BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1929.

General, Physical, and Inorganic Chemistry.

Stellar spectra in the far ultra-violet. S. Rosseland (Nature, 1929, **123**, 207).

Ionisation in stellar atmospheres. I. Generalised Saha formulæ, maximum intensities, and the determination of the coefficient of opacity. E. A. Milne (Month. Not. Roy. Astr. Soc., 1928, **89**, 17—49).—Mathematical. W. E. Downey.

Ionisation in stellar atmospheres. II. Absolute magnitude effects. E. A. Milne (Month. Not. Roy. Astr. Soc., 1928, **89**, 157—175).—Formulæ are obtained which determine the variation with g, at constant T, of the number of atoms responsible for the formation of a given absorption line. The behaviour depends on whether the coefficient of general absorption, κ, is constant throughout the stellar atmosphere or is proportional at each point to the electron pressure P. The fact that lines of both neutral and ionised atoms increase in intensity from dwarfs to giants favours the adoption of $\kappa \propto P$. When $\kappa \propto P$ the mass of the reversing layer increases with decreasing pressure and more than counterbalances the reduction in the proportion of neutral atoms due to increased ionisation. The observed strengthening of the Balmer lines from dwarfs to giants now receives theoretical explanation. C. J. Smithells.

Theoretical contours of absorption lines in stellar atmospheres. E. A. Milne (Month. Not. Roy. Astr. Soc., 1928, **89**, 3—17).—Mathematical. The number of atoms per c.c. in a stellar atmosphere is calculated on the assumption of no surface of demarcation between atmosphere and photosphere. W. E. Downey.

Relations between the most intense radiations and the highest chemical elements in the luminous atmosphere of the sun. H. Deslandres (Compt. rend., 1929, **188**, 20—24).—The wave-lengths of the ultimate radiations of the chemical elements in the solar chromosphere are tabulated, together with their intensities, heights, and series notations, and the author's conclusion (*ibid.*, 1924, **179**, 1066) that the corresponding frequencies are approximate multiples of the same elementary frequency $d_1=1062·5$ is confirmed. The light atoms (H, He, O) show intense radiations but have high excitation potentials, and the effect of the ionised heavy atoms (Ca^+, Sr^+, Ti^+) is very marked at great heights. J. Grant.

Presence of the absorption line D_3 in the solar spectrum. S. B. Nicholson and N. G. Perrakis (Compt. rend., 1929, **188**, 41—43).—Spectrograms of the sun taken with three Mt. Wilson plates show that the absorption due to helium is relatively strong in the immediate neighbourhood of the plate 3326 (Mt. Wilson notation), and in the interval separating members of the group 3333, whilst it is very faint in the space occupied by the faint markings. The presence of the atmospheric line (λ 5875·603) renders difficult the identification of the absorption line D_3 (λ 5785·620). J. Grant.

Elementary processes in emission and absorption of light. J. Stark (Ann. Physik, 1928, [iv], **87**, 909—926).—An earlier theory given by Stark is extended and applied to a series of experimental cases. In the process of emission of light three operations may be distinguished. First, the electron in its stationary state in the atom is displaced from equilibrium and approaches indefinitely close to a lower energy level. The time taken for this may be called the "Verweilzeit." Secondly, a light quant is formed in the electronic field. The time taken for this process ("Umformzeit") is independent of the order of magnitude of the period of the light. Thirdly, there is a mutual action between the electron and the light quant resulting in the emission of the quant in a definite direction with the velocity of light, and fixing of the electron in the new energy level. The time taken for this process ("Ablenkzeit") varies between a value of the order of the period and one many times this. The "Verweilzeit" can be estimated (*e.g.*, for H_γ) by examining the effect on spectra of an electric field acting on the given atom for a short time. In a field all energy levels are modified, transitions between a pair of modified levels giving a Stark component of the line concerned; but if the duration of the electric field is less than the "Verweilzeit" an electron may start from a modified and end in an unmodified level, or *vice versa*. In such circumstances components appear between normal and Stark modified lines. The time estimated for this operation for H_γ by this method is 10^{-9} sec. Consideration is given to excitation by cathode rays, and the theory predicts that the emission of characteristic frequencies in consequence of transfers of the atomic electron from one energy level to another is accompanied by the emission of a continuous spectrum in the infra-red or the beginning of the visible spectrum; also, that if the energy of the impinging electron is less than that required to raise the atomic electron to the next higher level an aggregate of atoms will give rise to a continuous spectrum. The theory provides an explanation of the continuous X-ray spectrum. The theory is applied to all kinds of absorption, including continuous, selective, and photo-electric absorption, and absorption due to scattering. A. J. Mee.

Spectral excitation by recombination in the electric arc. (Miss) J. M. Dewey (Physical Rev., 1928, [ii], 32, 918—921).—Measurements of electron velocities in arcs indicate that most of the light in the negative glow is due to the recombination of positive ions and electrons. Since the velocities of the positive ions are high, spectral lines emitted in this way should show Doppler broadening. This was measured photometrically for a hot cathode arc in helium in which measurements of electron velocities were also made and results obtained which can be explained by assuming all the light in the negative glow to result from recombination of ions having a temperature about one tenth that of the electrons.

N. M. Bligh.

Optical behaviour of hydrogen atoms in very strong electric fields. R. von Traubenberg (Physikal. Z., 1928, 29, 895).—The effect of sudden changes in field strengths up to 420,000 volts/cm. on hydrogen atoms has been studied by means of Stark's arrangement of separated fields, and the Stark effect measured in the second order for Balmer lines. The proportionality with the square of the field strength is confirmed for all components of H_γ. The results for the middle component agree better with the theory of Schrödinger than that of Epstein, but considerable deviations from Schrödinger's values are shown for the higher components. R. A. Morton.

Theory of the Stark effect in hydrogenic atoms. V. Rojansky (Physical Rev., 1929, [ii], **33**, 1—15).—Theoretical. Established formulæ give the relativity and spin corrections for a hydrogen-type atom perturbed by a weak electric field, and the energy levels without spin in the case of a strong field. Formulæ are here deduced for the energy levels in either a weak or a strong field, including both the relativity corrections and the Stark effect. The relativity and spin corrections for strong fields are deduced. The methods used are the matrix and wave mechanics. The results are similar, except in form, to those of Schlapp (cf. A., 1928, 806) using Darwin–Dirac wave methods. In the new, as opposed to the old, mechanics there is a linear Stark effect even in weak fields, because of the identity of energy for the ns and np_1 levels in the absence of external fields. This degeneracy is shown to account for the $2s$ level in hydrogen not being metastable. The coefficients are found for the development of the parabolic eigenfunctions in terms of the polar ones, and a set of values of these coefficients is tabulated. Methods are given for the calculation of the relative intensities in the Stark effect in terms of the already available theoretical fine-structure intensities in the absence of fields. N. M. Bligh.

Intensity measurements in the helium spectrum. C. Hodges and W. C. Michels (Physical Rev., 1928, [ii], 32, 913—917).—The absolute and relative intensities of thirteen lines of the helium spectrum, extending through the visible region, have been measured by the method developed by Ornstein and Dorgelo (A., 1924, ii, 282) modified by comparing each line directly with the known emission from a tungsten filament, operated under constant conditions. The results for a discharge in a capillary tube, with pressures from 1·92 to 34·3 mm., show that the absolute intensities increase rapidly to a maximum for pressures in the neighbourhood of 2—4 mm., below which they tend to zero. The relative intensities of the singlet system are favoured by lowered pressures, and the higher members of the triplet system are favoured over the lower members. The relative intensities within the singlet series are little affected by pressure. N. M. Bligh.

Influence of pressure and addition of foreign gases on the absorption in activated neon. L. Eckstein (Ann. Physik, 1928, [iv], 87, 1003—1034).—The influence of varying the pressure of gas in the absorption tube, keeping that in the emission tube constant, on the absorption of the neon lines 6402, 6266, 6163, 6143, 6096, and 5852 Å. has been investigated. The intensity of the spectral lines was measured by a photo-electric method. For all the above lines, the curves of absorption against gas pressure show maxima at a pressure of 1·2 mm. Hg. The maximum is greatest with the line 6402 Å. The influence of adding foreign gases to the absorption tube on the absorption of the lines 6402, 6266, 6163, and 6143 Å. has also been investigated. All four foreign gases used lowered the absorption, but whereas the decrease of absorption with increasing foreign gas pressure was slow with helium, it was very much quicker with water, nitrogen, and argon.

R. N. Kerr.

Experimental proof of "negative" dispersion. H. Kopfermann and R. Ladenburg (Z. physikal. Chem., 1928, **139**, 375—385).—By increasing the current density of a neon discharge up to 0·1 amp./cm.^{2} a rise in the anomalous dispersion has been found in the yellow-red $s-p$ lines (where p and s are the higher and lower energy levels, respectively). This signifies an increase of the active atoms in the s state. If, however, the current density be still further raised a gradual decrease in the anomalous dispersion in the different s_5-p_k lines (k=10, 9, 8, 6, 4, 2) with increasing current is observed. This is as expected from the dispersion formula of the quantum theory on account of the influence of "negative" dispersion, *i.e.*, due to greater activation of atoms in the p_k state. This is especially borne out by the systematic decrease of the dispersion for the s_5 lines combined with different p_k levels; the lower the p level considered and the more strongly it is activated the greater is the decrease of the accompanying anomalous dispersion. R. N. Kerr.

Absorption of ultra-violet light by metastable atoms. W. de Groot (Naturwiss., 1929, **17**, 13).—Since the ionisation energy of the metastable atoms of neon and argon is only 4·9 and 4·2 volts, respectively, corresponding with 2550 and 2950 Å., it is to be expected that there will be a continuous absorption of ultra-violet light from these wave-lengths up. Apparatus is described to test this. Light from a tungsten spiral at 3400° Abs. was passed through a tube containing the gas at 5 mm. pressure. The spectrum was photographed first of all with the absorption tube dark, and then with a current of

2 amp. flowing through the tube. There was no absorption in the part of the spectrum investigated either with neon or with argon. On the other hand, there was strong absorption corresponding with the $2s-2p$ lines in each gas with 50 milliamp. flowing through the tube. A. J. Mee.

Spectrum of doubly-ionised krypton. D. P. Acharya (Nature, 1929, **123**, 244).—A number of regularities have been observed, and three sets of terms are recorded. A. A. Eldridge.

Spectrum of doubly-ionised fluorine (F III). H. Dingle (Proc. Roy. Soc., 1929, **A**, **122**, 144—161; cf. A., 1927, 1; 1928, 98).—The lines of the spectrum of doubly-ionised fluorine appear when strongly condensed discharges are passed through silicon tetrafluoride at very low pressure. More than 300 lines, extending from 3267 to 2207 Å., have been measured and tabulated. The spectrum has been partly analysed into quadruplet and doublet systems of terms, which are correlated with the terms to be expected on the Heisenberg–Hund theory, and 82 lines have been classified. The resemblance between the spectrum and that of singly-ionised oxygen, which has the same electron structure as doubly-ionised fluorine, confirms its assignment to F^{++}. Most of the intervals in F III are almost exactly double the corresponding intervals in O II, but there are a few striking exceptions which are discussed. L. L. Bircumshaw.

Spectrum of doubly-ionised bromine. S. C. Deb (Nature, 1929, **123**, 244).—The lines of the spectrum of doubly-ionised bromine have been classified. A. A. Eldridge.

Absorption spectra of oxygen and of ozone in the ultra-violet region. J. Dufay (Compt. rend., 1929, **188**, 162—164).—The coincidence of bands in the ultra-violet absorption spectra of ozone and of compressed or liquid oxygen may be due to the same bands, enlarged in the latter case by the high density of the absorbing medium. This is supported by the fact that below 2400 Å. the absorption curve of ozone is continuous like that of compressed oxygen. J. Grant.

Intercombinations and new terms in the spark spectrum of sulphur (S II). L. Bloch and E. Bloch (Compt. rend., 1929, **188**, 160—162; cf. A., 1927, 1117; Gilles, A., 1928, 565).—New multiplets in the S II spectrum of sulphur detected by the use of an oscillating electrodeless discharge are recorded and include intercombinations and combinations of old and new terms. A correction of +317·20 must be applied to the doublet terms of Ingram to bring them to the same zero as the quadruplet terms. J. Grant.

Structure of the third order spectrum of sulphur (S III). J. Gilles (Compt. rend., 1929, **188**, 63—64; cf. A., 1928, 565).—The author has tabulated 40 lines (λ 4527·77—3323·97 Å.) and their intensities, based on the levels of multiplicity corresponding with the electronic configurations $a3d$, $a4s$, and $a4p$ of the S III spectrum. Eight multiplets are involved. J. Grant.

