be applied to the detection or approximate determination of β-phenylethyl alcohol in mixtures, *e.g.*, with rhodinol or geraniol, the styrene formed being converted into dibromide. R. Brightman.

Comparison of the stability of isomerides according to their absorption spectra. Allyl and *iso*allyl derivatives of the benzene series. (Mme.) Ramart-Lucas and (Mlle.) Amagat (Compt. rend., 1929, **188**, 638—640).—The *iso*allyl derivatives of the benzene series have the ascending branch of their ultra-violet absorption curves nearer the visible than those of the allyl isomerides and therefore conform to the rules suggested by Ramart-Lucas (A., 1928, 1000), the latter being transformed into the former by heat. It is shown that whilst γ-phenyl-*n*-propyl alcohol gives allylbenzene on dehydration with thionyl chloride, it will also give the *iso*-compound when dehydrated at a sufficiently high temperature. The following are prepared by reduction of the corresponding amides: *γ-anisyl-*n*-propyl alcohol*, b. p. 160°/15 mm., m. p. 26°; and *γ-piperonyl-*n*-propyl alcohol*, b. p. 180°/13 mm. J. Grant.

Ephedrine and structurally similar compounds. I. Synthesis of ephedrine. R. H. F. Manske and T. B. Johnson (J. Amer. Chem. Soc., 1929, **51**, 580—582).—α-Phenylpropane-αβ-dione, prepared from propiophenone and nitrogen peroxide, yields with anhydrous methylamine in light petroleum unstable *β-methylimino-α-phenylpropan-α-one*, which is hydrogenated (platinum) in alcohol to *dl*-ephedrine and (contrast other syntheses, A., 1920, i, 875; 1921, i, 45) only a little ψ-ephedrine. H. E. F. Notton.

Ultra-violet absorption of *p*-aminobenzoic esters in water solution. E. R. Riegel and K. W. Buchwald (J. Amer. Chem. Soc., 1929, **51**, 484—492).—Ultra-violet absorption spectra (to 2100 Å.) are recorded for aqueous solutions of (*a*) *p*-aminobenzoic acid and the following *p*-aminobenzoates: methyl, ethyl, propyl, butyl, γ-di-*n*-butylaminopropyl and its sulphate (butyn), β-diethylaminoethyl and its hydrochloride (procaine), γ-dimethylamino-αβ-dimethylpropyl and its hydrochloride (tutocaine); also *p*-hydroxybenzoic acid; (*b*) *p*-dimethylaminobenzoic acid, aniline and its hydrochloride, benzoic acid, α-methyl-α-dimethylaminomethylpropyl benzoate hydrochloride (stovaine), αα-bisdimethylaminomethylpropyl benzoate hydrochloride (alypine), cocaine sulphate, and benzene. The compounds in group (*a*) all show an intense absorption band which is of the same order of persistence as that previously found for substances of *p*-quinonoid structure (A., 1926, 734). It is therefore suggested that these exist in solution mainly in the form $NH{:}C_6H_4{:}C(OH)\cdot OR$, and this is confirmed by the observation that compounds which cannot isomerise in this way such as those in group (*b*) exhibit only a weak selective absorption. Nitro- and nitroamino-guanidine in water show an intense band, but guanidine carbonate has no selective absorption in this region. H. E. F. Notton.

Sulphonphthaleins. W. C. Harden and N. L. Drake (J. Amer. Chem. Soc., 1929, **51**, 562—566).—The following have been prepared by heating together a phenol and a tetrahalogeno-*o*-sulphobenzoic anhydride, alone, or in presence of stannic chloride at 120—140°: *phenoltetrachlorosulphonphthalein* (*tetrabromo*-derivative), *phenoltetrabromosulphonphthalein* (*tetrabromo*-derivative), *o-cresoltetrachlorosulphonphthalein* (*dibromo*-derivative), *o-cresoltetrabromosulphonphthalein* (*dibromo*-derivative), and *o-cresoltetraiodosulphonphthalein* (*dibromo*-derivative). The colour changes and useful p_H ranges of the products are tabulated. They are, in general, similar to those of the corresponding non-halogenated products. H. E. F. Notton.

Quinonoid tautomerism. Chlorination of *p*-nitrophenylacetonitrile. V. Nekrassov and A. V. Sokolov (Ber., 1929, **62**, [*B*], 463—466).—*p*-Nitrophenylacetonitrile is converted by chlorine at 120° in bright daylight into *dichloro-*p*-nitrophenylacetonitrile*, $NO_2\cdot C_6H_4\cdot CCl_2\cdot CN$, b. p. 149—149·5°/0·6 mm., d^{20} 1·4465, n^{20} 1·5710, hydrolysed by a boiling mixture of concentrated hydrochloric acid and ether to *dichloro-*p*-nitrophenylacetic acid*, m. p. 171—172° (slight decomp.). Oxidation of the nitrile by alkaline permanganate or hydrolysis of it by hydrobromic or sulphuric acid affords *p*-nitrobenzoic acid. Alcoholic solutions of the nitrile are coloured intensely permanganate-red by alkali and slowly become yellow when preserved. The colour disappears when the solutions are acidified but returns after addition of excess of alkali. Since a quinonoid or an imide structure cannot be attributed to the coloured salts, the constitution of the salt-like derivatives of the nitrophenylacetonitriles and analogous compounds cannot be regarded as established. H. Wren.

Nitrilotricarboxylic acids. G. L. Stadnikov and N. G. Titov (J. Russ. Phys. Chem. Soc., 1928, **60**, 1501—1503).—The behaviour of α-phenyl-α′α″-dimethylnitrilotriacetic acid (I) and the anhydride of α-phenyl-α′α′α″α″-tetramethylnitrilotriacetic acid (II) in the presence of concentrated hydrochloric acid at 160° was investigated, to determine their stability. The acids were readily decomposed first to α-phenyl-α′-methyliminodiacetic (III) and α-phenyl-α′α′-dimethyliminodiacetic (IV), and then finally to aminophenylacetic acid. M. Zvegintzov.

Synthesis of [2-]phenylindones from cinnamonitriles. P. Pfeiffer, H. Behr, H. Kübler, and H. Rüping (J. pr. Chem., 1929, [ii], **121**, 85—96).—The formation of 2-phenylindone derivatives by the action of sulphuric acid on phenylcinnamonitrile (Pfeiffer and others, this vol., 184) has been extended to substituted derivatives of the general type $(p)R_1\cdot C_6H_4\cdot CH{:}C(CN)\cdot C_6H_4\cdot R_2(p)$. Only the *cis*-compound, the cyano-group of which is not hydrolysed by alcoholic hydrogen chloride, yields the indene derivative and then only when R_1=H or, with less ease, Cl, but not when R_1=MeO, NMe_2, or NO_2. Thus from the appropriate phenylcinnamonitrile are obtained 2-p-*nitrophenylindone*, m. p. 156—157° (R_1=H, R_2=NO_2); 6-*chloro*-2-p-*nitrophenylindone*, m. p. 195°, together with p-*chloro*-α-p-*nitrophenylcinnamamide*, m. p. 230° (R_1=Cl, R_2=NO_2); 2-p-*carboxylamidophenylindone*, m. p. 198°, from α-p-*dicyanostilbene*, m. p. 146—147° (obtained by condensation of *p*-cyanophenylacetonitrile with benzaldehyde), which is converted by methyl-alcoholic hydrogen chloride into *methyl* α-*cyanostilbene*-p-*carboxylate*, m. p. 146—147° (*ethyl* ester, m. p. 133—134°). On the other hand, α : 4-*dicyano*-4′-*methoxystilbene*, m. p. 161—162° (R_1=MeO, R_2=CN), obtained by condensation of anisaldehyde with *p*-cyanophenylacetonitrile, yields no indone derivative, but is hydrolysed to *methyl* α-*cyano*-4′-*methoxystilbene*-4-*carboxylate*, m. p. 158°. Similarly, α : 4-dicyano-4′-dimethylaminostilbene is converted by sulphuric acid into the corresponding *diamide*, m. p. 268°, which is hydrolysed by boiling 10% sodium hydroxide to α-*carboxylamido*-4′-*dimethylaminostilbene*-4-*carboxylic acid*, m. p. 264° (*sodium* and *barium* salts; *methyl*, m. p. 217°, and *ethyl*, m. p. 185°, esters). J. W. BAKER.

Mechanism of the reaction between organomagnesium compounds and *N*-substituted cinnamanilides. N. MAXIM and N. IOANID (Bul. Soc. Chim. România, 1928, **10**, 116—126; cf. A., 1928, 1004).—To distinguish between 1 : 2- and 1 : 4-addition of magnesium alkyl halides to *N*-substituted cinnamanilides, $\underset{4}{\mathrm{CHPh}}{:}\underset{3}{\mathrm{CH}}\cdot\underset{2}{\mathrm{C}}(:\mathrm{O})\cdot\underset{1}{\mathrm{N}}\mathrm{RPh}$, decomposition of the organo-metallic complex has been effected with acetyl chloride; in the former case a ketone-anilide, yielding by hydrolysis a saturated ketonic acid, should result, whereas the product obtained is an unsaturated acetoxy-anilide, hydrolysed to a saturated acid, conforming to 1 : 4-addition. α-*Phenylmethylamino*-α-*acetoxy*-γγ-*diphenyl*-Δ^{α}-*propylene*, m. p. 154°, is obtained when the complex formed by magnesium phenyl bromide and *N*-methylcinnamanilide is treated with ethereal acetyl chloride; from the appropriate *N*-substituted cinnamanilides are obtained similarly: α-*phenylethylamino*-α-*acetoxy*-γγ-*diphenyl*-Δ^{α}-*propylene*, m. p. 138°, and α-*diphenylamino*-α-*acetoxy*-γγ-*diphenyl*-Δ^{α}-*propylene*, m. p. 148°. These acetoxy-compounds by hydrolysis with alcoholic potassium hydroxide yield respectively ββ-diphenylpropionmethylanilide, b. p. 261°/13 mm., ββ-diphenylpropionethylanilide, b. p. 278°/25 mm., and ββ-diphenylpropionic acid. The foregoing anilides are further hydrolysed by 40% hydrobromic acid to ββ-diphenylpropionic acid. C. W. SHOPPEE.

Hydrogenation of δ-lactones. C. MANNICH and A. BUTZ (Ber., 1929, 62, [*B*], 461—463; cf. this vol., 443).—Hydrogenation of the lactone of δ-hydroxy-βδ-diphenyl-Δ^{γ}-pentenoic acid in acetone in presence of palladised charcoal proceeds without noticeable break until 2 mols. of hydrogen have been absorbed and yields βδ-*diphenyl*-n-*valeric acid*, m. p. 109—110°, also obtained in moderate yield by reduction of γ-benzoyl-β-phenylbutyric acid by amalgamated zinc and concentrated hydrochloric acid. If hydrogenation is interrupted after 1 mol. of hydrogen has been absorbed, the product contains initial and fully hydrogenated substances together with the *lactone* of δ-*hydroxy*-βδ-*diphenyl*-n-*valeric acid*, m. p. 117°. Similarly, the lactone of δ-hydroxy-δ-phenyl-β-methylenedioxyphenyl-Δ^{γ}-pentenoic acid affords δ-*phenyl*-β-*methylenedioxyphenyl*-n-*valeric acid*, m. p. 138—139° (derived also from γ-benzoyl-β-methylenedioxyphenylbutyric acid), and the *lactone* of δ-*hydroxy*-δ-*phenyl*-β-*methylenedioxyphenyl*-n-*valeric acid*, m. p. 132—133°. The reduction does not appear general, since the lactone of α-hydroxy-β-phenyl-*n*-valeric acid is not hydrogenated in the presence of palladium; the presence of a phenyl group in the δ-position appears to be the determining factor. H. WREN.

Constituents of kawa root. VIII. Kawaic acid. W. BORSCHE and W. PEITZSCH (Ber., 1929, 62, [*B*], 368—373; cf. Borsche and Roth, A., 1921, i, 862; Murayama and others, A., 1922, i, 265).—Improved methods of treatment of kawa resin have yielded kawaic acid, m. p. 186° (decomp.), to which the composition $C_{14}H_{14}O_3$ instead of $C_{13}H_{12}O_3$ is now ascribed. The acid is distinguished from methystic acid by the absence of the methylenedioxy-group. Its stability towards alkali and ready conversion by acid into methyl alcohol and γ-cinnamylideneacetoacetic acid (or carbon dioxide and cinnamylideneacetone) show it to be β-*methoxy*-ζ-*phenyl*-$\Delta^{\alpha\gamma\epsilon}$-*heptatrienoic acid*, and this conception is confirmed by the partial demethylation of its *methyl* ester to methyl γ-cinnamylideneacetoacetate. Towards catalytic reduction, kawaic acid behaves similarly to methystic acid in that only two of its three ethylenic linkings are readily saturated. Tetrahydrokawaic acid (β-methoxy-ζ-phenyl-Δ^{α}-heptenoic acid), m. p. 109—110°, is smoothly decarboxylated when distilled under reduced pressure to β-methoxy-ζ-phenyl-Δ^{α}-hexene, b. p. 136—138°/16 mm. (converted by protracted boiling with alcoholic semicarbazide into the *semicarbazone* of ζ-*phenylhexan*-β-*one*, m. p. 141—142°), and decomposed by dilute acids into methyl alcohol, carbon dioxide, and ζ-phenylhexan-β-one. It is very slowly reduced to β-methoxy-ζ-phenylheptoic acid. Synthesis of tetrahydrokawaic acid is effected by the action of a large excess of diazomethane on methyl β-keto-ζ-phenylheptoate followed by hydrolysis of that portion of the product which is insoluble in alkali.

It appears probable that kawaic acid does not exist pre-formed in kawa resin, but as a doubly unsaturated lactone "kawain." H. WREN.

Catalytic hydrogenation of different types of unsaturated compounds. IV. Hydrogenation of conjugated systems: piperic acid. S. V. LEBEDEV and A. O. YAKUBCHIK (J.C.S., 1929, 220—225).—The catalytic hydrogenation of piperic acid as the potassium salt in aqueous solution with colloidal palladium (cf. Paal, A., 1912, i, 703) has been re-investigated, and found to conform to type II of the authors' classification (cf. A., 1928, 613). Hydrogenation proceeds similarly in alcoholic solution in the presence of platinum-black, and in both cases it is shown that dihydropiperic acids are formed prior to the tetrahydro-acid. Thus, using the former method, the product of 50% hydrogenation contains 34·3% of unchanged piperic acid, 31·4% of dihydro- and 34·3% of tetrahydro-acid; with the latter method the corresponding figures are 26·3%, 47·4%, and 26·3%. The position of the "critical point," *i.e.*, the point at which all piperic acid is exhausted, depends on the catalyst used and occurs at 75—76% of the hydrogen absorption in alcohol with platinum-black, and at 68—70% in water with palladium. The shapes of the hydrogenation curves, which are strikingly different beyond the critical point, and their interpretation are discussed.

C. W. SHOPPEE.

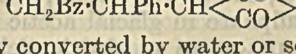
Molecular compounds of bile acids with fatty acids and alcohols. I. Deoxycholic and *apo*cholic acids. H. RHEINBOLDT [with E. FLUME and O. KÖNIG] (Z. physiol. Chem., 1929, **180**, 180—186).—Complex molecular *compounds* have been prepared from the following substances and deoxycholic acid, the number of mols. of the latter per 1 mol. of the former being given in parentheses: palmitic acid (8), m. p. 184—185°; stearic acid (8), m. p. 186—187°; cetyl alcohol (8), m. p. 185—186°, and from the same substances and *apo*cholic acid: palmitic acid (8), m. p. 184—185°; stearic acid (8), m. p. 185—186°; cetyl alcohol (8), m. p. 182·5°. H. BURTON.

Constituents of kawa root. VII. ψ-Methysticin. W. BORSCHE and W. PEITZSCH (Ber., 1929, **62**, [*B*], 360—367; cf. A., 1927, 1192; Winzheimer, A., 1908, i, 805).—ψ-Methysticin is dihydromethysticin containing methysticin, since the volume of hydrogen used in its catalytic hydrogenation is only a fraction of that required to convert an equal weight of methysticin into homogeneous dihydromethysticin. This conception of the change is in accordance with the evidence of optical activity and with the observation that the methyl ester of "ψ-methystic acid," obtained by the action of sodium methoxide on ψ-methysticin, is separable by ether into methyl dihydromethystate, m. p. 50—51°, and methyl methystate, m. p. 162—163°. ψ-Methysticin can be prepared artificially by crystallising a mixture of methysticin and its dihydro-compound from methyl alcohol. The mixed crystals thus obtained cannot be separated smoothly into their components by repeated crystallisation and, since both compounds are found in kawa root, it is doubtful if homogeneous methysticin has ever been isolated.

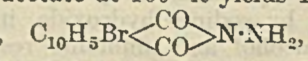
Catalytic reduction of methysticin proceeds in three distinct phases with very differing rapidities. Dihydromethysticin, m. p. 117—118°, $[\alpha]_D^{21}$ +20·57° in methyl alcohol, is the initial product. It is converted by sodium methoxide or *N*-potassium hydroxide into the optically inactive dihydromethystic acid (β-methoxy-ζ-methylenedioxyphenyl-$\Delta^{\alpha\gamma}$-heptadienoic acid), m. p. 146—147° (decomp.) [*methyl* ester, m. p. 50—51°], transformed by boiling *N*-sulphuric acid into dihydromethysticone (methyl δ-methylenedioxyphenyl-Δ^{α}-butenyl ketone), b. p. 196—198°/14 mm. [2 : 4-*dinitrophenylhydrazone*, m. p. 147—148°; *methysticone*-2 : 4-*dinitrophenylhydrazone* has m. p. 236—237° (decomp.)]. The quantitative conversion of methysticin into its dihydro-derivative appears impossible, since tetrahydromethystic acid is always produced even when only 1 mol. of hydrogen is used. The acid is more readily prepared by reduction of methystic acid. It is converted by distillation under diminished pressure into carbon dioxide and β-*methoxy*-ζ-*methylenedioxyphenyl*-Δ^{α}-*hexene*, b. p. 176—177°/14 mm., transformed by warm, dilute mineral acids into tetrahydromethysticone identified as the 2 : 4-*dinitrophenylhydrazone*, m. p. 129—130°. Catalytic reduction of the tetrahydro-acid to *hexahydromethystic acid* [β-*methoxy*-ζ-*methylenedioxyphenylheptoic acid*], m. p. 66—67°, is unexpectedly difficult. H. WREN.

Electrolytic reduction of the imides of cyclic acids. K. N. MENON and J. L. SIMONSEN (J.C.S., 1929, 302—305).—A preliminary account of work directed to the synthesis of cyclic 1-carboxy-2-acetic acids (cf. this vol., 52) by electrolytic reduction of cyclic dicarboxylamides in acid solution at 0—5° (cf. Tafel and Eckstein, A., 1902, i, 43). The imides were prepared by treatment of the anhydrides with dry ammonia at 180°. *Caronimide*, m. p. 120°, on reduction gave a 5% yield of 4 : 4-*dimethyl*-2-*piperidone*, liquid (*benzoyl* derivative, m. p. 114°; *phosphomolybdate*; *phosphotungstate*), with fission of the *cyclo*propane ring (cf. Iyer and Simonsen, A., 1926, 1042; Harihan, Menon, and Simonsen, A., 1928, 395). cyclo*Butane*-1 : 2-*dicarboxylimide*, m. p. 121°, yielded 15% of the γ-*lactam* of 2-*aminomethyl*cyclo*butane*-1-*carboxylic acid*, m. p. 127—128° (*nitroso*-derivative, liquid; *phosphomolybdate*; *phosphotungstate*); cyclo*pentane*-1 : 2-*dicarboxylimide*, m. p. 90°, gave a 25% yield of the γ-*lactam* of 2-*aminomethyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 83° (p-*nitrobenzoate*, m. p. 123°; *nitroso*-derivative, liquid), which was unaffected by 10% baryta at 180°. Conversion into the nitroso-derivatives followed by treatment with warm 10% sodium hydroxide yielded the sodium salts of 2-*hydroxymethyl*cyclo*butane*-1-*carboxylic acid*, and 2-*hydroxymethyl*cyclo*pentane*-1-*carboxylic acid*, respectively, isolated as the corresponding γ-lactones.

C. W. SHOPPEE.

Crystalline anhydrides of monosubstituted malonic acids. C. MANNICH and A. BUTZ (Ber., 1929, **62**, [*B*], 456—460).—β-Benzoyl-α-phenylethylmalonic acid is converted by thionyl chloride in benzene at 70° into β-*benzoyl*-α-*phenylethylmalonic anhydride*,  $CH_2Bz{\cdot}CHPh{\cdot}CH{<}^{CO}_{CO}{>}O$, m. p. 153—154°, slowly converted by water or sodium carbonate, rapidly by sodium hydroxide, into the acid. With ethyl alcohol and ammonia respectively it affords *ethyl hydrogen* β-*benzoyl*-α-*phenylethylmalonate*, m. p. 122° (obtained also by semi-hydrolysis of the di-ester) and β-*benzoyl*-α-*phenylethylmalonamic acid*, m. p. 151° (decomp.) (*ammonium* salt). The anhydride decomposes at 175—205°/vacuum into carbon dioxide and the lactone of δ-hydroxy-βδ-diphenyl-Δ^{γ}-pentenoic acid, m. p. 88—89°, converted into methyl γ-benzoyl-β-phenylbutyrate, m. p. 94°, and γ-benzoyl-β-phenylbutyramide, m. p. 159°. Piperonylideneacetophenone and ethyl malonate afford *ethyl* β-*benzoyl*-α-*methylenedioxyphenylethylmalonate*, m. p. 94°, hydrolysed to β-*benzoyl*-α-*methylenedioxyphenylethylmalonic acid*, m. p. 159° (decomp.) (*potassium hydrogen* salt), which is transformed by thionyl chloride into β-*benzoyl-α-methylenedioxyphenylethylmalonic anhydride*, m. p. 192° (decomp.). β-*Benzoyl-α-methylenedioxyphenylethylmalonamic acid*, m. p. 145° (*ammonium* salt), and the *lactone* of δ-*hydroxy-δ-phenyl-β-methylenedioxyphenyl-Δ^{γ}-pentenoic acid*, m. p. 94°, are described. The lactone is also prepared by boiling γ-*benzoyl-β-methylenedioxyphenylbutyric acid*, m. p. 154—155°, with acetic anhydride. γ-*Benzoyl-β-methylenedioxyphenylbutyramide*, m. p. 156°, is described. β-Acetyl-α-phenylethylmalonic acid yields the corresponding *anhydride*, m. p. 129°, from which *ethyl hydrogen β-acetyl-α-phenylethylmalonate*, m. p. 106°, and the lactone of δ-hydroxy-β-phenyl-Δ^{γ}-hexenoic acid, b. p. 167°/12 mm., are derived. H. Wren.

Chlorination of phthalic acid in alkaline solution. E. E. Ayling (J.C.S., 1929, 253—256).—Chlorination of phthalic acid in alkaline solution (cf. Auerbach, Chem.-Ztg., 1880, 4, 407; see also A., 1894, i, 289; 1913, i, 269; J.C.S., 1921, **119**, 1788) proceeds most satisfactorily with 3 mols. excess of potassium hydroxide, yielding mainly 4-chlorophthalic acid together with some 4 : 5-dichlorophthalic acid. The mixed acids are readily separated by conversion into the methyl esters and fractional distillation; methyl 4-chlorophthalate, b. p. 186—187°/32 mm., m. p. 38° (cf. lit.), yields on hydrolysis 4-chlorophthalic acid, m. p. 151° (cf. von Braun, A., 1924, i, 48, m. p. 157°), converted by acetyl chloride into 4-chlorophthalic anhydride, m. p. 97°. A neutral phthalate solution reacts with chlorine but not with hypochlorite (cf. A., 1913, i, 269) and the reaction is regarded as direct chlorination of the phthalate, the excess of alkali yielding alkali chloride which assists isolation of the chlorinated products by salting out. With sodium hydroxide a much larger proportion of dichloro-acid is formed, which is attributed to the smaller solubility of potassium hydrogen 4-chlorophthalate than the sodium hydrogen salt, and is considered to support the above view of the reaction mechanism. C. W. Shoppee.

Naphthalic acid derivatives. K. Dziewoński, O. Geschwindowna, and L. Schimmer (Bull. Acad. Polonaise, 1928, **A**, 507—522).—4-Bromonaphthalic anhydride, m. p. 221—222°, with methyl sulphate and aqueous sodium hydroxide furnishes *methyl 4-bromonaphthalate*, m. p. 102—103°; when treated with hydrazine sulphate in glacial acetic acid in the presence of sodium acetate at 100° it yields *4-bromonaphthalaminoimide*,  $C_{10}H_5Br\langle{}^{CO}_{CO}\rangle N{\cdot}NH_2$, m. p. 217°; nitration with nitric acid (*d* 1·52) and sulphuric acid affords a *dinitro-4-bromonaphthalic anhydride*, m. p. 234—235°; fusion with potassium hydroxide at 225—230° yields, contrary to the literature, 3-hydroxynaphthalic anhydride, m. p. 279—280° (characterised as 4-benzeneazo-3-hydroxynaphthalic anhydride), the wandering of the hydroxyl group being explained by the initial addition of the elements of water in the 3-position, followed by substitution of the bromine in the 4-position by hydroxyl and subsequent elimination of water. Sulphonation of 4-bromonaphthalic anhydride with fuming sulphuric acid (25% SO_3) gives *4-bromo-3-sulphonaphthalic anhydride* [*sodium* salt; *barium* salt; *aniline* salt, m. p. 270°; *sulphonyl chloride* (I), m. p. 183—184°; *4-bromo-3-amidosulphonylnaphthalimide*, m. p. 338°, by the action of concentrated aqueous ammonia on I at 100°]. 4-Chloronaphthalic anhydride, m. p. 216—217°, with fuming sulphuric acid (25% SO_3) gives *4-chloro-3-sulphonaphthalic anhydride* (*sodium* salt; *barium* salt; *aniline* salt, m. p. 257°; *sulphonyl chloride*, m. p. 180—181°; *4-chloro-3-amidosulphonylnaphthalimide*, m. p. 318°). 3 : 4-Disulphonaphthalic acid (*barium* salt) is prepared by the direct sulphonation of naphthalic acid with fuming sulphuric acid (*d* 1·9) or by the action of oleum (25% SO_3) on the 3-sulphonic acid. The anhydride forms a *sodium aniline* salt, m. p. above 360°, and a *disulphonyl chloride*, m. p. 192° (decomp.), giving *3 : 4-diamidosulphonylnaphthalimide*, m. p. above 350°. The *sodium* salt of the disulphonaphthalic acid when fused with excess of potassium hydroxide at 180° furnished *3 : 4-dihydroxynaphthalic anhydride* (II), m. p. 330°, identical with the product obtained at 240—260° from 4-bromo- and at 140—180° from 4-chloro-3-sulphonaphthalic acid by fusion with potassium hydroxide. The following derivatives of II are described: *dimethyl ether*, m. p. 280°; *diacetyl* derivative, m. p. 260°; *dibenzoyl* derivative, m. p. 235—236°; *monophenylhydrazone*, m. p. 252°; *dinitro*-derivative, m. p. 272° (decomp.), by the action of nitric acid (*d* 1·48) and glacial acetic acid at 40°; *3 : 4-dihydroxynaphthalphenylimide*, m. p. 363°. A. I. Vogel.

Diphenic acid series. III. H. W. Underwood, jun., and L. A. Clough (J. Amer. Chem. Soc., 1929, **51**, 583—587).—Methyl, methyl hydrogen, ethyl, and ethyl hydrogen diphenates do not react with acetic anhydride in glacial acetic acid at 145°. Diphenamic acid is converted by this mixture into diphenimide and a little *2-cyanodiphenyl-2′-carboxylic acid*, m. p. 168°, and diphenamide into *2 : 2′-dicyanodiphenyl*, m. p. 172°. 4 : 4′-Dibromodiphenic acid, unlike the 4 : 4′-dinitro-derivative, readily forms an anhydride. This indicates that anhydride formation is connected with the *op*-directing power of the substituents. In reply to Adkins' criticisms (A., 1924, i, 1198) it is shown that condensation of diphenic anhydride and resorcinol at 135° or 175° yields a mixture of products (cf. A., 1924, i, 176). The m. p. of resorcinoldiphenein is 178—179°, changing to 247—249° on keeping or heating. H. E. F. Notton.

Derivatives of cyclobutanol. L. Blanchard (Compt. rend., 1929, **188**, 503—504).—Condensation of αγ-dibromo*iso*propyl amyl ether with ethyl disodiomalonate yields *ethyl 3-amyloxy*cyclo*butane-1 : 1-dicarboxylate*, b. p. 175°/12 mm., d^{12} 1·011, n_D 1·44361, giving by hydrolysis *3-amyloxy*cyclo*butane-1 : 1-dicarboxylic acid* (*copper* salt). The acid loses 1 mol. of carbon dioxide at 155°, yielding *3-amyloxy*cyclo*butane-1-carboxylic acid*, b. p. 164—166°/10 mm., d^{12} 1·003, n_D 1·45112 (*silver* salt). B. W. Anderson.

Syringic acid and derivatives. M. T. Bogert and B. B. Coyne (J. Amer. Chem. Soc., 1929, **51**, 569—576).—Improved preparations of trimethylgallic (3 : 4 : 5-trimethoxybenzoic) acid, syringic acid (4-hydroxy-3 : 5-dimethoxybenzoic acid; cf. A., 1919, i, 483), methyl syringate, and acetylsyringic acid (methyl ester) are described. The last is nitrated in acetic anhydride by fuming nitric acid at −5° to *nitroacetylsyringic acid*, m. p. 190° (decomp.) [*methyl* ester, m. p. 107·5° (corr.)], which is hydrolysed by boiling 5% hydrochloric acid to *nitrosyringic acid*, m. p. 218°, softening at 213°. This gives a *methyl* ester, m. p. 210°, but the preparation of the ester of m. p. 68·3° (A., 1916, i, 146) could not be repeated. Nitrosyringic acid is reduced by stannous chloride and hydrochloric acid at 45° to *aminosyringic acid*, m. p. 169° (decomp.) (*hydrochloride*, m. p. 185°; *chlorostannate*), and by tin and boiling hydrochloric acid or by ferrous hydroxide to 3-*amino*-2 : 6-*dimethoxyphenol hydrochloride*, m. p. 198° (*benzoyl* derivative, m. p. 158·3°). Methyl aminosyringate, m. p. 126·5° (hydrochloride, m. p. 217°, darkening from 192°), gives on diazotisation and treatment with cuprous oxide methyl syringate. When kept with acetic anhydride and sodium acetate, aminosyringic acid yields the *diacetyl* derivative, m. p. 169°, of aminosyringic lactam, which is hydrolysed by hot water to *acetamidoacetylsyringic acid*, m. p. 193° (methyl ester, m. p. 154°; cf. *loc. cit.*). *Methyleneaminosyringic acid*, m. p. 195° (decomp.), from aminosyringic acid and formaldehyde in dilute hydrochloric acid, could not be converted into an indigotin derivative. H. E. F. NOTTON.