Structure of the third order spectrum of sulphur (S III). J. Gilles (Compt. rend., 1929, **188**, 320—321; cf. preceding abstract).—Lines of the $4d$ and $5s$ terms of the S III spectrum (2998·27—2442·65 Å.), based on the value 135600 for $4s^3P_2$, and corresponding with the multiplets ($4p^3S-4d^3P$), ($4p^3P-4d^3P$), ($4p^3D-4d^3P$), ($4p^3P-4d^3D$), ($4p^3D-4d^3D$), ($4p^3S-5s^3P$), and ($4p^3P-5s^3P$), are tabulated with their wave-lengths and intensities and include the line 2665·40 Å., hitherto attributed to the S V spectrum. J. Grant.

Further triplets of trebly-ionised arsenic. K. R. Rao (Nature, 1929, **123**, 244).—Two additional triplets due to As IV have been found. The values of $5pP_{012}$ are 168010, 167748, 166932. A. A. Eldridge.

Discontinuities of the *K*-absorption of simple substances. V. Dolejšek and K. Pestrecov (Compt. rend., 1929, **188**, 164—166).—Determinations of the limits of K-absorption of elements of atomic numbers (N) 12—30 in the same chemical state differ from the expression $\nu/R=a'+b'N+c'N^2+d'N^3+e'N^4$, where ν/R is the change of the frequencies of the K-level and the coefficients a', b' . . . e' are calculated from the frequencies of the rare gases, by amounts which vary periodically with N and show maxima for $N=12$, 21, and 29 and minima for $N=17$ and 25. J. Grant.

Diffraction of *X*-rays by ruled gratings. Spectrographic function of *X*-rays and ultra-violet rays. J. Thibaud (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, ii, 145—168).—An account of the author's work on the diffraction of X-rays and ultra-violet rays (cf. A., 1925—1928, numerous publications), showing the various stages in the development of the grating method with tangential incidence. This method is compared with the rotating-crystal method, and is shown to be very suitable for the investigation of the region between X-rays and ultra-violet rays. The theory of the diffraction grating with tangential incidence is summarised and a detailed description of the improved form of vacuum spectrograph with glass grating is given (cf. A., 1927, 286). O. J. Walker.

***D*-Line excitation by the green sodium band and the dissociation potential of sodium vapour.** E. L. Kinsey (Proc. Nat. Acad. Sci., 1929, **15**, 37—41).—The evidence is discussed for the dissociation of molecules into normal and excited atoms by the absorption of light in the fluorescence phenomena of sodium vapour. The conditions under which it is possible to excite the D-lines by the blue-green band of the sodium molecule were determined experimentally. The long and short wave-length limits of the exciting band and the wave-length of the band producing the maximum intensity were measured. The correspondence between the intensity variation of the D-lines and the blue-green bands shows that the process is probably the excitation of the atoms to the $2P$ levels by collisions of the second kind with excited molecules, and not by the dissociation of the molecules; the heat of dissociation is taken as 0·85 volt. N. M. Bligh.

Intensity relations in the spectra of titanium. I. Line intensities in the stronger multiplets

of Ti I and Ti II. G. R. Harrison (J. Opt. Soc. Amer., 1928, **17**, 389—416).—The relative intensities of the lines in a number of multiplets in the spectra of Ti I and Ti II have been measured. The apparatus used is described in detail and was capable of separating lines which were 0·24 Å. apart. The sources of error are discussed and are concluded to be less than 1%. Tables are given showing the measured and calculated intensities of these lines, 36 multiplets having been examined in all. J. L. Buchan.

Ground-terms in the spectrum of nickel II and proposed standard wave-lengths in the Schumann region. A. C. Menzies (Proc. Roy. Soc., 1929, A, **122**, 134—143; cf. Shenstone, A., 1927, 998).—During previous investigations of fuse spectra (A., 1928, 99, 806) it has been observed that this source is particularly suited to the study of low-level terms, and it is now applied to the analysis of the spectrum of Ni II. It was found that if the wires are mounted horizontally in the vacuum grating spectrograph, and very near the slit, the lines vary greatly in length, in spite of the astigmatic action of the grating, so allowing the application of the method of long and short lines. A number of lines, obviously connected on account of their length and strength, were found on analysis to belong to the hitherto missing ground-terms $^2D_3$ and $^2D_2$ of Ni II. Since the combining middle terms are accurately known, a determination of the values of $^2D_3$ and $^2D_2$ makes it possible to calculate the theoretical values of the wave-lengths of conveniently spaced lines, which can then be used as standards in the Schumann region. The lines extend from 1317 to 1940 Å.

L. L. Bircumshaw.

Reversals in the arc spectrum of nickel. A. C. Menzies (Phil. Mag., 1928, [vii], 6, 1210—1216).—An examination of the fuse spectra of nickel in air for the ultra-violet and in a vacuum for the Schumann region has been made to determine if the ground-term of the Ni I spectrum is $^1S_0$. Many reversals have been found in the ultra-violet region, but all of these can be accounted for from known data. In the Schumann region no lines attributable to the arc could be found. It is concluded that if the $^1S_0$ term does exist it must give rise to lines below the region examined. A. E. Mitchell.

Furnace spectrum of beryllium. R. F. Paton and G. M. Rassweiler (Physical Rev., 1929, [ii], **33**, 16—21).—Observations were made from 2150 to 7000 Å. and up to 2500° Abs., in both absorption and emission, using a specially designed high-temperature vacuum furnace. It is confirmed that the beryllium line 2348·62 Å. is the first line of the principal series of singlets for the neutral atom. The diffuse and sharp series of singlets of the element were discovered and tabulated. N. M. Bligh.

Spark doublets in the *K*-series. V. Dolejšek and (Mlle.) D. Engelmannova (Compt. rend., 1929, **188**, 318—320).—The experiments previously described (this vol., 225) have been extended to the heavier elements (atomic numbers 23—30) in the same state of valency, and the interval between the spark doublets of the *K*-series has been found to decrease with increase in atomic number. Dauvillier's results for copper (A., 1922, ii, 243) were confirmed, and the mean value found for the doublet constant $(\Delta\sqrt{\nu}/R)$ of 0·0074 is in good agreement with that already obtained (*loc. cit.*). J. Grant.

Continuous spectrum of mercury vapour. H. Volkringer (Compt. rend., 1929, **188**, 321—323).—The changes in the continuous spectrum of mercury vapour excited by an electrodeless discharge in a silica tube, the ends of which may be maintained at different temperatures, have been studied spectrographically. If the whole tube is at 230° the relative intensities of the several bands differ at various points of the tube, and are dependent on the exciting field. The production of the spectrum probably involves association of neutral and excited atoms rather than the simple passage from one atomic state to another.

J. Grant.

Power relation of the intensities of the lines in the optical excitation of mercury. I. E. Gaviola (Phil. Mag., 1928, [vii], 6, 1154—1167).—The intensities of the different lines of mercury vapour at the ordinary temperature when optically excited by a water-cooled mercury arc have been calculated as a function of the primary intensities and of the position of the emitting volume element in the tube. The special behaviour of lines like 3650 Å. is then explainable and the absorption laws for 4358, 3650 Å., and similar lines are calculable. A. E. Mitchell.

Influence of foreign gases on the optical excitation of mercury. II. E. Gaviola (Phil. Mag., 1928, [vii], 6, 1167—1191).—The alterations in the intensities of the lines in the optical excitation of mercury vapour caused by the presence of foreign gases are explained on the author's theory (cf. preceding abstract). The examination of the effects of various gases on the absorption of the line 4046 Å. by the metastable mercury atoms has demonstrated the long period of existence of these. The metastable level 2^3P_2 has an existence of 10^{-5} sec. when no foreign gases are present; its existence is, however, sensitive to their presence. In the presence of foreign gases the metastable level has a mean life of 1/300 sec., whilst under ideal conditions (as in stars) it should increase to about 10 sec. The result of Foote (A., 1927, 999) that the efficiency of quenching collisions of nitrogen with excited atoms in the resonance level is approximately 1 has been confirmed. The number of metastable atoms excited by the presence of a few mm. of nitrogen or water vapour is estimated to be about 10^2 times the number of excited atoms in the resonance level.

A. E. Mitchell.

Polarisation of canal-ray light. III. Mercury positive rays of the line 2537 Å. E. Rupp (Ann. Physik, 1929, [v], **1**, 289—300).—The polarisation ratio for the line 2537 Å. has been studied for mercury positive rays. Polarisation occurs in the fading light only when disturbances are allowed to occur at the positive-ray slit. By heating the slit the polarisation vanishes, so that it must be a secondary effect. The addition of foreign gases and the application of magnetic fields affect the polarisation ratio for the positive ray in the same way as they influence the resonance fluorescence of the line 2537 Å. The polarisation disappears when the positive-ray stream is diffused by an obstacle in its path.

R. A. Morton.

Heat spectrum of solid and liquid iron. R. Hase (Physikal. Z., 1928, **29**, 904—907).—The spectral energy distribution of the radiation emitted by solid and liquid iron resembles that from a black body, but the absolute intensity depends largely on surface oxidation. The wave-length of maximum emission for smooth solid iron is shifted in the direction of shorter wave-lengths as the temperature rises, so that Wien's law is obeyed. The intensity E at the maximum varies as CT^6, T being the absolute temperature and $C=2890$. Matt, slag-free iron emits approximately " grey " radiation approaching the black-body condition as the temperature rises. The heat spectrum of liquid iron closely resembles that of the smooth solid metal both as regards intensity and spectral distribution. R. A. Morton.

Excitation of *X*-ray spectra by means of α-particles. W. Bothe (Physikal. Z., 1928, **29**, 891—893).—The weak *X*-rays generated by the impact of α-particles on matter have been studied by means of a very sensitive apparatus, using argon in the counter. The following characteristic radiations were identified: *K*-radiation: Mg, Al, S, Ca, Cr, Fe, Zn; *L*-radiation: Se, Mo, Pd, Ag, Sb, Sn, Ta, Ir, Au, Bi; *M*-radiation: Bi. For some elements, the variation of the intensity of *X*-radiation with the range of the α-particles was determined, and was found to be closely related to the ionisation curve for the inner atomic electrons. The energy of the α-particles (from polonium) was insufficient for the maximum in the differential ionisation to be shown definitely, although the existence of such a maximum can be inferred for the curve obtained with aluminium. The results do not support Thomson's theory of ionisation, but are in agreement with Born's treatment of the quantum mechanics of collision processes.

R. A. Morton.

Some multiplets of singly-ionised thallium. S. Smith (Proc. Nat. Acad. Sci., 1928, **14**, 951—953).—Some of the lines arising from combinations of singlet and of singlet and triplet terms of Tl II were identified and classified, and compared with the lines predicted by an application of the regular and irregular *X*-ray doublet laws to the optical spectra of mercury-like atoms and interpolating between data for Hg I and Pb III. N. M. Bligh.

Influence of the presence of hydrogen on the L_{111} *X*-ray absorption edge of palladium. J. D. Hanawalt (Proc. Nat. Acad. Sci., 1928, **14**, 953—958).—*X*-Ray investigation shows that an outstanding distension of the palladium lattice exists due to absorbed hydrogen and corresponding with a compound Pd_2H. To decide whether the hydrogen atoms, are intimately combined with the palladium atoms the L_{111} absorption edge was studied using a vacuum spectrograph. Hydrogen was occluded in the palladium in two ways. Evidence indicates that the complex absorption edge corresponds with the superposition of two simple edges, one due to Pd atoms alone and the other due to Pd atoms combined with H atoms. The compound PdH is indicated, but the interpretation of the complex edge is inconclusive. N. M. Bligh.

Zeeman effect and term arrangement in the spectrum of singly-ionised chromium. E. Krömer (Z. Physik, 1928, **52**, 531—548).—Data for some 50 lines are tabulated, and from the results further contributions are made to the term arrangement in this spectrum. J. W. Smith.

***X*-Radiation excited by α-particles.** W. Bothe and H. Fränz (Z. Physik, 1928, **52**, 466—484).—The excitation of the *K*-, *L*-, and *M*-radiation by α-rays from polonium has been observed over the wave-length range 1·1—10 Å. for a number of elements. The relationship between the *K*- and *L*-excitation and the range of the α-particles is given graphically for some of the elements and the results are compared with Bragg's curve for the dependence of the ionisation in air on the range of the α-particles. The data obtained for the excitation limit are in opposition to Thomson's theory of ionisation (A., 1912, ii, 410), but not to Born's quantum theory of collision (A., 1926, 1078). The yield of aluminium *K*-radiation was measured in an absolute manner by an ionisation method, those of the other characteristic radiations being then compared with this. Both in the *K*- and *L*-series a general decrease in the yield was observed as the atomic number of the elements under investigation increased. From the observations made it is deduced that the probability of ionisation is essentially smaller for an *L* electron than for a *K* electron with equal energy of ionisation. J. W. Smith.

Precision measurements in the *K*-series of the elements zinc (30) to ruthenium (44). B. Edlén (Z. Physik, 1928, **52**, 364—371).—Using a precision tube spectrometer of the type employed by Siegbahn and by Larsson, measurements have been made of the *K* lines α_2, α_1, β_1, β_2 of the elements zinc, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, niobium, and ruthenium. The β_3 lines of the last six of these elements have also been measured. J. W. Smith.

Absolute *X*-ray wave-length measurements. A. P. R. Wadlund (Physical Rev., 1928, [ii], **32**, 841—849).—By means of a speculum metal grating ruled 50 lines to the mm., the wave-lengths of the $K\alpha_1$ line of copper, iron, and molybdenum were determined as 1·5373±0·0008, 1·937(6)±0·002(3), and 0·708(3)±0·001(1) Å., respectively. Using the $K\alpha_1$ line of copper the following constants were calculated: the grating space of calcite 3·0290±0·0016 Å., $N=(6{\cdot}061\pm0{\cdot}009)\times10^{23}$, and $e=(4{\cdot}774\pm0{\cdot}007)\times10^{-10}$. The sources of error involved are discussed, the chief being those due to the settings on the lines of the diffraction pattern and those due to the inexact setting of the grating. N. M. Bligh.

Evaporation at the cathode of the mercury arc. J. von Issendorf (Physikal. Z., 1928, **29**, 857—864).—By means of a special type of lamp it has been possible to determine the amount of mercury sputtered and vaporised from the cathode of the mercury arc, at various temperatures. The evaporation varies considerably with temperature and to a small extent with current, the whole cathode surface being apparently involved. Positive and negative limiting values for the vaporisation in the neighbourhood of the focal spot are given and it is shown that the loss of material from the focus is vanishingly small, an actual gain being not improbable owing to the effect of streams of ion. This supports Compton's assumption that, in considering the energy balance, volatilisation from the focus of the mercury discharge is negligible. The amount of mercury sputtered from the cathode shows a roughly linear increase with increasing current strength. The results are considered in relation to the problem of the energy balance at the cathode. R. A. Morton.

Transport of matter in the iron arc. H. Schmick and R. Seeliger (Physikal. Z., 1928, **29**, 864).—In the theory of the mechanism of the arc cathode, the energy balance plays an important part (cf. Issendorf, preceding abstract). Investigation of the loss of material from the iron arc shows that the phenomenon is complicated, but is definitely not proportional to the current and varies primarily as the degree of cooling of the cathode. In agreement with Issendorf's work, it would appear that the loss of material is not confined to the focal point, but is distributed over the whole neighbouring area.

R. A. Morton.

Geiger point counter. Influence of cathode material on the sparking potential. O. Klemperer (Physikal. Z., 1928, **29**, 947—948).—The sparking potential in the Geiger account varies to some extent with the material forming the " point " cathode. In carbon dioxide the limiting voltages were 600—650, no definite effect being traceable to the nature of the cathode. In air, platinum, gold, silver, and copper behaved similarly, but for steel and aluminium the voltage V_0 was lower. In hydrogen, the metals fell into a series, steel, however, being anomalous. The greatest differences in V_0 occurred in argon. The results are discussed in relation to the mode of action of the counter (cf. Curtiss, A., 1928, 985). R. A. Morton.

Calculation of the product of the halogen ions by means of their ultra-violet absorption in aqueous solution. G. Scheibe (Naturwiss., 1929, **17**, 86).

W. E. Downey.

Properties of ionised gases in high-frequency fields. H. Gutton (Compt. rend., 1929, **188**, 156—157; cf. A., 1927, 294).—Determinations of the conductivities corresponding with resonance of an ionised gas for λ 4830, 2528, 1834, and 1324 μμ show that the conductivity and elastic force are proportional to the number of ions per cm. and to number of ions to the power 0·75, respectively. The constitution of an ionised gas is analogous to that of a Lorentz dielectric in which the electrons are further apart, and the existence of an absorption band is due to resonance between the oscillations of the electrons and of the field. J. Grant.

Passage of the electric current through a Cooper-Hewitt mercury lamp. S. Ray (Z. Elektrochem., 1929, **35**, 89—93).—Theoretical. An attempt is made to explain the mechanism of the Copper-Hewitt mercury lamp in terms of a hypothetical compound HgZ, which is assumed to be formed in the lamp. The cause of the cessation of the current with time, especially at high voltages, is discussed. L. L. Bircumshaw.

Nature of streamers in electric sparks. M. Miyanishi (Japan. J. Phys., 1928, **5**, 67—82).—The streamers emanating from the anode and cathode of a spark have been examined spectrographically and found to consist of positively and negatively charged particles respectively. Their velocity and duration of luminosity have also been measured.

J. L. Buchan.

Ionisation through electronic collision. A. von Hippel (Ann. Physik, 1928, [iv], **87**, 1035—1086).—A theoretical discussion of the ionisation of atoms by electronic collision on the basis of classical theory is given. An ionisation function representing the probability of ionisation taking place through a collision is deduced. Under certain limiting conditions this function for a single atomic electron shows a maximum at a collision-electron speed corresponding with double the ionisation potential of the atom. Former experimental methods are critically discussed and a new one is described. A stream of electrons of homogeneous velocity hits perpendicularly a stream of atoms; the ions formed are carried on with the stream of atoms and are separated from the non-ionised atoms by passage through a mass spectrograph. The deflected ray of ions is then collected on a suitable ion collector. Mercury vapour has been examined afresh by this method, and the existence of a maximum of ionisation yield for an electronic speed in the neighbourhood of double the ionisation voltage of mercury is demonstrated. The measured collision yield, however, at this maximum is 8·3% compared with that predicted of 15%. A short description is also given of a high-frequency method suitable for the qualitative study of collision ionisation and also for experiments with streams of ions. R. N. Kerr.

Secondary electron emission produced by positive cæsium ions. J. M. Hyatt (Physical Rev., 1928, [ii], **32**, 922—928).—Experiments were made to determine the number of electrons emitted from a cæsium-covered grid and plate as a function of the accelerating potential, by positive cæsium ions from a tungsten filament maintained at about 1200 Abs. in the presence of cæsium vapour. The number of electrons emitted per positive ion was found to increase uniformly from 0·01 at 100 volts to 0·15 at 600 volts. The ratio, positive-ion current to plate/total emission current, was found to be independent of the plate and grid potentials for plate potentials greater than 0·2 of the grid potential. This ratio, 0·72, is the same as the ratio, total area of plate less projected area of grid/total plate area. Assuming the same distribution of electrons as positive ions, the ratio, plate current/grid current, in the type of tube used can be calculated. N. M. Bligh.

Critical photo-electric potential of clean mercury and the influence of gases and of the circulation of the mercury on it. W. B. Hales (Physical Rev., 1928, [ii], **32**, 950—960).—Experiments were made to test the theories of photo-electric fatigue after eliminating every possible source of contamination of the metal surface, using a reconstructed form of the apparatus of Kazda and Dunn (A., 1926, 3; 1927, 603). The long wave-length limit for running mercury was found to be 2735 and the critical frequency for stationary mercury 2735 ± 10 Å., in agreement with Kazda for flowing mercury. It is now found that a four-fold increase of photo-current is not reached until 80 hrs. after turning off the still, and remains constant indefinitely thereafter. The long wave-length limit for this maximum sensitivity was found to be 2910 Å. Traces of hydrogen, helium, argon, nitrogen, and water vapour had no influence on the photo-electric behaviour or on the rate of rise of sensitivity, except for a cleansing effect in reducing impurity which slowly contaminates the surface. Oxygen reduced the threshold value to 2555 Å. in 18 hrs. N. M. Bligh.

Ion-rays. J. Kahra (Ann. Physik, 1929, [v], **1**, 135—156).—In conformity with the view of Schmidt (A., 1924, ii, 727; 1925, ii, 251; 1926, 877) that only those ions capable of wandering in electrolysis are emitted on heating, it is found that at 400° lead bromide, iodide, and fluoride emit negative ions only. Experiments designed to increase the emission as a result of irreversible loosening of the crystal lattice were unsuccessful. The introduction of gases into the salt converted the falling portion of the emission curve into a rising portion, the change being due to irreversible processes. A number of glasses were found to emit positive ions exclusively, a separate negative emission being observed only at the highest temperatures. The data again support Schmidt's theory. The increase in emission with time arises from loosened structure following irreversible processes. R. A. Morton.

Change in emission of ion-rays with time. O. Birkenberg (Ann. Physik, 1929, [v], **1**, 157—168).—Dissolved or fused salts heated on a wire until the emission becomes constant maintain this constant value indefinitely in a vacuum or in contact with dry gases. In the presence of water vapour the emission from soluble salts is increased, whilst the emission from salts insoluble in water is unaffected. Salts which have been sublimed in air on to a wire and heated until the emission becomes constant revert to the normal in a vacuum or in contact with moist or dry gases, whereas if the sublimation has been carried out in a vacuum, reversion does not occur. The phenomena are all explained on the assumption that the salts can occlude foreign matter which results in the formation of loosened ions. R. A. Morton.

Photo-electric behaviour of mercury during the transition from the liquid to the solid state of aggregation. (Frl.) M. Grützmann (Ann. Physik, 1929, [v], **1**, 49—73).—The total photo-electric emission of mercury remains constant for temperatures on either side of the m. p., in contrast with the electrical behaviour of mercury in other respects. An electrical effect at the m. p., and independent of light, is shown to occur, and it is suggested that the phenomenon may be related to the liberation of mercury vapour. R. A. Morton.

Influence of hydrogen on the photo-electric electron emission of potassium. R. Suhrmann and N. Theissing (Z. Physik, 1928, **52**, 453—463).—Thoroughly purified and dried hydrogen exerts no influence on the photo-electric sensitivity of potassium in bulk. When the latter was in the form of a unimolecular film on the surface of platinum-black, the sensitivity was considerably reduced on admitting hydrogen. This effect diminished, however, as thicker films of potassium were built up. Hence it is concluded that the spectral maximum of the sensitivity curve observed with potassium is not attributable to the action of hydrogen molecules. J. W. Smith.

Theory of photo-electric action. H. Wolff (Z. Physik, 1928, **52**, 158—160).—The difference between limiting energies required to eject electrons from the surface of two metals equals e times the contact *P.D.* of the metals, and lightly bound electrons should suffer only Compton scattering. This, and other inconsistencies, suggests that photo-electric emission is caused by atoms, raised to a metastable state by light absorption, losing their energy to colliding and slowly moving electrons of the "electron-gas," which are then ejected as photo-electrons. A. B. D. Cassie.

Thermionic emission from clean platinum. L. A. DuBridge (Physical Rev., 1928, [ii], **32**, 961—966; cf. A., 1927, 391; 1928, 340).—Owing to previous inconsistent results for platinum, a greater precision and range of temperature and currents has been attempted. The thermionic emission from thoroughly outgassed platinum in high vacuum was measured to 0·5% over the temperature range 1360—1750° Abs. The values obtained for the thermionic constants of the equation $I=AT^2e^{-b/T}$, when corrected for the Schottky effect, are: $b=72820$ Abs., $\phi=6{\cdot}27$ volts, $A=17000$ amp./cm.^{2}deg.^{2} The value of the thermionic work function ϕ is correct to 1% and agrees within 0·5% with the value of the photo-electric work function previously obtained. The value of A is confirmed to be 250 times as great as the theoretical value of 60·2 amp./cm.^{2}deg.^{2} (cf. Bridgman, A., 1928, 682). N. M. Bligh.

Secondary electron emission from molybdenum. J. M. Hyatt and H. A. Smith (Physical Rev., 1928, [ii], **32**, 929—935).—The secondary electron emission from a clean molybdenum plate in a simple three-electrode tube was studied. The number of primary electrons striking the plate was calculated by the positive-ion calibration method (cf. this vol., 228). The number of secondary electrons per primary reaches a maximum of 1·15 at 600 volts and then decreases to 1·00 at 2000 volts. Petry (A., 1925, ii, 1017) reported discontinuities in the secondary emission curve at several accelerating potentials. One definite discontinuity is now found at 13·5 volts; the others are very small and not reproducible. The emission increases about 3% within a few minutes after heating if the gas pressure is very low and then remains constant for some time; it decreases with time when there is more gas present. The secondary emission appears to increase by about 4% when the temperature of the target is raised from that of normal operation to 1600° Abs. N. M. Bligh.

Thermionic emission constant *A*. R. H. Fowler (Proc. Roy. Soc., 1929, A, **122**, 36—49).—The relation between the constants *A* and χ of the thermionic emission formula, recently recorded by DuBridge for severely outgassed platinum (A., 1928, 340), is explained by the application of Nordheim's theory of the emission coefficient of electrons from metals. The necessary conditions for the proper application of the theory are formulated. Apart from the absolute value of *A* in certain cases, the theory gives a most satisfactory account of the whole range of thermionic emissions by clean surfaces, or surfaces so contaminated that the true work function is diminished. Certain apparent discrepancies in absolute magnitude between the observed and theoretical values of *A* are discussed.