6-Hydroxypiperonylic acid and allied compounds. M. T. BOGERT and F. R. ELDER (J. Amer. Chem. Soc., 1929, **51**, 532—539).—The oxime of 6-nitropiperonal (*diethylurethane*, m. p. 207—208°) has been reduced to 6-aminopiperonaloxime, m. p. 182—183° (cf. Haber, A., 1891, 704), which is converted by acetic anhydride and sodium acetate into 6-acetamidopiperylonitrile and on further action into 6-*diacetamidopiperylonitrile*, m. p. 146—147°. 6-Nitropiperonal has been converted into 6-aminopiperonal by the method of Rilliet and Kreitmann (A., 1913, i, 1355) and also by direct reduction with ferrous sulphate and ammonia. 6-Acetamidopiperonal is oxidised by neutral permanganate to 6-*acetamidopiperonylic acid*, m. p. 124—125°. The diazonium salt from methyl 6-aminopiperonylate (cf. Oertly and Pictet, A., 1910, i, 485) (*acetyl* derivative, m. p. 183—184°) is converted by boiling aqueous copper sulphate into *methyl* 6-*hydroxypiperonylate*, m. p. 99—100° (*acetyl* derivative, m. p. 97—98°), which is hydrolysed by 5% potassium hydroxide to 6-*hydroxypiperonylic acid*, m. p. 211—212° (*acetyl* derivative, m. p. 155·5—156·5°, which is prepared and purified with difficulty). H. E. F. NOTTON.

Indicators. XV. Phenolphthalein and some of its homologues. A. THIEL and L. JUNGFER (Z. anorg. Chem., 1929, **178**, 49—72; cf. this vol., 41).—Determinations have been made of the absorption maxima in the visible region of the spectrum, the extinction in the ultra-violet, and of the p_H at which the colour change and subsequent bleaching with excess of alkali takes place for phenolphthalein and some of its homologues and derivatives. The asymmetric *o*- or *m*-substituted (with respect to the central carbon atom of the side-chain) *p*-xylenolphthaleins are by far the most stable of these compounds towards alkalis. The mechanism of the bleaching action of excess of alkali on the phthaleins has been examined; the results indicate that the decolorisation is due to a splitting of the lactone ring and the entrance of a hydroxyl ion into the molecule to form a carbinolcarboxylic acid. An intermediate absorption of water into the molecule does not take place. A rise in the temperature of the solution displaces the equilibrium from the acid or from the alkaline colourless stage towards the intermediate coloured stage. The following new compounds have been prepared: *phenol*-m-*cresolphthalein* from *p*-hydroxybenzoyl-*o*-benzoic acid and *m*-cresol; m-*cresolphthalein*, m. p. 145°, from phthalyl chloride and *m*-cresol; and p-*xylenolphthalein*, m. p. 276°, from *p*-xylenol and phthalic anhydride. Condensation of *m*-cresol and phthalic anhydride with tin tetrachloride yields 2′ : 2″-*dimethylfluoran*, m. p. 206—207°, in colourless crystals. A. R. POWELL.

Synthesis of *cyclo*butane acids. I. Norpinic acid. C. A. KERR (J. Amer. Chem. Soc., 1929, **51**, 614—619).—Attempts to prepare *cyclo*butane derivatives from methylene iodide and ethyl αγ-dibromo-αββ-trimethylglutarate or ethyl ββ-dimethylpropane-ααγγ-tetracarboxylate were unsuccessful. The sodio-derivative of αγ-dicyano-ββ-dimethylglutarimide (cf. Kon and Thorpe, J.C.S., 1919, **115**, 686) is converted by methylene iodide in methyl alcohol into *dicyanonorpinimide* (1 : 3-dicyano-2 : 2-dimethyl*cyclo*butane-1 : 3-dicarboxylimide), m. p. 305—306° (*silver* salt). This is hydrolysed by acids with ring fission and by 2% sodium hydroxide to a mixture of s-*dicyanonorpinic acid* (1 : 3-dicyano-2 : 2-dimethyl*cyclo*butane-1 : 3-dicarboxylic acid), m. p. 225—226° (*methyl* ester, m. p. 139—140°), and s-*dicarbamylnorpinic acid*, m. p. 190°. This is further hydrolysed by boiling water to *ammonium dihydrogen* 1-*carbamyl*-2 : 2-*dimethyl*cyclo*butane*-1 : 3 : 3-*tricarboxylate* (free *acid* ?), and by aqueous sodium hydroxide to 2 : 2-*dimethyl*cyclo*butane*-1 : 1 : 3 : 3-*tetracarboxylic acid*, m. p. 200° (*silver* salt; *methyl* ester, b. p. 100°/25 mm.), which is also obtained from the *s*-dicyano-derivative. It is decarboxylated at 200—205° to *trans*-norpinic acid (cf. Perkin and Simonsen, J.C.S., 1909, **95**, 1176). H. E. F. NOTTON.

Synthesis of truxinic and truxillic acids. F. BACHÉR (J. pr. Chem., 1929, [ii], **120**, 301—338; cf. A., 1928, 521).—Attempts have been made, generally without success, to synthesise truxinic and truxillic acids by direct methods. Thus, attempted condensation of stilbene dibromide and ethyl dipotassioethane-ααγγ-tetracarboxylate yields stilbene; benzil and ethyl dibromosuccinate in presence of zinc afford hydrobenzoin; ethyl disodio-β-phenylpropane-ααββ-tetracarboxylate and benzylidene chloride give ethyl benzylidenemalonate. When methyl benzylidenemalonate is reduced with aluminium amalgam in methyl alcohol about 20% of the two forms of methyl βγ-diphenylbutane-ααδδ-tetracarboxylate, m. p. 163—164° and 167—168°, respectively, are obtained (cf. *loc. cit.*). The previously described (*loc. cit.*) dimethyl dihydrogen 3 : 4-diphenyl*cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate, m. p. 203—205°, after elimination of carbon dioxide at 210° affords, in addition to methyl ζ-truxinate, a small amount of methyl δ-truxinate, m. p. 75—76°. Thus, two of the three theoretically possible truxinates are obtained from the *r*-diphenylbutanetetracarboxylate. The above methyl ester, m. p. 167—168°, is not convertible into a *cyclo*butane derivative, but on hydrolysis and elimination of carbon dioxide it yields the high-melting (*meso*) form of βγ-diphenyladipic acid, thus demonstrating that the original ester is probably the *meso*-form, and that ring formation is not possible unless there is a swinging of the spatial configuration.

Addition of potassium to methyl benzylidenemalonate in toluene solution in an atmosphere of hydrogen, and decomposition of the resulting product with hydrochloric acid gives, in addition to oily products, some methyl βγ-diphenylbutane-ααδδ-tetracarboxylate, m. p. 165—167°. The intermediate potassium derivative does not appear to be identical with that derived from the ester and potassium alkoxide. Condensation of benzil with ethyl cyanoacetate in presence of a small amount of piperidine or diethylamine gives *ethyl desylidenecyanoacetate* (I), CPhBz⁚C(CN)·CO_2Et, m. p. 141° [*methyl* ester (II), m. p. 125°], also formed from benzil and ethyl bromocyanoacetate in presence of zinc and benzene. When a relatively large amount of base is used in the above condensation by-products are obtained, one of which is probably *ethyl αα′-dicyano-β-benzoyl-β-phenylglutarate*, m. p. 172°. Hydrolysis of I and II with alcoholic potassium hydroxide affords *desylidenecyanoacetic acid* (III), m. p. 135°, whilst reduction with hydrogen in presence of alcohol and palladised barium sulphate affords *ethyl* (IV) and *methyl α-cyano-β-benzoyl-β-phenylpropionates*, m. p. 83° and 118°, respectively. Similar reduction of the sodium salt of III in aqueous solution gives *α-cyano-β-benzoyl-β-phenylpropionic acid*, m. p. 190° (decomp.). When bromodeoxybenzoin is condensed with ethyl sodiocyanoacetate IV results. When IV is dissolved in piperidine or diethylamine a *substance*, m. p. 150°, having the same composition as the original ester, is obtained. The analogous *compound* from the corresponding methyl ester has m. p. 152°.

When ethyl disodioethane-ααββ-tetracarboxylate is treated with benzoyl chloride in presence of toluene *ethyl αβ-dibenzoylethane-ααββ-tetracarboxylate*, m. p. 91°, results. Attempts to reduce this compound caused elimination of the benzoyl groups. Treatment of both forms of αδ-dihydroxy-αδ-diphenylbutane with phosphorus pentabromide gives a single αδ-dibromo-αδ-diphenylbutane, m. p. 139°. This is converted by treatment with potassium iodide in acetone into the corresponding di-iodo-derivative, m. p. 140°. When an acetone solution of the dibromo-derivative is treated with zinc dust either in absence or presence of potassium iodide 1 : 2-diphenyl*cyclo*butane(?) is formed. H. BURTON.

Photochemical decomposition of benzaldehyde. A. DE HEMPTINNE.—See this vol., 409.

Colour and constitution. IV. Absorption spectra of nitrophenylhydrazones in alcohol and in alcoholic potassium hydroxide. H. H. HODGSON and K. E. COOPER (J.C.S., 1929, 231—234).—The suggestion of Chattaway and Clemo (*ibid.*, 1923, **123**, 3041), that the intense coloration developed by *p*-nitrophenylhydrazones in the presence of hydroxyl ions is due to conversion into a quinonoid ion, has been utilised to investigate the influence of a series of substituents R in the benzaldehyde nucleus on the colour of the ion. It is assumed that the greater the incipient ionisation of the molecule due to the substituent R the less will be the energy required to produce the quinonoid ion and the lower the frequency of the light absorbed by the ion. The wave-length of the head of the absorption band in alcoholic potassium hydroxide decreases through the sequence R=$NMe_3^{\oplus}$, Cl, OMe, NMe_2, Me, $O^{\ominus}$, which is also the serial order for the decreasing effect of these groups on ease of ionisation.

In absence of alkali the effect is in the order $NMe_2>OH=OMe>Cl=Me>NMe_3^{\oplus}$, the frequency absorbed increasing through the series. Minimum and maximum restraint of the electronic structure by the NMe_2 and $NMe_3^{\oplus}$ groups, respectively, is thus accompanied by absorption of minimum and maximum frequency.

The following are described: *benzaldehyde*-p-*trimethylammonium iodide*, m. p. 152°; *benzaldehyde*-p-*trimethylammonium chloride* p-*nitrophenylhydrazone*, m. p. 196°; p-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 262°. C. W. SHOPPEE.

Carbohydrates and polysaccharides. XXII. Isomeric cinnamylideneglycerols. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, **51**, 620—625).—Cinnamaldehyde and glycerol yield in presence of a little sulphuric acid at 100° a mixture of *αγ-cinnamylideneglycerol*, m. p. 121° (cf. Peacock, J.C.S., 1915, **107**, 816), and oily *αβ-cinnamylideneglycerol*. These appear to be interconvertible on keeping and are identified by the very ready hydrolysis of their *methyl ethers*, m. p. 79—80°, and b. p. 164—165°, n_D^{20} 1·5455, respectively, by boiling dilute acid to β- and α-methyl glyceryl ethers.

H. E. F. NOTTON.

Hadromal, lignin, and coniferaldehyde; preparation and identification. Higher alkali condensates of acetaldehyde. H. PAULY and K. FEUERSTEIN (Ber., 1929, **62**, [*B*], 297—311).—The main difficulty in the preparation of coniferaldehyde lies in the condensation of 3-methoxy-4-methoxymethoxybenzaldehyde with acetaldehyde (cf. Pauly and Wäscher, A., 1923, i, 342); the necessary conditions are now described in greater detail. Pure coniferaldehyde forms sulphur-yellow crystals, b. p. 157°/2·5 mm., m. p. 82·5°, $d_4^{100·5}$ 1·1562, n_α 1·63973, n_{He} 1·65635, whereas vanillin crystallises in colourless, monoclinic crystals, b. p. 131°/2·7 mm., m. p. 82·5°, $d_4^{100·1}$ 1·1772, n_α 1·56398, n_{He} 1·57294, n_β 1·59748. The differentiating behaviour of vanillin and coniferaldehyde towards a long series of reagents is described in detail. 3-Methoxy-4-methoxymethoxycinnamaldehyde is reduced in a fermenting mixture of sugar, ammonium phosphate, water, and yeast at 36° to *3-methoxy-4-methoxymethoxycinnamyl alcohol*, b. p. 166—168°/2·5 mm. (*phenylurethane*, m. p. 86°), whereas under similar conditions coniferaldehyde affords non-crystalline coniferyl alcohol (ammonium salt; *phenylurethane*, m. p. 108°). Coniferaldehyde is converted by a solution of phloroglucinol in 5*N*-hydrochloric acid into the dark carmine-red *powder*, $C_{22}H_{20}O_8$, m. p. not below 300°. With benzidine in boiling methyl alcohol, coniferaldehyde yields *di-4-hydroxy-3-methoxycinnamylidenebenzidine*, $[\cdot C_6H_4\cdot N{:}CH\cdot CH{:}CH\cdot C_6H_3(OMe)\cdot OH]_2$, m. p. 216° (*dihydrochloride*), whereas vanillin gives *di-4-hydroxy-3-methoxybenzylidenebenzidine*, m. p. 225·5° (*dihydrochloride*). A method for the detection of very small amounts of coniferaldehyde in the presence of much vanillin is based on the widely-differing solubilities of the respective benzidine derivatives in boiling benzene.

Repetition of the work of Hoffmeister (A., 1927, 1189) leads to the conclusion that hadromal does not contain even traces of coniferaldehyde, but consists mainly of vanillin mixed with wood gum, tannin (oak), pyrocatechol (pine), and minute amounts of other phenolic compounds. The m. p. after admixture with an equal quantity of vanillin is 82°, whilst with an equal amount of coniferaldehyde depressions of 20—24° are observed. The m. p. 86° recorded by Hoffmeister is higher than that of vanillin or coniferaldehyde. Further, the ability of hadromal to add 2 atoms of iodine is not shared by coniferaldehyde or its parent cinnamaldehyde. Hoffmeister's process for the synthesis of coniferaldehyde by the condensation of vanillin with acetaldehyde in the presence of sodium hydroxide gives unchanged vanillin to the extent of at least 97%. The isolation of coniferaldehyde as described would require condensation to have proceeded with at least 97% yield.

Repetition of the work of Klason (A., 1928, 277) shows that methoxymethylvanillin does not react quantitatively with acetaldehyde in dilute alkaline solution, but confirms the production of a substance with the properties and approximate composition of the supposed β-naphthylamine salt of coniferaldehydesulphonic acid. This, however, is not derived from intermediately-formed coniferaldehyde, but from two previously unknown substances formed by the autocondensation of acetaldehyde. Klason's compound cannot be derived from coniferaldehyde and aqueous sulphurous acid. Polymerisation of coniferaldehyde to Klason's "paraconiferaldehyde" does not appear to have taken place after preservation during 2 years, in the course of which vanillin is slowly produced.

The gradual addition of potassium hydroxide to an aqueous solution of acetaldehyde at 66—68° affords aldehyde resin, an *aldehyde*, $C_8H_{12}O_2$, b. p. 72—74°/14 mm., 176—178°/atmos. pressure, $d_4^{20\cdot3}$ 0·9767, n_{He}^{20} 1·4967 (*semicarbazone*, m. p. 195°), and an *aldehyde*, $C_{10}H_{14}O_2$, b. p. 116—120°/12 mm., d_4^{20} 1·035, n_{He}^{20} 1·5447 (*semicarbazone*, m. p. 133°).

H. WREN.

Organic compounds of sulphur. XII. Formation of mercaptols by the action of aliphatic diazo-compounds on disulphides. A. SCHÖNBERG, O. SCHÜTZ, and J. PETER (Ber., 1929, 62, [*B*], 440—441; cf. this vol., 316).—Diphenyl disulphide is converted by diphenyldiazomethane in boiling anhydrous benzene in an atmosphere of carbon dioxide and absence of light into diphenylthioldiphenylmethane, m. p. 138°, which decomposes at 230° with production of thiobenzophenone.

H. WREN.

Synthesis of methyl ketones from *p-tert.*-butyltoluene and *p*-cymene by the Friedel–Crafts reaction. A. LACOURT (Bull. Soc. chim. Belg., 1929, 38, 1—24).—The reaction between *p-tert.*-butyltoluene, b. p. 192—193°/760 mm., n_D^{20} 1·49187, d_{20}^{20} 0·8614, and dry, finely-powdered aluminium chloride under reduced pressure has been studied at 20—35°. The following products were isolated: *iso*butane, b. p. —11°, toluene, *tert.*-butyltoluene, a liquid, $C_{15}H_{24}$, b. p. 245—249°/760 mm., $d_{13\cdot5}^{18\cdot5}$ 0·9069, $n_D^{18\cdot5}$ 1·5164, probably 2 : 4-dibutyltoluene, a fraction b. p. 120—160°/6 mm., n_D^{17} 1·5460, not definitely identified, and a fraction b. p. 160—170°/4 mm., $n_D^{17\cdot5}$ 1·5852, which contained a considerable proportion of 2 : 4 : 5-tributyltoluene, giving by oxidation with chromic and acetic acids terephthalic acid, with alkaline permanganate at 100° a toluenetricarboxylic acid (?), m. p. about 290°, and with concentrated aqueous permanganate, pyromellitic acid. The reaction between *p*-cymene, b. p. 176·2—177·2°, n_D^{20} 1·49083, d_{20}^{20} 0·8583, and powdered aluminium chloride was similarly studied; no gas was evolved during 10 days' contact at the ordinary temperature, and after decomposition of the reaction product with ice, benzene, toluene, xylene, *p*-cymene, and di*iso*propyltoluene were isolated. These experiments explain why a homogeneous product is not always obtained in the Friedel–Crafts reaction, and it is concluded that the most favourable conditions for the elimination of secondary products are low temperature and carrying out the reaction as rapidly as possible. Equimolecular mixtures of aluminium chloride, *tert.*-butyltoluene, and acetyl chloride under the above conditions give *iso*butane, b. p. —13·5° to —10°, *p*-acetyltoluene, b. p. 97—101°/10 mm., d_{20}^{20} 0·9943, d_0^0 1·0100, n_D^{19} 1·530 (oxime, m. p. 87·5—88°); acetyl-*p-tert.*-butyltoluene, b. p. 131—134°/10 mm. (*semicarbazone*, m. p. 189·8—190°; *oxime*, m. p. 121·8—122°), and products of high b. p. which were not identified with certainty. The reaction between an equimolecular mixture of aluminium chloride, *p*-cymene, and acetyl chloride under similar conditions gives *p*-acetyltoluene, b. p. 97°/12 mm., d_0^0 1·0160, n_D^{18} 1·5350, unchanged *p*-cymene, an intermediate ketonic fraction, b. p. 126—132·5°/16 mm., n_D^{18} 1·5228, acetyl-*p*-cymene, b. p. 132·5—137·4°/16 mm., a fraction of b. p. 138—145°/16 mm., n_D^{18} 1·512, and a brown, viscous residue. The best yields of ketone, in which the by-products are reduced to a minimum, are obtained by adding an equimolecular mixture of the hydrocarbon and acetyl chloride to aluminium chloride in carbon disulphide at —10° to —15°. Pure acetyl-*p-tert.*-butyltoluene has b. p. 133·2—135°/12 mm., m. p. —1° to —3°, d_0^0 0·9757, d_{20}^{20} 0·9615, n_D^{20} 1·52071, whilst pure acetyl-*p*-cymene has b. p. 124·2—125·2°/12 mm., d_0^0 0·9864, d_{20}^{20} 0·9654, n_D^{20} 1·51849 (semicarbazone, m. p. 147°; oxime, m. p. 91—92·5°). Oxidation of the former with nitric acid (*d* 1·15) gave toluene-2 : 4-dicarboxylic acid, m. p. 332°, whilst oxidation of the latter indicated that the keto-group is *ortho* to methyl.

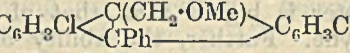
A. I. VOGEL.

Interpretation of rearrangements of pinacols and tertiary amino-alcohols from the electron theory of valency. M. MIGITA (Bull. Chem. Soc. Japan, 1928, **3**, 308—316).—An electronic interpretation of the rearrangement of pinacols to ketones is offered. Since the change does not take place in neutral or alkaline solution it is assumed that the acid behaves both as a catalyst and a dehydrating agent. The order of " electro-negativity " of the groups which determines their wandering is taken as $\alpha C_{10}H_7 > p\text{-}MeO\cdot C_6H_4 > o,p\text{-}MeC_6H_4 > Ph > Me > Et,Pr > CH_2Ph$ (Kharasch and Marker, A., 1927, 165). A similar interpretation is given of the semipinacolinic deamination of tertiary amino-alcohols such as γ-amino-βγ-diphenyl*iso*propyl alcohol, and of the normal displacement of the amino-group in γ-amino-ααγ-triphenylpropyl alcohol. The behaviour of γ-amino-αγ-diphenyl-β-benzyl*iso*propyl alcohol towards nitrous acid is not in harmony with the electronic interpretation. A. I. VOGEL.

Relative affinity capacities of various radicals in the transformation of trisubstituted ethylene oxides. (MLLE.) J. LÉVY and A. TABART (Compt. rend., 1929, **188**, 402—404; cf. A., 1926, 383, 818).—In addition to previous results the following transformations of ethylene oxides by heat are recorded; no experimental details are given. α-Phenyl-β-ethyl-Δ^{α}-butylene oxide gives α-phenyl-α-ethylbutaldehyde and α-phenyl-*n*-propyl ethyl ketone; α-phenyl-β-methyl-Δ^{α}-butylene oxide gives α-phenyl-α-methylbutaldehyde and α-phenyl-*n*-propyl methyl ketone (migration of an ethyl group); α-phenyl-β-methyl-Δ^{α}-*n*-amylene oxide gives α-phenyl-α-methylvaleraldehyde and α-phenylethyl *n*-propyl ketone (migration of a methyl group); α-phenyl-β-benzyl-Δ^{α}-propylene oxide, αβ-diphenylethyl methyl ketone; α-phenyl-β-benzyl-Δ^{α}-*n*-butylene oxide, αβ-diphenylethyl ethyl ketone; α-phenyl-β-benzyl-Δ^{α}-*n*-amylene oxide, αβ-diphenylethyl *n*-propyl ketone. In the three last examples the migration of a benzyl group is involved. G. A. C. GOUGH.

Additive properties of diacetylenic hydrocarbons. V. GRIGNARD and TCHÉOUFAKI (Compt. rend., 1929, **188**, 527—530).—When an aqueous-alcoholic solution of $\Delta^{\alpha\gamma}$-αδ-di-4-*m*-xylylbutadi-inene is agitated with oxygen, 4-m-*xylyl* 4-m-*xylylmethylacetylenyl ketone*, m. p. 125°, is formed, which yields an ozonide decomposing in carbon tetrachloride solution to give in turn 4-*m*-xylylacetic acid, m. p. 106°, and 4-m-*xylylglyoxylic acid*, m. p. 75° ($+H_2O$, m. p. 53—54°) (*sodium hydrogen sulphite* compound described). It is suggested that αδ-addition precedes the formation of the above ketone. Agitation of $\Delta^{\delta\zeta}$-decadi-inene with a 40% acetic acid solution of concentrated sulphuric acid yields *deca*-δζ-*dione*, m. p. 147°. Tetradeca-$\Delta^{\epsilon\eta}$-di-inene yields similarly *tetradeca*-ζθ-*dione*, m. p. 237°, which affords the additive *compound*, $C_{16}H_{14}Hg_2Cl_4$.
G. A. C. GOUGH.

Is 2 : 3-diphenylindone resolvable into optically active antipodes? J. MEISENHEIMER and W. THEILACKER (Annalen, 1929, **469**, 26—30).—The authors have been unable to repeat Schlenk, Bergmann, and Müller's resolution of 2 : 3-diphenylindone (A., 1928, 1035). The small rotation observed by these authors is probably due to impurity. *N*-Diphenylindenylidenebornylamide has m. p. 126°, $[\alpha]_D^{15}$ +232° in chloroform (cf. *loc. cit.*). H. BURTON.

***ms*-Alkylanthracenes and "transannular tautomerism."** V. E. DE B. BARNETT and N. F. GOODWAY (Ber., 1929, **62**, [*B*], 423—431; cf. A., 1927, 140; 1928, 52).—1 : 5-Dichloro-9-bromo-9-phenylanthrone is converted by methyl or ethyl alcohol in presence of calcium carbonate into 1 : 5-*dichloro*-9-*methoxy*-9-*phenylanthrone*, m. p. 213°, or 1 : 5-*dichloro*-9-*ethoxy*-9-*phenylanthrone*, m. p. 150°. With magnesium methyl iodide the methoxy-compound affords 1 : 5-*dichloro*-9-*hydroxy*-10-*methoxy*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 215°, converted by boiling methyl alcohol containing hydrochloric acid into a colourless *substance*, $(C_{22}H_{18}O_2Cl_2)_2,MeOH$, m. p. 191° (also $+CH_3\cdot CO\cdot CH_3$). 1 : 5-*Dichloro*-9-*hydroxy*-10-*ethoxy*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 205°, is described. Treatment of the methoxy-compound with methyl alcohol and hydrochloric acid at 100° or of the methoxy- or ethoxy-derivative with boiling ethyl alcohol and hydrochloric acid affords respectively 1 : 5-*dichloro*-10-*phenyl*-9-*methoxymethylanthracene*,  $C_6H_3Cl<\begin{matrix}C(CH_2\cdot OMe)\\CPh\end{matrix}>C_6H_3Cl$, m. p. 154°, and 1 : 5-*dichloro*-10-*phenyl*-9-*ethoxymethylanthracene*, m. p. 124°. The possibility of transannular migration of alkoxy-groups is thus established.

1 : 5-Dichloro-9-bromoanthrone is converted by benzyl alcohol in the presence of calcium carbonate into 1 : 5-*dichloro*-9-*benzyloxyanthrone*, m. p. 157°; 1 : 5-*dichloro*-9-*benzyloxymethylanthracene*, m. p. 118°, is prepared similarly from 1 : 5-dichloro-9-bromomethylanthracene. Treatment of 1 : 5-dichloro-9-ethoxy-(or benzyloxy-)anthrone with ethereal magnesium benzyl chloride causes de-alkylation and the oils thus produced when dissolved in glacial acetic acid and treated with concentrated hydrochloric acid at the ordinary temperature yield 1 : 5 : 10-*trichloro*-9-*hydroxy*-9-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 135° (decomp.), identified by conversion into 1 : 5-*dichloro*-9-*hydroxy*-10-*piperidino*-9-*benzyl*-9 : 10-*dihydroanthracene* (+1MeOH or $1CH_3\cdot CO\cdot CH_3$), m. p. 169°, also prepared from 1 : 5-dichloro-9-piperidinoanthrone and magnesium benzyl chloride. (In a single instance, 1 : 5-dichloro-9-ethoxyanthrone was converted into a colourless *substance*, m. p. 144°, probably 1 : 5-*dichloro*-10-*ethoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene* but differing from the product derived from ethyl alcohol, calcium carbonate, and dichlorobromobenzylanthracene.) Magnesium methyl iodide and 1 : 5-dichloro-9-benzyloxyanthrone yield 1 : 5-dichloroanthrone. The trichloro-compound (see above) is transformed by methyl alcohol in the presence of calcium carbonate into 1 : 5-*dichloro*-9-*hydroxy*-10-*methoxy*-9-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 144°, and by aqueous acetone and calcium carbonate into 1 : 5-*dichloro*-9-*benzyl*-9 : 10-*dihydroanthraquinol*, m. p. 172°. 1 : 5-*Dichloro*-10-*piperidino*-9-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 194°, is described.
H. WREN.

Tautomerism of α-diketones. Two tautomeric forms of phenylbenzylglyoxal and phenyl-

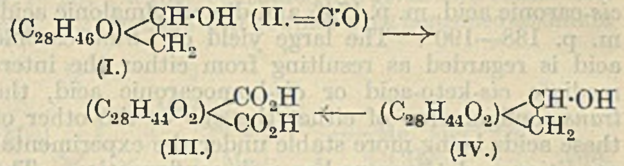
anisylglyoxal. H. Moureu (Compt. rend., 1929, 188, 504—506).—The form of phenylanisylglyoxal, m. p. 70° ($A\alpha$), when heated slowly above its m. p. recrystallises as its *isomeride*, m. p. 82° ($A\beta$). These keto–enolic A forms are transformed by distillation under pressures of about 1 mm. into a true ketonic *isomeride*, m. p. 23—24° (B), extracted from the resultant liquid by crystallisation at low temperature. The corresponding A forms of phenylbenzylglyoxal (cf. A., 1928, 180) are similarly transformed into a B-*isomeride*, m. p. 35—36°. The action of heat partly changes the B forms into the A forms. These transformations are markedly affected by alkaline catalysts (*e.g.*, ordinary glass). B. W. Anderson.

Structure of dihydroxybenzanthrone obtained from the condensation of alizarin with glycerol and sulphuric acid (G.P. 187,495). J. Turski and J. Grynwasser (Rocz. Chem., 1929, 9, 78—82).—2 : 3-*Dihydroxyphenyl* α-*naphthyl ketone*, m. p. 118° (*diacetyl* derivative, m. p. 135°), prepared by the action of α-naphthoyl chloride on pyrocatechol, yields when fused with aluminium chloride 5 : 6-dihydroxydihydro-1 : 9-benzanthrone, which on oxidation gives 5 : 6-*dihydroxy*-1 : 9-*benzanthrone*, m. p. 185° (*diacetyl* derivative, m. p. 109°). *Phenyl* 2 : 3-*dihydroxy*-α-*naphthyl ketone*, m. p. 179°, prepared by the Friedel–Crafts reaction from dihydroxynaphthalene and benzoyl chloride, is in a similar way to the above converted into 3 : 4-*dihydroxy*-1 : 9-*benzanthrone*, m. p. 285°. If Scholl's reaction is substituted for that of Friedel and Crafts in the above condensation, the product is 2 : 3-*dibenzoyloxynaphthalene*, m. p. 235°, which can be further condensed to Bz-2 : 3-*dihydroxy*-1 : 9-*benzanthrone*, m. p. 192° (*dibenzoyl* derivative, decomp. 320°). A comparison of these benzanthrones with the product obtained by the method described in G.P. 187,495 shows that the latter is 5 : 6-dihydroxy-1 : 9-benzanthrone. R. Truszkowski.

Manufacture of anthraquinone derivatives [1-*o*-carboxyphenylanthraquinone]. I. G. Farbenind. A.-G.—See B., 1929, 164.

Manufacture of aminated sulphur-containing benzanthrone derivatives. I. G. Farbenind. A.-G.—See B., 1929, 164.