L. L. Bircumshaw.

What happens during an electron jump? D. S. Villars (Nature, 1929, **123**, 240).—It is considered that in an electron " jump " the electron does not suddenly change its position, but merely undergoes a change in momentum and obeys a new force law; its behaviour is compared with that of a vibrating molecule after absorbing light. By Pauli's interpretation of Schrödinger's theory the electron orbit represents a cloud in space, the centre of gravity being the locus of a Bohr orbit. A. A. Eldridge.

Polarisation of the light emitted in electron collisions in inert gases. K. Steiner (Z. Physik, 1928, **52**, 516—530).—The degree of polarisation of the light produced by electron collisions in neon and helium has been investigated experimentally. In the case of neon, very definite effects were observed, the lines of some of the spectral series showing a tendency to become polarised parallel to the electron beam, and others at right angles to it. Indications of a similar effect have been obtained with helium.

J. W. Smith.

Absorption of *X*-rays. H. R. Robinson and C. L. Young (Nature, 1929, **123**, 203—204).—By a method of " magnetic spectrometry " it is shown that the two *K*-electrons of a zinc atom absorb probably more (almost certainly not less) *X*-radiation of wave-length 0·56 Å. than the eight *L*-electrons of tungsten. Simplifying assumptions associated with all theories so far proposed may account for the deviations between experimental and theoretical values. A. A. Eldridge.

Some transient effects with ions of low mobility. H. P. Walmsley (Mem. Manchester Phil. Soc., 1927—1928, **72**, 29—41).—The mathematical theory of the motion of ions of low mobility is discussed and approximate equations are derived which lead to curves for the time variation of the saturation exhibiting the same type of distortion from the normal as do the author's experimental curves relating to ions of low mobility. R. W. Lunt.

Range of *H*-particles. W. Bothe (Z. Physik, 1928, **51**, 613—617).—Calculations based on the energy exchanges which take place when a α-particle collides with a neutral molecule resulting in the liberation of an *H*-particle lead to values of the range of *H*-particles in agreement with experiment if it be assumed that after collision the α-particle becomes attached to the nucleus of the atom with which collision has taken place. Such an hypothesis was suggested by Blackett in order to account for the apparent disappearance of α-particles after collision in nitrogen. R. W. Lunt.

Dispersion electrons of lithium. J. Hargreaves (Proc. Camb. Phil. Soc., 1929, **25**, 75—96).—Mathematical. The method of Hartree (cf. A., 1928, 216) has been used to determine the number of dispersing electrons corresponding with the lines of the principal series of the optical spectrum of lithium, and also to the continuous spectrum at the head of the series. W. E. Downey.

Measurement of the life of the metastable mercury atom. M. L. Pool (Physical Rev., 1929, [ii], **33**, 22—26).—An interrupted optical excitation method was used for measuring the life of the metastable 2^3P_0 state. The line 4047 Å. ($2^3P_0-2^3S_1$) showed strong absorption when a few mm. of nitrogen were introduced into the resonance tube, whilst the lines 4077, 4358, 5461, 5770, and 5790 Å. showed no measurable absorption. The rate of decay of the amount of 4047 Å. absorbed with respect to the delay after excitation of the mercury vapour was taken as the rate of decay of the metastable 2^3P_0 state. The life or half-value time of the state varied markedly with the pressure of admixed nitrogen. The maximum life, $4{\cdot}2\times10^{-4}$ sec., occurred for 6·8 mm. of nitrogen. No absorption of 4047 Å. was observed on introducing hydrogen, argon, neon, or helium into the resonance tube. N. M. Bligh.

Counting of α-particles by Wulf's method. (Mlle.) M. Desmet and (Mlle.) M. van Haeperen (Ann. Soc. Sci. Bruxelles, 1928, **48**, B, i, 100—113).—A comparison of the improved ionisation chamber method of counting α-particles of Wulf (Physikal. Z. 1925, **26**, 382) with the scintillation method. Using as a constant source of α-particles a small sphere of polished steel activated by means of radium emanation, the optical method gave 15 particles/min. Wulf's method gave values of 10—13 in the most favourable cases using dull-pointed needles, and only 3—5 with fine-pointed needles. Particular attention was paid to the cleaning of the needles, shape of the point, and sign and magnitude of the voltage applied. Since the scintillation method almost certainly gives a low result, Wulf's method is not considered suitable as an accurate quantitative method.

O. J. Walker.

Diamagnetism of ions of the rare gas type. H. Kulenkampff (Ann. Physik, 1929, [v], **1**, 192—194).—The value of c_1 in the work of Ikenmeyer (cf. this vol., 247) can be obtained as follows: the susceptibility $\chi=\Sigma_i r_i^2(e^2L/6mc^2)=Z_E\bar{r}^2e^2L/6mc^2$, r_i being the distance from the nucleus of the *i*-th electron, $\bar{r}^2$ the mean distance for all electrons, and Z_E the number of electrons. As a first approximation, $\bar{r}^2$ is independent of Z_E and $\bar{r}^2=0{\cdot}282\times10^{-16}=(0{\cdot}531\times10^{-8}$ cm.$)^2$, agreeing with $a_1=0{\cdot}532\times10^{-8}$ cm., where a_1 is the ground orbit of the Bohr hydrogen atom. It is then shown that $\bar{r}^2=a_1^2[1+(1/Z_E)(c_2'-c_1)/c_1]=a_1^2[1+(7{\cdot}35/Z_E)]$ for halogen ions. For alkali ions and alkaline-earth ions the values 3·0 and 4·35, respectively, replace 7·35, $2c_1$ replacing c_1 in the numerator in the latter case. R. A. Morton.

Motion of electrons in pentane. J. D. McGee and J. C. Jaeger (Phil. Mag., 1928, [vii], 6, 1107—1117).—The method of Bailey (A., 1925, ii, 1019) has been employed to investigate the motion of electrons in pentane vapour. The phenomena observed are very similar to those previously obtained with ethylene. The fraction of the energy lost in collision rapidly approaches a maximum as the agitation velocity increases and then decreases rapidly. It is suggested that this may be due to the formation of ions. The "ageing" effect of the gas, when left in the apparatus, reported by Wellish (Phil. Trans., 1909, A., 209, 249) was absent. A. E. Mitchell.

Capture of electrons by molecules. V. A. Bailey and J. D. McGee (Phil. Mag., 1928, [vii], 6, 1073—1089).—The apparatus previously described by Bailey (A., 1925, ii, 1019) has been modified to simplify the procedure of measurement. The measurements of Bailey and Higgs (to be published later) on ammonia have been repeated and it is shown that the probability of attachment of an electron at a collision with a molecule may vary very considerably with the energy of the electron. This result is in disagreement with that of Loeb and others, who consider the probability of attachment to be a characteristic constant for a gas.

A. E. Mitchell.

Electronic waves and electrons. (Sir) J. J. Thomson (Phil. Mag., 1928, [vii], 6, 1254—1281).—It is shown that if the structure of the electron were such that the usually accepted point charge, or something analogous to it, formed a nucleus surrounded by a system made up of parts which can be set in motion by electric forces and when in motion produce the effects of electric currents, then the motion of the electron would, from the ordinary laws of electro-dynamics, give rise to a train of waves, the relationship between the wave-length of this train and the velocity of the electron being exactly as indicated by the experiments of G. P. Thomson. This surrounding structure might comprise either a distribution of discrete lines of force or of a number of positively and negatively charged particles which would behave like free particles. The sphere surrounding the nucleus will have a definite period of vibration, the frequency of which is proportional to the square root of the number of electrified systems per unit of volume. The vibrations form an oscillating electric field in which there is no transmission of energy. Both the nucleus and the sphere can vibrate, and in the steady state of the electron the vibrations are in resonance. The total energy of the electron is that due to the charge on the nucleus plus that due to the oscillating field, the importance of which conception is pointed out in connexion with the calculation of the size of the electron.

A. E. Mitchell.

Wave mechanics of rotating electrons and the fundamental equation of the electromagnetic field. J. Frenkel (Z. Physik, 1928, 52, 356—363).—Mathematical. In continuation of a previous communication (A., 1928, 570) the fundamental equation of the wave mechanics of an electron is shown to be a generalised form of Maxwell's equation and the corresponding d'Alembert equation. By modifying slightly the previous work, a system of eight equations is obtained which may be combined into pairs yielding the four equations of Dirac's theory.

J. W. Smith.

Anomalous magnetic rotation of excited neon. R. N. Jones (Nature, 1929, 123, 278).—Erroneous values of the dispersion constants determined from the anomalous magnetic rotation in excited neon (A., 1928, 1310) are replaced by corrected values. A. A. Eldridge.

Charge of an electron. A. S. Eddington (Proc. Roy. Soc., 1929, A, 122, 358—369).—The ratio of hc to e^2 is a pure number, and although the usual methods of macroscopic physics break up this number so that its dimensionless character appears curious, in the wave theory of the interaction of electrons the number is kept intact. In the wave equation for two electrons (or an electron and a proton) e occurs in the expression $hc/2\pi e^2$ as the coefficient of certain terms. The present investigation of the interaction of two electrons is based on the exclusion principle and the Fermi–Dirac statistics, and it is not considered necessary to postulate electric charge. A wider principle of relativity is conceived, which allows, in addition to a rotation of space and time, a "rotation" which will interchange the identity of two electrons; or the two electrons become two indistinguishable entities. This treatment leads to an equation containing $2\pi e^2/hc$ as a coefficient of one term, which according to the theory must have the value 1/136. The experimentally determined value of e gives, however, 137·1 for $hc/2\pi e^2$. L. L. Bircumshaw.

Longitudinal magnetic actions on beams of slow electrons (periodic concentrations and dilatations). J. Thibaud (Compt. rend., 1929, 188, 54—56).—The blue fluorescence shown by a beam of electrons traversing an evacuated cylinder containing a wire-wound coil in a high vacuum and at a voltage below 500 shows periodic variations between a thin, bright uniform thread of light (state of concentration) and a luminous cone (state of dilatation) when varying magnetic fields are applied. The phenomenon is unaffected by the sense of the field and the type of coil used to generate it, and a linear relation exists between the spread of the electrons and the field strength producing concentration (or dilatation) for each successive phase. J. Grant.

Concentration and dilatation effect produced by a longitudinal magnetic field on a beam of slow electrons. J. Thibaud (Compt. rend., 1929, 188, 158—160).

Diffusion of slow-moving electrons in the inert gases. H. Pose (Z. Physik, 1928, 52, 428—447).—The diffusion of electrons in an inert gas has been investigated by passing a beam of thermally emitted electrons through a hole in the centre of one plate, and measuring the ratio of the number of electrons striking an opposite parallel plate to the number returning to the plate through which the electrons enter, both plates being maintained at the same potential. According to the diffusion theory of Hertz (Z. Physik, 1925, 32, 298), this ratio should be equal to $4\lambda/3a$, where a is the distance between the plates and λ the mean free path of the electrons. After correction for the dimensions of the source, which were necessarily large compared with the mean free path of the electrons, the values obtained for the mean free path in the gases investigated, viz., neon, argon, and a mixture of neon and helium, were in good agreement with those obtained by direct measurement. They also showed very clearly the phenomenon observed by Ramsauer (A., 1921, ii, 324) of the strong dependence of the mean free path in argon on the electronic velocity.

Measurements were also carried out with an electrostatic field between the two plates, the dependence of the above-named ratio on the potential between the plates being measured. In this case, also, the results were in good agreement with the diffusion theory. The deviations observed, especially at high electronic velocity, are explainable on the ground of reflexion at the plates. In argon the deviations were of the order to be anticipated according to the diffusion theory from the change in the mean free path with electron velocity. It is concluded that, to the degree of accuracy obtainable, the motion of slow-moving electrons through the inert gases is correctly expressed by the diffusion theory.

J. W. Smith.

Polarisability of an electron pencil. F. Wolf (Z. Physik, 1928, 52, 314—317).—If an electron is a magnetic dipole an electron pencil must come into a state of polarisation when it is passed through a magnetic field. Experimental analysis of such a pencil carried out by allowing it to impinge on a metallic reflector with its face at an angle of 45° to the pencil and connected to an electrometer failed to show any such effect. J. W. Smith.

Theory of electron scattering and excitation by collision. J. Holoymark (Z. Physik, 1928, 52, 485—495).—Mathematical. These phenomena are discussed from the point of view of wave mechanics.

J. W. Smith.

Refractive index of electrons and diamagnetism. L. Rosenfeld (Naturwiss., 1929, 17, 49—50). —By further application of the principles of wave mechanics to the considerations of Bethe (A., 1928, 1303) a relationship is deduced connecting the diamagnetic susceptibility of an element with its refractive index with respect to electrons. The experimentally observed susceptibility can be regarded as the difference between a paramagnetic component and a diamagnetic component. Since the former can also be calculated from wave mechanics, this difference can be deduced theoretically. Calculations have been made for six metals, and the theoretical figures compared with practical data. In the cases of copper, silver, gold, and lead, values of the right order of magnitude are obtained, but considerable discrepancies are found in the cases of chromium and aluminium. J. W. Smith.

Magnetism and nuclear structure. D. Enskog (Z. Physik, 1928, 52, 203—220; cf. A., 1928, 343). —Both kinetic and potential terms of the classical Hamilton energy function are modified when electrically-charged particles, moving under their mutual influence, are supposed possessed of magnetic doublets. The energy of emission of an α-particle, as measured by Rutherford and others, from radioactive atoms seems given by this modified expression for closed quantised orbits. A non-magnetic planet moving in a magnetic field has kinetic modification, and the maximum core charge suggested by considerations of stability of this system is two electronic units. Larger nuclei ought, therefore, to be formed of helium and smaller nuclei. The positive energy of this non-magnetic-planet system disagrees with Aston's results on "packing." Magnetic-planet systems may have negative energy, and a planet with two magnetic units gives quantitative agreement with experiment. The decrease in energy is greater when a second single proton planet is added to a two-proton core, indicating stability of the helium group. The magnetic number for the helium nucleus is 2, for an α-particle 1, indicating instability of binding for an α-particle. The formation of more complex nuclei is considered. A. B. D. Cassie.

Free and bound electrons in metals. R. Ruedy (Physical Rev., 1928, [ii], 32, 974—978).—Theoretical. It is found when the theory of dispersion in an absorbing medium is applied to recent values for the optical properties of different metals (copper, gold, nickel) that bound electrons exist inside the metal comparable in number with that of the free electrons. N. M. Bligh.

Number of recoil electrons and intensity of modified scattering. E. J. Williams (Mem. Manchester Phil. Soc., 1927—1928, 72, 1—16).—Scattered radiation consists of modified and unmodified radiation; the modified radiation, according to the quantum theory, should be accompanied by production of β-rays or recoil electrons. X-Ray properties of the elements show a periodicity, and on this basis the coefficients of modified scattering for oxygen and nitrogen and radiation of wave-length 0·6 Å. have been calculated from results for carbon and aluminium. The values agree to within the experimental error (10%) with those determined experimentally from the expression $\tau \times N_R/N_P$, where τ is the coefficient of photo-electric absorption, and N_R and N_P are the numbers of recoil and photo-electrons, respectively. This proves that β-rays are produced distinct from the photo-electrons and equal numerically to the number of modified quanta scattered. Comparison of σ_m calculated from the wave mechanics with values of $\tau \times N_R/N_P$ shows discrepancies of 10%. The error is greater in the case of carbon. G. E. Wentworth.

Ninth report of the German Commission on atomic weights. M. Bodenstein, O. Hahn, O. Hönigschmid, and R. J. Meyer (Ber., 1929, 62, [*B*], 1—23).—The report is divided into three sections dealing respectively with atomic weights determined by physico-chemical methods, with those dependent on chemical processes, and with progress in the question of isotopes of non-radioactive elements. Under their respective headings, detailed consideration is given to neon, argon; potassium, cæsium, copper, silver, barium, cerium, erbium, titanium, uranium, rhenium; neon, potassium, zinc, and germanium.

New determinations of the ratio Ag : O are regarded as establishing the value Ag=107·880 with an uncertainty not exceeding ±0·001. Atomic weights on the silver basis, in so far as they have been determined with all the refinements of the halogen process, have been re-calculated to the adopted at. wt. of silver and are now given to so many decimal places that the last figure may be regarded as accurate at any rate to within a few units. Changes are adopted for the following elements, to which the at. wts. assigned are : Ba=137·36; Cd=112·41; C=12·000; Ce=140·13, Co=58·94; Dy=162·46; Er=167·64; H=1·0078; He=4·002; I=126·93; Li=6·940; Ne=20·18; Ni=58·69; P=31·02; Pb=207·21; Pt=195·23; S=32·06; Sm=150·43; U=238·14; V=50·95; Zn=65·38; Zr=91·22. H. Wren.

Numerical regularities in the atomic weights of elements. S. M. Lozanić (Bull. Acad. Sci. Bohême, 1928, Reprint, 9 pp.).—Regularities of the type $a=2m+b$, where a is the at. wt., m the atomic number, and b is 0, 1, 2 or 3, appear in the first part of the periodic table. As the at. wt. increases, regularities of the same type appear to persist, with high values for b. These considerations are regarded as supporting the view that the at. wts. are whole numbers. The number of isotopes possessed by a given element is connected with its place in the table. R. A. Morton.

Isotopy of lead. (Mme.) B. Perrette–Montamat (Ann. Physique, 1928, [x], **10**, 349—407).—The behaviour of two samples of lead, one from galena and having an at. wt. of 207·2, the other from pitchblende from the Belgian Congo and having an at. wt. of 206·14, has been investigated. The carefully purified samples were spectroscopically examined and the line at 4058 Å. was found to vary by 0·0076±0·0008 Å. between the two specimens. The ordinary lead had d 11·336±0·0004, the pitchblende lead, 11·278±0·0004. The nitrates, crystallised at 0°, had d 4·536±0·0005, 4·523±0·0005, respectively. The values of n_{5890} for the two nitrates do not vary by more than 0·00015 from 1·78185 at 10°. W. E. Downey.

Is there a stable radium isotope in barium minerals? O. Kahn and K. Donat (Z. physikal. Chem., 1928, **139**, 143—150).—Since calcium, strontium, and barium, of even atomic numbers, occur in large quantities and since uranium and thorium occur in amounts comparable with those of their next lower homologues tungsten and hafnium, the possibility of the existence of a stable isotope of radium is discussed. A concentration of the active isotope, a stable element of atomic number 88, was attempted by methods of radium-fractionation using barium bromide; the product was examined spectroscopically for radium lines, but no such lines were recognisable. G. E. Wentworth.

γ-Rays of radium. J. A. Gray (Nature, 1929, **123**, 241—242).—It is concluded that the theory of Cave and Gray (A., 1927, 1004) can be employed in the interpretation of cosmic-ray experiments; Dirac's theory of scattering is considered to be incorrect. The results of cosmic-ray experiments have been examined. The author's method for the determination of γ-ray wave-lengths is outlined. A. A. Eldridge.

Measurement of the active deposit of radium by the penetrating γ-radiation. (Mme.) I. Curie (Compt. rend., 1929, **188**, 64—66; cf. A., 1928, 810).—The number of millicuries of radium-C in a source of radium $(B+C)$ in radioactive equilibrium may be determined from the fraction of ionisation (K) attributable to radium-B. The correction to be applied is obtained from the electrometric measurement of the difference in the ionisation currents produced in two chambers, in one of which the β-radiation of radium-B is absorbed by a lead sheet 27 mm. thick. The correction is applied by division by $[1-K(1-\alpha)]$, where $\alpha=bB/cC$, B and C being the number of atoms of radium-B and radium-C, and b and c their radioactive constants, respectively. At equilibrium $(1-\alpha)=0{\cdot}735$. J. Grant.

Quantum mechanics of radioactive nuclei. G. Gamow and F. G. Houtermans (Z. Physik, 1928, **52**, 496—509).—Mathematical. From the point of view of Gamow's previous theory (this vol., 7) the disintegration constant of an α-radiator is calculated from the energy of the α-particle, the atomic number, and the characteristic nuclear radius. In each radioactive series the observed rate of disintegration of the emanations was assumed and hence the nuclear radius was calculated. Using these values the disintegration constants of the remaining α-ray emitters in the series could be calculated without any supposition as to the change of potential in the immediate neighbourhood of the nucleus. The results obtained are in approximate agreement with the experimental values. They are also compared with the values calculated from the Geiger–Nuttall relation. A qualitative view of the mechanism of radioactive disintegration is also developed. J. W. Smith.

Blue rock salt. K. Przibram (Nature, 1929, **123**, 243).—Guthrie's observations (this vol., 168) confirm those of the author (Sitzungsber. Akad. Wiss. Wien, 1923, II*a*, **132**, 261), whose recent principal results concerning the coloration of salts are summarised. A. A. Eldridge.

Passage of α-rays through matter. S. Rosenblum (Ann. Physique, 1928, [x], **10**, 408—471).—The effect of passage through matter on α-rays has been examined by the method of the magnetic field. The total distance traversed by α-rays from thorium-C' is equal to $36{\cdot}3K$, where K is a constant characteristic of the metal and is a function of the atomic number of the metal. The power of various metals in stopping α-rays is found to be expressed by $N/\sqrt{(N+4)}$. W. E. Downey.

Positive ion currents in the positive column of the glow-discharge in the noble gases. W. Uyterhoeven (Proc. Nat. Acad. Sci., 1929, **15**, 32—37).—Langmuir's method for the use of collectors in gas discharge was employed to study the positive column of the glow in neon, argon, and helium. The positive ion current increased with decrease of the potential of the collector, and there was a difference between the measured and calculated values of the positive ion current amounting to one half of the former. A number of possible explanations of these discrepancies are summarised and discussed.

N. M. Bligh.

Discharge of canal rays and the influence of metal walls. J. Koenigsberger (Z. Physik, 1928, **51**, 565—569).

Yield of *H*-particles. G. Kirsch and H. Pettersson (Z. Physik, 1928, **51**, 669—695).—Elaborate experiments are described by means of which the authors have sought an explanation of the discrepancies in the yields of *H*-particles between their results and those of Bothe and Fränz. It is claimed that the experiments establish that the scintillation counting method is free from the objection that β-particles may be confused with *H*-particles, and counter-objections are made to the Geiger counter method. R. W. Lunt.

Passage of β-rays through matter. C. E. Eddy (Proc. Camb. Phil. Soc., 1929, **25**, 50—61).—The form of the absorption curves of homogeneous β-rays in aluminium has been investigated by means of a Geiger counter. The main portion of the curve is linear with pronounced initial and final flattenings. Similar initial flattenings were found for copper and silver, but not for gold. The range of β-rays emergent at different angles has been determined, and it appears that the loss of range is due to the increased path consequent on scattering. Some evidence of the angular distribution of plurally scattered particles was obtained; also evidence of a most probable angle of scattering, similar to that found for α-rays by Geiger. W. E. Downey.

Light from hydrogen canal rays. B. Dasannacharya (Ann. Physik, 1929, [v], **1**, 74—92).—A simple deduction is given of Wien's formula for the intensity of the positive-ray Balmer spectrum of hydrogen for equilibrium between rays and pressure in an observation space behind the cathode. A correction factor applicable to earlier work by the author (*ibid.*, 1925, [iv], **77**, 613) is introduced. A new magnitude c_0, the free path of the total disturbance in a collision, is introduced and values are calculated for H_β and H_γ and compared with those for H_α. It is calculated that the ratio of the intensities of the hydrogen lines is H_α/H_β, 8·4—21·5; H_β/H_γ, 4—5·8; and H_γ/H_δ 2·8—3·4. R. A. Morton.

Refraction of material waves from the point of view of special relativity theory. H. Bauer (Z. Physik, 1928, **52**, 221—224).

Transference of energy in collisions between nuclei. W. Kuhn (Z. Physik, 1928, **52**, 151—155).—Mathematical.

Laws of scattering of canal-rays in their passage through solid bodies. C. Gerthsen (Ann. Physik, 1928, [iv], **87**, 1000—1002).—The units used in calculating the most probable angle of deflexion should not be rings of a plane as taken by Homma (A., 1926, 880), but spherical zones. On correction of that author's results in this way the resemblance obtained between these laws and the laws of scattering for α-particles disappears.

R. N. Kerr.

Structure of the helium atom. J. Stark (Ann. Physik, 1928, [iv], **87**, 927—934).—Consideration of the results of experiments on the splitting of helium lines in an electric field enables a generalisation to be made concerning the displacement of lines belonging to either an ortho series of one of the groups $2p^2$ or $2s$ or a para series of one of the groups $2P^2$ or $2S$. Measured with reference to a common zero, the displacement depends on the product of the field strength at the higher energy level of the emitting electron inside the atom, and a parameter characteristic of the atomic structure, whether the field is applied externally or is intrinsic. In the case of the helium atom the parameter is opposite in sign for the para and ortho cases. The parameter might describe the direction of rotation of the electron; this would then be opposite for para and ortho. The work is in agreement with a structure proposed earlier by Stark, and with the observations of Ishida and Kamijima on the splitting of helium lines. A. J. Mee.