Phytochemistry. V. *allo*Betulin. O. Dischendorfer and O. Polak (Monatsh., 1929, 51, 43—58; cf. A., 1927, 249).—Oxidation of *allo*betulin formate with chromic and acetic acids yields directly crystalline *oxy*allo*betulin formate*, m. p. 347—348° (decomp.), $[\alpha]_D^{18}$ +57·6° in chloroform. Similarly, *allo*betulin acetate is oxidised either by chromic acid (cf. Schulze and Pieroh, A., 1922, i, 1045) or nitric acid (*d* 1·52) at −5° to oxy*allo*betulin acetate, $[\alpha]_D^{18}$ +63° in chloroform. Oxy*allo*betulin, m. p. 360° (decomp.), $[\alpha]_D^{18}$ +47° in pyridine, is obtained by hydrolysis of either ester and has the composition $C_{30}H_{48}O_3$ and not that assigned by Schulze and Pieroh (*loc. cit.*). Oxidation of *allo*betulin (I) with a mixture of nitric acid (*d* 1·52) and acetic acid at 0° yields the dibasic *oxy*allo*betulinic acid* (III), m. p. 283—284° (decomp.), $[\alpha]_D^{18}$ +57° in pyridine (*dimethyl* ester, m. p. 230—231°, $[\alpha]_D^{18}$ +48·7°; *diethyl* ester, m. p. 191—193°, $[\alpha]_D^{18}$ +53°). The same acid is obtained by oxidation of *allo*betulone (II), m. p. 239—241° (Schultze and Pieroh, *loc. cit.*, give 230—231°), with nitric acid (*d* 1·52) at −5°, or of oxy*allo*betulin (IV) with nitric (*d* 1·50) and acetic acids at −5°. These reactions are represented by the partial formulæ,



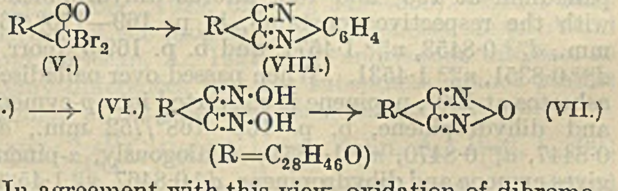
$$(C_{28}H_{46}O){<}\begin{matrix}CH{\cdot}OH\\ CH_2\end{matrix}\ (II.=C{:}O)\longrightarrow$$

(I.)

$$(C_{28}H_{44}O_2){<}\begin{matrix}CO_2H\\ CO_2H\end{matrix}\longleftarrow(C_{28}H_{44}O_2){<}\begin{matrix}CH{\cdot}OH\\ CH_2\end{matrix}$$

(III.) (IV.)

two hydrogen atoms in the C_{28} residue in I and II being replaced by oxygen. The acid III when heated with acetic anhydride yields an *anhydride*, m. p. 290—292° (decomp.), $[\alpha]_D^{18}$ +86° in pyridine, and by distillation in an atmosphere of carbon dioxide above 300° yields a *ketone*, $C_{29}H_{44}O_3$, m. p. 340—342° (decomp.), $[\alpha]_D^{18}$ +153·5° in pyridine [*oxime*, m. p. 304—306° (decomp.)]. The acid III is therefore most probably an azelaic acid and the ring which is opened in its formation a six-membered one (less probably a seven- or an eight-membered ring). Since this ketone is unchanged by treatment with nitric acid under normal oxidation conditions it is improbable that there is another methylene group next to the $-CO{\cdot}CH_2-$ grouping in *allo*betulone. Reduction of the latter by Clemmensen's method gives a *substance*, $C_{30}H_{50}O$, m. p. 232—233°, $[\alpha]_D^{18}$ +45°, in which the carbonyl group has been reduced to a methylene group. The action of less concentrated nitric acid on *allo*betulone (above) yields a *substance*, $C_{30}H_{44}O_7N_2$, m. p. 223—224° (decomp.), which is probably dinitro-oxy*allo*betulone. Dibromo*allo*betulone (V) (Dischendorfer and Grillmayer, A., 1927, 59) on prolonged heating with hydroxylamine yields a bromine-free *dioxime* (VI), m. p. 194—196° (decomp.), $[\alpha]_D^{18}$ +77·7° in pyridine, which is oxidised by sodium nitrite in acetic acid to the *furoxan* (VII), m. p. 258—261° (decomp.), and condenses with *o*-phenylenediamine to yield a *phenazine* (VIII), m. p. 269—273° (decomp.). Hence (V) is an αα'-dibromo-compound.



$$R{<}\begin{matrix}CO\\ CBr_2\end{matrix}\longrightarrow R{<}\begin{matrix}C{:}N\\ C{:}N\end{matrix}{>}C_6H_4$$

(V.) (VIII.)

$$(V.)\longrightarrow(VI.)\ R{<}\begin{matrix}C{:}N{\cdot}OH\\ C{:}N{\cdot}OH\end{matrix}\longrightarrow R{<}\begin{matrix}C{:}N\\ C{:}N\end{matrix}{>}O\quad(VII.)$$

$$(R=C_{28}H_{46}O)$$

In agreement with this view, oxidation of dibromo*allo*betulone with nitric (*d* 1·52) and acetic acids at −5° yields, not a brominated oxy*allo*betulinic acid, but αα'-*dibromo-oxy*allo*betulone*, $C_{30}H_{44}O_3Br_2$, m. p. 300—310° (decomp.). J. W. Baker.

Indian turpentine from *Pinus longifolia*, Roxb. V. Oxidation of *d*-Δ³-carene with Beckmann's chromic acid mixture. C. S. Gibson and J. L. Simonsen (J.C.S., 1929, 305—311).—Treatment of *d*-Δ³-carene (1 part) with Beckmann's reagent (20 parts; cf. Henry and Paget, A., 1928, 295) afforded *l*-*trans*-caronic acid, m. p. 201—202°, $[\alpha]_{5461}^{20}$ −12·3° in alcohol (the optical purity could not be increased by crystallising the strychnine salt; compare Ruzicka and Staudinger, A., 1924, i, 510), and terpenylic acid, m. p. 57°, rising after dehydration over sulphuric acid to 90° (ethyl ester, m. p. 37—38°), in relatively large yield, together with small quantities of *d*-homoterpenyl methyl ketone, m. p. 42—43°, $[\alpha]_{5461}^{20}$ +55·7° in water [*semicarbazone*, m. p. 195—196° (decomp.), $[\alpha]_{5461}^{20}$ +49·9° in alcohol], terebic acid, m. p. 173—174°, *cis*-caronic acid, m. p. 174°, and dimethylmalonic acid, m. p. 188—190°. The large yield of *l*-*trans*-caronic acid is regarded as resulting from either the intermediate *cis*-keto-acid or *cis*-homocaronic acid, the *trans*-configuration of either the one or the other of these acids being more stable under the experimental conditions; *d*-Δ^3-carene has a *cis*-configuration. The isolation of *d*-homoterpenyl methyl ketone confirms the constitution of the hydrocarbon and eliminates the possibility of the ethylenic group occupying the Δ^2-position. When *d*-Δ^3-carene (10 parts), acetic acid (25 parts), and 50% sulphuric acid (1 part) are heated together at 60°, the main product is a *diterpene*, $C_{20}H_{32}$, b. p. 175°/10 mm., d_{30}^{30} 0·9309, n_D^{30} 1·5168, $[\alpha]_{5461}^{20}$ +5·69°; a small quantity of a monocyclic terpene, b. p. 174—176°/755 mm., d_{20}^{20} 0·8500, n_D^{20} 1·4750, $[\alpha]_{5461}^{20}$ −6·5° (hydrochloride, b. p. about 115°/15 mm.), together with a trace of *l*-borneol, m. p. 204—205°, $[\alpha]_{5461}^{20}$ −26·9° (*p*-nitrobenzoyl derivative, m. p. 136—137°), the latter being probably due to the presence of a little pinene or camphene in the *d*-Δ^3-carene, are also formed.

A. I. Vogel.

Irreversible catalysis of unsaturated cyclic hydrocarbons. VI. Contact transformations of nopinene, terpinene, and terpinolene. N. D. Zelinski and R. J. Levina (Ber., 1929, 62, [*B*], 339—343; cf. A., 1927, 670).—Nopinene, b. p. 163·5—165·5°/742 mm., $n_D^{20.5}$ 1·4766, is hydrogenated in the presence of palladised charcoal at 170—175° to dihydronopinene, b. p. 167—167·5°/737 mm., d_4^{20} 0·8521, n_D^{16} 1·4628, the hydrocarbon thus yielding a single product in contrast with pinene. The latter compound in presence of nickel at 155—158° gives dihydro-α-pinene, b. p. 168·5°/748 mm., d_4^{20} 0·8392, n_D^{20} 1·4541, whereas hydrogenation in presence of palladium at 195° and 158° affords dihydropinenes with the respective constants, b. p. 169—170°/768 mm., $d_4^{18.5}$ 0·8453, $n_D^{18.5}$ 1·4577, and b. p. 169·5° (corr.), $d_4^{19.5}$ 0·8351, $n_D^{18.5}$ 1·4531. When passed over palladised asbestos at 190°, nopinene is converted into *p*-cymene and dihydropinene, b. p. 166—168°/752 mm., d_4^{21} 0·8447, d_4^{18} 0·8470, n_D^{21} 1·4554; analogously, α-pinene gives cymene and dihydropinene, d_4^{18} 0·8467, n_D^{18} 1·4589. It is probable, therefore, that nopinene is initially isomerised to α-pinene. Terpinene, b. p. 178·5—180·5°/740 mm., 65·5—68°/14 mm., d_4^{20} 0·855, n_D^{21} 1·4783, is converted in presence of palladised asbestos at 190° into *p*-cymene and menthane, b. p. 168·5—169·5°/745 mm., $n_D^{16.5}$ 1·4452, whilst the same products are similarly derived from terpinolene, b. p. 75°/14 mm., d_4^{20} 0·8628, n_D^{21} 1·4802, at 160—170°/40 mm. The differing positions of the two double linkings, within or outside the nucleus, in monocyclic terpene hydrocarbons appear without influence on the final products of their contact transformations.

Palladised charcoal may be used in place of palladised asbestos in contact transformations, but the former adsorbs an appreciable proportion of the molecules and protects them from contact with the active surface of the catalyst, thus rendering repeated treatment necessary.

H. Wren.

Individuality of humulene. A. C. Chapman (J.C.S., 1929, 359—360; cf. A., 1928, 646).—A reply to Deussen (A., 1928, 1378). The author maintains that clove oil and also hop oil contain " humulene," a hydrocarbon which is not identical with caryophyllene, although the two hydrocarbons are closely related and may undergo intramolecular change in certain reactions, the one being transformed into the other.

A. I. Vogel.

Sylvestrenes and carenes. J. L. Kondakov (Perfumerie Mod., 1927, 3—15).—A polemical discussion (mainly against W. H. Perkin and Wallach) of the generic relationships of these terpenes.

J. W. Baker.

Syntheses and degradations in tetrahydrodiphenylene oxide series. F. Ebel (Helv. Chim. Acta, 1929, 12, 3—16).—Chlorination of *cyclo*hexanol in presence of water and calcium carbonate affords 2-chloro*cyclo*hexanone, b. p. 84—85°, which reacts with sodium phenoxide in light petroleum, yielding *cyclo*hexanolone phenyl-lactolide, m. p. 64·5° (osazone, m. p. 152—153°) (cf. Kötz and others, A., 1913, i, 1201). When the reaction is carried out in phenol at 120°, 50% of the theoretical yield of 1 : 2 : 3 : 4-tetrahydrodiphenylene oxide (I) (cf. Hönigschmid, A., 1901, i, 700) is obtained. Nitration of I by a 33% solution of concentrated nitric acid in acetic acid gives a *mononitro*-derivative, m. p. 120·5°. Hydrogenation of I with hydrogen and a platinum–palladium catalyst affords a hexahydrodiphenylene oxide, b. p. 137°/10 mm., identical with that described by von Braun (A., 1923, i, 103), whilst dehydrogenation with sulphur at 200—260° yields diphenylene oxide. When a solution of I in carbon tetrachloride containing small amounts of acetic acid and bromine is treated with ozone, δ-salicoylvaleric acid is obtained, demonstrating that I is definitely the 1 : 2 : 3 : 4-tetrahydro-derivative. δ-*Salicoylvalerolactone peroxide* has m. p. 191° (decomp.). δ-3 : 5-*Dibromosalicoylvaleric acid*, m. p. 128·4°, is oxidised by hot nitric acid, yielding adipic acid, and by bromine water at 90° giving an acid, m. p. 88—89°, and a substance, m. p. 175—180°, both containing bromine.

2-Chloro*cyclo*hexanone and sodium *o*-methoxyphenoxide react in toluene giving cyclo*hexanolone* o-*methoxyphenyl-lactolide*, m. p. 67·5° [*osazone*(?), m. p. 159°], which when treated with concentrated sulphuric acid in the cold affords 8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrodiphenylene oxide*, m. p. 39·5°. With sodium β-naphthoxide cyclo*hexanolone* β-*naphthyl-lactolide*, m. p. 135°, is produced; this yields *tetrahydrophenylenenaphthylene oxide*, m. p. 60° (*picrate*, m. p. 145°).

H. Burton.

Furan compounds derived from sugars. II. Acetyl derivative of hydroxymethylfurfuraldehyde. J. Karashima (Z. physiol. Chem., 1929, 180, 241—248).—Acetylation of ω-hydroxymethylfurfuraldehyde with acetic anhydride in presence of anhydrous sodium acetate gives the corresponding acetyl derivative (I) (Fenton and Gostling, J.C.S., 1901, 79, 807), which is oxidised by copper, silver, and mercuric oxides to hydroxymethylpyromucic acid, and by alkaline potassium permanganate to muconic and oxalic acids. Condensation of I with acetic anhydride and sodium acetate at 160—170° gives *acetoxyfurfurylideneacetic acid*, m. p. 134°, hydrolysed by barium hydroxide solution to *hydroxyfurfurylideneacetic acid*, m. p. 139°. Administration of I to the dog, rabbit, or hen leads to the excretion in the urine of considerable amounts (49·7—73·3%) of hydroxymethylpyromucic acid (cf. A., 1927, 1107).

H. BURTON.

α[3]-Phenylcoumarins. G. BARGELLINI and (SIGNA.) L. MONTI (Atti R. Accad. Lincei, 1928, [vi], 8, 395—399; cf. A., 1927, 883).—3-p-*Anisylcoumarin*, prepared by the condensation of salicylaldehyde and sodium *p*-methoxyphenylacetate in presence of acetic anhydride, has m. p. 142—144°; 3-(3′ : 4′-*methylenedioxyphenyl*)*coumarin*, m. p. 170—172°, is obtained similarly from methylenedioxyphenylacetic acid. 7-*Hydroxy*-3-(3′ : 4′-*methylenedioxy*)*phenylcoumarin*, m. p. 238—239°, obtained as *acetyl* derivative, m. p. 191—192°, from resorcylaldehyde and methylenedioxyphenylacetic acid, forms a *methyl ether*, m. p. 195—196°. 5 : 7-*Dihydroxy*-3-(3′ : 4′-*methylenedioxy*)-*phenylcoumarin*, decomp. from 260°, obtained as *diacetyl* derivative, m. p. 198—199°, from phloroglucinaldehyde and methylenedioxyphenylacetic acid, forms a *methyl ether*, m. p. about 170°.

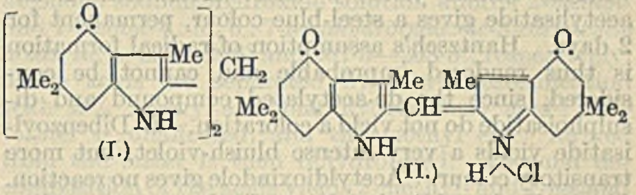
T. H. POPE.

Grape pigments. II. Anthocyans in Clinton grapes. R. J. ANDERSON and F. P. NABENHAUER. **III. Anthocyans in Seibel grapes.** R. J. ANDERSON (N.Y. Agric. Exp. Sta., Tech. Bull. 146, July, 1928, 21 pp.).—See A., 1924, i, 1152, 1390.

Derivatives of 4 : 5 : 6 : 7-tetrahydroindole. I. C. D. NENITZESCU. **II. Derivatives of 4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole.** C. D. NENITZESCU and V. SCORTZEANU. **III. Polynuclear derivatives of 4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole.** C. D. NENITZESCU (Bul. Soc. Chim. România, 1928, 10, 131—133, 134—140, 141—148).—I. Ethyl sodioacetoacetate and 2-bromo*cyclo*hexanone condense in alcoholic solution to yield a product containing *ethyl* cyclo*hexanonylacetoacetate*, which is converted into *ethyl 2-methyl-4 : 5 : 6 : 7-tetrahydroindole-3-carboxylate*, m. p. 132°, when treated with ammonium acetate in boiling glacial acetic acid.

II. Condensation of ethyl α-aminoacetoacetate and *cyclo*hexane-1 : 3-dione furnishes *ethyl 4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole-2-carboxylate*, m. p. 171°, oxidised by warm nitric acid (*d* 1·40) to an alkali-soluble *substance*, $C_{13}H_{17}O_8N_3$, m. p. 193° (decomp.), and hydrolysed by aqueous-alcoholic potassium hydroxide to *4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole-2-carboxylic acid*. The latter melts at 253°, giving carbon dioxide and *4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole*, m. p. 162°. When the above indolecarboxylic ester is treated with bromine in glacial acetic acid or in chloroform, an orange-red *compound*, $[C_{14}H_{19}O_3N,Br_{2\cdot5}]$, m. p. 132°, is obtained which loses bromine in a vacuum or in aqueous solution to regenerate the parent ester; in boiling glacial acetic acid, the compound gives hydrogen bromide and a *compound*, m. p. 202° (decomp.), whilst in boiling alcoholic solution a second colourless *compound*, m. p. 208°, is obtained.

III. 4-Keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole and formaldehyde afford *bis-(4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindyl)methane* (I), m. p. 267°, whilst benzaldehyde gives two *substances*, m. p. 172° and 254°; it couples with benzenediazonium chloride, giving *2-benzeneazo-4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole*, m. p. 224° (decomp.). The substance I could not be converted into II by treatment with formic acid in the presence of hydrochloric or perchloric acid. 4-Keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole condensed with ethyl orthoformate yields *tri-(4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindyl)methane*, m. p. 284°, readily converted by dissolution in hydrochloric acid (*d* 1·19) into *2-(4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindyl)-2-(4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindolenyl)methene hydrochloride* (II), m. p. 264°. To investigate the effect of the 4-keto-group on the ease of conversion of the pyrrole form into the pyrrolene form (occurring in II), 4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole was converted by hydrazine followed by sodium methoxide at 150—160° into *3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole*, m. p. 63° [*picrate*, m. p. 140° (decomp.)]; owing to the ease with which this substance oxidises, attempts to obtain a product by condensation with formic acid gave inconclusive results. In the Wolff–Kishner process described above, the *azine* of *4-keto-3 : 6 : 6-trimethyl-4 : 5 : 6 : 7-tetrahydroindole*, m. p. above 300°, was also obtained.



(I.) (II.)

C. W. SHOPPEE.

Isatide or isatinpinacol. G. HELLER and H. LAUTH (Ber., 1929, 62, [*B*], 343—350).—Exact comparison of the properties of disulphoisatide (cf. Wahl and Féricéan, A., 1927, 470) and isatide discloses so many differences that the substances cannot possess similar structures and hence the constitution $\left|NH<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}>C(OH)\cdot\right]_2$ (cf. Kohn, A., 1912, i, 800; 1916, i, 607; Hantzsch, A., 1921, i, 598) cannot be ascribed to isatide. The constitution $C_6H_4<\begin{smallmatrix}CO\\NH\end{smallmatrix}>CO$ — + $C_6H_4<\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}>C\cdot OH$ or $NH<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}>CO<\begin{smallmatrix}OH\cdot C\cdot C_6H_4\\OH\cdot C-NH\end{smallmatrix}$ is suggested. During acetylation of isatide, a transformation into the pinacol form probably occurs and the compound is therefore regarded with some reserve as tetra-acetylisatinpinacol.

Tetra-acetylisatinpinacol (tetra-acetylisatide) is converted by glacial acetic and hydrochloric acids at 50—60° or by phenylhydrazine (together with isatinphenylhydrazone) into *diacetylisatinpinacol*, m. p. about 317° after darkening at 280°. Complete de-acetylation of the diacetyl compound is effected by 85—90% sulphuric acid, acetic acid, and hydrochloric acid or, preferably, acetic and phosphoric acids at 125°, but the product, decomp. about 265—270°, is not homogeneous, and, when re-acetylated, gives the tetra-acetyl compound in moderate yield. Isatide and 90% sulphuric acid appear also to yield isatinpinacol. Dioxindole does not become coloured by pyridine–barium hydroxide in the absence of oxygen, whereas isatide yields a violet coloration. *N*-Diacetylisatide gives a steel-blue colour, permanent for 2 days. Hantzsch's assumption of radical formation is thus rendered improbable and cannot be considered, since the de-acetylated compound and disulphoisatide do not yield a coloration. *N*-Dibenzoylisatide yields a very intense bluish-violet, but more transitory colour. Acetyldioxindole gives no reaction. Since *N*-phenyldioxindole and the corresponding isatide give a similar blue colour with alkali, it is probable that the action is due to the –NH·C(OH):C(OH)– group. Prolonged treatment of *N*-benzoylisatin or *N*-dibenzoylisatide with phenylhydrazine yields "iso-N-*benzoylisatinosazone*," $C_{27}H_{21}ON_5$, pale yellow crystals, m. p. 211—212°, converted by bromine in hot, glacial acetic acid into a *substance*, m. p. 266°. Similarly, *N*-acetylisatin and *N*-diacetylisatide afford "iso-N-*acetylisatinosazone*," m. p. about 130° (also $+1COMe_2$); if the duration of the action is curtailed *N*-acetylisatin-3-phenylhydrazone can be isolated.

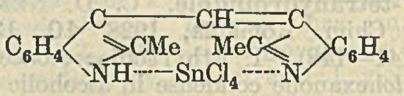
o-Benzoyldioxindole, m. p. 134°, is prepared by converting dioxindole by means of alcoholic potassium hydroxide into its potassium salt, which is treated with benzoyl chloride. *O*-Acetyldioxindole, m. p. 127°, is obtained similarly or from dioxindole and a slight excess of acetic anhydride in presence of a little concentrated sulphuric acid. The attachment of the acyl groups to the oxygen is established by the conversion of both substances into isatin-3-phenylhydrazone.

H. WREN.

N-Arylisatins and isomeric acridinemesocarboxylic acids. J. MARTINET and A. DANSETTE (Bull. Soc. chim., 1929, [iv], 45, 101—109).—When *N*-phenyl-β-naphthylamine and ethyl mesoxalate are fused at 150°, or when the acetic acid solution of the mixture is boiled, there is formed *ethyl* 1-*phenyl*-4 : 5-*benzodioxindole*-3-*carboxylate*, m. p. 171° (? 181°) [*ethyl* 1-*hydroxy*-2-*keto*-3-*phenyl*-1 : 2-*dihydro*-β-*naphthindole*-1-*carboxylate*] (*acetyl* derivative, m. p. 177°) converted by potassium hydroxide in the absence of air into 1-*hydroxy*-2-*keto*-3-*phenyl*-1 : 2-*dihydro*-β-*naphthindole*, m. p. 95—102° (*acetyl* derivative, m. p. 150°), by 2% sodium or potassium hydroxide in 15 min. into 1-phenyl-β-naphthoisatin (1 : 2-diketo-3-phenyl-1 : 2-dihydro-β-naphthindole) (Stollé, A., 1923, i, 1125), m. p. 227° (*phenylhydrazone*, m. p. 195°), and by 10% potassium hydroxide into β-*naphthacridine*-12-*carboxylic acid*, m. p. above 300° (decomp.) (*potassium*, *copper*, *barium*, and *lead* salts), yielding naphthacridine, m. p. 131° (Ullmann and Baezner, A., 1902, i, 694), when distilled alone or with soda-lime. The isatin and naphthacridinecarboxylic acid are obtained in yields of 96—97%, 2-anilinonaphthalene-1-glyoxylic acid being probably an intermediate stage (cf. Friedländer and Kunz, A., 1922, i, 765; Stollé, *loc. cit.*), since *potassium* 2-*anilinonaphthalene*-1-*glyoxylate* ($+3H_2O$) is obtained by the action of 30% potassium hydroxide on 1-phenyl-β-naphthoisatin. Reduction with sodium hyposulphite in alcohol converts the isatin into the above hydroxy-compound, m. p. 95—102°, the acetyl derivative being obtained (yield 65—94%) by reduction in presence of acetic anhydride.

R. BRIGHTMAN.

Subsidiary valency forces of indole nitrogen. O. SCHMITZ-DUMONT and E. MOTZKUS (Ber., 1929, 62, [*B*], 466—473; cf. this vol., 328).—Indole differs from pyrrole in its behaviour towards stannic chloride, since it yields a normal additive *compound*, $(C_8H_7N)_2,SnCl_4$, m. p. 153° (decomp.) after softening at 133°, from which the indole may be almost quantitatively regenerated; the product is coloured blue by the presence of an impurity which can be removed by treatment with nitrobenzene. Indole does not yield a stable compound with stannic bromide, but with titanium tetrachloride and aluminium bromide gives the *substances* $(C_8H_7N)_2,TiCl_4$ and $C_8H_7N,AlBr_3$, m. p. 140° after darkening at 130°. The dark violet colour of the titanium product is attributed to the particular valency of the metal in the compound; a reduction to the tervalent stage does not enter into the question. Polymerisation enhances the additive capacity of indole nitrogen, since tri-indole gives the *compounds* $(C_8H_7N)_3,SnCl_4$, m. p. 166—168°, $2(C_8H_7N)_3,SnCl_4$, m. p. about 150° after softening at 130°, $2(C_8H_7N)_3,SnBr_4$, m. p. 120—133° (decomp.), $2(C_8H_7N)_3,TiCl_4$, and $(C_8H_7N)_3,AlBr_3$. Introduction of the methyl group in position 1 depresses rather than enhances the additive power, since 1-methylindole does not give a normal product with stannic chloride, but with aluminium bromide affords the *substance* $C_8H_6MeN,AlBr_3$, from which the base is regenerated unchanged. 2-Methylindole unexpectedly yields the *compounds* $C_9H_8N,SnCl_3$, m. p. 149°, and $2C_9H_9N,HSnCl_5$, m. p. 207°, from each of which the base is smoothly regenerated. Di-2-methylindylmethene with stannic chloride gives the *compound* I,



(I.)

m. p. 201°, but could not be caused to react with stannic bromide. Di-2-methylindyldimethylmethane gives an additive *product* (1 : 1) with stannic chloride from which the initial material cannot be regenerated.

H. WREN.

Manufacture of 1 : 8-naphthoxypenthiophen. I. G. FARBENIND.—See B., 1929, 200.

Derivatives of 5-aminoquinoline. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 237—246).—5-Aminoquinoline and ethylcarbimide, when heated in ethereal solution at 100°, formed N-5-*quinolyl*-N′-*ethylcarbamide*, m. p. 219—220° (resolidification occurred at 220—260° with sublimation and remelting at 300°; these phenomena are ascribed to fission by heat: $C_9H_6N{\cdot}NH_2+Et{\cdot}NCO \rightleftharpoons C_9H_6N{\cdot}NH{\cdot}CO{\cdot}NHEt \rightleftharpoons C_9H_6N{\cdot}NCO+NH_2Et$; *s*-di-5-quinolylcarbamide and *s*-diethylcarbamide are then formed).

5-Aminoquinoline reacted with methyl and ethyl chloroformates in acetic acid–sodium acetate solution to give *methyl quinoline*-5-*carbamate*, m. p. 134°, and *ethyl quinoline*-5-*carbamate*, m. p. 137°. 5-Aminoquinoline and potassium cyanate in dilute acetic acid solution formed 5-*quinolylcarbamide*, m. p. 280° after changing somewhat at 224°, together with a biuret *derivative*, $C_9H_6N\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2$, m. p. 305°.

Absolute nitric acid converted the above quinolylethylcarbamide into N-*nitro*-N′-8-*nitro*-5-*quinolyl*-N-*ethylcarbamide*, m. p. 173° (decomp.), which, when heated with alcoholic ammonia or with water, gave 8-nitro-5-aminoquinoline, m. p. 280°, and ethylnitroamine. Nitration with absolute nitric acid and sulphuric acid and treatment of the product with aqueous ammonia led to 6 : 8-*dinitro*-5-*aminoquinoline*, m. p. 273—277° (decomp.).

Nitration of methyl quinoline-5-carbamate with absolute nitric acid gave small yields of *methyl* 8-*nitroquinoline*-5-*carbamate*, m. p. 180° (decomposition with sulphuric acid gave 8-nitro-5-aminoquinoline), accompanied by *methyl* 6 : 8-*dinitroquinoline*-5-*carbamate*, m. p. 195° (decomp.) (sulphuric acid decomposition led to 6 : 8-dinitro-5-aminoquinoline, m. p. 273°). Similar treatment of ethylquinoline-5-carbamate gave *ethyl* 8-*nitroquinoline*-5-*carbamate*, m. p. 156°, mixed-acid nitration giving *ethyl* 6 : 8-*dinitroquinolyl*-5-*carbamate*, m. p. 180—183° (decomp.).

R. J. W. Le Fèvre.

N-Aminoalkylation of amines. [Preparation of 8-(β-hydroxy-1′-γ-piperidylpropylamino)quinoline.]—I. G. Farbenind.—See B., 1929, 164.

Carbazole. T. V. Aristov (J. Chem. Ind. Moscow, 1928, 5, 721).—In purification of carbazole with sulphuric acid, partial sulphonation appears to take place.

Chemical Abstracts.

Identification of alkylbarbituric acids. E. Lyons and A. W. Dox (J. Amer. Chem. Soc., 1929, 51, 288—291).—The following compounds have been prepared by heating barbituric acids with *p*-nitrobenzyl chloride or bromide in aqueous alcohol in presence of sodium carbonate: 1 : 3-*Di*-p-*nitrobenzyl*-5 : 5-*diethyl*-, m. p. 192°, -5-*ethyl*-5-iso*propyl*-, m. p. 160°, -5 : 5-*diallyl*-, m. p. 190°, -5-*ethyl*-5-*butyl*-, m. p. 146°, -5-*ethyl*-5-iso*amyl*-, m. p. 138°, -5-*butyl*-5-*allyl*-, m. p. 169°, -5-*ethyl*-5-*amyl*-, m. p. 131°; 5-*phenyl*-1 : 3-*di*-p-*nitrobenzyl*-5-*ethyl*-, m. p. 182°; 1-p-*nitrobenzyl*-5 : 5-*diethyl*-, m. p. 192°, -3-*methyl*-5 : 5-*diethyl*-, m. p. 104°, -3 : 5 : 5-*triethyl*-, m. p. 69°; 3-*phenyl*-1-p-*nitrobenzyl*-5 : 5-*diethyl*-, m. p. 133°; 3 : 5-*di*-p-*nitrobenzyl*-1-*methyl*-5-*hexyl*-, m. p. 139°; 1 : 3 : 5-*tri*-p-*nitrobenzyl*-5-iso*propyl*-, m. p. 187°, -5-*butyl*-, m. p. 180°; 1 : 3-*diphenyl*-5-p-*nitrobenzyl*-5-*ethyl*-, m. p. 218°; 1 : 3 : 5 : 5-*tetra*-p-*nitrobenzyl*- (not melting); and a *poly*-p-*nitrobenzyl-barbituric acid*, m. p. 264° (265° ?).

The original contains several apparent misprints.