Isobaric elements. H. Herszfinkel (Naturwiss., 1929, **17**, 50—51).—With reference to the work of Meitner (*ibid.*, 1926, **30**, 719) it is pointed out that it is uncertain whether any neighbouring atoms are isobaric with cæsium, so predictions cannot be made concerning its radioactivity. In the case of elements of medium at. wt. it is important whether the isobars are among the principal isotopes of their respective elements. Isobars of bromine and iodine certainly exist, and although these elements are practically non-radioactive it may be assumed that they possess a certain instability and may give rise to a β-ray change. Such changes would produce the inert gases krypton and xenon, which are much more readily detectable than, *e.g.*, calcium, which is the product of the disintegration of potassium. Assuming the radioactivity of these elements to be one hundredth of that of potassium, it is calculated that compact bromine and iodine minerals 10^6—10^7 years old should contain 10^{-5}—10^{-6} mg. of krypton or xenon per gram; this is quite a detectable amount. J. W. Smith.

Quantum theory of atomic disentegration. G. Gamow (Z. Physik, 1928, **50**, 510—515).—From the point of view of wave mechanics it is shown that atomic disintegration may be brought about by α-particles with an energy lower than the potential maximum of the atom struck. An upper limit is deduced for the amount of atomic disintegration produced in dependence on the energy of the α-rays and the nuclear charge of the scattered atom. The results obtained are in good agreement with practical data. J. W. Smith.

Fusibility and atomic number of the elements. P. Vinassa (Atti R. Accad. Lincei, 1928, [vi], **8**, 121—125).—The ratio of the absolute fusion temperature of helium to its at. wt. is 0·5. Referred to this coefficient as unity the analogous ratios for the great majority of the elements are integers. Attempts have been made to correlate this regularity with the electronic configuration of the elements.

F. G. Tryhorn.

Electromagnetic equations in the quantum theory. C. G. Darwin (Nature, 1929, **123**, 203).—Mathematical. A. A. Eldridge.

Nuclear motions associated with electron transitions in diatomic molecules. E. U. Condon (Physical Rev., 1928, [ii], **32**, 858—872).—Theoretical. A mechanism for the direct dissociation of molecules by light absorption has been proposed by Franck (cf. A., 1925, ii, 1077), and extended by Condon to the theory of intensity distribution in band systems (cf. A., 1927, 89). Franck's postulate has been derived from the new quantum mechanics, and is here described, and discussed with reference to wave mechanics. It appears that Heisenberg's indetermination principle gives the clue to the inexactitude of the earlier method of predicting electron transitions and intensities based on Franck's postulate, since its strict application calls for a violation of the principle. The quantum-mechanical formula is applied, for the halogens, to the continuous spectrum accompanying molecular dissociation, and additional applications to band systems are made. The existence of an entirely new type of band spectrum due to the wave nature of matter is predicted, and the interpretation of Rayleigh's mercury band at 2476—2482 Å. (cf. A., 1928, 806) as of this type is suggested. It is shown that although Franck's postulate is also true for electron jumps in atoms, it is of minor interest because its inexactitude is much greater for the electrons than for the heavy nuclei.

N. M. Bligh.

Molecular constants of hydrogen. H. H. Hyman and R. T. Birge (Nature, 1919, **123**, 277—278).—New observations show that the B—A system bands consist of R and P branches only. A complete verification of the combination principle has been obtained. For the zero vibrational level of the B state, it is computed that $B_0=19{\cdot}46\pm0{\cdot}04$, whence $I_0=1{\cdot}423(\pm0{\cdot}003)\times10^{-40}$ g.cm.², a value of the moment of inertia which is considered to be trustworthy.

A. A. Eldridge.

Intensity measurements in the secondary spectrum of hydrogen. II. W. Kapuscinski and (Miss) J. G. Eymers (Proc. Roy. Soc., 1929, A, **122**, 58—68).—An extension of previous work (Ornstein, Kapuscinski, and Eymers, A., 1928, 678). The intensities of 1427 lines in the secondary spectrum of hydrogen have been determined over the region 3652 to 6441 Å. The whole spectrum was taken at a pressure of hydrogen of about 0·17 mm., the times of exposure ranging from ½ min. to 5 hrs. It was found that, on taking several photographs on the same plate, only differing in time of exposure, the ratios of the intensities of the lines on each pair of photographs were dependent on the density. A correction was made for this phenomenon, which is probably due to "developer-effects," causing the density curves (obtained by means of continuous density marks) to have a too small inclination at high intensities and a too large inclination at lower intensities.

L. L. Bircumshaw.

Interpretation of the atmospheric absorption bands of oxygen. R. S. Mulliken (Physical Rev., 1928, [ii], **32**, 880—887).—Theoretical. The atmospheric oxygen absorption bands can be attributed to a $^3S\longrightarrow{}^1S$ transition from the normal ^3S to a metastable ^1S excited state of O_2. This accounts for all the strong lines and explains missing lines, without conflict with existing theory. Certain very weak series are, however, not yet explained. Of the three rotational levels for each value of j_k in the ^3S normal state, the two for which $j=j_k\pm1$ show only a very small separation, which increases slowly with j_k, whilst the third is separated from the other two by an interval of about two wave numbers which does not change with j_k. The ^3S and ^1S states involved in the atmospheric bands are probably both due to the same electron configuration (cf. A., 1928, 1067). If so, it is likely that a metastable ^1D state derived from the same configuration also exists, and that infra-red atmospheric bands corresponding with the transition $^3S\longrightarrow{}^1D$ should be found.

N. M. Bligh.

Infra-red emission spectra of Bunsen and allied flames. C. R. Bailey and K. H. Lih (Trans. Faraday Soc., 1929, **25**, 29—32).—Using a rock-salt prism spectrometer the emission spectra of the Bunsen and Méker flames have been examined in the infra-red (1—7 μ) and compared with those of the carbon monoxide, hydrogen, and methane flames. Particular attention was paid to constancy of atmospheric temperature and of source of radiation. The more important maxima in the flame spectra are tabulated. The ratio of the intensities of radiation from the two most prominent bands at 4·46 and 2·8 μ varies greatly from flame to flame. Measurements of the spectra from known mixtures of carbon monoxide and hydrogen show that this ratio passes through a maximum at about 10% of hydrogen and falls to zero for the hydrogen flame.

O. J. Walker.

Infra-red emission spectra of separated cones in methane and Bunsen flames. C. R. Bailey and K. H. Lih (Trans. Faraday Soc., 1929, **25**, 32—36).—By means of a modified Smithells separator provided with a rock-salt window the emission spectra of the inner and outer cones of the methane and Bunsen flames have been examined in the region 0·5—8 μ. The radiation from the outer cone is more intense in spite of its lower temperature. There is no trace of emission from new-formed molecules of carbon monoxide in the inner cone, but the water-vapour spectrum is much more prominent than in the outer cone. A band in the Bunsen and inner cone flames of methane at 3·35 μ is attributed to thermal emission from heated methane.

O. J. Walker.

Infra-red emission spectra of flames in nitrous oxide. C. R. Bailey and K. H. Lih (J.C.S., 1929, 51—56).—Examination of the infra-red emission spectra of flames of hydrogen, carbon monoxide, and coal gas in nitrous oxide supports the assumption that, as far as the end-products are concerned, the combustible gas burns in oxygen furnished by the decomposition of nitrous oxide. Hydrogen presents anomalous features in that, whilst carbon monoxide and coal gas give the same spectra whether they are mixed with nitrous oxide or burned directly in an atmosphere of it, the spectra obtained from hydrogen differ in the two cases. Further, the spectrum obtained by burning hydrogen directly in an atmosphere of nitrous oxide is different in type from those obtained with carbon monoxide and coal gas. The new spectrum is attributed to some form of stimulation by the burning hydrogen molecules. F. J. Wilkins.

Absorption of ultra-violet light by liquid carbon dioxide. G. Harig (Physikal. Z., 1929, **30**, 8—20).—A method has been devised for the quantitative determination of the absorption spectra of liquefied gases, using high pressures and temperatures and small thicknesses of liquid. Carbon dioxide, whether liquid or gaseous, is quite transparent to visible light; the gas under ordinary conditions shows no measurable absorption of wave-lengths greater than 2195 Å., in agreement with Kreusler (Ann. Physik, 1901, [iv], 6, 412). Liquid carbon dioxide, however, absorbs in the region 2195—2552 Å. about 10^3 times as strongly as the gas at the same pressure. The data are interpreted by assuming the existence of two kinds of carbon dioxide molecules, differing widely in absorptive power, the " gas " molecules showing negligible absorption, whilst the molecular species present in the liquid shows a broad absorption band with a maximum near 2265 Å., and a second weaker band with maximum at 2435 Å. Both types of molecules can exist in the supercritical state, the reversible transformation occurring at the points where the isotherms and isobars intersect. The absorptive power of the liquid remains about the same at constant temperature, although the pressure may vary, but near the critical temperature a very sudden, but not discontinuous, change occurs. R. A. Morton.

Band spectrum of lanthanum oxide. R. Mecke (Naturwiss., 1929, **17**, 86—87).—Seven band systems at 4372, 4418, 5600, 7380, 7403, 7877, and 7910 Å. have been observed and ascribed to lanthanum oxide. W. E. Downey.

Change in the cathode-ray spectrum of nitrogen by cooling with liquid air. J. Aars (Ann. Physik, 1929, [v], **1**, 216—228).—Investigation of bands belonging to the second positive system of N_2 and the negative band system of N_2^+ shows that, under the conditions obtaining in the work, the distribution of line intensities depends solely on the temperature and not on pressure or on the velocity of the cathode rays. R. A. Morton.

Absorption spectrum of vitamin-*D*. T. A. Webster and R. B. Bourdillon (Nature, 1929, **123**, 244).—The observation that irradiation of ergosterol produces three substances in succession is confirmed; the first shows intense absorption at 2500—2900 Å. and great antirachitic power, the second shows intense absorption at 2400 Å. and no antirachitic power, whilst the final product (or products) shows no absorption and has no antirachitic power. Intensity of absorption of irradiated ergosterol between 2700 and 2900 Å. is parallel with its antirachitic activity; moreover, further irradiation of such solutions with exclusion of radiation of wave-lengths less than 2600 Å. affords a product showing intense absorption at 2400 Å., but no antirachitic activity. A. A. Eldridge.

Structure and activation of the molecules of aliphatic aldehydes. I. Analysis of the spectrum of the vapour of formaldehyde. S. A. Schou (J. Chim. phys., 1928, **25**, 665—721).—The absorption spectrum of formaldehyde in the gaseous state has been measured by means of two quartz spectrographs of high dispersion. For a concentration of vapour of 60 mg. per litre the spectrum consists of 35 bands between 3700 and 2500 Å. The intensity of these bands varies periodically throughout the range of wave-length. The bands consist of large numbers of fine lines arising from rotation of the molecule. The structure of each band in the middle and in the part nearest the visible is very complicated, but towards the ultra-violet both the distribution and intensity of the lines show a distinct regularity. The band in this part is made up of two series of lines and this double structure is attributed to the molecule of formaldehyde having a rotation about two axes, the first a line joining the carbon and oxygen atoms and the second a line perpendicular to this. The theoretical formula for a molecule of this type having two different moments of inertia has been worked out from the quantum theory and good agreement is obtained between the wave-lengths of the lines calculated from it and the observed values. R. N. Kerr.

Infra-red arc spectra. H. Auerbach (Naturwiss., 1929, **17**, 84—85).—A group of bands believed to be due to lanthanum oxide has been observed between 7876 and 8638 Å. W. E. Downey.

Absorption spectra of certain organic liquids in the near infra-red. J. W. Sappenfield (Physical Rev., 1929, [ii], **33**, 37—47).—Absorption spectra were studied from 0·8 to 2·5 μ with an accuracy of 0·002 μ for nine alcohols, six esters, two ethers, two aldehydes, and five other organic liquids, and the bands tabulated and plotted. The sources of absorption and relative intensities of the band heads are discussed. An attempt is made to obtain a relation between different band heads of a particular compound. The anharmonic oscillator and a relation due to Gapon (cf. A., 1927, 1007) modified to $\nu_n=\nu_0/(n)^{\frac{1}{2}}$ were applied with moderate success. N. M. Bligh.

Combination frequencies of the infra-red bands of quartz. E. K. Plyler (Physical Rev., 1929, [ii], **33**, 48—51).—Two new bands at 2·72 and 3·18 μ have been found. By combining the frequencies, assumed to be fundamental, of bands at 9, 12·5, 20, and 26 μ, six bands in the region 3—9 μ in addition to the new bands are accounted for. This gives a total of eleven absorption bands, the remainder being at 2·96, 3·75, 4·10, 4·35, and 8·40 μ, for the ordinary ray of quartz, the frequencies agreeing, with only small differences, with the calculated values. N. M. Bligh.