E. E. Turner.

N-Alkyl- and -aryl-4 : 5 : 6 : 7-tetrahydroindazoles. K. von Auwers, J. Conrad, A. Ernecke, and B. Ottens (Annalen, 1929, 469, 57—82).—A continuation of the indazole syntheses previously described (A., 1924, i, 325; 1925, i, 1181). Condensation of substituted ethyl *cyclo*hexanone-2-oxalates with alkyl- and aryl-hydrazines affords a mixture of 1- and 2-alkyl- or -aryl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylates. When hydrazine is used tetrahydroindazole-3-carboxylates result. Subsequent alkylation of these affords mixtures of the 1- and 2-derivatives. Elimination of carbon dioxide from the alkylated indazolecarboxylic acids gives the corresponding indazoles. Ethyl *cyclo*hexanone-2-oxalate and methylhydrazine acetate react in presence of alcohol and dilute sodium hydroxide solution, giving a mixture of esters which after hydrolysis with alcoholic sodium hydroxide solution affords 2-*methyl*- and 1-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylic acids*, m. p. 205—206° and 207·5—208·5°, respectively. These acids are separated by partial esterification with 3% methyl-alcoholic hydrochloric acid: the former is unaffected, and the methyl ester formed from the latter is then rehydrolysed. Thermal decomposition of the acids yields 2-methyl- and 1-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*, b. p. 109—110°/11 mm. (*picrate*, m. p. 141—142°), respectively. *Ethyl tetrahydroindazole*-3-*carboxylate*, m. p. 106—107°, is ethylated by ethyl bromide and sodium ethoxide, affording after the above treatment 2-*ethyl*-, m. p. 148—149°, and 1-*ethyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. 183—186° (*methyl* ester, m. p. 108—109°). The picrates of 2- and 1-ethyltetrahydroindazole, m. p. 103—104° and 150—151°, respectively, have been described previously (A., 1924, i, 328) as the 1- and 2-derivatives, respectively. 2-*Benzyl*-, m. p. 187—187·5°, and 1-*benzyl-tetrahydroindazole*-3-*carboxylic acid*, m. p. 157·5—158·5° (*methyl* ester, m. p. 69—70°), are obtained similarly. The corresponding indazole *picrates* have m. p. 132—133° and 128—129°, respectively. Ethyl 4-methyl*cyclo*hexanone-2-oxalate and hydrazine hydrate afford *ethyl* 5-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylate* (I), b. p. 208—210°/14 mm., m. p. 110—111° (free *acid*, m. p. 274°), whilst condensation with methylhydrazine in presence of acetic acid gives after hydrolysis 2 : 5-*dimethyl-tetrahydroindazole*-3-*carboxylic acid*, m. p. 195—195·5°, as the chief product. If the condensation with methylhydrazine is effected in sulphuric acid at 0° 1 : 5-*dimethyltetrahydroindazole*-3-*carboxylic acid*, m. p. 185—186° (*methyl* ester, m. p. 114—115°), is the main product. Methylation of I with methyl iodide and alkali gives about equal quantities of the 1 : 5- and 2 : 5-derivatives. 1 : 5-*Dimethyltetrahydroindazole* (*picrate*, m. p. 155°) has b. p. 115—116°/12 mm. Ethylation of I gives 5-*methyl*-2-*ethyl*-, m. p. 184—185°, and 5-*methyl*-1-*ethyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. 147·5—149·5° (*methyl* ester, m. p. 44·5—45·5°). The m. p. of the corresponding indazole picrates (A., 1925, i, 1183) should be interchanged. Benzylation of I gives 40% of 2-*benzyl*-5-*methyl*-, m. p. 186—187°, and 60% of 1-*benzyl*-5-*methyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. 142·5—143·5° (*methyl* ester, m. p. 98—99°), which when decarboxylated yield 2-benzyl-5-methyl- (*picrates*, m. p. 115—116° and 135—136°), and 1-*benzyl*-5-*methyl-tetrahydroindazoles*, b. p. 191—192°/12 mm. [*picrate*, m. p. 128—129° (cf. *loc. cit.*)]. Condensation of the above oxalate with phenylhydrazine gives 80% of *ethyl* 1-*phenyl*-5-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylate*, m. p. 128—129° (*methyl* ester, m. p. 119—120°; free *acid*, m. p. 196·5—198·5°), together with 20% of 2-*phenyl*-5-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylic acid*, m. p. 202—203°.

Ethyl 6-methyl*cyclo*hexanone-2-oxalate and hydrazine hydrate afford 43% of *ethyl* 7-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylate*, b. p. 182°/11 mm., m. p. 87—88° (free *acid*, m. p. 212—214°), which with methyl iodide and sodium methoxide yields approximately equal amounts of 2 : 7-*dimethyl*-, m. p. 128—130°, and 1 : 7-*dimethyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. 169·5—170·5° (*methyl* ester, b. p. 185—187°/11 mm.). 1 : 7 - *Dimethyltetrahydroindazole* (*picrate*, m. p. 155·5°) has b. p. 111—112°/11 mm. Ethylation gives about equal amounts of 7-*methyl*-2-*ethyl*-, m. p. 43—49°, and 7-*methyl*-1-*ethyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. (+H_2O) 94°, (anhydrous) 127·5—128·5° (*methyl* ester, b. p. 182—183°/10 mm., $d_4^{17\cdot6}$ 1·0899, $n^{17\cdot6}$ 1·50485). 7-*Methyl*-1-*ethyltetrahydroindazole* (*picrate*, m. p. 136—137°) has b. p. 111—111·5°/10 mm. Benzylation gives 80% of 1-*benzyl*-7-*methyltetrahydroindazole*-3-*carboxylic acid*, m. p. (+H_2O) 119—121° (*methyl* ester, b. p. 242—246°/11 mm.), together with 20% of the 2-*benzyl* derivative, m. p. 154—154·5°. 1- and 2-*Benzyl*-7-*methyltetrahydroindazoles*, b. p. 188—191°/11 mm. and 189—190°/12 mm., respectively, are obtained in the usual way. Condensation of the above oxalate with phenylhydrazine in presence of hydrochloric or acetic acid yields 65% of 1-*phenyl*-7-*methyltetrahydroindazole*-3-*carboxylic acid*, m. p. 177—178° (*methyl* ester, b. p. 238—240°/12 mm.), and 35% of the 2-*phenyl-acid*, m. p. 180—181°.

Methylation of *ethyl* 4 : 6-*dimethyl*-4 : 5 : 6 : 7-*tetrahydroindazole*-3-*carboxylate*, b. p. 197°/12 mm. (*methyl* ester, b. p. 197°/12 mm., m. p. 90—91°; free *acid*, m. p. 269—270°), affords 83% of 1 : 4 : 6-*trimethyltetrahydroindazole*-3-*carboxylic acid*, m. p. 176—177° (*methyl* ester, m. p. 73—75°), together with 17% of the 2 : 4 : 6-*trimethyl* derivative, m. p. 179—180°. The *picrates* of 1 : 4 : 6- and 2 : 4 : 6-trimethyltetrahydroindazoles, m. p. 175—176·5° and 145—146°, respectively, have been previously described (*loc. cit.*) as the 2 : 4 : 6- and 1 : 4 : 6-derivatives. 4 : 6-*Dimethyl*-1-*ethyltetrahydroindazole*-3-*carboxylic acid*, m. p. 141—141·5° (*methyl* ester, b. p. 188—189°/11 mm., m. p. 64·5—65·5°), gives 4 : 6-dimethyl-1-ethyltetrahydroindazole, b. p. 126°/11 mm. [*picrate*, m. p. 137—138°, previously named 2-picrate (*loc. cit.*)], and 4 : 6-*dimethyl*-2-*ethyltetrahydroindazole*-3-*carboxylic acid*, m. p. 145—146·5°, yields the corresponding indazole [*picrate*, m. p. 117—118°, previously termed the 1-picrate (*loc. cit.*)]. 2-*Benzyl*-4 : 6-*dimethyl*-, m. p. 159·5—160·5°, and 1-*benzyl*-4 : 6-*dimethyl-tetrahydroindazole*-3-*carboxylic acids*, m. p. 137—138° (*methyl* ester, b. p. 242—243°/11 mm., m. p. 112—113°), are also described. 1-Phenyl-4 : 6-dimethyltetrahydroindazole [perchlorate, m. p. 183—184° (cf. *loc. cit.*)] is obtained from the corresponding 3-*carboxylic acid*, m. p. 192·5—193·5° (*methyl* ester, b. p. 240°/11 mm., m. p. 87—88°). 2-*Phenyl*-4 : 6-*dimethyltetrahydroindazole*-3-*carboxylic acid* has m. p. 223° (decomp.). Spectrochemical data for 14 substituted tetrahydroindazoles are given.

H. BURTON.

Synthesis and fission of quaternary tetrahydroindazolium salts. K. von Auwers, J. Conrad, and A. Ernecke (Annalen, 1929, 469, 82—92).—The following substituted 4 : 5 : 6 : 7-*tetrahydroindazolium iodides* have been prepared from the requisite indazole and alkyl or aralkyl iodide at 100° : 1 : 2-*dibenzyl*-, m. p. 153°; 1-*benzyl*-2-*ethyl*-, m. p. 125—127°; 1 : 2 : 5-*trimethyl*-, m. p. 137·5° (*bromide*, an oil); 1 : 5-*dimethyl*-2-*ethyl*-, m. p. 84°; 2 : 5-*dimethyl*-1-*ethyl*-, m. p. 67—69°; 5-*methyl*-1 : 2-*diethyl*-, m. p. 115—117°; 2-*benzyl*-1 : 5-*dimethyl*-, m. p. 139—140°; 1-*benzyl*-2 : 5-*dimethyl*-, m. p. 175—176°; 2-*benzyl*-5-*methyl*-1-*ethyl*-, m. p. 167—168°; 1-*benzyl*-5-*methyl*-2-*ethyl*-, m. p. 142—144°; 1 : 2 : 7-*trimethyl*-, m. p. 121—123°; 7-*methyl*-1 : 2-*diethyl*-, an oil; 2-*benzyl*-1 : 7-*dimethyl*-, m. p. 175°; 1-*benzyl*-2 : 7-*dimethyl*-; 1 : 2 : 4 : 6-*tetramethyl*-, m. p. 155°; 1 : 4 : 6-*trimethyl*-2-*ethyl*-, an oil; 2 : 4 : 6-*trimethyl*-1-*ethyl*-, m. p. 116—118°; 2-*benzyl*-1 : 4 : 6-*trimethyl*-, an oil, and 1-*benzyl*-2 : 4 : 6-*trimethyl*-, m. p. 119·5—120·5°. The compounds previously described as 1-benzyl-1-ethyl- and 2-benzyl-2-ethyl-tetrahydroindazolium iodides (A., 1924, i, 329) are the 1-benzyl-2-ethyl- and 2-benzyl-1-ethyl derivatives, respectively. The methiodide of 7-methyl-2-ethyltetrahydroindazole, m. p. 102—103° (*loc. cit.*), is the quaternary 2 : 7-dimethyl-1-ethyl salt. The methiodide, m. p. 175°, from 2-benzyl-7-methyltetrahydroindazole (*loc. cit.*) is also obtained from 1 : 7-dimethyltetrahydroindazole and benzyl iodide, and is, therefore, 2-benzyl-1 : 7-dimethyltetrahydroindazolium iodide. Fission of the above salts is accomplished by heating in a vacuum above the m. p. and converting the bases formed into the picrates. With the 1 : 2-dimethyl, 1 : 2-diethyl, and 1 : 2-dibenzyl derivatives approximately equal amounts of the 1- and 2-alkyltetrahydroindazoles are produced; occasionally an excess of the 2-derivative results. When dissimilar groups are attached to the 1- and 2-positions the one with the least affinity demand (*e.g.*, benzyl) is eliminated, in agreement with the results previously obtained (cf. A., 1926, 847). In some of the decompositions a partial wandering of an alkyl group occurs. Thus, 1-benzyl-2 : 7-dimethyltetrahydroindazolium iodide affords in addition to 2 : 7-dimethyltetrahydroindazole a small amount of the 1 : 7-dimethyl derivative. 1 : 4 : 6-Trimethyl-2-ethyltetrahydroindazolium iodide gives 1 : 4 : 6-trimethyl-, 4 : 6-dimethyl-1-ethyl-, and 4 : 6-dimethyl-2-ethyl-tetrahydroindazoles in the ratio of 2 : 1 : 3. Similarly, 2 : 4 : 6-trimethyl-1-ethyltetrahydroindazolium iodide yields 1 : 4 : 6-trimethyl-, 4 : 6-dimethyl-1-ethyl-, and 2 : 4 : 6-trimethyl-tetrahydroindazoles in the proportion 3 : 3 : 1.

H. BURTON.

Acridine. III. Hydrogenation of acridine with sodium amalgam. K. Lehmstedt and H. Hundertmark (Ber., 1929, 62, [*B*], 414—418; cf. A., 1927, 776; 1928, 1259).—Acridine is reduced by sodium and alcohol to a mixture of 9 : 10-dihydroacridine (acridan) and "insoluble hydroacridine." The former compound readily yields additive *products*, $C_{13}H_{11}N,AgNO_3$; $C_{13}H_{11}N,HgCl_2$; $(C_{13}H_{11}N_2)_2,EtONa$, m. p. 170°; with acridine hydrochloride in alcohol it affords the quinhydrone-like *compound*, $C_{13}H_{11}N,C_{13}H_9N,HCl,1\cdot5H_2O$, immediately decomposed into its components by water or ether. Analyses of "insoluble hydroacridine" indicate the composition $C_{26}H_{22}ON_2$, the sodium amalgam thus appearing to operate as oxygen carrier. The compound is somewhat unstable and decomposes when heated or continuously warmed with concentrated sulphuric acid into dihydroacridine, acridine, and water. The constitution $\begin{matrix}C_{13}H_{10}{>}NH\\ C_{13}H_{10}{>}NH\end{matrix}{>}O$ is suggested. " Insoluble hydroacridine " loses water when dissolved in boiling pyridine and becomes transformed into the non-basic 9 : 9′ : 10 : 10′-*tetrahydro*-10 : 10′-*diacridyl*, m. p. 220° when placed in a bath pre-heated to 205° or m. p. 208—210° (decomp.) after softening when more slowly heated. It decomposes when heated into acridine and dihydroacridine, but does not suffer fission when warmed with sulphuric acid, which causes production of a new *base*, not yet examined completely. H. WREN.

Porphyrins. XVIII. Porphyrin formation from β-hæmin. W. KÜSTER and W. VON DEGENFELD. **XIX. Porphyrin fission of substituted hæmins and constitution of hæmin.** W. KUSTER and K. SCHLAYER (Z. physiol. Chem., 1929, **180**, 259—269, 270—285).—XVIII. The crude hæmin from the blood of a horse inoculated with erysipelas culture has been examined. The chloroform-insoluble portion is soluble in 5% sodium hydroxide solution and is therefore not an ester. By the action of diazomethane only one methyl group is introduced into the double molecule, and treatment of a pyridine solution with alcoholic hydrochloric acid gives a monoethylhæmin, $(C_{36}H_{33}O_4N_4ClFe)_2$. The chloroform-soluble part is a monoethylhæmin, partly methylated by diazomethane. Porphyrin fission of the crude hæmin by treatment with hydrogen bromide and acetic acid and finally water affords, in addition to unchanged hæmin, hæmatoporphyrin and an insoluble product, probably a β-*bromo*-αα′-*dihydroxymesoporphyrin*, $C_{34}H_{37}O_6N_4Br$ (*copper*, *zinc*, and *hydroxyiron* salts), formed by initial addition of 2 mols. of hydrogen bromide to the acetylene residue and 1 mol. of hydrogen bromide to the vinyl group. This new porphyrin is methylated with diazomethane in chloroform suspension, yielding a *dimethyl* ester; it forms a *dihydrochloride*, completely hydrolysed by water at the ordinary temperature. The bromine is removed by successive treatment with hot 5% sodium hydroxide solution. When decomposed with hydrobromic and acetic acids and the residue, after removal of acid under reduced pressure, treated with methyl alcohol at 60° a small amount of *bromodimethoxyporphyrin dimethyl* ester, $C_{38}H_{45}O_6N_4Br$, is obtained.

XIX. Treatment of dichloro-α-dimethyl(chloro)-hæmin with a very large excess of boiling methyl alcohol gives a soluble *chloromethoxydimethylhæmin* (I), $C_{37}H_{37}O_5N_4Cl_2Fe$, together with 10% of an insoluble *substance* (II), $C_{36}H_{33}O_4N_4Cl_2Fe$, apparently formed by elimination of hydrogen chloride. Treatment of I with a mixture of hydrobromic and acetic acids and then with methyl alcohol affords chlorohæmatoporphyrin dimethyl ether (Küster and Fleischmann, A., 1928, 657) [complex *zinc*, *copper*, and *iron chloride* salts; *dimethyl* ester, m. p. 112° after sintering at 63° (complex *iron chloride* salt, m. p. 177° after sintering at 131°)], together with a bromine-containing product, which after the action of hydrobromic and acetic acids and methyl alcohol gives chlorobromodimethoxymesoporphyrin together with the monomethoxy-ether and a " hæmin." When the residue from the hydrobromic–acetic acid treatment of I is treated with water or 1% hydrobromic acid a soluble chlorobromo-derivative (containing no methoxyl) and an insoluble chlorobromo-compound are obtained. Treatment of the latter with disodium hydrogen phosphate eliminates bromine, yielding a *chlorohæmatoporphyrin*, $C_{34}H_{35}O_6N_4Cl$ [*dimethyl* ester (complex *zinc, copper*, and *iron chloride* salts)]. When a pyridine solution of I is treated with dilute hydrochloric acid there appears to be formed (spectrum) a dichlorodimethylhæmin. Some change occurs in pyridine solution, since fission of the resulting product with hydrobromic and acetic acids gives a chlorobromodimethoxymesoporphyrin. Fission of II gave impure chlorobromodimethoxymesoporphyrin and the hydrobromide of a substance containing iron. Oxidation of chlorohæmatoporphyrin dimethyl ether with chromic anhydride and 30% sulphuric acid yields methyl(chloromethoxy)ethylmaleinimide, m. p. 65°. The formation of chlorohæmatoporphyrin dimethyl ether from I indicates that fission occurs thus: $\cdot CH(OMe)\cdot CH⋮C\cdot CH_2Cl \longrightarrow \cdot CH_2Br\cdot CH_2Br + \cdot CH(OMe)\cdot CH_2Cl$, with subsequent elimination of hydrogen bromide from the dibrominated residue and replacement of bromine by methoxyl, viz., $\cdot CH{:}CHBr \longrightarrow \cdot CH{:}CH\cdot OMe$. H. BURTON.

Protoporphyrin. A. HAMSÍK (Z. physiol. Chem., 1929, **180**, 308—318).—When α-hydroxyhæmin (A., 1928, 1148) is treated with iron powder in presence of formic acid (cf. Fischer and Pützer, A., 1926, 854) protoporphyrin is formed together with by-products. Treatment with acetic, formic, or alcoholic hydrochloric acid and hydrazine hydrate, or hydrochloric acid and stannous chloride in acetone, gives varying amounts of protoporphyrin. Aqueous or acetic acid solutions of stannous chloride and hydrochloric acid are unsuitable. Similar experiments carried out with β- and ψ-hydroxyhæmins and α-chlorohæmin do not give such satisfactory results. Protoporphyrin is affected by treatment with dilute hydrochloric acid in acetone or hot acetic acid, the colour of the solution becoming reddish-brown. With reducing agents, except formic acid and hydrazine hydrate, there is also a colour change. The complex protoporphyrin tin salt previously described (A., 1926, 1265) is altered by dilute hydrochloric acid, giving a substance soluble in formic acid to a greenish-blue solution. H. BURTON.

Derivatives of 2 : 5-diphenyloxazole. S. MINOVICI, C. D. NENITZESCU, and B. ANGELESCU (Bul. Soc. Chim. România, 1928, **10**, 149—159).—Synthesis of 2 : 5-diphenyloxazoles by condensation of aromatic aldehydecyanohydrins with aromatic aldehydes in the presence of dry hydrogen chloride (cf. Fischer, A., 1896, i, 262; Minovici, A., 1896, i, 703; Ingham, A., 1927, 459) has been extended to various substituted aldehydes and aldehydecyanohydrins. From benzaldehydecyanohydrin and *p*-nitrobenzaldehyde a considerable quantity of p-*nitrobenzylidenemandelamide*, m. p. 168°, is obtained, and with *p*-anisaldehydecyanohydrin and *p*-nitrobenzaldehyde the sole product is p-*nitrobenzylidene*-p-

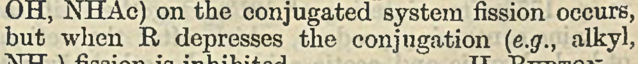
methoxymandelamide, m. p. 168°. The basicity of these oxazoles is largely diminished by the presence of negative substituents in the two phenyl groups; thus the hydrochlorides of phenyloxazoles can be recrystallised from absolute alcohol, whilst those of nitrophenyloxazoles lose hydrogen chloride. The following substances have already been obtained by Lister and Robinson (J.C.S., 1912, **101**, 1297) using a method other than that given above; the m. p. in parentheses are theirs. 5-Phenyl-2-*p*-tolyloxazole, m. p. 74° (77°) [*hydrochloride*, m. p. 160—161° (decomp.)]; 5-phenyl-2-*o*-chlorophenyloxazole, m. p. 83° (80—81°); 5-phenyl-2-*o*-nitrophenyloxazole, m. p. 123° (125°); 5-phenyl-2-*m*-nitrophenyloxazole, m. p. 154—155° (149°); 5-phenyl-2-*p*-nitrophenyloxazole, m. p. 208° (202—204°). The following are described: 2-*phenyl*-5-p-*tolyloxazole*, m. p. 81° [*hydrochloride*, m. p. 180° (decomp.)]; 2-p-*anisyl*-5-p-*tolyloxazole*, m. p. 88°; 5-*phenyl*-2-*piperonyloxazole*, m. p. 116—117° [*hydrochloride*, m. p. 193° (decomp.)]; 5-*phenyl*-2-m-*chlorophenyloxazole*, m. p. 107°; 5-p-*anisyl*-2-p-*tolyloxazole*, m. p. 90° [*hydrochloride*, m. p. 179° (decomp.)]; 5-p-*anisyl*-2-*piperonyloxazole*, m. p. 145°; 2-o-*nitrophenyl*-5-p-*methoxyphenyloxazole*, m. p. 116°; 2-m-*nitrophenyl*-5-p-*methoxyphenyloxazole*, m. p. 163°; 2-o-*chlorophenyl*-5-p-*methoxyphenyloxazole*, m. p. 108° (*hydrochloride*, m. p. 127°); 2-m-*chlorophenyl*-5-p-*anisyloxazole*, m. p. 123° [*hydrochloride*, m. p. 162° (decomp.)]; 2-phenyl-5-*p*-nitrophenyloxazole, m. p. 187° (cf. Minovici, *loc. cit.*), which is also obtained by nitration of 2 : 5-diphenyloxazole, and yields *p*-nitrobenzoic acid when oxidised. C. W. Shoppee.

o-Benzidine rearrangement of 4-phenylhydrazino-5-phenyl-3-methyl*iso*oxazole. G. Wittig, H. Kleiner, and J. Conrad (Annalen, 1929, **469**, 1—16).—Reduction of 4-benzeneazo-5-phenyl-3-methyl*iso*oxazole (A., 1928, 779) either electrolytically or with aluminium powder and a small amount of sodium hydroxide solution in alcoholic solution affords 4-*phenylhydrazino*-5-*phenyl*-3-*methyl*isooxazole, m. p. 136° (decomp.). When this is warmed with *N*-hydrochloric acid there is formed a mixture of 5-*anilino*-5-*phenyl*-3-*methyl*isooxazol-4-*one* (I), m. p. 130° (decomp.), and 5-*phenyl*-5-o-*aminophenyl*-3-*methyl*isooxazole-4-*ketimine* (II), m. p. 179—180° (decomp.; *benzylidene* derivative, m. p. 195·5—196°; *acetyl* derivative, m. p. 254°; *chlorostannate*, m. p. 127°). Thermal decomposition of I at 130° gives carbon monoxide and benzanilide, whilst acid or alkaline hydrolysis affords benzoic acid and aniline. The compound is unaffected by potassium permanganate or by hydroxylamine. Bromination of I in acetic acid solution yields benz-2 : 4-dibromoanilide, m. p. 139·5°, and magnesium phenyl bromide converts it into 4-*hydroxy*-5-*anilino*-4 : 5-*diphenyl*-3-*methyl*iso*oxazoline*, m. p. 173·5° (slight decomp.). Hydrolysis of this last compound with *N*-acetic acid in acetone gives an *oxime*, $C_{16}H_{15}O_3N$, m. p. 179—180° (decomp.), converted by further hydrolysis with 2*N*-sulphuric acid into benzil. Magnesium methyl iodide and I yield 4-*hydroxy*-5-*anilino*-5-*phenyl*-3 : 4-*dimethyl*iso*oxazoline*, m. p. 201° (slight decomp.), hydrolysed by 2*N*-sulphuric acid, forming aniline and γ-*nitroso*-β-*benzoylbutan*-β-*ol*, m. p. 145°. Bromination of II in dry chloroform yields the *hydrobromide*, m. p. 172·5° (decomp.), of 5-*phenyl*-5-p-*bromo*-o-*aminophenyl*-3-*methyl*isooxazole-4-*ketimine*, m. p. 175°, whilst hydrolysis with 30% potassium hydroxide solution gives 2-*amino*-3-*hydroxy*-3-*phenylindole*, m. p. 204° (decomp.), also formed by the action of an excess of magnesium methyl iodide on II. When this indole derivative is fused with alkali hydroxide *o*-aminobenzophenone and hydrogen cyanide are produced. Treatment of II with boiling dilute acetic acid affords 2 : 3-dihydroxy-3-phenylindole, m. p. 209—210° (*N*-acetyl derivative, m. p. 140—140·5°). H. Burton.

Fission of the benz*iso*oxazole ring. H. Lindemann and H. Cissée (Annalen, 1929, **469**, 44—57).—Methyl 6-nitrobenz*iso*oxazole-3-carboxylate (Borsche, A., 1912, i, 652), when heated with slightly diluted sulphuric acid at 100°, gives 6-*nitrobenz*isooxazole-3-*carboxylic acid* (I), m. p. 189—190° with elimination of carbon dioxide. Alkaline hydrolysis affords an *acid* (II), $C_8H_4O_5N_2,H_2O$, m. p. 167—168° (cf. Borsche, *loc. cit.*), which when dried in a vacuum over phosphorus pentoxide loses water and gives I. Treatment of I with water affords II, indicating simple hydration. 4-Nitro-2-hydroxyphenylglyoximic acid (Borsche, *loc. cit.*) is probably II.

Treatment of an alcoholic solution of methyl 6-nitrobenz*iso*oxazole-3-carboxylate with hydrazine hydrate affords the corresponding *hydrazide*, m. p. 170° (*acetyl* derivative, m. p. 213—214°), converted by nitrous acid into the corresponding *azide*, m. p. 135° (decomp.). Decomposition of this with acetic acid affords *di*-(6-*nitrobenz*isooxazole-3)-*carbamide*, m.p. 342°, whilst with acetic anhydride and a small amount of concentrated sulphuric acid 6-*nitro*-3-*acetamido*-, m. p. 230° (not sharp), and 6-*nitro*-3-*di-acetamido-benz*iso*oxazoles*, m. p. 133°, are produced. When either of these acetyl derivatives is warmed with 2*N*-sodium hydroxide solution 3-4′-*nitro*-2′-*hydroxyphenyl*-5-*methyl*-1 : 2 : 4-*oxdiazole*, m. p. 124° (*acetyl* derivative, m. p. 162°), results, thus demonstrating fission of the *iso*oxazole ring and subsequent reaction between the oximino- and acetamido-groupings. Hydrolysis of the acetyl derivatives with fairly concentrated sulphuric acid gives 6-*nitro*-3-*aminobenz*iso*oxazole*, m. p. 234°, converted by treatment with nitrous acid into 6-*nitro*-3-*hydroxybenz*iso-*oxazole*, m. p. 85—88° (decomp.). Treatment of this last compound with acetic acid or the above amino-derivative with nitrous acid in presence of acetic acid gives 4-*nitro*-2-*hydroxybenzacetylhydroxamic acid*, $(NO_2)(OH)C_6H_3\cdot C(:N\cdot OAc)\cdot OH$, m. p. 184° resolidifying with m. p. 241°, hydrolysed by 10% sodium hydroxide solution to the corresponding *hydroxamic acid*, m. p. 214°. When either of these acids is heated with methyl-alcoholic potassium hydroxide solution 6-*nitrobenzoxazol*-2-*one*, m. p. 241°, results.

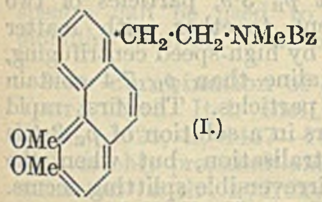
Fission of the benz*iso*oxazole ring is explained by postulating the addition of 1 mol. of water:



$$\begin{array}{l}\cdot C\!-\!CR\\ \;\|\quad\;\|\\ \cdot C\cdot O\cdot N\end{array}\longrightarrow\begin{array}{l}\cdot C\!=\!CR\\ \;|\qquad\;|\\ \cdot CH\cdot O\cdot N\cdot OH\end{array}\longrightarrow\begin{array}{l}\cdot C\!-\!CR\\ \;\|\qquad\;\|\\ \cdot C\cdot OH\;\; N\cdot OH\end{array}$$

If the group R has no depressant action (*e.g.*, OH, NHAc) on the conjugated system fission occurs, but when R depresses the conjugation (*e.g.*, alkyl, NH$_2$) fission is inhibited. H. Burton.

Opium alkaloids. X. Syntheses of *dl-apo*morphine dimethyl ether. E. Späth and O. Hromatka (Ber., 1929, 62, [*B*], 325—332).—2-Nitrohomoveratric acid is converted by phosphorus pentachloride into the non-crystalline chloride and thence by β-phenylethylamine in aqueous-alkaline solution according to the method of Kay and Pictet (J.C.S., 1913, **103**, 947) into nitrohomoveratryl-β-phenylethylamide, m. p. 79° (lit. m. p. 98°); preferably, the acid is treated successively with thionyl chloride and an excess of β-phenylethylamine in benzene, whereby the amide, m. p. 79°, is obtained, although in a single instance the product had m. p. 118° after softening at 116°. Treatment of either amide with phosphoric oxide in boiling xylene or, preferably, toluene yields a mixture of 1 : 2′-*nitro*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 129° (vac.), and a non-basic compound, $C_{19}H_{18}O_4N_2$, m. p. 124—126°, probably identical with that described by Kay and Pictet (*loc. cit.*). The dihydro-base is transformed through the *methiodide*, m. p. 203° (decomp.), into the *methochloride*. Reduction of the latter compound with tin and hydrochloric acid followed by treatment with nitrous acid and copper powder gives dl-apo*morphine dimethyl ether*. Since this product is not readily obtainable from natural sources, it is transformed by boiling benzoyl chloride into the *benzoyl* compound (I), m. p. 164·5—165°. The same treatment of *l-apo*morphine dimethyl ether yields this compound, since the nitrogen ring is ruptured at the position of the asymmetric carbon atom and an optically inactive compound is thus produced.



(I.)

Complete methylation of *l-apo*morphine to non-crystalline *l-apo*morphine dimethyl ether is effected by prolonged treatment of a solution of the base in methyl alcohol with an excess of ethereal diazomethane; the *hydrogen* d-*tartrate*, m. p. 177—178° (vac., decomp.), is described.

Attempts to racemise l-*apo*morphine dimethyl ether by protracted heating of the base, by the action of alcoholic iodine and subsequent hydrogenation, or by oxidation with mercuric acetate were unsuccessful.

H. Wren.

Synthesis of *dl-apo*morphine dimethyl ether. H. Avenarius and R. Pschorr [and, in part, H. Herz] (Ber., 1929, 62, [*B*], 321—325; cf. Pschorr, A., 1906, i, 878; 1907, i, 635).—*vic*-2-Nitrovanillin methyl ether is condensed with hippuric acid in the presence of sodium acetate and acetic anhydride to 2-nitro-α-benzamido-3 : 4-dimethoxycinnamolactone (+1EtOH), m. p. 169°, converted by sodium hydroxide or 75% acetic acid into 2-*nitro-α-benzamido*-3 : 4-*dimethoxycinnamic acid*, decomp. 215° (*ethyl* ester, m. p. 149°). The lactone is transformed by aqueous-alcoholic hydrochloric acid at 100° into 2-*nitro*-3 : 4-*dimethoxyphenylpyruvic acid*, m. p. 172° (*ethyl* ester, m. p. 109°, and its *oxime*, m. p. 108°). The *oxime* of the acid, m. p. 156—157°, is converted at 150—160° into 2-*nitro*-3 : 4-*dimethoxyphenylacetonitrile*, m. p. 66°. β-Phenylethylamine is transformed by anhydrous formic acid at 150—180° into its *formyl* derivative, b. p. 210—214°/35 mm., which, when treated successively with potassium and methyl iodide, affords N-*formyl*-N-*methyl*-β-*phenylethylamine*. The latter compound is isomerised by thionyl chloride in boiling toluene to 1-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 110—111°. Condensation of molecular quantities of 2-nitro-3 : 4-dimethoxyphenylacetonitrile with 1-hydroxy-2-methyltetrahydro*iso*quinoline in presence of sodium ethoxide followed by successive hydrolysis of the cyano-group and elimination of carbon dioxide by boiling hydrochloric acid and reduction by tin foil yields 1 : 2′-*amino*-3′ : 4′-*dimethoxybenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (*dihydrochloride*, m. p. 198—199°). Treatment of the dihydrochloride with sodium nitrite and copper powder and of the product with methyl iodide affords the methiodide of *apo*morphine dimethyl ether, m. p. 195°, identical with the product derived from natural sources.

H. Wren.

***Strychnos* alkaloids. XLVIII. Fission of the oxime of brucinonic acid by alkali.** H. Leuchs (Ber., 1929, 62, [*B*], 407—409).—The oxime of brucinonic acid is converted by the prolonged action of *N*-alkali hydroxide mainly into a *compound*, $C_{21}H_{21}O_5N_3$, m. p. 295—300° (decomp.) after changing at 280°, which yields an *acetyl* derivative, $C_{23}H_{23}O_6N_3$, decomp. 240° after darkening at 225°. In addition, an *isomeride*, m. p. 250—258° (decomp.), is obtained, whilst about 50% of the acid is recovered unchanged.

H. Wren.

Action of magnesium phenyl bromide on phosphorus pentachloride. J. H. Kolitowska (Rocz. Chem., 1928, 8, 568—575).—The products of the action of magnesium phenyl bromide on phosphorus pentachloride are diphenyl, triphenylphosphine, triphenyldihydroxyphosphine, *phosphorus tetraphenyl bromide*, $PBrPh_4,2H_2O$, m. p. 286—288°, and a crystalline complex, $PhMgBr,MgBr_2,MgCl_2,4Et_2O$. The double compound formed between triphenylphosphine has the composition $(PPh_3)_2,HgCl_2$, and not $PPh_3,HgCl_2$, as stated by Michaelis and Soden (A., 1885, i, 1134).

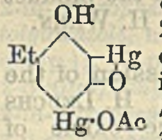
R. Truszkowski.

Derivatives of mono- and di-aminohydroxyphenylarsinic acids. B. C. Fisher and G. W. Raiziss (J. Amer. Chem. Soc., 1929, 51, 527—532).—3-Acetamido-4-hydroxyphenylarsinic acid gives *lithium* (+2H_2O), *calcium* (+2H_2O), *barium*, and *strontium* salts. 3-Nitro-4-hydroxyphenylarsinic acid is brominated in methyl alcohol in presence of iron to 5-*bromo*-3-*nitro*-4-*hydroxyphenylarsinic acid*, decomp. 280°, which is reduced by sodium hyposulphite to 5-*bromo*-3-*amino*-4-*hydroxyphenylarsinic acid* (N-*acetyl* derivative, decomp. 267—270°). 3 : 5-Diamino-4-hydroxyphenylarsinic acid (cf. A., 1921, i, 370) is readily acylated to 3 : 5-*diformamido*-, decomp. 200°; 3 : 5-*diacetamido*-, darkens at 235—240° (toxicity relatively low), 3 : 5-*dipropionamido*-, m. p. 197—198°; 3 : 5-*dibutyramido*-, m. p. 177°, and 3 : 5-*dichloroacetamido*-, m. p. 210—211° (decomp.), -4-*hydroxyphenylarsinic acids* (corresponding *sodium* salts).

H. E. F. Notton.

Derivatives of tri-*p*-tolylsilicane. A. R. Steele and F. S. Kipping (J.C.S., 1929, 357—358).—The fraction b. p. 250—300° isolated from the crude product of the interaction of silicon tetrachloride and magnesium *p*-tolyl bromide when kept for several weeks yields *tri-*p*-tolylsilicyl chloride*, m. p. 115—116°, slowly decomposed by cold water and converted by dilute ammonia in aqueous acetone into *tri-*p*-tolylsilicol*, m. p. 99—100°. When an alcoholic solution of the silicol containing a little aqueous sodium hydroxide is evaporated at 100° and the residue is then heated *tri-*p*-tolylsilicyl oxide*, m. p. 223—224°, is produced. A. I. Vogel.

Mercuration of resorcinol and alkylresorcinols. R. B. Sandin (J. Amer. Chem. Soc., 1929, 51, 479—483).—Ethylresorcinol (1 mol.) and mercuric acetate (2 mols.) in ethyl alcohol give quantitatively yellow *acetoxymercurianhydromercuriethylresorcinol* (? annexed formula), which darkens at 180°. This is converted by dilute hydrochloric acid into 2 : 6-*dichloromercuri-4-ethylresorcinol*, decomp. 207—209°, and by carbon dioxide in alkaline solution into dark brown *hydroxymercurianhydromercuriethylresorcinol.* The phenol gives with 0·5 mol. of mercuric acetate in hot acetic acid 6(2)-*acetoxymercuriethylresorcinol*, m. p. 163—164° (decomp.), which is converted by aqueous sodium chloride into 6(2)-*chloromercuriethylresorcinol*, m. p. 145—146° (corr.). Hexylresorcinol (A., 1926, 838) affords similarly yellow *acetoxymercurianhydromercurihexylresorcinol* (darkens at 200°), 2 : 6-*dichloromercuri-4-hexylresorcinol*, m. p. 137—138°, and 6(2)-*acetoxymercurihexylresorcinol*, m. p. 177—178° (decomp.). Resorcinol (cf. Dimroth, A., 1902, i, 849; Leys, A., 1905, i, 433) yields with mercuric acetate (3 mols.) in alcohol yellow *diacetoxymercurianhydromercuriresorcinol* (darkens at 210°). H. E. F. Notton.



Replacement of carboxyl by mercury in 3-substituted phthalic acids. I. F. C. Whitmore and P. J. Culhane (J. Amer. Chem. Soc., 1928, 51, 602—605).—The mercuration of 3-substituted phthalic acids has been examined in order to show that in the formation of the inner anhydride of *o*-hydroxymercuribenzoic acid from mercuric acetate and phthalic acid (Pesci, A., 1901, i, 576) the mercury displaces a carboxyl group and not an *o*-hydrogen atom. Prolonged refluxing of sodium 3-nitrophthalate with aqueous mercuric acetate gives the *anhydride* of 3-*nitro-2-hydroxymercuribenzoic acid*, which is not attacked by fuming nitric acid, but yields with boiling hydrochloric acid *m*-nitrobenzoic acid and with halogens the 2-halogeno-3-nitrobenzoic acid. 3-Bromo- and 3-chloro-phthalic acids also give gelatinous mercuration *products* which are hydrolysed by hydrochloric acid to 3-bromo- and 3-chloro-benzoic acids. H. E. F. Notton.

Mol. wt. of hæmocyanin of *Limulus Polyphemus*. T. Svedberg and F. F. Heyroth (J. Amer. Chem. Soc., 1929, 51, 539—550).—The protein (I) has a partial specific vol. of 0·735 at 20° and a mol. wt. of 2·04 × 10^6 by the sedimentation velocity method in 0·98% solution in phosphate buffer at p_H 6·63. This is about one third of that of *Helix* hæmocyanin (II) at p_H 5·62 (cf. following abstract). At concentrations of 0·65—0·03% a progressive disintegration occurs with formation of increasing amounts of non-centrifugable matter. The change is largely, if not quantitatively, reversed when the protein is reprecipitated by dialysis. The decomposition is also shown by sedimentation equilibrium measurements and by the fact that the dilute solutions do not obey Beer's law. The absorption spectra of I and II near the isoelectric point are similar, but the spectrum of II is more intense throughout. In the visible region the curve for I approaches more nearly to that of the acid degradation product of II. The molecules of I, unlike those of II, deviate considerably from the spherical shape. H. E. F. Notton.

Hydrogen-ion activity and the stability of the hæmocyanin of *Helix pomatia*. T. Svedberg and F. F. Heyroth (J. Amer. Chem. Soc., 1929, 51, 550—561).—The mol. wt. by the sedimentation velocity method of *Helix* hæmocyanin (cf. A., 1928, 783) in 0·089% solutions in dilute acetate and phosphate buffers is 5·0 × 10^6 between p_H 4·5 and p_H 7·4. As these limits are approached the molecules become hydrated and then break down into heterogeneous products. These are also the limits beyond which *Helix* serum increases rapidly in viscosity (cf. Stedman, A., 1927, 689). At p_H 3·9, particles of two different sizes are present together with matter which is precipitated only by high-speed centrifuging, whilst solutions more alkaline than p_H 7·4 contain in addition still smaller particles. The first rapid decomposition which occurs in a solution of p_H 3·4 is mainly reversed by neutralisation, but when the solution is kept a further irreversible splitting occurs. H. E. F. Notton.

Correlation between total nitrogen of bases and arginine-nitrogen and between total nitrogen of bases and lysine-nitrogen of various proteins. R. K. Larmour (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 349—363).—A statistical examination of 214 results obtained by different authors of the total basic nitrogen and arginine-nitrogen values for different proteins gives a coefficient of correlation +0·794 ± 0·017. The coefficient between total basic nitrogen and the deviation of arginine-nitrogen from the mean is +0·211 ±0·044. Considering 213 cases the coefficient of correlation between total basic nitrogen and lysine-nitrogen was found to be +0·548±0·032, and between total basic nitrogen and the deviation of lysine from the mean, +0·03±0·046. It is suggested that these results support Kossel's hypothesis that arginine is the nucleus of the protein molecule. F. C. Happold.

Nitrogen distribution of gelatin. F. S. Daft (Biochem. J., 1929, 23, 149—160).—Certain modifications of the method of analysis of proteins are advocated. Preliminary treatment of gelatin with acid or alkali has no effect on the percentage of non-amino-nitrogen and of basic nitrogen. S. S. Zilva.

Fractionation of gelatin. M. Kunitz and J. H. Northrop (J. Gen. Physiol., 1929, 12, 379—390).—When gelatin is repeatedly washed with water at p_H 4·7 and 23° a residue which is insoluble in water even at 80°, and a soluble fraction result. The insoluble fraction contains some soluble protein, does not swell in water, but swells in acid and in alkali. Alkaline gels of the insoluble fraction shrink more in acid than do similar gels of normal gelatin. As the two fractions cannot be converted back into gelatin it is assumed that they are bound together in the micellæ. Partial hydrolysis of gelatin at 90° yields a similar, although probably not identical, insoluble substance. E. BOYLAND.

Absorption of ultra-violet light by some proteins. L. MARCHLEWSKI and J. WIERZUCHOWSKA (Bull. Acad. Polonaise, 1928, **A**, 471—478).—The absorption spectra of some proteins, in neutral aqueous solution unless otherwise stated, have been measured. Ovalbumin gives a band between 3109 and 2415 Å., serum-albumin a band at 2960 and 2411 Å., egg-globulin a band at 2975 and 2417 Å., serum-globulin a band at 3071 and 2434 Å., caseinogen in 0·02*N*-sodium hydroxide a band at 3176 and 2628 Å., vitellin in 0·04*N*-sodium hydroxide a band at 3441 and 2645 Å., whilst the nucleoprotein of the liver in 0·1*N*-sodium hydroxide gives a faint band at 3212 and 2295 Å. which is quite different from those given by the above proteins. It is concluded that albumins, globulins, caseinogen, and vitellin behave similarly towards ultra-violet light and that the absorption spectra can be used to distinguish albumins and globulins from phosphoproteins. A. I. VOGEL.

New combination of sulphæmoglobin. A. D. VOLTA (Arch. Ital. Biol., 1926, **77**, 6 pp.; Chem. Zentr., 1928, ii, 1467—1468).—Treatment of blood with freshly-prepared ammonium sulphide solution saturated with hydroxylamine hydrochloride or sulphate affords an olive-green coloration, due to "chlorohæmoglobin." Addition of pyridine changes the green colour to brick-red, and the hæmochromogen spectrum may then be observed. Spectrographic measurements are recorded. A. A. ELDRIDGE.

Denaturation of proteins. VII. Denaturation versus coagulation. H. WU (Chinese J. Physiol., 1929, **3**, 1—6).—After flocculation, denatured egg-albumin differs from coagulated egg-albumin in its solubility in acids, alkalis, or in concentrated carbamide solution. Denatured egg-albumin differs from the native protein in not being coagulated by alcohol or by shaking. Therefore, probably, denaturation is not a step in the coagulation of protein but the essential step in denaturation is hydrolytic fission, whilst in coagulation it is molecular condensation. W. O. KERMACK.

Denaturation of proteins. IX. Liberation of non-protein substances on denaturation and coagulation of proteins. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, **3**, 75—79).—Highly purified egg-albumin was heated at 100° for 15 min. with various quantities of acid or alkali. The cooled and neutralised solutions were filtered from protein which had been coagulated or denatured and flocculated. Any conalbumin precipitated by further heating for 15 min. was removed by filtration. The filtrates were tested by the phenol reagent and sodium carbonate; at the isoelectric point there was no liberation of chromogenic substances on heating, but on either side of this point there is some liberation, much more on the alkaline than on the acid side. W. O. KERMACK.

Denaturation of proteins. V. Denaturation by acid. H. K. CUBIN (Biochem. J., 1929, **23**, 25—30).—Determination of the velocity coefficients at different temperatures and for varying values of p_H of the denaturation shows that the critical increment for oxyhæmoglobin is 12,000 g.-cal. and for egg-albumin 36,000—48,000 g.-cal., *i.e.*, lower values than those obtained by heat-denaturation. Formaldehyde diminishes the p_H range over which precipitation of denatured protein occurs. S. S. ZILVA.

Protein denaturation. I. Denaturation by alcohol. M. SPIEGEL-ADOLF (Biochem. Z., 1929, **204**, 1—13).—In contrast to serum-albumin, pseudo-globulin when precipitated by heat only partly regains its water-solubility on treatment with alkali. Even using high alcohol concentrations (88%) for long periods (6 weeks) only about 60—70% of serum-albumin remains insoluble; by treatment with alkali and electrodialysis it regains its water-solubility and typical properties. Under similar conditions egg-albumin remains practically insoluble; pseudo-globulin occupies an intermediate position. The presence of acid increases and of neutral salt diminishes the proportion of the alcohol precipitate of serum-albumin, which becomes soluble when treated with alkali. J. H. BIRKINSHAW.

Capsule for incinerating [organic materials]. KÖNIG (Chem.-Ztg., 1929, **43**, 130).—The ordinary small porcelain capsule is provided with an outside flange so as to permit the operator to grip it with the crucible tongs without danger of touching the contents of the capsule. A. R. POWELL.

Device for carbon and hydrogen analysis of volatile, explosive, and easily carbonisable organic liquids. M. G. SEVAG (Ind. Eng. Chem. [Anal.], 1929, **1**, 16—17).—The usual capillary bulb is replaced by a pyrex or silica tube packed with kieselguhr held in position by asbestos pads. The ends are closed by glass or rubber stoppers during weighing, and the liquid is dropped on the kieselguhr by removing one pad. No appreciable loss of even a volatile liquid occurs in handling and the combustion proceeds without either explosion or incomplete burning of the carbon content. C. IRWIN.

Quantitative gas analysis. W. H. BENNETT.—See this vol., 420.

Micro-determination of iodine. J. F. REITH.—See this vol., 414.

Volumetric determination of dextrose. C. A. AMICK (Chemist-Analyst, 1928, **17**, No. 4, 10—11).—The dextrose solution (10 c.c.) and 6*N*-sodium hydroxide solution are added to boiling 2*N*-copper sulphate solution (30 c.c.) and water (50 c.c.); carbonate must be absent. The mixture is heated on the water-bath for 15 min., then cooled to the ordinary temperature. Phosphomolybdate solution (50 c.c.; 100 g. of Na_2MoO_4 in 500 c.c. of water, 75 c.c. of 85% phosphoric acid, 275 c.c. of concentrated sulphuric acid, and water to 1750 c.c.) is added, and the tervalent molybdenum is titrated with permanganate similarly standardised with dextrose.

CHEMICAL ABSTRACTS.

Determination of formaldehyde. F. LIPPICH (Z. anal. Chem., 1929, 76, 241—254).—The method is based on the principle that formaldehyde reacts with potassium cyanide to form the potassium compound of hydroxyacetonitrile which is stable in boiling 20% tartaric acid solution, whereas the excess of potassium cyanide is thereby decomposed. The reaction is carried out in a distillation flask provided with a side tube which passes down to the bottom and connected through a reflux condenser to an absorption flask containing 50 c.c. of 60% potassium hydroxide solution; a measured volume of 0·25*N*-potassium cyanide solution is placed in the distillation flask and the formaldehyde is added slowly with agitation. After 5 min. a 40% solution of tartaric acid is added in quantity sufficient to give a 20% solution of the acid in the flask. The liquid is boiled for 1—2 hrs., while a rapid current of air is passed through the apparatus to expel excess of hydrogen cyanide. The contents of the absorption flask are rinsed into a beaker, diluted to 200 c.c., treated with a little potassium iodide, and titrated with silver nitrate, about 0·5 c.c. of ammonia being added towards the end of the titration. Acetone causes the results to be slightly high and acetaldehyde reacts quantitatively with cyanide in the same way as formaldehyde, so that the sum of both aldehydes may be obtained by this method. Formaldehyde may then be determined in a separate sample by Romijn's method (A., 1897, ii, 166).

A. R. POWELL.

Applications of the nitrile method. I. Fixation of hydrocyanic acid by protein, determination of formaldehyde in presence of pure proteins, and quantitative relationship between formaldehyde and protein. F. LIPPICH (Z. anal. Chem., 1929, 76, 255—260; cf. preceding abstract).—In the determination of formaldehyde by the nitrile method the presence of proteins in the solution causes only a very slight error due to irreversible combination of the cyanide with protein, but more serious errors are introduced by combination of the formaldehyde with the protein molecule, especially in the cases of gelatin and casein.

A. R. POWELL.

Micro-chemistry [detection] of theophylline. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 131—133).—The most suitable reactions are those with mercuric chloride, iodine, and bromine, which will detect 5 mg. at a concentration of 1 in 1000. Potassium antimony iodide will detect 1 mg. at the same concentration.

S. I. LEVY.

Biochemistry.

Seasonal influence on the respiratory combustion of the dog. F. MAIGNON and A. PAINVIN (Compt. rend., 1929, 188, 573—575).—The amount of oxygen used in respiration by a fasting dog shows maxima in the spring and the autumn; on a meat diet the effect is similar but less pronounced.

G. A. C. GOUGH.

Carbon dioxide capacity of human body. E. F. ADOLPH, F. D. NANCE, and M. S. SHILING (Amer. J. Physiol., 1929, 87, 532—541).—When the human body is saturated or desaturated to a new level of carbon dioxide tension, carbon dioxide is retained or given up by the body amounting to between 40 and 700 c.c. for each mm. change in alveolar carbon dioxide tension.

B. A. EAGLES.

Gas tension at skin surface of man. J. A. CAMPBELL (J. Physiol., 1929, 67, Proc. Physiol. Soc., viii—ix).—The carbon dioxide tension at the skin surface is about 40 mm. mercury, resembling that in the alveolar air. The skin is permeable outwards or inwards to carbon dioxide, but impermeable outwards to oxygen. It is slightly permeable inwards to oxygen at higher pressures.

B. A. EAGLES.

Hydrogen in tissues. J. A. CAMPBELL (J. Physiol., 1929, 67, Proc. Physiol Soc., vi—vii).—Tensions of hydrogen, carbon dioxide, and oxygen in the gut and peritoneal cavity were determined. The gases in the gut differed in composition from gases in the peritoneal cavity, carbon dioxide and hydrogen being present at much greater tension in the gut, whilst oxygen was at much lower tension than in the peritoneal cavity.

B. A. EAGLES.

Carbon dioxide in venous blood. I. Effect of oxygenation and critical oxygen tension. M. C. G. ISRAËLS and F. W. LAMB (J. Physiol., 1929, 67, 49—61).—Attention is directed to the effect of insufficient oxygenation of the lung blood in rebreathing experiments for determining the carbon dioxide content of the mixed venous blood. A method for carrying out rebreathing experiments without a rapid lowering of the oxygen tension in the rebreathing bag is described.

B. A. EAGLES.

Blood-cell metabolism. III. Effect of methylene-blue on oxygen consumption of eggs of sea urchin and starfish; mechanism of the action of methylene-blue. E. S. G. BARRON (J. Biol. Chem., 1929, 81, 445—457).—The oxygen consumption of the eggs of the sea urchin and starfish is increased by the presence of methylene-blue; the action of the dye is inhibited by narcotics (urethane derivatives), but is not affected by cyanides, which indicates that it is concerned with the anaërobic metabolism of the cells. In agreement with this, the effect of methylene-blue on the oxygen consumption of mammalian red blood-corpuscles is considerable and on avian blood-corpuscles negligible. The rôle of methylene-blue is that of a reversible hydrogen acceptor.

C. R. HARINGTON.

Effect of removal of liver on alkali reserve and lactic acid content of blood. L. G. KILBORN, S. SOSKIN, and J. C. THOMAS (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 159—161).—There is a close relationship between the rise in the lactic acid content and the fall in carbon dioxide capacity of the blood. After removal of the kidneys there was a small initial rise in lactic acid accompanied by a fall in the carbon dioxide capacity; these values then remained fairly constant. After evisceration or hepatectomy, the lactic acid content of the blood increased considerably with a corresponding decrease in the carbon dioxide capacity. It is suggested that the respiratory quotient is of doubtful value as an index of the type of metabolism proceeding in such preparations.

F. C. Happold.

Detection of specific blood. A. D. Volta (Arch. Ital. Biol., 1928, **79**, 4 pp.; Chem. Zentr., 1928, ii, 1468).—The " chlorohæmoglobin " reaction is applied to the blood of various animal species.

A. A. Eldridge.

Spectrographic study of the " chlorohæmoglobins " in the blood of various animals. A. D. Volta and E. Viterbi (Arch. Ital. Biol., 1928, **79**, 4 pp.; Chem. Zentr., 1928, ii, 1468).

Diffusion of hæmoglobin. R. E. Liesegang and O. Mastbaum (Biochem. Z., 1929, **205**, 451—456).—Hæmoglobin diffuses into a gelatin gel much more readily than would be expected from the size of the molecule. J. H. Birkinshaw.

Oxidase in the blood-leucocytes and the stability of the enzyme in various types of leucocytes. J. B. Goldman (Zhur. exp. Biol. Med., 1928, **9**, 552—558).—All myelocytes and monocytes give a positive oxidase reaction; basophiles are generally negative. The stability of the enzyme is greatest in eosinophiles, intermediate in neutrophiles, and least in monocytes. Chemical Abstracts.

Seasonal variation in calcium content of the blood-serum of the young white rat. A. T. Cameron [with K. R. Turner] (Trans. Roy. Soc. Canada, 1928, (iii), **22**, V, 135—144).—A constant serum-calcium content is found throughout the year in the adult rat, irrespective of sex. The younger the rat the more susceptible it appears to be to influences which depress the serum-calcium content, and in animals of weight varying between 30 and 50 g. a normal figure was maintained only during the height of summer. This seasonal variation is possibly controlled by the effect of the solar ultra-violet radiation on the rats' food. F. C. Happold.

Rotatory power of serum as a function of temperature. P. L. Du Noüy (Compt. rend., 1929, **188**, 660—662).—The lævo-rotation of normal horse serum is constant between 0° and 50° at $[\alpha]_{\text{Hg yellow}}$ $-49°$. Slight variations are produced by heating for 10 min. at 50—55°, whilst above 55° there is a progressive increase which is rapid above 59° and increases with the duration of heating. The results are correlated with the changes in viscosity with temperature (A., 1926, 423), and with the probable changes in molecular structure of the protein constituents associated with the suppression of the " complementary power " of the serum.

J. Grant.

Serum-albumin; crystallisation in the absence of ions. M. Piettre (Compt. rend., 1929, **188**, 463—465).—After separation of serum-globulin (A., 1928, 912), the serum-albumin is purified by four precipitations with acetone. It then gives a solution of about p_H 6·5 and contains no ionic impurities. When an aqueous solution is evaporated in a vacuum over sulphuric acid, a gummy mass is obtained which becomes crystalline (long prisms, softening with decomp. at 225—230°) when subjected to a series of sudden shocks. This preparation causes no immediate anaphylaxis in goats or dogs. G. A. C. Gough.

Decomposition of adrenaline by serum. M. Chikano and M. Kominami (Biochem. Z., 1929, **205**, 176—179).—The decomposition of adrenaline in serum is followed by the chemical (iodic acid method; cf. this vol., 474) and the biological methods. The decomposition curves proceed almost identically for the first 48 hrs. and then the rate becomes somewhat less as determined by the chemical than by the biological method. Adrenaline in phosphate buffer solution of the same p_H as blood is decomposed with almost the same velocity as in serum, but the velocity is considerably less in Ringer–Locke solution.

P. W. Clutterbuck.

Choline content of blood at different points in the circulation. M. Maxim and C. Vasiliu (Bull. Soc. Chim. biol., 1929, **11**, 70—73).—The choline contents of the blood of a normal dog in the abdominal aorta, the inferior vena cava, the portal vein, and the hepatic vein are 21, 25, 32·1, and 18·1 mg. per litre, respectively. It is suggested that the liver is concerned in these variations. G. A. C. Gough.

Separation and determination of constituents of blood by means of selective adsorption. B. Sjollema and A. Emmerie (Biochem. Z., 1929, **204**, 275—285).—Constituents of blood such as ergothioneine and glutathione can be separated and determined in the same blood filtrate by the use of two adsorbents which are free from sulphur, nitrogen, and phosphorus, the sulphur content of the filtrate before and after adsorption having been found. Similarly, from determinations of nitrogen, phosphorus, and reducing power the concentration of other constituents of blood can be deduced. The adsorbents are a sugar charcoal and aluminium hydroxide, prepared according to directions given.

W. McCartney.

Amide-nitrogen of blood. IV. S. Bliss (J. Biol. Chem., 1929, **81**, 405—406).—Amide-nitrogen of blood (this vol., 339) is better expressed as mg. per 100 g. of blood-protein, rather than as mg. per 100 c.c.

C. R. Harington.

Ultrafiltration for removal of protein in the determination of amino- and residual nitrogen in blood. B. A. Wilenski (Biochem. Z., 1929, **204**, 433—438).—By means of a simple ultrafiltering apparatus which is easily prepared and cleaned, proteins can be removed at a satisfactory rate from biological fluids. Determinations of amino- and residual nitrogen in the ultrafiltrates show that this ultrafiltration method gives more constant and more satisfactory results than do precipitation methods.

W. McCartney.

Deproteinisation of blood for determination of total non-protein nitrogen and the index of polypeptidæmia. P. Cristol (Bull. Soc. Chim. biol., 1929, **11**, 92—110).—Non-protein-nitrogen is determined in the filtrate from deproteinisation with 20% trichloroacetic acid. The difference between this value and that of the filtrate after treatment with 0·6*N*-phosphotungstic acid is shown to be due probably to polypeptides. The consequent polypeptide-nitrogen is termed the "index of polypeptidæmia" and the value of this index in various pathological states is determined.

G. A. C. Gough.

Characterisation of the proteins of blood, muscles, and internal organs of rabbits and chickens by means of colour reactions. M. A. Rakuzin and T. A. Genke (Zhur. exp. Biol. Med., 1928, 9, 225—229). Chemical Abstracts.

Blood-sugar. O. Folin (J. Biol. Chem., 1929, **81**, 377—379).—The conclusions of Somogyi and Kramer (this vol., 207) are criticised.

C. R. Harington.

Ferricyanide method for determination of blood-sugar. O. Folin (J. Biol. Chem., 1929, **81**, 231—236).—Further technical details are given in connexion with the author's recent method for the determination of blood-sugar (A., 1928, 786); it is important that toluene be not used as a preservative for the tungstic acid solution, especially if the latter be exposed to light; gum ghatti is recommended in place of gum arabic as a protective colloid for the ferric phosphate solution. C. R. Harington.

Determination of reducing sugars in blood and urine. J. A. Hawkins and D. D. Van Slyke (J. Biol. Chem., 1929, **81**, 459—467).—The rate of decolorisation of an alkaline solution of potassium ferricyanide on heating with a solution containing reducing sugars bears, within wide limits, a definite relationship to the concentration of the latter. On this fact is based a rapid method for the determination of reducing sugars in urine, or in protein-free blood filtrates, with an error of ±5%.

C. R. Harington.

Blood-sugar regulation in mammals. II. Effect of fasting on alimentary hyperglycæmia. B. Kisch, A Simons, and P. Weyl (Biochem. Z., 1929, **205**, 349—359; cf. this vol., 339).—The feeding of oats or dextrose to fasting rabbits produces only a slight hyperglycæmia which is perhaps more marked after 16 hrs.' than 9 days' fast. Dextrose administered to the fasting dog produces marked reaction, hyperglycæmia followed by hypoglycæmia, which is strong after 1—3½ days' fast, weak after 16 hrs., and negligible after 7½—10½ days.

J. H. Birkinshaw.

Daily variations of blood-sugar values in man. L. M. Krasnjanskij (Biochem. Z., 1929, **205**, 180—185).—Curves show the variations on a normal diet and during starvation. P. W. Clutterbuck.

Alimentary blood-sugar curves. IV. Sucrose in blood. V. Lævulose in blood. W. W. Oppel (Biochem. Z., 1929, **205**, 31—46, 47—62).—IV. After enteral administration of sucrose (2—4 g./kg.) dextrose and lævulose, but not sucrose, could be detected in the blood. Injection of sucrose directly into the jejunum, however, causes sucrose to appear in the blood and the intestine is therefore permeable to it. After intravenous injection of sucrose a regular curve is obtained showing its disappearance. Sucrose must remain therefore sufficiently long in the intestinal tract for the action of invertase to be completed.

V.—Lævulose, after enteral administration to rabbits, can be detected in the blood, its appearance in the peripheral circulation depending on the amount administered. With a dose of 2—3·5 g./kg., the first traces of lævulose are detected in the blood within 5 min. of administration; the maximal increase in blood-lævulose is 8—10 mg./100 c.c. of blood, and the sugar disappears in 2·5—3 hrs. After intravenous injection of 0·2—0·4 g. of lævulose, the sugar disappears from the blood in 30—60 min., part being retained by the liver and part appearing in the circulation.

P. W. Clutterbuck.

Imitation of organic forms by means of albumin. L. A. Herrera (Atti R. Accad. Lincei, 1928, [vi], 8, 637—639).—Further details are recorded (cf. this vol., 208).

Low cholesterol content of fatty substances of the chrysalides of Lepidoptera. A. Courtois (Compt. rend., 1929, **188**, 666—668).—The ratio unsaponifiable matter/total fatty acids for the fatty substances of the chrysalides of the Lepidoptera is of the same order as that for the invertebrates, but for those species of the former studied (*Attacus Pernyi*, *Sphinx Ligustri*, and *Saturnia Pyri*) the cholesterol content of the unsaponifiable matter is so small that the lipocytic coefficient (100 × cholesterol/fatty acids) is less than one tenth of the smallest value recorded for the animal series. J. Grant.

Isolation of methylhydantoin from extract of ox testes. J. P. Collip and R. Sandin (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 185—186).—A crystalline substance isolated from an extract of ox testes has been shown to be β-methylhydantoin.