Absorption spectra and fluorescence of fats. W. Sproesser.—See B., 1929, 101.

Energies of dissociation of cadmium and zinc molecules. J. G. Winans (Nature, 1929, **123**, 279).—The difference in energy between the limiting band at 2212 Å. and the atomic line at 2288 Å. gives the value 0·200 volt for the energy of dissociation of the normal Cd_2 molecule. The value for Zn_2 is 0·246 volt. A. A. Eldridge.

Diffraction of *X*-rays by aqueous solutions of sucrose, lævulose, and dextrose. P. Krishnamurti (Indian J. Physics, 1928, **3**, 209—223; cf. A., 1928, 1079).—Dilute solutions give an outer ring due to the water, and a corona surrounding the central spot, due to relatively intense scattering at small angles, and increasing in intensity with increasing solution concentration. The corona is attributed to molecules of the solute distributed at random in the solvent, thus giving direct experimental verification of the well-known analogy between the gaseous and dissolved states as deduced by van 't Hoff. At higher concentrations the corona develops into a halo on account of a diminution of the intensity of scattering at small angles, and interpreted as due to the molecules acquiring a roughly uniform spatial arrangement. As concentration increases the halo develops into a ring of increasing diameter, the pattern ultimately resembling that for the powder. The angular radius of the disc round the central spot is a measure of the average size of the dissolved molecule. The influence of the hydration of the molecules is considered.

N. M. Bligh.

Continuous spectrum of mercury. J. K. Robertson, K. A. MacKinnon, and W. H. Zinn (J. Opt. Soc. Amer., 1928, **17**, 417—427).—Two methods for producing the continuous spectrum are described. In the first a drop of mercury was caused to move to and fro in an evacuated cylindrical quartz tube which was heated by a small electric oven. The intensity of the glow increased as the temperature was raised, reaching a maximum at about 200° and finally disappearing at red heat. Three characteristic bands were observed, two broad and with maxima at about 4600 and 3340 Å., respectively, and one narrow band ending abruptly at 1942 Å. A method is also described for producing the continuous spectrum by means of an electrodeless discharge. The appearance of the spectrum at various temperatures is described. In general the same three bands as before were found and in some cases also one at about 2650 Å. The origin of the spectrum is discussed and it is concluded that it is molecular.

J. L. Buchan.

Band spectra of the alkaline-earth halides. I. Calcium fluoride, strontium fluoride. II. Barium fluoride, magnesium fluoride. R. C. Johnson (Proc. Roy. Soc., 1929, **A**, **122**, 161—188, 189—200).—I. An extension of Mecke's work (A., 1927, 495). The whole of the known band spectra of the fluorides of calcium and strontium have now been completely analysed and ordered in regard to their gross structure. A re-measurement of about 250 band-heads has been made from first-order plates taken on a 21-foot Rowland grating, and the sequences have been fitted to cubic formulæ by the method of least squares. A notable feature of these spectra is the existence of unusually prolonged sequences in which the lines are packed close together. The sequence $\Delta n=0$ is always dominant, and $\Delta n=\pm 1$ sometimes occur but are much weaker. This is explained by the fact that the vibration frequencies in the initial and final states of the molecule differ very little. The characteristic "tail" phenomenon exhibited by many of the sequences has been shown to accord with theoretical expectations. In each case the molecules give rise to at least three band systems, one in the ultra-violet, one in the green, and one in the orange. The first two groups are degraded to the red side and the third to the violet. They appear to arise from the electronic transitions $3^2S\longrightarrow 1^2S$, $2^2S\longrightarrow 1^2S$, and $2^2P\longrightarrow 1^2S$, respectively. All the systems exhibit minor doublet intervals due to the presence of Q branches, and the Q heads are always stronger than the associated P or R heads. Several exceptional features are observed, such as the occurrence of strong Q branches in ${}^2S\longrightarrow {}^2S$ transitions, and a definite discrepancy in (n'') as evaluated from ${}^2S\longrightarrow {}^2S$ and ${}^2P\longrightarrow {}^2S$ systems. Applying the methods of Birge and Sponer (A., 1926, 993), the energy of dissociation of the CaF molecule, evaluated from the vibrational structure of the various electronic levels, has been found to be approximately 3·36 volts (77460 g.-cal.), and that of SrF is of the same order. The value found gives a satisfactory explanation, in the case of CaF, of the sudden fall of intensity and termination of the B_1 sequence with the 20th member.

II. A quantum analysis has been made of the gross structure of the band spectra of barium and magnesium fluorides, and for BaF new measurements have been made from first-order plates taken on a 21-foot Rowland grating. In the case of magnesium fluoride, Datta's experimental data (cf. A., 1921, ii, 529) have been used. The familiar BaF bands in the green region are believed to represent two systems, arising respectively from the electronic transitions $2^2S\longrightarrow 1^3S$ and $3^3D\longrightarrow 1^3S$. A number of bands measured by George (A., 1913, ii, 646) and attributed by him to barium oxide have been analysed, and their final state has been identified with that determined for BaF, thus proving their fluoride origin. This system is attributed to the transition $2^2D\longrightarrow 1^2S$, since it is found in about the expected region and has the same structural characteristics as the $3^2D\longrightarrow 1^2S$ transition. The suggested ${}^2D\longrightarrow {}^2S$ transitions are discussed; they are believed to be new to band spectra. The system $2^2P\longrightarrow 1^2S$, which is so dominant in CaF and SrF, is unrecorded in BaF. It is possible that the 2^2P level lies below the 2^2D level in the BaF molecule. The recorded emission bands for MgF constitute a $2^2P\longrightarrow 1^2S$ system in which $\Delta 2^2P=18\cdot 6\nu$. The vibrational constants for these two states are given. Evidence of the vibrational isotope effect occurs in the D_1 sequence, and the theoretical value of the isotope coefficient, calculated on the basis of two isotopes of magnesium of masses 24 and 25, agrees satisfactorily with the experimental value.

L. L. Bircumshaw.

Band spectra associated with zinc, cadmium, and mercury. J. M. Walter and S. Barratt (Proc. Roy. Soc., 1929, **A**, **122**, 201—210; cf. A., 1928, 812).—With the view of determining the origin of the extensive band systems ascribed to zinc, cadmium, and mercury (cf. Mohler and Moore, A., 1927, 917), the vapours of these metals have been examined spectroscopically, using the apparatus previously described (*loc. cit.*). Criteria are given for true metal spectra, and the non-metallic origin of most of the spectra under investigation was proved by observing their total disappearance on the introduction of a trace of sodium or potassium vapour into the absorbing column. This indicated that the molecules responsible for the repressed bands contained electronegative elements, and the impurities were identified by increasing the quantity of each probable electronegative element in turn until every one of the band spectra had been obtained in an enhanced form. It was thus found that the majority of the supposed band spectra of zinc and cadmium (with the exception of two weak and diffuse bands, one at 2212 Å. for cadmium and one at 3050 Å. for zinc), and one band system previously attributed to mercury (3000—2750 Å.), were probably oxide and chloride spectra. There is, however, no doubt that mercury vapour contains diatomic molecules. The bromides of the three metals and the iodide of cadmium all yield absorption band systems analogous to the chloride bands. L. L. Bircumshaw.

Band systems of the fluorides of beryllium and magnesium. W. Jevons (Proc. Roy. Soc., 1929, A, **122**, 211—227).—Evidence is cited in support of the following interpretation of the band-heads of the BeF doublet system, those in parentheses being missing: R_2, R_1, Q_2, (Q_1), with a doublet separation of the order $R_2-R_1=3$ cm.$^{-1}$, rather than R_2, Q_2, (R_1), Q_1, with a separation $Q_2-Q_1=$about 35 cm.$^{-1}$, as suggested by Mulliken (cf. A., 1926, 8). With this interpretation there is now a steady increase of the origin separations $\Delta\nu_e$ with the number of electrons in the alkaline-earth fluoride molecules BeF to BaF. The spectra given by the flame surrounding the arc between carbon poles fed with several beryllium salts have been examined under varying conditions. With the fluoride, for a few minutes after charging the arc is surrounded by a yellow flame, showing the band systems of both BeO and BeF, the latter being specially well developed. Subsequently a bright blue flame appears, with the visible BeO system strongly developed and scarcely a trace of the BeF system, and the region between the CN λ 3590 sequence and the 0 sequence of the BeF system is now occupied by a new set of bands which, like the BeF bands, are also degraded towards the red. Other beryllium salts tested give similar results, although less satisfactorily. The new bands do not form a number of regular sequences such as characterise the known band systems of diatomic emitters, but they occur in separate groups not wholly unlike those sequences. The emitting molecule is considered to be either an oxide or a fluoride of beryllium, possibly BeO or BeF_2. No bands attributable to BeCl and no further bands of BeF have been detected. The data for the BeO band-system are extended by the recognition of four bands of the hitherto unrecorded sequence $n''-n'=-2$, of which the strongest band-head occurs between the λ 4216 and 4197 heads of the CN violet system. With magnesium fluoride in the carbon arc in air the outer flame develops, in addition to the MgF doublet system, a new more refrangible system of three sequences of bands degraded to the further ultra-violet from heads at 2741·6, 2689·3, and 2636·4 Å., respectively, the middle sequence being the strongest. The heads appear single under the dispersion used. *P*-head data and n', n'' values are tabulated for the new system, which is also due to MgF, and may have for its final state the initial state for the doublet system. If ${}^2P\longrightarrow{}^2S$ is assumed for the doublet system, the new system may be ${}^2P\longrightarrow{}^2P$. The spectrograms of the new system show no evidence of the vibrational Mg-isotope effect. L. L. Bircumshaw.

Structure of the violet bands of silicon nitride. F. A. Jenkins and H. de Laszlo (Proc. Roy. Soc., 1929, A, **122**, 103—121; cf. Mulliken, A., 1925, ii, 1020).—The spectrum of the luminescence produced when silicon tetrachloride vapour reacts with glowing active nitrogen has been investigated, using an instrument of high resolving power. The wave-numbers (in vacuum) of the lines of the ten strongest bands due to the molecule containing the most abundant isotope, $Si^{28}N$, are tabulated. The line structure of the bands is in accord with that to be expected for a ${}^2S\longrightarrow{}^2S$ system. One line is missing at the origin, and the members of each branch are resolved into narrow doublets at higher rotational quantum numbers. The components of these doublets are in general of equal intensity. Several interesting perturbations occur, as in the analogous CN bands, which usually take the form of an exceptionally wide or narrow doublet, and faint satellite lines are often visible in the immediate neighbourhood of the perturbed line. These irregularities are connected in every case with the initial electronic state. One of them is of a new type, and suggests an intimate connexion between the perturbations and the rotational doubling. The combination relations between *P* and *R* lines are applied to find the term differences, from which the rotational constants are evaluated. The moment of inertia of the vibrationless molecule is found to be 38·29 and 37·89$\times10^{-40}$ g.cm.^{2} in the initial and final states, respectively. Assuming this molecule to be $Si^{28}N$, the corresponding internuclear distances are 1·576 and 1·568$\times10^{-8}$ cm. Accurate values are obtained for the band origins, and an equation is derived from these, giving the vibrational energy in the initial and final states. The isotope effect is well marked for $Si^{28}N$, $Si^{29}N$, and $Si^{30}N$. From this effect in three bands of the strongest sequence, quantitative evidence is adduced in support of the quantum mechanics formulation for the vibrational energy, which is developed in powers of $(n+\frac{1}{2})$.

L. L. Bircumshaw.

Excitation of solid bodies by slow-speed electrons. S. Ziemecki (Bull. Acad. Polonaise, 1928, *A*, 367—375).—The cathodo-luminescence of calcium oxide, zirconium oxide, calcium sulphide, willemite, and a samarium preparation has been examined using slow-speed electrons. The excitation potentials are found to be of the same order as the excitation potential of gases. W. E. Downey.

Absorption of ultra-violet light by the inversion products of sucrose. L. Kwieciński and L. Marchlewski (Biochem. Z., 1929, **204**, 192—196).—See this vol., 9.

Energy increase in elementary processes. H. Beutler and B. Josephy (Z. physikal. Chem., 1928, **139**, 482—496).—A study of energy exchange between activated atoms and molecules. The fluorescence of irradiated mercury vapour to which nitrogen has been added shows spectrum lines derived from atoms containing double the energy of metastable mercury atoms; this corresponds with $A^*+A^*=A^{**}+A$.

The chemiluminescence produced in the reactions $Na+HgCl_2$, $Na+Cl_2$, and $K+Cl_2$ has been studied. Mercury vapour was added and the spectrum obtained showed the presence of mercury atoms of greatly increased energy, the amount being characteristic of each reaction. It is shown that the energy change may be represented by $A^*+A^*+B=B^{**}+2A$. Evidence of the transfer of energy from several molecules to a single atom has also been obtained.