F. C. Happold.

Non-specific pressor substance. J. P. Collip (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 181—184; see also this vol., 208).—A highly potent pressor substance can be extracted from skeletal muscle, liver, kidney, spleen, ovary, testes, stomach, intestine, whole fœtus, and several commercial preparations of both pepsin and pancreatin, by boiling the minced tissue with neutral or acidulated water. The active substance is freed from inorganic matter and much of the depressor substances by repeated extraction with acetone. Further methods of purification of the pressor substance and its stability to such treatment as exposure to acetic anhydride, heating with acid and alkali, etc. are described. Gynergen in doses of 0·5 mg. produces marked enhancement of the pressor action, with nicotine the action is slight, with atropine no effect is apparent, and with cocaine a marked, but transient antagonism is observed. The pressor extract obtained from the prostate glands of oxen is not antagonised by cocaine. F. C. Happold.

Determination of adrenaline in human adrenals after death. M. Paget and P. Lohéac (Compt. rend. Soc. Biol., 1928, **98**, 1421—1423; Chem. Zentr., 1928, ii, 1346).—The finely-divided material is ground with three times its weight of anhydrous sodium sulphate and 5—10 c.c. of "4/10" sulphuric acid; after 5 min. the mixture is diluted with water, frequently shaken during 15 min., and filtered. An aliquot part of the filtrate is treated with sodium acetate and a little mercuric chloride, when a red colour is produced (maximum in 45 min.) and compared with that produced by a solution of adrenaline. A. A. Eldridge.

Existence of adrenaline, free and otherwise, in human adrenals after death. Langeron, M. Paget, and P. Lohéac (Compt. rend. Soc. Biol., 1928, 98, 1424—1426; Chem. Zentr., 1928, ii, 1346).—On incipient decomposition the adrenaline rapidly disappears (cf. preceding abstract).

A. A. Eldridge.

Preparation of chondroitin-sulphuric acid. E. Jorpes (Biochem. Z., 1929, 204, 354—360).—Tracheal cartilage from cattle after being treated with alcohol, dried in air, and ground was extracted for 8—10 hrs. at 0—3° with 2% sodium hydroxide solution. The extract was made faintly acid with acetic acid, filtered, and the filtrate treated with kaolin to remove protein. The filtrate then gave no biuret reaction and alcohol precipitated biuret-free calcium sodium salt of the acid. The yield of substance (4·5% S) was 50—80 g. from 1 kg. of cartilage. This substance was shaken with cold 10% sodium chloride solution for 12 hrs., 1·0—1·5% acetic acid was added, the liquid was filtered, and the filtrate treated with kaolin. After further filtration the product was precipitated with alcohol. A further quantity was obtained from the original powder by a slightly modified treatment. The method gives a purer product than previously used methods.

W. McCartney.

Tissue calcification. N. W. Taylor and C. Sheard (J. Biol. Chem., 1929, 81, 479—493).—Determination of the refractive index of bone, dentine, and dental enamel indicates that the inorganic basis of these materials is of the apatite type; this conclusion is supported by X-ray diffraction photographs of various samples of normal and pathological bone powders. C. R. Harington.

Characteristic colour reaction of thymus-nucleic acid. Z. Dische (Biochem. Z., 1929, 204, 431—432).—When a 0·25% solution of thymus-nucleic acid containing 0·5% of hydrochloric acid is heated at 100° for 5 min. with 0·1—0·2 c.c. of a 1% alcoholic solution of indole an intense orange colour develops and, on cooling, the liquid becomes turbid. If the turbid liquid is shaken with chloroform this remains colourless, but thick red flocks appear at the interface. If less than 0·5% of hydrochloric acid is present heating must be continued longer and the colour produced is reddish-brown. Sugars and aliphatic aldehydes give the test, although often only when present in high concentrations, and in the case of these substances the colours can be completely extracted with chloroform. It is concluded that the reaction is due to the carbohydrate component of the nucleic acid. W. McCartney.

Pentosenucleic acids in the animal organism; pancreas-nucleic acids. E. Jorpes (Veröffentl. Chem. Abt. Karol. Inst. Stockholm, 1928, 253—573; Chem. Zentr., 1928, ii, 1343).—Fresh pancreas contains about 0·0437% of free phosphate-phosphorus and 0·1267% of lipin-phosphorus. Fresh (ox) pancreas contains 0·223% of nucleic acid-phosphorus, corresponding values being: liver 0·104, spleen 0·145, parotid 0·107, mucous membrane of fundus ventriculi 0·088%. When heated for 2·5 hrs. on the water-bath with 5% sulphuric acid, the phosphorus in purine-nucleotides is quantitatively removed, whilst only a portion is removed from pyrimidine-nucleotides. Half of the thymus-nucleic acid-phosphorus is removable by acid hydrolysis. The nucleic acid-phosphorus of the thymus amounting to 0·441%, the pentosenucleic acids, reckoned as pentosetetranucleotide, constitute 14·2% of the total nucleic acid-phosphorus. In the pancreas, with a pentose content of 0·445%, pentosenucleic acids form the major portion. About half of the pancreas-nucleic acid undergoes fission by acid hydrolysis; hence the pentosenucleic acids of the animal organism are considered to have a tetranucleotide character. No differences between carnivorous and herbivorous animals were observed. The nature of the pancreas-nucleic acids is discussed, and analytical methods are described. A. A. Eldridge.

Analysis of the liver of *Raja clavata*. O. Flössner and F. Kutscher (Z. Biol., 1929, 88, 390—394).—The following substances have been isolated: adenine, choline, neosine, histidine, acanthine, lactic and *n*-valeric acids. E. A. Lunt.

Alleged presence of carotin in pig's liver. L. S. Palmer (Amer. J. Physiol., 1929, 87, 553—557).—Pig's liver contains a minute quantity of unsaponifiable pigment soluble in light petroleum which resembles carotin in solubility and adsorption properties and gives some colour reactions, but not others, given by carotinoids. Its spectroscopic properties are both qualitatively and quantitatively unlike those of carotin and therefore the liver pigment cannot be carotin. B. A. Eagles.

Micro-determination of total creatinine in muscle. S. Ochoa and J. G. Valdecasas (J. Biol. Chem., 1929, 81, 351—357).—Muscle is autoclaved for 25 min. at 125° with 0·2N-hydrochloric acid, the solution is treated with picric acid and filtered, and the filtrate made alkaline with sodium hydroxide; the resulting colour is compared with that obtained from a known amount of creatinine. The method is applicable to 5—100 mg. of muscle with an error of ±2%. C. R. Harington.

Hydrogen-ion concentration of isolated uterus. P. T. Kerridge and F. R. Winton (J. Physiol., 1929, 67, 66—76).—The effect of the p_H of a solution on the tone of a uterus cannot be attributed to the sign or magnitude of the difference of p_H between the muscle and the solution. The hydrogen-ion concentration of an isolated uterus is greater than that of the uterus *in situ*. This acid formation is largely irreversible and takes place during excision and before immersion in saline solutions.

B. A. Eagles.

Body fluids of elasmobranchs. H. W. Smith [with J. T. Baker and H. Silvette] (J. Biol. Chem., 1929, 81, 407—419).—Figures are given for the concentrations of carbamide and of inorganic salts in the blood, cerebrospinal fluid, and pericardial and perivisceral fluids of various elasmobranchs. As found by previous workers, carbamide is present throughout in very large amount. Whilst the cerebrospinal fluid is practically an ultrafiltrate of the blood-plasma, differences between the composition of the latter and of the pericardial and peritoneal fluids indicate a probable excretory function of the pericardial and peritoneal membranes.

C. R. Harington.

Nitrogenous constituents of the urine of the goosefish (*Lophius piscatorius*); presence of trimethylamine oxide. A. Grollman (J. Biol. Chem., 1929, **81**, 267—278).—The urine of the goosefish contains but little ammonia, carbamide, or uric acid; the nitrogen is present chiefly in the form of amino-acids, creatine, creatinine, and trimethylamine oxide. The urine of specimens kept in an aquarium contained less nitrogen and more salts (especially magnesium salts and chlorides) than that of specimens freshly caught. C. R. Harington.

Determination of hippuric acid in urine. A. von Beznák (Biochem. Z., 1929, **205**, 409—413).—The total ethereal extract of the urine is dissolved in 10 c.c. of water, 1 c.c. of sulphuric acid is added, and the mixture autoclaved for 3 hrs. at 2½ kg./cm.^{2} The amino-nitrogen of the hydrolysate determined by Van Slyke's method gives the hippuric acid originally present. J. H. Birkinshaw.

Preparation of urea from urine. S. Kannegieter (Pharm. Weekblad, 1929, **66**, 129—131).—The urine is shaken with 2—3% by weight of "norit," filtered, evaporated to one sixth of its original volume, cooled, and treated with nitric acid. Pure urea nitrate is obtained directly. The base is obtained by treatment with barium carbonate and extraction with alcohol. S. I. Levy.

Uric acid and its determination in blood and urine. Fischer (Süddeut. Apoth.-Ztg., 1928, **68**, 448—450; Chem. Zentr., 1928, ii, 1468).—A discussion, particularly of the degradation of nucleoproteins. A. A. Eldridge.

Does the oxidation quotient of dextrose-free urine change on keeping owing to decomposition? L. Chaskin and G. Nigmann (Biochem. Z., 1929, **205**, 473—480).—Rabbit's or human urine kept for 24 hrs. at the ordinary temperature undergoes no change in oxidation quotient.

J. H. Birkinshaw.

Application of Grossfeld's method for the determination of fat to fæces. W. Heupke (Arch. Verdauungskrankh., 1927, **41**, 329—335; Chem. Zentr., 1928, ii, 1469).—By weighing the residue from an aliquot part of the filtered solution of fat in solvent, sufficiently good accord with results obtained by Soxhlet's method can be obtained.

A. A. Eldridge.

Lipin excretion. V. Partition of fæcal lipins with reference to bacteria. W. M. Sperry (J. Biol. Chem., 1929, **81**, 299—319).—The fæces of dogs on a lipin-free diet were suspended in dilute hydrochloric acid, and separated by fractional centrifuging into bacteria, non-bacterial solids, and soluble substances. On the average, 40% of the total lipins were present in the bacteria, the greater part of the remainder being contained in the non-bacterial solids. Under these conditions, therefore, the lipins are associated entirely with the formed elements. Extraction and fractionation of the lipins revealed no significant difference between those of the bacteria and those of the non-bacterial residue; it is therefore possible that they represent a secretion into the intestine which is adsorbed on the formed elements of the fæces. C. R. Harington.

Blood regeneration in severe anæmia. XV. Liver fractions and potent factors. W. M. Sperry, C. A. Elden, F. S. Robscheit-Robbins, and G. H. Whipple (J. Biol. Chem., 1929, **81**, 251—265).—The increased formation of hæmoglobin in dogs suffering from simple anæmia (as the result of hæmorrhage) which is obtained by administration of liver is observed also on administration of extracts of liver prepared by a variety of methods (*e.g.*, extraction with alcoholic hydrochloric or aqueous sulphuric acid, enzymic digestion or autolysis of the liver, and extraction with alkali). The acid extracts are the most potent, containing more than 50% of the activity of the original liver; of the digests, the peptic hydrolysate is the most active. The activity of all fractions is in part due to salts, particularly those of iron; in general the therapeutic effect is complex. The purified extract, shown by Cohn and others (A., 1928, 790) to be effective in relieving human pernicious anæmia, represents 10—20% of the activity of the original liver with respect to the simple experimental anæmia in dogs.

C. R. Harington.

Circulation during hyperæmia following anæmia. A. Jarisch and F. Gaisböck (Arch. exp. Path. Pharm., 1929, **139**, 159—178).—From experiments determining the effect on the circulation and respiratory exchange of tying off the limbs and freeing them again it appears that in man the circulation through the extremities amounts to 28 c.c. per kg. per min. and that resting human skeletal muscle requires between 0·8 and 1·0 c.c. of oxygen per g. per hr. W. O. Kermack.

Cytolysis in cancer. III. N. Waterman, L. De Kromme, and J. F. Lemmens (Biochem. Z., 1929, **205**, 1—20).—In cancer a spontaneous but small amount of lysis occurs which can be artificially increased. In the disintegration of pure cancer cells in suspensions, substances are formed which make fresh cells resistant to lysis and agglutination. A lytic substance may be extracted from all normal organs and from serum, the best yield being obtained from lymph glands, spleen, and thymus. It is combined with lipoprotein, is not identifiable with any simple known enzyme system, and is both activated and destroyed by exposure to *X*-radiation, the radiation effect being greater with the impure than with the purified preparation (cf. A., 1927, 1215; 1928, 86). P. W. Clutterbuck.

Is aërobic glycolysis specific for tumours? O. Warburg (Biochem. Z., 1929, **204**, 482—483).—Aërobic glycolysis is not specific for tumours. When normal cells undergo aërobic glycolysis, they die, whereas cells of tumours undergoing glycolysis live and grow without limit while using the chemical energy of the glycolysis. The classification of body-tissues according to the magnitude of their respiration should be abandoned. The two kinds of disturbance to respiration which can be produced artificially in normal cells occur naturally in tumours.

W. McCartney.

Carbohydrate exchange in tumours and normal tissue and its relation to the lactic acid economy of the body. C. Fahrig (Z. Krebsforsch., 1927, 25, 146—228; Chem. Zentr., 1928, ii, 1357).—Noorden and Embden's postulated carbohydrate cycle is supported. In cancer a high lactic acid value is found only in pathological conditions of the liver. The content of glycogen, lower carbohydrates, and buffers in myoma, sarcoma, and carcinoma does not differ markedly from that in normal tissue.

A. A. Eldridge.

Catalase of malignant tissue. M. R. Lewis and H. Cossman (Amer. J. Physiol., 1929, 87, 584—593).—The infectious tumour of the chicken contains only a feeble catalase, in this respect being like the muscle. The tumour virus, however, is inactivated by hydrogen peroxide. B. A. Eagles.

Differentiation between normal and pathological sera; ease of oxidation of sera. R. Douris, C. Mondain, and M. Plessis (Compt. rend., 1929, **188**, 587—588).—The reducing capacity of sera is determined empirically by oxidation by the method of Cordebard (A., 1928, 661) followed by back-titration with ferrous ammonium sulphate. The average values are found to increase in the order: cancerous, syphilitic, and normal serum.

G. A. C. Gough.

Metabolism of sulphur. XIV. Cystinuria. H. B. Lewis and S. A. Lough (J. Biol. Chem., 1929, 81, 285—297).—The excretion of cystine by a cystinuric was independent of the amount of cystine in the diet; administration of a high protein–low cystine diet, however, led to increased excretion of cystine. Cystine, administered as such, was completely oxidised to the extent of 2—3 g. per day. The cystine excreted is therefore regarded as being principally of endogenous origin.

C. R. Harington.

Blood-sugar during the night and morning [in diabetics]. H. Lange and J. Schloss (Arch. exp. Path. Pharm., 1929, **139**, 274—289).—The blood-sugar of diabetics has been followed at short intervals during the night and morning hours. A marked rise in the curve occurs in the early morning, beginning between 3 a.m. and 5 a.m. The theoretical and clinical significance of this observation is discussed.

W. O. Kermack.

Significance of cholesterol in the formation of gall-stones. S. Hansen (Acta chir. Scand., 1927, 67, 483—542; Chem. Zentr., 1928, ii, 1352).—A critical discussion. A. A. Eldridge.

[Cause of] the Millon reaction given by urine in mental disease. E. Scheiner (Biochem. Z., 1929, **204**, 361—370).—Normal urine contains small quantities of a *substance*, m. p. 40°, b. p. 70°, which is present in much larger amounts in the urine of mentally diseased persons. The substance gives a strong reaction with Millon's reagent and is found in the "histidine" fraction of the urine. Its properties resemble those of the glyoxaline derivatives. It can be adsorbed on charcoal and quantitatively recovered with acetone. W. McCartney.

Composition of tissues in avitaminosis-*A*: phosphorus, lipoid extract, and cholesterol. M. Javillier, S. Rousseau, and L. Émerique (Compt. rend., 1929, **188**, 580—582).—The course of avitaminosis-*A* in rats does not lead to any appreciable alteration in the nucleoprotein-phosphorus content of separate organs. In general the ratios cholesterol/lipoid extract and cholesterol/fatty acids increase and the ratio cholesterol/lecithin decreases. The lipin content of the skin, liver, and the muscle falls; that of the spleen, kidney, lungs, and heart remains almost constant, and that of the brain and bone increases. With the exception of the skin, the cholesterol content of all the organs falls.

G. A. C. Gough.

Total proteins (serum-albumin and serum-globulin) of the serum of scorbutic guinea-pigs. Presence of albumin and hæmoglobin in urine in the final pathological state. A. Michaux (Compt. rend., 1929, **188**, 582—584).—The albumin and globulin content of the serum of scorbutic guinea-pigs shows a slight temporary decrease at the beginning of the avitaminosis. After a certain period the urine decreases greatly in volume and shows the presence of small amounts of protein, including hæmoglobin. G. A. C. Gough.

Tissue respiration. V. Utilisation of protein in tissue respiration. K. Singer and O. Pöppelmann (Biochem. Z., 1929, **205**, 63—70).—In a variety of animals, viz., mouse, cat, rabbit, dog, man, cow, and ox, the amounts of protein utilised as determined in the intact animal by the nitrogen excretion and in the respiration of surviving tissue by the formation of ammonia are compared. In each case the nitrogen excreted or formed varies within narrow limits and is independent of the kind and size of animal and of the intensity of the animal's metabolism. In the dog no definite difference could be established between the protein utilisation of living and surviving tissue, but in the larger animals the protein utilised in tissue respiration was much greater than in the intact animal. P. W. Clutterbuck.

Rôle of free oxygen in [egg] development. L. Rapkine (Compt. rend., 1929, **188**, 650—652).—The development of fertile sea-urchin eggs in air-free sea-water at 20° is inhibited if methylene-blue is absent. Molecular oxygen can therefore act as an acceptor of hydrogen provided by donators. Since the r_H of the cellular medium remains constant, the principal rôle of oxygen is to ensure a definite cellular potential, and it may therefore substitute any other acceptor.

J. Grant.

Water evaporated during work. J. A. Campbell and T. C. Angus (J. Physiol., 1929, 67, Proc. Physiol. Soc., x—xi).—A study of the total water evaporated in subjects during work under various atmospheric conditions. B. A. Eagles.

Metabolism in athletes. O. Flössner and F. Kutscher (Z. Biol., 1928, 88, 382—389).—The urine from athletes has been examined and the following substances have been detected : hippuric acid, lactic acid, adenine, methylguanidine, γ-butyrobetaine, and choline. The lactic acid, adenine, and methylguanidine contents decrease after exercise, whilst the appearance of phenylalanine and γ-butyrobetaine is noted. E. A. Lunt.

Metabolism of the retina of the frog and determination of Meyerhof quotients at different temperatures. F. Kubowitz (Biochem. Z., 1929, 204, 475—478).—At temperatures above 35° the frog retina behaves similarly to the retina of warm-blooded animals. Within the range of temperatures which do not injure the cells the Meyerhof quotient (which is independent of the action of respiration on the fermentation) increases with rise of temperature. W. McCartney.

Metabolism of the retina of the fish at different temperatures. M. Nakashima (Biochem. Z., 1929, 204, 479—481; cf. preceding abstract).—The fish retina behaves like that of the frog, but at 37° the respiration of the former is not small. It is concluded that, according to the species of animal, the same kind of injury to the retina produces aërobic glycolysis by arresting either respiration or the Pasteur reaction. W. McCartney.

Utilisation of sulphur by animals. H. R. Marston and T. B. Robertson (Council Sci. Res., Australia, 1928, Bull. 39, 5—51).—A review of the literature dealing with sulphur metabolism, compiled with the object of laying a foundation for research into the problem of the economic importance of sulphur in wool production. B. A. Eagles.

Phosphagen [in muscle]. W. Dulière (Compt. rend. Soc. Biol., 1928, 98, 1252—1254; Chem. Zentr., 1928, ii, 1351).—Rigor is not associated with the presence of phosphagen; it may disappear while the phosphagen is intact. Phosphagen disappears in the course of rigor or exertion. Addition of dextrose to the Ringer solution does not affect the phosphagen content of the muscle.
A. A. Eldridge.

Muscle-phosphorus. II. Acid hydrolysis of lactacidogen. H. A. Davenport and J. Sacks (J. Biol. Chem., 1929, 81, 469—477).—Fresh resting muscle was rapidly extracted with trichloroacetic acid solution and the extract hydrolysed with *N*-sulphuric acid at 100°; there resulted a rapid liberation of phosphoric acid during the first hour, followed by a prolonged and very much slower hydrolysis. The phosphoric acid rapidly liberated corresponds with that set free on incubation of the muscle extract, and represents a part of the lactacidogen (I); the portion hydrolysable with difficulty (designated lactacidogen II) corresponds with the ester examined by Lohmann (A., 1928, 1054); the suggestion of Lohmann that the first acid-labile portion is pyrophosphate could not be confirmed. Brief stimulation of muscle resulted in a rise in lactacidogen II and in little or no change in lactacidogen I.
C. R. Harington.

Determination of digestibility of protein by Bergeim's method. W. D. Gallup (J. Biol. Chem., 1929, 81, 321—324).—Silica has been successfully substituted for the ferric oxide employed by Bergeim (A., 1926, 1170). C. R. Harington.

Oxidation of glutamic acid in the animal body. A. von Beznák (Biochem. Z., 1929, 205, 420—432).—β-Phenylglutamic acid given subcutaneously to dogs and rabbits increases the hippuric acid excretion. It is concluded that glutamic acid is oxidised in the animal body, not only at the α-carbon, but also at the β-carbon atom. γ-Phenylglutamic acid is lethal to dogs and rabbits in doses of 0·5 g./kg. body-weight.
J. H. Birkinshaw.

Relation of various organs to cholesterol, fat, and lecithins. S. V. Nedsvedsky and A. K. Alexandry (Pflüger's Archiv, 1928, 219, 619—625; Chem. Zentr., 1928, ii, 1459).—In fasting dogs the adrenals synthesise and deliver 8 mg. of cholesterol to 100 c.c. of perfusing blood. The other organs neither take up cholesterol from the blood nor give it up. During digestion all the organs except the kidneys accumulate cholesterol. The lecithin content of arterial blood (2·6 mg. per 100 c.c.) remains unchanged after feeding. Of venous blood that of the hepatic vein contains most lecithin (0·10—0·28 mg.-%). A. A. Eldridge.

Resorption. II. Significance of bile acids for fat resorption. F. Verzár and A. Kúthy. **III. Acceleration of resorption by yeast extract.** E. von Kokas and G. Gál (Biochem. Z., 1929, 205, 369—379, 380—387).—II. Palmitic, stearic, and oleic acids when finely emulsified in water give, in presence of sodium taurocholate and glycocholate, clear, diffusible, molecular-disperse solutions which are stable at acid reactions down to p_H 6·2. The function of the complex bile acids in fat resorption is therefore to render soluble the fatty acids at the slightly acid reaction of the intestine.

III. The effect of yeast extract (Harris powder) on the resorption of dextrose and peptone in the stomach and intestine of the rat was studied. The average resorption of dextrose was increased from 37·3% to 46·8% and of peptone from 31·5% to 57·6% in presence of the extract. J. H. Birkinshaw.

Basal metabolism and specific dynamic action after extirpation of adrenals in rats. A. von Arvay (Biochem. Z., 1929, 205, 441—448).—Extirpation of both adrenals of rats leads to a fall (max. —26%) in the basal metabolism to a minimum at the sixth day, followed by a rise to the normal value at about the twentieth day in the survivors. The specific dynamic action reaches its minimum (about half normal) at the third day and attains the normal value at the same time as the basal metabolism.
J. H. Birkinshaw.

Behaviour of blood-sugar in experimental adrenal insufficiency. H. Lange and E. Grossmann (Biochem. Z., 1929, 205, 306—317).—Fasting cats deprived of one adrenal show no diminution in blood-sugar. Removal of both adrenals reduces the blood-sugar to about one quarter of its original value. The convulsions ensuing can be cured by intravenous dextrose injections. J. H. Birkinshaw.

Effect of electrolytes on sugar metabolism. I. Abelin (Biochem. Z., 1929, **205**, 457—466; cf. A., 1927, 276, 897).—The addition of phosphate, sodium hydrogen carbonate, or natural Carlsbad salt to a sucrose diet produces in rats a fall in the amount of glycogen deposited in the liver and in the respiratory quotient. A relationship is suggested between this phenomenon and the strong ketogenic action of sodium hydrogen carbonate and other alkaline salts.

J. H. Birkinshaw.

Physiology of surviving mammalian hearts. V. Sugar consumption of the surviving hearts of normal cats. G. Ambrus (Biochem. Z., 1929, **204**, 467—473).—The sugar consumption of the surviving hearts is greater than previously stated by other workers. The original view that the consumption is greatest in the earliest period of survival should, for various reasons, be modified and the second period should be regarded as that of greatest consumption. Small hearts consume relatively more sugar than large ones and results should be expressed in such a way as to allow for this and other facts.

W. McCartney.

Physiology of surviving mammalian hearts. VI. Sugar utilisation of the hearts of normal and thyroidectomised cats after administration of thyroxine. G. Ambrus (Biochem. Z., 1929, **205**, 194—213; cf. preceding abstract).—The sugar utilisation of surviving hearts of thyroidectomised cats is considerably smaller than that of the hearts of normal animals, the decrease being the greater the sooner the experiment is carried out after extirpation. The hearts of normal and of thyroidectomised cats to which thyroxine has previously been administered use more sugar than the hearts of corresponding animals not receiving such treatment.

P. W. Clutterbuck.

Influence of food on regulation of blood-sugar. E. Geiger and H. Kropf (Arch. exp. Path. Pharm., 1929, **139**, 290—301).—The sugar tolerance of rabbits as shown by the blood-sugar curves obtained after giving dextrose by mouth is increased by feeding on oats or administration of alkali, but is decreased after feeding on green food or administration of acid. These results render doubtful the validity of the method of Staub (Z. klin. Med., 1922, **93**, 123; 1926, **104**, 587) for ascertaining the efficiency of the insulin apparatus in the human subject.

W. O. Kermack.

Utilisation of pentoses in the animal organism. P. Thomas, A. Gradinescu, and (Mlle.) R. Imas (Compt. rend., 1929, **188**, 664—666).—The proportions of glycogen fixed in the liver and muscles of the male frog after ingestion of 4% solutions of certain pentoses have been determined by Pflüger's method. Assuming 1 mol. of pentose provides 1 mol. of lactic acid, which is subsequently transformed into glycogen, then the maximum possible yield of glycogen is 54%. Actually 51·24% of glycogen was formed from xylose and 54·90% from arabinose. J. Grant.

Hepatic glycogen formation from *d*- and *l*-lactic acid. C. F. Cori and G. T. Cori (J. Biol. Chem., 1929, **81**, 389—403).—The glycogen content of the liver of 24-hr. fasting rats shows marked increase after oral or subcutaneous administration of sodium *d*-lactate, a less pronounced effect after sodium *r*-lactate, and no change after sodium *l*-lactate; this confirms the recent suggestion (A., 1928, 1286) that adrenaline stimulates the transformation of muscle-glycogen into liver-glycogen through the stage of lactic acid. C. R. Harington.

Muscle-glycogen in mammals. M. E. McKay (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 329—333).—The fall in glycogen content of the sartorius, gracilis, and gastrocnemius muscles of the rabbit and dog has been studied. With the intact muscle this fall is not rapid; it is greatest in the sartorius and least in the gastrocnemius. Decapitate and decerebrate cats and cats the spinal cord of which was severed between the seventh cervical and first dorsal vertebræ were stimulated for periods of 1—30 min. There was little evidence of the restoration of glycogen to the muscles following a period for recovery of 1 or 2 hrs. F. C. Happold.

Removal of glycogen from living muscle. V. J. M. Hershey and M. D. Orr (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 151—157).—The effect of starvation, starvation and muscular exercise, severe exercise accompanied by cold, severe exercise and induced prolonged shivering on the liver- and muscle-glycogen of rats has been studied. None of these processes removed all the glycogen. There is a more thorough removal of glycogen when strychnine is injected due to the combined muscular convulsions and respiratory embarrassment; the removal is not, however, complete. F. C. Happold.

Hæmopoietic action of bilirubin and other hæmoglobin derivatives. F. Verzár and A. Zih (Biochem. Z., 1929, **205**, 388—401).—Bilirubin and hemibilirubin, and also hæmoglobin and hæmatin (which give rise to bilirubin in the body), fed to rabbits have a hæmopoietic action, but biliverdin has a much weaker action. Lower degradation products of bilirubin, as the porphyrins and bilirubinic acid, are without action. Bilirubin in large doses has a hæmolytic action in common with hæmopoietic extracts of spleen and bone-marrow and with bile. Bilirubin is active even after removal of the spleen. It is suggested that the bilirubin and related products arising from the decomposition of the blood act as physiological stimulants for the formation of red blood-corpuscles. J. H. Birkinshaw.

Hæmopoietic action of various organs. A. Zih (Biochem. Z., 1929, **205**, 402—408).—Bone-marrow, spleen, and lymph glands fed to rabbits have a variable hæmopoietic or hæmolytic action in contrast to lung and muscle, which are inactive. All hæmopoietically active organs belong to the reticulo-endothelial apparatus and breakdown products of hæmoglobin may be present in the extracts.

J. H. Birkinshaw.

Pharmacological synergism of stereoisomerides. D. I. Macht (Proc. Nat. Acad. Sci., 1929, **15**, 63—70).—Synergism is the term applied to the phenomenon exhibited by two or more drugs in which the pharmacodynamic effect of the mixture is not a simple summation of the effects of the components. A study was made of the effects of a number of stereoisomerides on certain animals and plants. Timed observations showed in general that the toxic and pharmacological effects of the *d*-, *l*-, and racemic forms varied considerably, and that a *dl*-mixture exhibited a definite synergism.

N. M. Bligh.

Physiological action of derivatives of salicylic acid. I. K. Kase. **II.** K. Kase and K. Seki (Biochem. Z., 1929, **205**, 21—26, 27—30).—I. The methyl esters and the amides of *o*- and *p*-hydroxybenzoic acids are more toxic than the corresponding free acids and their action resembles more closely that of the corresponding phenols.

II. The non-poisonous character of the hydroxybenzoic acids depends on the presence of a free carboxyl group. P. W. Clutterbuck.

Toxic effects of amines. A. R. Johnston (J. Infect. Dis., 1928, **42**, 473—484).—The toxic effects of pyridine, quinoline, fuchsin, *p*-phenylenediamine, and amines generally are described. No relationship exists between the number of amino-groups in the molecule and its toxicity. Chemical Abstracts.

Effects of derivatives of betaineamide and of choline ethers on the autonomic nervous system. R. Hunt and R. R. Renshaw (J. Pharm. Exp. Ther., 1929, **35**, 99—128).—The effect on the blood pressure of the anæsthetised or decerebrated cat of a large number of derivatives of betaine of the general formula $NMe_3X\cdot CO\cdot NHR$, (R = an aliphatic or aromatic radical and X=Cl or Br) as well as of several derivatives of choline and homocholine, has been studied. The muscarine-like action and the nicotine stimulating action are influenced by the substituents, the phenyl group in particular decreasing the muscarine action and increasing the nicotine stimulating action. W. O. Kermack.

Action of choline on gaseous metabolism. H. Tangl (Arch. exp. Path. Pharm., 1929, **139**, 220—225).—Subcutaneous injection of choline into fasting rats increases the metabolism, the maximum effect occurring 2—6 hrs. after administration.

W. O. Kermack.

Guanidine structure and hypoglycæmia. F. Bischoff, M. Sahyun, and M. L. Long (J. Biol. Chem., 1929, **81**, 325—349).—A number of guanidine derivatives have been studied with respect to their hypoglycæmic activity and their toxic effect on the liver and kidney, the latter being measured by changes in the carbamide- and amino-acid-nitrogen of the blood. In the aliphatic and alicyclic series, the toxicity towards the kidney appears to be characteristic of the guanidine group, whilst hepatic injury is produced by those derivatives which cause hypoglycæmia, and in a parallel degree. Aliphatic guanidine derivatives containing cyano-, carbonyl, carboxyl, or hydroxyl groups are devoid of toxicity and of hypoglycæmic activity; acylation reduces the toxicity of guanidine. Aromatic guanidine derivatives exercise a toxic effect distinct from that of the aliphatic compounds; some of them have also a hypoglycæmic action. The diguanidinopolymethylenes (homologues of synthalin) show a higher degree of hypoglycæmic activity than other derivatives, the activity increasing with the length of the carbon chain. Of the compounds studied so far, guanylpiperidine is unique in showing a definitely greater hypoglycæmic than toxic action, and in producing a rapid hypoglycæmia (preceding depletion of the glycogen stores) in which respect its action simulates that of insulin. C. R. Harington.

Substances producing hypoglycæmia. I. Syntheses of guanidine derivatives. T. Kumagai, S. Kawai, Y. Shikinami, and T. Hosono (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **9**, 271—275).—Hexamethylenediguanidine, octamethylenediguanidine, and decamethylenediguanidine (" synthalin ") are approximately equally effective in producing hypoglycæmia in rabbits. Octamethylenediguanidine is slightly more active than the other two compounds. The following compounds are described, the guanidine derivatives being produced by the condensation of *S*-methyl-ψ-thiocarbamide with the appropriate amine; β-3-*indolylethylguanidine hydriodide*, m. p. 141—142°; *pentamethylenediguanidine sulphate*, decomp. 330°; *hexamethylenediguanidine hydrochloride*, m. p. 179—180°; *dibenzoyloctamethylenediamine*, m. p. 169·5°; *octamethylenediamine hydrochloride*, m. p. 284° (decomp.); *octamethylenediguanidine hydrochloride*, m. p. 176·5; *decamethylenediamine hydrochloride*, m. p. 309—310°, and *decamethylenediguanidine hydrochloride*, m. p. 193°. W. O. Kermack.

Distribution of quinine in the blood. O. S. Gibbs (Proc. Nova Scotian Inst. Sci., 1928, **17**, 114—115).—Blood containing quinine was separated by centrifuging into a serum layer and a blood-cell layer. The quinine was found to be equally distributed between the two layers. When the blood is hæmolysed before being centrifuged, the lower layer, containing the " ghosts " of cells, has 6—40% more quinine, owing probably to adsorption on the cells. A modification of Ramsden and Lipkin's method for the determination of quinine gave unsatisfactory results (cf. King and Acton, A., 1921, i, 474).

B. W. Anderson.

Action of vapours of ethyl and methyl alcohols, ether, and chloroform, and of illuminating gas on leucocytes. (Signa.) C. Forti (Atti R. Accad. Lincei, 1928, [vi], **8**, 700—705).—The amœboid activity of the leucocytes of toad's blood is paralysed in a few minutes by the vapour emitted by small quantities of ethyl or methyl alcohol, ether, or chloroform. Illuminating gas (40—50% of carbon monoxide) produces first increased, and later gradually diminishing movement of the leucocytes, complete arrest setting in only after 8 or 9 hrs. According to the duration of the action, these effects may be either permanent or transitory. T. H. Pope.

Combined narcosis. I. Ether and chloroform. II. Nitrous oxide and ether. III. Acetylene and ether. L. Lendle (Arch. exp. Path. Pharm., 1929, **139**, 179—200, 201—210, 211—219).—I. When white mice are anæsthetised by mixtures of chloroform and ether the speed of narcotisation increases, whilst, relatively to the dose necessary for light narcosis, the narcotic range (cf. A., 1928, 920) decreases, as the proportion of ether in the mixture is increased. The secondary toxic action of the anæsthetic also decreases with increase in the proportion of ether.

II. With mixtures of nitrous oxide and ether the anæsthetic action is not additive, but with addition of nitrous oxide to the mixture the total anæsthetic effect tends to decrease. The narcotic ranges of the mixtures investigated were approximately the same as that of pure ether.

III. The relative narcotic range of mixtures of acetylene and ether is approximately independent of the proportion of the two anæsthetics. The anæsthetic effect of such mixtures is an additive function of the constituents. W. O. Kermack.

Relative physiological properties of certain 5 : 5-dialkyl- and 1-aryl-5 : 5-dialkylbarbituric acids. A. M. Hjort and A. W. Dox (J. Pharm. Exp. Ther., 1929, **35**, 155—164).—The anæsthetic action on mice has been studied. In the case of 5 : 5-diethylbarbituric acid the introduction of a 1-aryl group does not improve hypnotic properties, but in the cases of 5-ethyl-5-*n*-propyl- 5-ethyl-5-*n*-butyl-, 5-ethyl-5-*iso*butyl-, and 5-ethyl-5-*iso*amylbarbituric acids, the presence of a 1-aryl group decreases the toxicity of the compound and hence improves it as a hypnotic. Neither 1 : 3-diphenyl-5-ethylbarbituric acid nor the *p*-ethoxyphenylmonoureide of ethyl-*n*-butylmalonic acid has anæsthetic action. The following barbituric acids have been prepared: 1-p-*tolyl*-5 : 5-*diethyl*-, m. p. 152—153°; 1-p-*anisyl*-5 : 5-*diethyl*-, m. p. 126—127°; 1-p-*ethoxyphenyl*-5 : 5-*diethyl*-, m. p. 152—153°; 1-p-*chlorophenyl*-5 : 5-*diethyl*-, m. p. 135—136°; 1-p-*bromophenyl*-5 : 5-*diethyl*-, m. p. 186°; 1-*phenyl*-5-*ethyl*-5-*propyl*-, m. p. 152—153°; 1-*phenyl*-5-*ethyl*-5-iso*butyl*-, m. p. 149°; 1-*phenyl*-5-*ethyl*-5-n-*butyl*-, gummy; 1-*phenyl*-5-*ethyl*-5-iso*amyl*-, m. p. 130°; 1 : 3-*diphenyl*-5-*ethyl*-, m. p. 145°; also the p-*ethoxyphenylmonoureide* of *ethyl*-n-*butylmalonic acid*, m. p. 124—125°.

W. O. Kermack.

"Noctal" and "pernocton." III. Behaviour in the organism. IV. Determination of the activity of similar barbituric acids. V. Influence of the structure of the alkyl group on the activity. F. Boedecker and H. Ludwig (Arch. exp. Path. Pharm., 1929, **139**, 353—356, 357—360, 361—372).—III. 5-*iso*Propyl-5-acetonylbarbituric acid and 5-*iso*propyl-5-carboxymethylbarbituric acid, into which "noctal" (5-*iso*propyl-5-β-bromoallylbarbituric acid) is presumably converted in the animal organism, are without toxic action. The corresponding *sec.*-butyl compounds derived from "pernocton" (5-*sec.*-butyl-5-β-bromoallylbarbituric acid) are likewise inactive.

IV. The following compounds are all strong hypnotics: 5-*iso*propyl-5-γ-bromoallyl-, 5-*iso*propyl-5-β-chloroallyl-, 5-*iso*propyl-5-βγ-dibromoallyl-, 5-di-(β-bromoallyl)-, and 5 : 5-di(chloroallyl)-barbituric acids.

V. Of the following barbituric acids: 5-α-methylbutyl-5-allyl-, 5-α-methylbutyl-β-bromoallyl-, 5-*sec.*-butyl-5-allyl-, 5-*sec.*-butyl-5-β-chloroallyl-, 5-α-phenylpropyl-5-allyl-, 5-*iso*propyl-5-β-bromoallyl-, 5-*iso*propyl-5-β-chloroallyl-, 5-α-ethylpropyl-5-β-bromoallyl-, and 5-dimethylpropyl-5-β-bromoallyl-, those containing an asymmetric carbon atom are particularly potent hypnotics. The physiological and pharmacological actions of "pernocton" have been investigated. W. O. Kermack.

"Avertin." A. Welsch (Arch. exp. Path. Pharm., 1929, **139**, 302—312).—After administration of "avertin" the bromine of the compound is quantitatively excreted in the urine within 48 hrs. The urine gives Arnold's reaction (with sodium nitroprusside and alkali) much more markedly than does normal urine and it contains a substance which inhibits the reduction of Fehling's solution. From the urine after precipitation with lead acetate a barium salt was obtained which was apparently an impure mixture of the barium salts of cystine and of "avertin"-glycuronic acid from which this latter acid was isolated. W. O. Kermack.

Use of magnesium as an aid in anæsthesia. I. Neuwirth and G. B. Wallace (J. Pharm. Exp. Ther., 1929, **35**, 171—187).—Administration of magnesium sulphate or lactate to dogs by mouth or *per rectum* does not raise the magnesium content of the serum to the level at which analgesic action is produced, viz., 5 mg. per 100 c.c. This level is reached by the administration subcutaneously of 0·25 g. of magnesium sulphate per kg. body-weight. Profound anæsthesia occurs when the serum-magnesium is 20 mg. or more per 100 c.c. It is considered unlikely that magnesium salts are of use in colonic anæsthesia mixtures or in obstetrical analgesia when employed in the usual doses. W. O. Kermack.

Action of large amounts of iron. II. Action on blood, growth, fertility, and lactation. K. Waltner (Biochem. Z., 1929, **205**, 467—472; cf. *ibid.*, 1927, **188**, 38).—Rats receiving an addition of 2% of reduced iron to a complete diet show no change in the blood, but with a rachitic diet anæmia develops. The iron also delays growth at the age susceptible to rickets. The lessened fertility and secretion of milk produced by the reduced iron are cured by vitamin-*D*. J. H. Birkinshaw.

[Physiological] action of sulphur. L. Pincussen and E. Gornitzkaja (Z. klin. Med., 1928, **108**, 369—377; Chem. Zentr., 1928, ii, 1347).—After application of sulphur the blood-sugar, -diastase, and -catalase are unchanged, but the tributyrin esterase is diminished. A. A. Eldridge.

Toxicology of bismuth. II. Distribution in the organism after injection of aqueous solutions of bismuth compounds. R. Fabre and M. Picon (J. Pharm. Chim., 1928, [viii], **9**, 97—112; cf. A., 1928, 1280).—A study of the distribution of bismuth in the tissues after intravenous injections of aqueous solutions of bismuth cacodylate, "bismuth camphocarbonate," and ammoniacal bismuth citrate.

B. A. Eagles.

Excretion of bismuth from the human organism. W. Engelhardt (Arch. Dermat. Syphilis, 1928, **156**, 1—42; Chem. Zentr., 1928, ii, 1461).—Considerable quantities of bismuth are excreted in the fæces and urine during treatment of syphilis by bismuth preparations. Up to 50% is so excreted, most rapid excretion taking place after intravenous injection. Oil suspensions are irregularly excreted.

A. A. Eldridge.

Electrolytic determination of lead in urine. T. Cooksey and S. G. Walton (Analyst, 1929, 54, 97—99).—The urine is made acid with acetic acid and lead deposited electrolytically. The deposit is dissolved in nitric acid and converted into chloride, and lead is determined by comparing the turbidity resulting on addition of a solution of potassium metabisulphite against a standard. The lead content of normal urine varies between 0·02 and 0·05 mg./litre; mean, 0·04. J. S. Carter.

Resistance of the nematode, *Anguillula aceti*, Ehrenberg, to various protoplasmic poisons. J. Bělehrádek and V. Nečásova (Bull. Soc. Chim. biol., 1929, **11**, 65—69; cf. A., 1928, 1279).—*Anguillula aceti* resists the action of 2·5% aluminium chloride and 2% barium chloride solutions for considerable periods. The times of survival to potassium cyanide, mercuric chloride, and cupric chloride are greater than those of *Cypris* and *Tubifex*. The resistance is probably connected with the constitution of the epidermal tissue. G. A. C. Gough.

Strontium thioacetate as an antidote in poisoning by mercuric chloride. C. C. Haskell and J. C. Forbes (J. Pharm. Exp. Ther., 1929, **35**, 147—153).—Dogs poisoned by mercuric chloride administered either orally or intravenously were apparently not benefited by the administration of strontium thioacetate. W. O. Kermack.

Effect of *X*-rays on the process of enzyme formation in the isolated pancreas. A. I. Bogayevski and B. Goldstein (Zhur. exp. Biol. Med., 1928, 9, 328—334).—Stimulation of the gland cells by the action of *X*-rays on the perfused pancreas yields a fluid containing a greater concentration of amylase and lipase. An excessive dose diminishes the activity. Chemical Abstracts.

Absolute absorption spectrum of the respiratory enzyme. Photochemical dissociation of iron pentacarbonyl. O. Warburg and E. Negelein (Biochem. Z., 1929, **204**, 495—499).—Certain results communicated in former papers (cf. A., 1928, 549, 851, 1390; this vol., 216) require to be multiplied by the factor 2·2. The photochemical dissociation of iron pentacarbonyl has been reinvestigated and it has been found that one molecule of carbon monoxide per quantum of light is split off. W. McCartney.

Cytochrome and respiratory enzymes. D. Keilin (Proc. Roy. Soc., 1929, B, **104**, 206—252).—Yeast cells contain a powerful indophenol-oxidase system which is easily revealed by the oxidation of *p*-phenylenediamine. The oxidase is thermolabile, being irreversibly destroyed by boiling or heating to 70°, is strongly inhibited by potassium cyanide and hydrogen sulphide but not by sodium pyrophosphate. This oxidase system is inhibited by the reducing systems of the cells and so is active only in presence of various narcotics such as urethane or after the cells have been warmed for 1½ hrs. at 52° or cooled to −2°. Dried yeast and zymin give only feeble reactions. The oxidase system is inhibited by carbon monoxide, which appears to form an inactive compound with it. This compound is, however, readily destroyed by oxygen and by light. Quantitative measurements by means of a Barcroft manometer demonstrate that the amount of carbon monoxide combined with the yeast oxidase is proportional to the partial pressure of the carbon monoxide and that the oxidase molecule has much greater affinity for oxygen than for carbon monoxide. The oxidase activity of yeast-cells and the total respiratory activity are with a few exceptions similarly affected by reagents. An oxidase system with properties similar to but not identical with that found in yeast is present in a preparation of washed heart-muscle. The properties of polyphenol-oxidase from potato have also been investigated. This enzyme can be obtained as a clear solution unlike the former two, which it has not so far been possible to separate from cellular material. It is considered that the indophenol-oxidase plays an important rôle in cell metabolism. The properties of the components of living cells which are derivatives of hæmatin are described. Cytochrome is composed of three hæmatin compounds, a^1, b^1, and c^1, and an unbound hæmatin compound similar to the protohæmatin of hæmoglobin, of which the components a^1 and c^1 are not, whilst the other two are autoxidisable. It appears that the factors, *e.g.*, potassium cyanide, propionitrile, hydrogen sulphide, carbon monoxide, drying the cells, treating them with alcohol or acetone, which inhibit the activity of indophenol also inhibit the oxidation of cytochrome, whilst the factors, *e.g.*, narcotics or warming to 52°, which have little effect on the activity of indophenol-oxidase do not inhibit the oxidation of cytochrome. It is concluded that cytochrome is oxidised by the indophenol-oxidase. Cytochrome in the living cell is reduced in presence of dehydrases by the hydrogen donators present, which are themselves oxidised. Cytochrome is thus considered to act as an oxygen carrier in the oxidation of the cell metabolites, being alternately oxidised through the action of the oxidase and reduced through the action of the dehydrase. Some other possible functions of intracellular hæmatin compounds are discussed as well as the nature of the oxidase. W. O. Kermack.

Dextrose-oxidase. II. D. Müller (Biochem. Z., 1929, **205**, 111—143).—In the press juice and in the alcohol, alcohol-ether, and acetone precipitates of the press juice of *Aspergillus niger* an enzyme is present which can oxidise dextrose to gluconic acid, atmospheric oxygen being absorbed. The enzyme oxidises mannose and galactose less readily, but does not attack lævulose, xylose, arabinose, calcium gluconate, dihydroxyacetone, glycerol, and acetaldehyde. The oxidase does not act in an atmosphere of hydrogen. Its p_H optimum is 5·5—6·5 and its action increases from 0 to 30°, inactivation occurring at 73°. Its action is not assisted by phosphate or insulin. The activity of the oxidase rapidly decreases on keeping. The enzyme is also present in the press juice of *Penicillium glaucum*.

P. W. Clutterbuck.

Action of ptyalin on starch. I. J. R. Broeze (Biochem. Z., 1929, **204**, 286—302).—The decomposition of starch by ptyalin has been followed by means of viscosity measurements. The velocity of enzymic hydrolysis was proportional to the concentration of the enzyme. The enzyme was not reduced in activity by its action on the starch. The temperature coefficient of the velocity of the reaction at 20—30° was 2. No regeneration of the heated enzyme could be observed. Evidence is given for supposing that the flocculation of the starch and the checking of the reaction which occur during the process are due, respectively, to the existence of sensitive spots on the starch particles and to the enveloping action of some of the particles, when swelling, on others.

W. McCartney.

Action of fluorescent dyes in the dark on diastase. G. Claus (Biochem. Z., 1929, 204, 456—466).—Diastase from germinating roots grown from seeds treated with eosin is more active than that from normally grown roots. The dyes of the fluorescein series and phenosafranine added to starch-diastase solution accelerate the decomposition of the starch, the magnitude of acceleration varying according to the dye used and being greatest with phenosafranine and eosin and least with phloxin and erythrosin. The acceleration of decomposition occurs only at p_H values removed from the optimum for the action of diastase, but it exceeds considerably that produced at the most favourable p_H without addition of eosin. Diastases of different origins may, in consequence of the presence of impurities, produce different effects and malt diastase should always be employed. The action of diastase from saliva can also be stimulated by the dyes, although negative results were obtained with extract of *Aspergillus oryzæ*. W. McCartney.

Determination of catalase in barley-malt. M. O. Charmandarian (Biochem. Z., 1929, 204, 389—396).—On continued extraction the catalase of malt from barley loses some of its power to decompose hydrogen peroxide, but the length of the period of extraction does not influence the reaction of the medium and hence factors which might affect the activity of the catalase are not introduced. Unextracted barley-malt always decomposes more hydrogen peroxide than do extracts and it is concluded that the variations which occur in the power of the catalase are chiefly due to the degree of its dispersion in the medium. W. McCartney.

Action of proteolytic enzymes on the benzoyl and phthalyl derivatives of polypeptides. I. Action of intestinal erepsin and of yeast protease on phthalylglycylglycine and phthalyldiglycylglycine. II. Action of tissue proteases on benzoyl- and phthalyl-glycylglycine. III. Action of pancreatic proteases on benzoyl- and phthalyl-glycylglycine. S. Utzino (J. Biochem. Japan, 1928, 9, 453—463).—I. Yeast protease attacks both compounds, but intestinal erepsin hydrolyses only the latter.

II. Phthalylglycine and phthalylglycylglycine were not hydrolysed. Maceration juice hydrolyses glycylglycine and leucylglycine; pig-kidney maceration juice hydrolyses benzoylglycine, benzoylglycylglycine, and glycylglycine. Benzoyl- and phthalyl-glycylglycine are not hydrolysed by beef muscle or pig-liver press juice, rabbit-muscle or -liver maceration juice, or rabbit-liver pulp.

III. The compounds are hydrolysed by pancreatin, pig-pancreas pulp, pancreas press-juice, and glycerol extracts of dry pancreas preparations, and by the trypsin fraction which hydrolyses edestin but not glycylglycine. Chemical Abstracts.

Effect of alkaloids on an alcoholic extract of fibrin peptone (peptic digest). M. A. Rakuzin and T. A. Genke (Zhur. exp. Biol. Med., 1928, 9, 221—223).—Strychnine, brucine, quinine, codeine, morphine, or theobromine removes tyrosine from the extract. The action of the alkaloid is similar to that of enzymes, and it is suggested that alkaloids are crystalline toxins. Some alkaloids of high mol. wt. are considered to be colloidal.

Chemical Abstracts.

Stereochemical action of animal phosphatase. A. Gualdi (Biochem. Z., 1929, 205, 320—324).—Phosphatase from the liver and from the kidney of the rabbit, like mould phosphatase, first sets free *l*-borneol from salts of *dl*-borneolphosphoric acid.

J. H. Birkinshaw.

Sulphatase. X. F. Weinmann (Biochem. Z., 1929, 205, 214—218).—The preparation of potassium 3-methyl*cyclo*hexylphenyl sulphate and its hydrolysis by takasulphatase are described, the hydrolysis being practically complete. P. W. Clutterbuck.

Significance of some auxo-substances in the urease reaction. M. Kitagawa (J. Biochem. Japan, 1928, 9, 347—352).—Urease free from auxo-substance retains its activity provided that the inhibitor is completely removed from the system. Since the addition of an auxo-substance causes the formation of an undissociable compound with the inhibitor and liberates free active urease, the activity is determined by the relative amounts of auxo-substance and inhibitor in the system.

Chemical Abstracts.

Systematic study of some *Torulæ*. F. C. Harrison (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 187—225).

Plant phosphatides. VIII. Phosphatides of yeast. V. Grafe (Biochem. Z., 1929, 205, 256—258).—Pure cultures of yeast are subject to autolysis at 28—30° for 36 hrs. and dialysed against distilled water. The dialysate contained considerable amounts of phosphatide but no protein.

P. W. Clutterbuck.

Relation between the production of lactic acid and the growth of yeast. E. Aubel (Compt. rend., 1929, 188, 578—580).—The hypothesis that the energy absorbed in the growth of yeast arises from the conversion of dextrose into lactic acid (A., 1926, 1277) is shown to be untenable, since the amount of the last-named product appears to possess no relation to the amount of growth.

G. A. C. Gough.

Sporulation of yeast. H. Stantial (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 257—261).—Experiments to determine the conditions of sporulation of yeast are discussed. Whether yeast will form spores or not depends on the presence or absence of some constituent of wort, fruit juices, lettuce, etc. The juice of grape-fruit gave the best results.

A. J. Mee.

Persistence of acclimatisation to fluoride, after sporulation of yeast. H. Stantial (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 263—265).—Experiments are described which prove that yeast from "fluoride spores," *i.e.*, yeast formed by the germination in fluoride-free wort of spores which had been formed in the absence of fluoride from acclimatised yeast, is much more tolerant of fluoride than is yeast formed in parallel experiments from unacclimatised yeast. A. J. Mee.

Isolation and identification of bios I; its absorption by and recovery from yeast. E. V. Eastcott (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 267).—Pure bios I has been obtained from tea-dust and shown to be identical with inactive inositol. The amount of inositol taken up by yeast is $1{\cdot}2\times 10^{-13}$ g. per cell. A. J. Mee.

Chemical derivatives of bios II. E. M. Sparling (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 271).—Bios II may be purified by conversion into some derivative which can itself be more easily purified, and then treating this with alkali. Acylation seems the most promising method. The product of this treatment is without effect on the rate of reproduction of yeast until "activated" by sodium hydroxide. A. J. Mee.

Giant yeast cells. M. Holt (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 269—270).—Yeast left to bud in a solution of sugar and salts to which certain amino-acids have been added gives rise to abnormally large cells. The substances capable of promoting this growth are aspartic acid, glutamic acid, glycine, and alanine. This reaction may be peculiar to certain races of yeast. A. J. Mee.

Extraction and purification of co-zymase from yeast. K. Myrbäck (Svensk Kem. Tidskr., 1929, 41, 3—8; cf. A., 1924, i, 918; 1927, 993; 1928, 1284).—Brewer's yeast is washed in running water until the effluent is almost colourless, filtered, and pressed. The powdered material is stirred with 4 vols. of water at 80° for 10 min., and the solution filtered hot, whereby an average extraction of 60% of the total co-zymase is obtained. For further purification the extract is evaporated in a vacuum and dialysed, the co-zymase passing through the collodion membrane. After removal of inactive impurities from the dialysate by precipitation with neutral lead acetate, the co-zymase can be precipitated by the addition of lead acetate and sodium hydroxide to the filtrate, but as an excess of either reagent prevents complete precipitation it is difficult to obtain a good yield. A better method is to precipitate the excess of lead with hydrogen sulphide, and remove the latter from the filtrate by a current of air. An excess of mercuric acetate is added, the precipitate separated by centrifuging after keeping for 2 hrs., suspended in water, and treated with hydrogen sulphide. The filtrate after removal of hydrogen sulphide contains 90% of the co-zymase originally present. The purity of the product can be determined by the method of Euler and Myrbäck (A., 1924, i, 918). Attempts to separate co-zymase, in view of the marked pentose reactions it exhibits, by precipitation with a mixture of copper sulphate and calcium hydroxide were not successful.

H. F. Harwood.

Regulated enzymic dismutation by the ketoaldehyde mutase of *B. subtilis*. A. Gualdi (Biochem. Z., 1929, 205, 318—319).—Dismutation of phenylglyoxal hydrate by *B. subtilis* gives a preponderance (84%) of *d*-mandelic acid. J. H. Birkinshaw.

Question of the identity of mutase and ketoaldehyde mutase. C. Neuberg and M. Kobel (Z. physikal. Chem., 1928, 139, 631—646).—A kinetic study of the dismutation of acetaldehyde and methylglyoxal by the action of various bacteria. Experiments with freshly-prepared suspensions of bacteria were carried out at 37° with solutions $0{\cdot}01M$, $0{\cdot}02M$, $0{\cdot}04M$ for methylglyoxal and $0{\cdot}02M$, $0{\cdot}04M$, $0{\cdot}08M$ for acetaldehyde. The course of the reaction was followed by determining the amount of unchanged substance by titration, using the hydroxylamine sulphate method for acetaldehyde and the iodometric method for methylglyoxal. Two series of experiments were carried out; to the first only the bacterial suspension was added but to the second calcium carbonate was also added in order to maintain a constant p_H throughout the reaction. With *B. Pasteurianum* and *B. ascendens* transformation of both substances follows the same course; it is also the same with these two bacteria whether the solution is acid or neutral. On the other hand with *B. Delbrücki* the dismutation of methylglyoxal proceeds much more quickly than that of acetaldehyde, whether in neutral or acid solution. The same difference is found with *B. lactis aërogenes*, but not to such a marked extent. Using yeast the change of both substances proceeds at nearly the same rate in dilute solution, but in more concentrated solutions methylglyoxal is transformed more quickly than acetaldehyde.

R. N. Kerr.

Characterisation of the group of *Aspergillus niger*. II. Importance of acid substrates for the characterisation and growth of the mould. K. Bernhauer (Biochem. Z., 1929, 205, 240—244).—*A. niger* is very sensitive to acids and only small amounts are formed unless some means for its neutralisation, *e.g.*, calcium carbonate, is present. The mould is differently resistant to different acids. Successive sowing of spores on acid substrates increases the acid-forming power. P. W. Clutterbuck.

Formation of citric and oxalic acids by *Aspergillus niger*. S. Kostytschev and V. Tscheskokov (Planta, Arch. wiss. Bot., 1927, 4, 181—200; Chem. Zentr., 1928, ii, 1452).—Formation of citric acid is favoured by acidity, and of oxalic acid by alkalinity, of the medium. In young cultures citric acid is not formed so long as nitrogen is utilised from the nutrient solution. Citric acid is considered to be necessary for the synthesis of amino-acids.

A. A. Eldridge.

Fermentative hydrolysis of asparagine by the mycelium of *Aspergillus niger*. D. Bach (Bull. Soc. Chim. biol., 1929, 11, 119—145).—A more detailed account of work already published (this vol., 108).

Formation of diastase by *Aspergillus oryzæ*. G. L. Funke (Rec. trav. bot., 1927, **24**, 583—630; Chem. Zentr., 1928, ii, 1444).—On buffered solutions (0·5% of potassium monohydrogen phosphate) *A. oryzæ* forms large quantities of diastase; the chemical composition of the nutrient solution is without influence. On unbuffered solutions the mould grows less readily, forms more acid and scarcely any diastase; aërobic respiration takes place. The acid is apparently oxalic, which may inactivate the enzyme by chemical union. A. A. Eldridge.

Chemical constituents of the spores of *Aspergillus oryzæ*. M. Sumi (Biochem. Z., 1929, **204**, 412—413).—The sterol isolated from the spores (cf. A., 1928, 927) is now found to be ergosterol.

W. McCartney.

***Penicillium glaucum*. Production of methyl ketones from triglycerides or fatty acids in the metabolism of the mould. II.** O. Acklin (Biochem. Z., 1929, **204**, 253—274).—The normal fatty acids (except butyric and valeric acids) are decomposed by *P. glaucum* in such a way that corresponding methyl ketones are formed. β-Hydroxy-acids are not formed as intermediate stages in the process and evidence is given for supposing that keto-acids are first produced. These, if stable, are converted directly or indirectly into methyl ketones (or even, finally, into secondary alcohols by reduction); if unstable, they are converted first into β-hydroxy-acids, then into carbon dioxide and water. Quantitative experiments on the decomposition by *P. glaucum* of hexoic acid (or of trihexoin) show that the course of the process depends greatly on the concentration of the acid (or glyceride) and of the nutrient medium as well as on the p_H of the system, the production of methyl propyl ketone being most favoured by low concentrations of the acid (or glyceride), high concentration of the medium, and p_H on the alkaline side. Hæmin has no catalytic effect on the formation of the ketone. In general, it is concluded that both qualitatively and quantitatively the course of the decomposition of normal fatty acids to methyl ketones by *P. glaucum* depends on the lengths of the carbon chains of the acids concerned.

W. McCartney.

Dissimilation of salts of fatty acids and carbohydrates by thermophilic bacteria. C. Coolhaas (Zentr. Bakt. Par., 1928, II, **75**, 161—170; Chem. Zentr., 1928, ii, 1342—1343).—A mixture of ammonium chloride (1 g.), potassium monohydrogen phosphate (1 g.), magnesium sulphate (0·5 g.), and calcium acetate (10 g. per litre), inoculated with mud and kept at 63°, exhibited fermentation in 5—14 days, yielding 50—60 c.c. of a mixture (2 : 1 vols.) of methane and carbon dioxide per hr. The reaction was: $CaC_4H_6O_4+H_2O = 2CH_4+CO_2+CaCO_3$. With calcium formate, $2CaC_2H_2O_4=CH_4+CO_2+2CaCO_3$, 94·4% of the theoretical quantity of methane being obtained, together with small amounts of hydrogen. Calcium *iso*butyrate, oxalate, lactate, and gluconate were readily, propionate more slowly, and butyrate very slowly, fermented. When sucrose, in an inorganic nutrient medium, was inoculated with canal mud, the gas produced consisted of carbon dioxide and hydrogen. Inoculation with acetate-fermenting bacteria, however, produced the fermentation $C_{12}H_{22}O_{11}+H_2O=6CO_2+6CH_4$, the process gradually reverting to the hydrogen fermentation. Cellulose, inoculated with fæces, at 60° gives varying proportions of methane and hydrogen. Cabbage waste yields thus more methane at 60° than at 26°.

A. A. Eldridge.

***Bacterium gluconicum*, occurring in "Kombucha" (Japanese or Indian tea fungus).** S. Hermann (Biochem. Z., 1929, **205**, 297—305; cf. A., 1928, 330).—*B. gluconicum* is a Gram-negative non-sporing organism with ovoid cells 0·8/0·6 μ. Its physiological behaviour on various sugars is given; in its reactions it closely resembles *B. xylinum*. On dextrose it gives a transitory Selivanov reaction for keto-groups. J. H. Birkinshaw.

Cellulose as source of energy for nitrogen-fixing micro-organisms. P. Tuorila (Zentr. Bakt. Par., 1928, II, **75**, 178—182; Chem. Zentr., 1928, ii, 1340).—With a mixture of cellulose (5 g.), calcium carbonate (0·2 g.), potassium monohydrogen phosphate (150 c.c. of 0·075% solution), garden soil (0·5 g.), and varying quantities of ammonium chloride kept for 30 days at 31°, the micro-organisms assimilated considerable quantities (up to 18 mg.) of atmospheric nitrogen only when the concentration of ammonium chloride was small or zero. The chief source of energy was the degradation products of cellulose. In a culture containing cellulose and mannitol the latter was the sole source of energy for a pure culture of *Azotobacter*. Mixed cultures of soil bacteria and *Azotobacter* with cellulose as principal nutrient fix much nitrogen; apparently certain bacteria decompose the cellulose and others, *e.g.*, *Azotobacter*, utilise the products. A. A. Eldridge.

Fixation of atmospheric nitrogen by *Azotobacter*. O. Meyerhof and D. Burk (Z. physikal. Chem., 1928, **139**, 117—142).—The growth and respiration of *A. chroococcum* under varying experimental conditions have been studied in liquid cultures for short periods of time at 28°. A deficiency of calcium or phosphate in the culture medium is accompanied by decreased respiration. The optimum p_H of the solution lies at 6·8—7·6. Respiration in the presence of dextrose, lævulose, galactose, and mannitol is ten to fifteen times as great as in solutions free from carbohydrate, is almost independent of concentration between 0·1 and 5%, but is reduced considerably at a concentration of 10%. It is retarded by even small amounts of ammonium sulphate, narcotics, and potassium cyanide. The effect of potassium cyanide is less marked in pure oxygen than in air. Respiration measured with respect to unit dry weight falls rapidly with an increase in age of the culture, whilst the rate of growth decreases after the first 24 hrs., which is attributed to aggregation of the bacteria. Under average conditions the increase in number of bacteria, the increase in dry weight, and that of nitrogen fixed run parallel. Maximum respiration occurs at 15—20% of oxygen and outside these limits falls rapidly. In pure oxygen it is one third to one half that in air, but on the other hand is independent, for short periods of time, of the presence of nitrogen; in mixtures of oxygen and hydrogen it equals that in oxygen–nitrogen mixtures. In the absence of ammonium salts, the increase in respiration, taken as a measure of growth, is dependent on the nitrogen content. In oxygen–hydrogen mixtures this increase is nil during the first 6 hrs., with 5% of nitrogen it becomes noticeable, and with 20% is approximately as large as in air. The oxygen concentration has an important effect on the nitrogen fixation and on the ratio nitrogen fixed/oxygen used. Maximum fixation and growth occur with 4—5% of oxygen, but the ratio increases continuously with decreasing pressure of oxygen. The assimilation of ammonia in a nitrogen-free atmosphere also increases with decreasing oxygen pressure, but the ratio nitrogen assimilated/oxygen used is practically unaltered. L. S. Theobald.

Diphtheria toxin. A. Locke and E. R. Main (J. Infect. Dis., 1928, **43**, 41—59).—Toxin is not accumulated in cultures in the absence of a definite growth momentum, of a concomitant growth inhibition, and of buffers, *e.g.*, proteoses. Toxin preparations were of lipoprotein character and contained no carbohydrate. Antigenicity, antitoxin-binding power, and toxicity of bacterial toxins may be manifestations of their combining avidity.
Chemical Abstracts.

Action of hæmotoxins on oxygenated and reduced blood. I. *Bacillus Welchii* toxin. G. B. Reed, J. H. Orr, and W. A. Campbell (J. Infect. Dis., 1927, **41**, 434—438).—Atmospheric oxidation of *B. Welchii* toxin causes considerable loss of hæmotoxic action. A higher concentration of the toxin is required for hæmolysis of oxygenated red cell suspensions than for that of reduced red cell emulsions. Chemical Abstracts.

Determination of indole in bacterial cultures. H. B. Pierce and R. B. Kilborn (J. Biol. Chem., 1929, **81**, 381—387).—Indole can be successfully determined in bacterial cultures by a slight modification of the method employed by Bergeim (A., 1918, ii, 23) for fæces. Added indole can be recovered from water and from bacterial cultures in peptone-water to the extent of 95% and 91%, respectively.
C. R. Harington.

Pneumin. A respiratory autacoid from the adrenal cortex. S. Vincent and J. H. Thompson (J. Physiol., 1929, **67**, Proc. Physiol. Soc., iii—iv).—Extirpation of both adrenals or ligation of the total blood supply to them causes rapid death in decerebrate cats due to cessation of respiration. It is concluded that a substance, for which the name *pneumin* is proposed, essential for the normal movements of respiration, is secreted by the adrenal cortex and passes into the veins by way of the lymphatics.
B. A. Eagles.

Attempt to concentrate the active principle of the adrenal cortex. A. T. Cameron and F. D. White (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 145—149).—An active fraction, capable of accelerating growth, is obtained when the fresh whole adrenal gland of the ox is extracted with 0·1N-hydrochloric acid, concentrated to dryness, and extracted with 95% alcohol. The fraction precipitated by 80% alcohol and not by 60% and that precipitated by 90% but not by 80% show a definite increase in growth-promoting value; this increase, it is suggested, is due to a removal of adrenaline, which has an antagonising action. Concentration of the active factor has been effected by extracting with methyl alcohol. The antagonising action of adrenaline is removed by simple oxidation. F. C. Happold.

Action of adrenaline on the creatine-phosphoric acid content of muscles. O. Feinschmidt and D. Ferdmann (Biochem. Z., 1929, **205**, 325—328).—Injection of adrenaline into the breast-muscle of the pigeon causes an increase in inorganic phosphorus which is not accounted for by the increased creatine-phosphoric acid hydrolysis. There is also an increase in the phosphorus compounds which yield phosphoric acid after hydrolysis for 2 hrs. with 2% sodium hydrogen carbonate solution and a decrease in the residual phosphoric acid. The higher lactic acid content is not directly related to the augmented creatine-phosphoric acid hydrolysis.
J. H. Birkinshaw.

Influence of adrenaline in gluconeogenesis. E. Wertheimer (Arch. exp. Path. Pharm., 1929, **139**, 378—380).—Polemical against Geiger and Schmidt (cf. A., 1928, 1160). W. O. Kermack.

Influence of amino-acids and their derivatives on adrenaline hyperglycæmia. M. Chikano (Biochem. Z., 1929, **205**, 154—165).—Tyrosine has no effect on the blood-sugar level, but increases 3—4 hrs. after subcutaneous injection into rabbits the hyperglycæmia caused by adrenaline. Tryptophan causes a slight hyperglycæmia and increases adrenaline hyperglycæmia. Dihydroxyphenylalanine causes considerable hyperglycæmia. Leucine and histidine inhibit hyperglycæmia by adrenaline. Phenylalanine, glutamic acid, and glycine have no action on the blood-sugar level. *p*-Hydroxyphenylpyruvic acid increases adrenaline hyperglycæmia, but *p*-hydroxyphenyl-lactic acid does not. Pyrocatechol causes considerable hyperglycæmia but protocatechuic and anthranilic acids have no effect.
P. W. Clutterbuck.

Antagonism between adrenaline and ergotamine. U. von Euler (Arch. exp. Path. Pharm., 1929, **139**, 373—377).—In exceedingly small concentrations (1 in 10^{12}) ergotamine tartrate and ergotoxin phosphate increase cell oxidation as measured by the methylene-blue technique. The rise in cell oxidation caused by adrenaline (1 in 10^{12}) is prevented by ergotamine in similar concentration.
W. O. Kermack.

Micro-determination of adrenaline, and its application in the investigation of intermediate metabolism. M. Chikano (Biochem. Z., 1929, **205**, 166—175).—Adrenaline can readily be determined in aqueous solutions by adding iodic acid and determining the excess of the acid by titration with thiosulphate in acid solution after addition of potassium iodide. With normal rabbit's serum, blank determinations gave a value for the substances present which react with iodic acid, and when known amounts of adrenaline were then added to serum the difference in value corresponded very closely with the amount added. With fresh defibrinated rabbits' blood, however, and with suspensions of washed corpuscles, the blank value was about five times as large as for serum and the percentage of adrenaline found by analysis was only 56—32% of that added, the value decreasing with decreasing amount of adrenaline added. The substances reacting with iodic acid are therefore present chiefly in the corpuscles and include the so-called adrenaline-like substances, urea and uric acid, and some end and intermediate products of protein metabolism.

P. W. Clutterbuck.

Hormone of heart motion. X. Experiments with warm-blooded animals. L. Haberlandt (Pflüger's Archiv, 1928, 220, 203—211; Chem. Zentr., 1928, ii, 1345).

Influence on the heart of a substance present in heart muscle and other tissues. A. N. Drury and A. Szent-Györgyi (J. Physiol., 1929, **67**, Proc. Physiol. Soc., xiv—xv).—A crystalline *substance*, m. p. 190—200° (decomp.), which when injected intravenously in the frog, dog, rabbit, or cat produces a transient sinus brachycardia and in the guinea-pig a transient high-grade heart block, has been isolated from heart muscle. It is probably a derivative of nucleic acid. Elementary analyses and calculation of the residue as metaphosphoric acid gives the formula $C_{16}H_{21}O_{12}N_8,HPO_3$. B. A. Eagles.

Effect of insulin on distribution of non-protein-nitrogen of blood. S. E. Kerr and V. H. Krikorian (J. Biol. Chem., 1929, **81**, 421—424).—Administration of insulin to dogs causes a preliminary fall in the carbamide and increase in the amino-acids of the blood, these changes being reversed as the hypoglycæmia increases (cf. Luck and others, A., 1928, 676, 1058). C. R. Harington.

Glycogenic function of skeletal muscle in dehepatised dog and rôle of insulin. J. Markowitz, F. C. Mann, and J. L. Bollman (Amer. J. Physiol., 1929, **87**, 566—583).—In a dehepatised dog, administration of dextrose (1 g. per kg. body-weight per hr.) for several hours leads to a definite rise in muscle-glycogen. This rise in the glycogen content of muscle cannot be demonstrated in dehepatised and depancreatised dogs. Administration of large doses of insulin to such dogs may produce a rise in muscle-glycogen. Unless relatively enormous doses of insulin are injected into dehepatised dogs which have received several administrations of dextrose, no hypoglycæmic effect can be demonstrated. It is suggested that the liver possibly plays a major part in the action of insulin in the intact animal.

B. A. Eagles.

Behaviour of insulin on irradiation with *X*-, radium, and ultra-violet rays. D. den Hoed, S. E. de Jongh, and A. E. J. Peek (Biochem. Z., 1929, **205**, 144—153).—In the absence of air insulin is stable to *X*-, radium, and ultra-violet irradiation, but in presence of air, whereas *X*-rays have no effect, radium, and still more so ultra-violet, irradiation destroys it gradually. P. W. Clutterbuck.

Œstrus-producing hormone in bile. M. A. Gsell-Busse (Arch. exp. Path. Pharm., 1929, **139**, 328—340).—Certain commercial samples of purified bile salts contain the œstrus-producing hormone, but this is probably present as an adsorbed impurity. Ether extracts of the bile of various animals including man contain the hormone, the activity being particularly great in the extracts of human bile, especially that of females. Extracts of the bile of patients suffering from various diseases have reduced activity or none at all. No hormone could be extracted from 0·5 kg. of fresh liver. Meconium is particularly rich in the hormone. W. O. Kermack.

Effect of parathyroid hormone on the structure of bone. C. G. Lambie, W. O. Kermack, and W. F. Harvey (Nature, 1929, **123**, 348).—Administration of parathyroid hormone to rats appears to cause a change in the form in which calcium exists in the bones. A. A. Eldridge.

Action of secretin on gaseous metabolism. H. Tangl and F. Than (Arch. exp. Path. Pharm., 1929, **139**, 226—230).—Subcutaneous injection of secretin into fasting rats decreases the rate of consumption of oxygen and thus raises the respiratory quotient.

W. O. Kermack.

Effect of minimal doses of thyroxine on gaseous metabolism in invertebrates. B. Romeis and J. Wüst (Naturwiss., 1929, **17**, 104—105).—In contrast with its action on vertebrates, thyroxine appears to be without influence on the morphology of invertebrates. The respiration of butterfly pupæ (*Papilio podalirius*) has now been studied, definite concentrations of thyroxine in solutions isotonic with the lymph being injected. Relatively concentrated solutions caused a 30—50% increase in oxygen consumption. With much more dilute solutions the gas consumption remained at first unchanged, but after the fourth or fifth day following the injection a sudden increase occurred to as much as 30—40 times the normal value. The high rate was maintained for 1—2 days and then rapidly fell to even below the normal value in 1—2 days. Further dilution merely delayed the appearance of the sudden increase without affecting the order or magnitude of the change. The effect was obtained with 2×10^{-11} g. of thyroxine on pupæ weighing 0·8 g. In spite of the great change in gaseous metabolism no shortening of the period of metamorphosis was noticed. Apparently, therefore, the primary action of thyroxine is on the respiration process, whilst the normal morphological effect is connected with secondary factors absent in this case.

R. A. Morton.

Effect of thyroxine on the metabolism of surviving tissue. K. J. Anselmino, O. Eichler, and H. Schlossmann (Biochem. Z., 1929, **205**, 481—488).—The respiration of sections of the surviving liver, spleen, and kidney of rats is unaffected by previous subcutaneous injection of thyroxine into the animals. The anaërobic glycolysis of these organs is increased only in the case of the kidney. The thyroid hormone affects principally the anaërobic phase of metabolism. J. H. Birkinshaw.

Incretion and avitaminosis. X. Action of thyroxine and pituitary extract on basal metabol-

ism and specific dynamic action after thyroid extirpation and in avitaminosis. A. von Arvay (Biochem. Z., 1929, **205**, 433—440).—There is strong similarity in the decrease in basal metabolism, specific dynamic action, and action of thyroxine in thyroidectomised rats and in rats deprived of vitamin-*A* and -*B*. Thyroxine restores the basal metabolism and specific dynamic action to normal in both cases, pituitary extract is without effect. Extirpation of the hypertrophied adrenals in avitaminosis leads to death of the animal. J. H. Birkinshaw.

Action of vitamins and surface activity. I. Vitamin-free substances which have surface activity in avitaminosis in guinea-pigs. N. E. Schepilevskaja (Biochem. Z., 1929, **204**, 371—388).—Phenolphthalein, alcohol, magnesium sulphate, and (except in solutions of the order of 0·015%) sodium oleate have no prophylactic or therapeutic effect in experimental scurvy in guinea-pigs. Consequently the views of Hahn (cf. A., 1925, ii, 664) concerning the vitamin-like action of substances having high surface activity are not confirmed as far as substances not used as food are concerned. W. McCartney.

Experimental hypervitaminosis in rats caused by large doses of irradiated ergosterol. J. A. Collazo, P. Rubino, and B. Varela (Biochem. Z., 1929, **204**, 347—353).—A daily dose of 5 mg. of the vitamin-*D* preparation "vigantol" per animal produces hypervitaminosis and eventually death in rats, and hence excess as well as lack of vitamin may have pathological results. W. McCartney.

Oxidative capacity and peroxidic-oxygen content of cod-liver oil: influence of ultra-violet light. P. Delore (Bull. Soc. Chim. biol., 1929, **11**, 74—91).—Olive, linseed, and especially cod-liver oil gain weight owing to absorption of oxygen on exposure to air in the absence of light. Possibly some volatile substances are lost in the process. Preliminary irradiation of the oils by ultra-violet light enhances the rate of autoxidation up to a limit beyond which it is decreased. In these experiments and in comparison with other oils, cod-liver oil behaves as if it had been already irradiated. The autoxidation is accompanied by a decrease in the iodine value and increases in the viscosity and refractive index. The peroxidic-oxygen content of the oils, determined by the liberation of iodine from potassium iodide acidified with acetic acid, shows a relation to the time of irradiation similar to that of the increase in weight. G. A. C. Gough.

Experimental blacktongue and the blacktongue preventive in yeast. J. Goldberger, G. A. Wheeler, R. D. Lillie, and L. M. Rogers (U.S. Public Health Service, 1928, Reprint No. 1216, 1—38).—Experiments indicate that blacktongue in dogs is due to a dietary deficiency capable of correction by a preventive present in yeast. This preventive, which can be distinguished from the antineuritic factor, shows considerable heat-resistance, and is probably identical with the anti-pellagra vitamin. E. A. Lunt.

Velocity of absorption of ions by plants. M. von Wrangell (Z. physikal. Chem., 1928, **139**, 351—367).—The velocity of absorption of the phosphate and ammonium ions by plants, especially maize, has been measured colorimetrically in nutrient solutions of various concentrations and composition. From very dilute solutions (0·1 mg./litre), the absorption of the phosphate ion is slow, but that of ammonia is much quicker and is complete in 0·5—2 hrs. The optimum concentrations for absorption lie between 0·001 and 0·01 g./litre. During short time-intervals, the absorption is independent of the usual growth factors such as light, and the nutrient ions potassium, nitrate, etc., but the absorption of phosphate is increased by the presence of calcium. Temperature has a significant influence on salt absorption, which appears to be primarily a physico-chemical and not a physiological process. The velocity is not governed apparently by the diffusion of the ions or by Henry's or the Fechner–Weber law and is best interpreted as an adsorption process. L. S. Theobald.

The $p_{\rm H}$ of the cell sap of flowers. B. H. Buxton and F. V. Darbishire (J. Roy. Hort. Soc., 1929, **54**, 203—213).—Colorimetric determinations have been made of the variation with time of the $p_{\rm H}$ of aqueous solutions of dried petals from various flowers. E. A. Lunt.

Origin of chlorophyll and its relation to blood pigments. K. Noack (Naturwiss., 1929, **17**, 104).—The magnesium of protochlorophyll can be removed by means of acid and re-introduced through the Grignard reaction. The magnesium-free compound is a red dye practically identical with phylloerythrin (bilipurpurin) as regards absorption spectrum. Phylloerythrin, obtained from the bile of herbivorous animals, has been converted into a green pigment as a result of the introduction of magnesium and the material possesses almost the same absorption maxima as protochlorophyll. One or more carboxyl groups can be set free in phylloerythrin, lactone or lactam groups being probably present initially. By reduction in acid solution phæophytins (the magnesium-free derivatives of chlorophyll *a* and *b*) are readily converted into magnesium-free protochlorophyll derivatives, without hydrolysis of the ester groups in the phæophytin. Hydrolysis of the reduction products yields substances which can be identified spectroscopically with phylloerythrin derivatives. The acids undergo photo-oxidation to form green substances. Thus a simple reduction forms a bridge between blood and leaf pigments. Further, it would appear that in the animal, phylloerythrin is a reduction product of chlorophyll, and that in the plant the last step in the synthesis of chlorophyll is a photo-oxidation. An explanation is also provided for the rôle of iron in the formation of chlorophyll, since minimal quantities of the metal are known to catalyse the photo-oxidation of fluorescent colouring matters. R. A. Morton.

Determination of small quantities of starch in vegetable tissue. E. J. B. Bish (Biochem. J., 1929, **23**, 31—34).—The dried powdered tissue is extracted with absolute alcohol to remove sugars, chlorophyll, and some proteins. It is then hydrolysed with takadiastase and the remaining proteins, tannins, and mucilages are removed by either lead acetate or mercury salts. The copper-reducing power of the hydrolysed starch is compared with the reducing power of known quantities of a carefully purified starch preparation. S. S. ZILVA.

Physiology of the organic acids in green plants. III. *Rheum hybridum hort.* W. RUHLAND and K. WETZEL (Planta, Arch. wiss. Bot., 1927, E, 3, 765—769; Chem. Zentr., 1928, ii, 1222—1223).—Of the nitrogen in resting rhizomes, two thirds is soluble. Considerable synthesis of protein takes place in the stalks of young leaves, amino-acids being supplied from the rhizome. Old stems contain much ammonia-nitrogen. In deficiency of carbohydrate or of light there is increase of ammonia formation. The rhizome contains about 0·90% of oxalic acid and 0·73% of succinic and malic acids, the latter diminishing with development of the aerial organs. Young stems contain little oxalic acid. In growing stems vigorous deamination produces ammonia, which is removed by acid formation; succinic and malic acids appear first, and diminish in quantity as oxalic acid is produced.

A. A. ELDRIDGE.

l*-Asparagine in the fresh flowers of *Ulex europæus. M. BRIDEL (Bull. Soc. Chim. biol., 1928, 10, 1378—1379).—*l*-Asparagine (7·7 g. from 25 kg. of fresh flowers) is obtained from the mother-liquor from the preparation of ulexoside (A., 1926, 1183). G. A. C. GOUGH.

Alkaloids of *Corydalis ambigua* (Yen-Hu-So). II. *Corydalis.* F. G. CHOU and T. Q. CHOU (Chinese J. Physiol., 1929, 3, 69—74).—In addition to the five alkaloids (corydalis *A*, or corydaline, corydalis *B*, *C*, *D*, and *E*) previously isolated from the tubers of *C. ambigua* (A., 1928, 927) there have now been isolated three more alkaloids, *corydalis* F, $C_{26}H_{23}O_4N$, m. p. 237° $[\alpha]_D^{25}$ −250° in chloroform (*hydrobromide*, m. p. 222°; *hydrochloride*, m. p. 234°), *corydalis* G, m. p. 237°, $[\alpha]_D^{25}$ +300° in chloroform, possibly identical with corypalmine isolated by Späth, Mosettig, and Tröthandl (cf. A., 1923, i, 593) from *C. tuberosa*, and *corydalis* H, obtained as *bromide*, m. p. 235°, optically inactive. Corydalis *F* and *G* are phenolic. Corydalis *H* when treated with barium hydroxide and extracted with chloroform yields a *base*, m. p. 153° (*hydrobromide*, m. p. 228°). Two *sulphates* of corydalis *B* are described, one acid, m. p. 238°, and one neutral, m. p. 220°. W. O. KERMACK.

Alkaloids of *Bocconia frutescens*, L. E. R. MILLER (J. Amer. Pharm. Assoc., 1929, 18, 12—14).—The leaves of *B. frutescens*, L., contain at least four alkaloids, γ-homochelidonine, m. p. 168—169°, protopine, m. p. 206—207°, a third, probably β-homochelidonine, m. p. 159—160°, and probably chelerythrine. The bark of the large plants is rich in alkaloids and on account of the large leaves and their high alkaloidal content the plant is probably the best known source of protopine. E. H. SHARPLES.

Jute seeds (*Corchorus capsularis*). II. Composition of corchorus oil. N. K. SEN (J. Indian Chem. Soc., 1928, 5, 759—767).—Extraction of jute seeds with light petroleum gives 14·73% of an oil which after purification with alkali has the following constants: d^{28} 0·923, $n^{29·7}$ 1·4615, solidifying pt. −20°, iodine value 102·6, saponification value 184·6, acid value 1·5, acetyl value 27·3, Reichert–Meissl value 0·16. The oil contains a small amount of unsaponifiable matter, probably a mixture of sterols, small quantities of palmitic, stearic, and "crude arachidic" acids, triolein (39·18%), and trilinolein (44·63%). The refined oil is suitable as a food and burns satisfactorily. H. BURTON.

Rind of California oranges. M. B. MATLACK (J. Amer. Pharm. Assoc., 1929, 18, 24—31).—The following substances have been identified in the fat from the rind of sweet oranges: oleic, linoleic, linolenic, stearic, and palmitic acids, sitosterol, a sterol, m. p. 150° (acetyl derivative, m. p. 113·5—114°), probably identical with paraphytosterol, a phytosterolin, m. p. 280° (benzoyl derivative, m. p. 198°; acetyl derivative, m. p. 164—164·5°), which is probably sitosterol-*d*-glucoside, ceryl alcohol, and small amounts of resin and carotinoid colouring matter. E. H. SHARPLES.

Mineral constituents of cranberries. F. W. MORSE (J. Biol. Chem., 1929, 81, 77—79; cf. A., 1928, 1407).—Figures are given for the constituents of the ash of cranberries grown on Cape Cod.

C. R. HARINGTON.

Action of thorium-*X* on the content of active principles in certain medicinal plants. AVERSENQ, JALOUSTRE, and MAURIN (Compt. rend., 1929, 188, 345—347).—The alkaloid contents of the root and the stems of the pomegranate and the leaves and the seeds of *Datura stramonium* increase when the plant is treated with aqueous suspensions of thorium-*X*. Similar increases in the fat contents of the seeds of the castor-oil plant and the total anthraquinone derivatives of the stem of French rhubarb are observed. The treatment leads to a decrease in the allylthiocarbimide content of seeds of black mustard.

G. A. C. GOUGH.

Conversion of starch granules into calcium oxalate crystals in plant cells by ultra-violet light. G. NADSON and E. ROCHLINE (Compt. rend. Soc. Biol., 1928, 99, 131—133; Chem. Zentr., 1928, ii, 1108).—Ultra-violet light stimulates oxidation processes in the cell; thus oxalic acid is produced from starch, sugar being an intermediate stage.

A. A. ELDRIDGE.

Characterisation of the anthocyanins and anthocyanidins by means of their colour reactions in alkaline solutions. A. ROBERTSON and R. ROBINSON (Biochem. J., 1929, 23, 35—40).—The examination of the colour reactions of apigeninidin chloride, pelargonidin chloride, cyanidin chloride, 5-*o*-benzoylcyanidin chloride, peonidin chloride, malvidin chloride, cyanin chloride, and malvin chloride in a range of buffer solutions has shown that this method is by far the most trustworthy for purposes of comparison and characterisation. Various properties such as ψ-base formation and colour base precipitation, ease of oxidation are incidentally revealed in this examination. Fear and Nierenstein's observation (A., 1928, 646) that cyanidin chloride from cyanin behaves differently from synthetic 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride is not confirmed.

S. S. ZILVA.

Action of certain substances on the zoospores of *Pseudoperonospora humuli* (Miy et Takah), Wils. W. GOODWIN, E. S. SALMON, and W. M. WARE

(J. Agric. Sci., 1929, **19**, 185—200).—Zoospores of *Pseudoperonospora humuli* and *Phytophthora infestans* are extremely susceptible to the action of dilute solutions of soap or saponin. In solutions containing 0·1% of soft soap disintegration occurs within 60 sec. Glycerol, iodine, bromine, and aluminum–lime mixtures also killed the spores rapidly. A. G. POLLARD.

Sodium nitrate and development of chlorosis in rice. W. H. METZGER and G. JANSSEN (J. Agric. Res., 1928, **37**, 589—602).—Rice plants become chlorotic when they suffer from a lack of available nitrogen, particularly ammonia, in the early stages of growth. B. A. EAGLES.

Biochemistry of dry-rot in wood. G. C. BARTON-WRIGHT and J. G. BOSWELL (Biochem. J., 1929, **23**, 110—114).—A comparison of analytical data of sound spruce and spruce decayed by the action of the fungus *Merulius lachrymans*. There is a removal in the latter of galactan, mannan, and cellulose fractions. The hemicelluloses and lignin are not affected by the fungus. S. S. ZILVA.

Behaviour of lignins in the natural disintegration of plants. F. FISCHER and R. LIESKE (Biochem. Z., 1928, **203**, 351—362).—In the natural disintegration of plants (decayed pinewood, ferns, etc.) the hydrolysable constituents are first decomposed and the lignin substances concentrated. The microscopic structure of the wood is not destroyed during the decomposition of the cellulose. During natural disintegration the p_H does not diminish as far as in experiments with pure cultures of moulds, the acid formed initially being removed naturally either by washing or by the action of micro-organisms. Bacteria sensitive to acid can therefore take part in the disintegration. P. W. CLUTTERBUCK.

Double staining of mitochondria and bacteria in plant tissues. J. DUFRENOY (Stain Tech., 1929, **4**, 13—15).—A favourable report on the use of Milovidov's technique (Compt. rend. Soc. Biol., 1928, **98**, 555). H. W. DUDLEY.

Jena filter plates of porous glass in biological analysis. E. CATTELAIN (J. Pharm. Chim., 1928, [viii], **8**, 549—550, and Bull. Soc. Chim. biol., 1928, **10**, 1385—1386).—Jena porous glass filter crucibles can replace Gooch crucibles in biological analysis. E. H. SHARPLES.

General apparatus for micro-analysis. I. Ashing in a sealed system. E. TSCHOPP (Biochem. Z., 1928, **203**, 267—277).—An apparatus is described in which organic substances may be ashed in a closed space and without using large amounts of sulphuric acid and the inorganic content determined. P. W. CLUTTERBUCK.

Modification of the Northrop–Kunitz microcataphoresis cell. H. A. ABRAMSON (J. Gen. Physiol., 1929, **12**, 469—472).—The original cell (*ibid.*, 1925, **7**, 729) is made more compact; agar reversible electrodes and the lowest possible *E.M.F.* are used. E. BOYLAND.

Application of the method of Hagedorn and Jensen to the determination of larger quantities of reducing sugars. C. S. HANES (Biochem. J., 1929, **23**, 99—106).—The method has been extended to permit the determination of about ten times the amount of reducing sugar. Standardisation data are given for dextrose and maltose. The amounts of dissolved oxygen in sugar solutions do not affect the reducing values found by this method. S. S. ZILVA.

Microscopical differentiation of neutral and hydrolysed fat. W. HEUPKE (Arch. Verdauungskrankh., 1927, **40**, 357—364; Chem. Zentr., 1928, ii, 1018).—The material, *e.g.*, fæces, is treated while hot with cupric nitrate and mixed on the slide with alcoholic dimethylaminoazobenzene; green copper soaps are formed, the neutral fat being coloured yellow. A. A. ELDRIDGE.

Salicylates. XVII. Phosphoric acid distillation method of determining salicylic and salicyluric acids. C. C. JOHNSON (J. Pharm. Exp. Ther., 1928, **34**, 437—444).—The Thoburn–Hanzlik method of phosphoric acid distillation (A., 1916, ii, 58) gave 88% of salicylic acid from salicyluric acid, whilst the Holmes method (A., 1926, 90) gave a much lower recovery. The results of determinations in urine after administration of salicylic acid indicate that some salicylic acid is decomposed in the body. E. BOYLAND.

Determination of tryptophan by means of *p*-dimethylaminobenzaldehyde. W. J. BOYD (Biochem. J., 1929, **23**, 78—82).—Errors can arise in the determination of tryptophan in proteins by May and Rose's method (A., 1923, i, 160) through unequal illumination of the reacting mixture and through the presence of reducing substances such as hydrogen sulphide or aldehydes. In carrying out the test 3 drops of 0·5% sodium nitrite solution should be added to the reaction mixture after 24 hrs.' incubation at 36° and 3 days at the ordinary temperature and again after a further 3 days, the colorimetric comparison being made next day or later. By this modification higher values are obtained for cod-muscle protein and edestin. S. S. ZILVA.

Occurrence of iodine and fluorine in the organism. I. A. MAYRHOFER and A. WASITZKY (Biochem. Z., 1929, **204**, 62—77).—A review is given of the principal methods for the determination of iodine and fluorine in organic matter. The method recommended consists in ashing the substance with sodium hydroxide. The residue is then ground up with 90% alcohol which dissolves the sodium iodide. The iodine in the alcohol may be determined volumetrically after oxidation to iodate and liberation of iodine by addition of potassium iodide and acidification. The iodine-free residue is dissolved in acetic acid and the fluorine precipitated with lanthanum acetate. Hydrogen fluoride set free by sulphuric acid is allowed to etch glass and determined by the loss of weight of the glass thus treated. J. H. BIRKINSHAW.

Determination of organic arsinic acids. E. URBSCHAT (Biochem. Z., 1928, **203**, 223—225).—A method is described for the nephelometric determination of 2-hydroxypyridine-5-arsinic acid and used for its determination in the urine of animals to which it had been administered. P. W. CLUTTERBUCK.