R. N. Kerr.

Alkali halide phosphors containing copper. A. M. MacMahon (Z. Physik, 1928, 52, 336—341).—Sodium chloride and potassium chloride phosphors containing copper as the active cation are rather unstable when the lattice is strongly mechanically disturbed by high copper concentration. The excitation bands show a strong depression after some time. The influence of cooling on the absorption bands of phosphors containing copper is generally similar to that in the case of phosphors containing thallium and lead (cf. Lorenz, A., 1928, 347). It was found, however, that the relatively broad bands emitted by phosphors containing copper were split up on cooling into two or three components. The narrowing of the band widths by cooling is not always associated with a rise in the absorption constant at the maximum. In sodium chloride phosphors the bands were both narrower and less intense on cooling.

J. W. Smith.

Structure of colouring matter. N. Nyberg (Z. Physik, 1928, 52, 406—419).—A new theory is given of the structure of pigments, based on Helmholtz' theory of light sensitivity. Ostwald's theory of colour is criticised mathematically.

J. W. Smith.

Electronic states and band spectrum structure in diatomic molecules. VII. $^2P\longrightarrow{}^2S$ and $^2S\longrightarrow{}^2P$ transitions. A correction. R. S. Mulliken (Physical Rev., 1928, [ii], 32, 997; cf. A., 1928, 1166). N. M. Bligh.

Visible absorption bands of colourless liquids and their relation to infra-red bands. J. W. Ellis (Physical Rev., 1928, [ii], 32, 906—912).—The absorption of ten representative organic liquids, hexane, *cyclo*hexane, benzene, toluene, *m*-xylene, chlorobenzene, chloroform, acetone, ethyl acetate, and aniline, was studied in the visible spectrum by photographic means, with cell-lengths up to 6½ metres. The effect of unsaturation and substitution in the molecule was examined. The near infra-red spectra of these substances was obtained. A good correlation of the bands of the two regions has been secured. The bands of the visible region seem to be higher members of series previously detected in the infra-red. N. M. Bligh.

Infra-red absorption spectra of the methyl halides. W. H. Bennett and C. F. Meyer (Physical Rev., 1928, [ii], 32, 888—905).—The molecules are considered as symmetrical tops having one low moment of inertia. Two types of bands are expected, arising from vibration parallel to and perpendicular to the axis of symmetry, || and ⊥ bands, respectively. The appearance of each type is described. There are seven bands for each of the four compounds. The twenty-eight bands fall into seven series, *A* to *G* inclusive. Two of the four bands of series *A* lie beyond the range of observation. Series *A*, *C*, *E*, and *F* are made up of bands of the || type, and series *B*, *D*, and *G* of the ⊥ type. The series converge towards the known bands of methane with decrease in the atomic weight of the halogen in the halide. The envelopes of the || type bands show the existence of *P*, *Q*, and *R* branches. With the possible exception of the chloride, the doublet separations for the various bands of the same compound appear to be the same, increasing from compound to compound with decreasing atomic weight of the halogen in the halide. The methyl fluoride *A* series band has been resolved and the *P* and *R* branches have been shown to consist of a single series of lines. Strong convergence in the spacing is present. The bands of the ⊥ type have all been resolved. Every third line is more intense than the others. The spacing converges in series *B* towards lower frequencies, and in series *D* and *G* towards higher frequencies. The mean frequency intervals from band to band of the same compound show a marked and unexplained variation. N. M. Bligh.

Red band system of sodium. F. W. Loomis and S. W. Nile, jun. (Physical Rev., 1928, [ii], 32, 873—879).—The red band system of Na_2 is found to extend into the infra-red, and terminates in a fairly sharp edge at 8150 Å. This edge, which is not an ordinary convergence limit, can be explained by an unusual distribution of intensities of vibrational transitions which can be deduced from the Franck–Condon theory of intensity distribution, when account is taken of the shape of the potential energy curves as dissociation is approached. The same theory explains a head of the red system in the yellow-green, the reappearance of the orange cathode-ray fluorescence series in the infra-red, and the observed asymmetry in the two branches of the Condon parabola.

N. M. Bligh.

Photosensitised band fluorescence of OH, HgH, NH, H_2O, and NH_3 molecules. E. Gaviola and R. W. Wood (Phil. Mag., 1928, [vii], 6, 1191—1210).—A more detailed study of the photosensitised band fluorescence previously examined by Wood and Gaviola (A., 1927, 1117, etc.) has been made. The fluorescence of HgH, OH, NH, Hg–H_2O, and Hg–NH_3 molecules has been observed and the conditions for the exhibition of the various bands and the most probable chemical processes causing them have been suggested. The concentration of OH and NH in the fluorescence tube is, under the best conditions, of the same order as that of excited mercury atoms (10^{-5} mm.). The dissociation energy of a water molecule into H^+ and OH^- is probably about 5·2 volts and not less than 4·9 volts as given by Senftleben and Rehren (cf. A., 1926, 768), whilst the corresponding dissociation energy of the nitrogen molecule is approximately 9·8 volts and not 11·4 volts as calculated by Sponer and Birge. Collisions of excited mercury atoms in the resonance level 2^3P_1 with normal water vapour molecules may lead to three different results. In most cases the mercury atom is reduced to the metastable 2^3P_0 level, in about 1 per 10,000 collisions the water molecule is dissociated to H^+ and OH^-, and in less than 1 per 1000 collisions a quasi-molecule $Hg-H_2O$ is formed which emits the continuous band at 2800 Å. when dissociating. Such collisions with nitrogen molecules reduce the mercury atoms to the metastable state, whilst collisions of two such mercury atoms with nitrogen molecules may give dissociation of the nitrogen molecule. A. E. Mitchell.

Deterioration of quartz mercury-vapour lamps and the luminescence of fused quartz. A. E. Gillam and R. A. Morton (Phil. Mag., 1928, [vii], 6, 1123—1132).—The factors operating in the deterioration of quartz mercury-vapour lamps are found to be a shortening of the spectrum confined to the extreme ultra-violet and a non-selective loss in transmission. The first factor exhibits itself in a rapid fall in output and preponderates for the first 150—200 hrs. of use. It is suggested that it is due to the formation of silicon monoxide vapour within the lamp. The second factor manifests itself more slowly, but plays an increasingly important part in the subsequent history. Its origin is suggested in the gradual deposition of a film of opaque elementary silicon. No exact connexion between this deterioration and the luminescence properties of fused quartz has been found. Transparent fused quartz has been shown to exhibit three types of luminescence: a brief visible phosphorescence, a phosphorescence of long duration, and a thermoluminescence, the origin of which is attributed to traces of impurities in the material.

A. E. Mitchell.

Relation between luminosity and concentration in luminescent solid solutions. J. Ewles (Proc. Leeds Phil. Soc., 1929, **1**, 341—345).—The relation between the intensity of luminescence of a solid solution of bismuth oxide in calcium oxide, illuminated by a mercury-vapour lamp, and the concentration of the solution has been studied. On the assumption that a luminescent solid solution consists of a number of active particles distributed in accordance with the laws of chance in a transparent lattice, and that the luminescent centre consists of one atom of an active metal associated with a definite number (n) of lattice points (this number being characteristic of a given band), the expression $I=Ace^{-n_1c}+Bce^{-n_2c}+$ etc. is deduced, where I=intensity of luminescence, $c=N/M=$ the atomic concentration, and A and B are constants (cf. Bruninghaus, Compt. rend., 1909, **149**, 1375). In the example studied the observed points lie closely on the theoretical curve so plotted ($A=2{\cdot}34\times10^4$, $B=1{\cdot}58\times10^3$, $n_1=5012$, $n_2=331$) which shows two maxima (at c Bi/Ca $0{\cdot}0_3 2233$ and $0{\cdot}0_2 4000$). The range of action of the first centre extends across about 11 unit cells and of the second across 4—5 unit cells each way. J. W. Baker.

Phosphorescence of fused quartz. A. C. Bailey and J. W. Woodrow (Phil. Mag., 1928, [vii], 6, 1104—1107).—Many samples of fused quartz are shown to possess the property of phosphorescence, emitting phosphorescent radiation when heated after illumination by ultra-violet light. Heating at a red heat completely deactivates the material. Quartz crystals may be made to exhibit the phenomenon after being heated slowly to 1600°. Similar phosphorescent activity is exhibited by pyrex glass, calcite, and fluorite, but not by gypsum.

A. E. Mitchell.

Phosphorometer for the rapid measurements of the intensities of phosphorescences. R. Coustal (Compt. rend., 1929, **188**, 326—327).—The intensity or decrease of phosphorescence of the substance to be examined is matched by means of mixtures, in known proportions, of varying amounts of two zinc sulphides from the same batch, of which one only has been rendered phosphorescent. The surface densities of such mixtures are proportional to the concentrations of the active sulphide. The intensities of phosphorescence show the same rates of decrease with time and the Güntz formula was confirmed. J. Grant.

Raman effect in quartz. M. Czerny (Naturwiss., 1929, **17**, 12—13).—The transmissibility of quartz in the long-wave infra-red has been determined by means of a grating spectrometer, and absorption was found at 38 and 78 μ as is required by the Raman effect. There is no anomaly in the transmissibility curve at 48 μ which others appear to have observed. There is considerable deviation between the relative intensities of the infra-red absorption bands and the corresponding Raman lines. According to Pringsheim and Rosen the Raman lines corresponding with 80 and 48 μ should be equally strong, and the 38 μ line weaker, but it is found that in the infra-red spectrum the 38 μ band is apparently stronger than the 80 μ band, whilst the 48 μ band is so weak that it is not measurable. A. J. Mee.

Secondary radiations in the molecular diffusion of light (Raman effect). P. Daure (Compt. rend., 1929, **188**, 61—62).—Solutions of antimony chloride in hydrochloric acid show Raman spectra, in which the lines spread out with increasing dilution so that beyond the dilution of 50% the *b* band is completely covered by the *a* band, and the spectrum is comparable with that of dissolved bismuth trichloride. Aqueous solutions of magnesium or aluminium chloride, of calcium bromide, or of liquid oxygen showed no Raman effect, whilst liquid ammonia and methane gave wide bands and a single fine line, respectively. J. Grant.

Production of new radiations by light scattering. I. C. V. Raman and K. S. Krishnan (Proc. Roy. Soc., 1929, **A**, **122**, 23—35).—Further studies have been made on the radiations previously described (A., 1928, 1075). Spectrograms are reproduced of the scattering of monochromatic light by benzene, toluene, and carbon tetrachloride. The characteristic infra-red frequencies of the molecules, calculated from the frequencies of the modified lines, are in satisfactory agreement with the values obtained from direct measurements of infra-red absorption. Whilst most of the modified lines have frequencies lower than the exciting line, there appear in all three spectrograms (and particularly conspicuously in that of carbon tetrachloride) some relatively feeble lines of which the frequencies exceed that of the exciting line by an infra-red frequency of the molecule. It is considered that the existence of these lines of enhanced frequency yields the first direct experimental proof of induced emission (or negative absorption) of radiation by molecules. A visual examination with a direct-vision spectroscope of benzene, toluene, and some other liquids showed a nebulosity or continuous spectrum accompanying the prominent lines in the scattered spectrum, extending unsymmetrically on the two sides of the exciting line. Its origin is discussed; it is possibly due to a combination of the rotational frequencies of the molecule with the frequency of the incident radiation. The modified radiations scattered at 90° exhibit striking polarisation, the lines corresponding with different frequency shifts being polarised to different extents. The intensity of the weaker component varies from almost zero to about 40 or 50% of that of the stronger line. The negative lines (of enhanced frequency) are polarised to the same extent as the corresponding positive lines. A tentative explanation of these results is suggested. The usefulness of light-scattering as a convenient and accurate method of exploring molecular spectra is indicated, and some preliminary remarks are made with regard to the dependence of the intensity of the modified radiation on the wave-length of the exciting lines. L. L. Bircumshaw.

Raman spectra for certain substances. M. Kimura and Y. Uchida (Japan. J. Physics, 1928, 5, 97—101).—The Raman spectra have been examined for commercial xylene, calcite, water, and salts of neodymium. Tables are given showing the wave-lengths of the Raman lines and the calculated infra-red absorption bands derived from them. J. L. Buchan.

Raman lines under high dispersion. R. W. Wood (Phil. Mag., 1928, [vii], 6, 1282—1283).—Previous work (A., 1928, 1306) has been extended by photographing the spectra scattered by benzene and carbon tetrachloride under very high dispersion. The line at 4618 Å., excited by the mercury line 4046 Å., is shown to be a strong line about 1 Å. wide with a faint line 2·5 Å. wide close to it on the violet side. The wave-lengths of the strongest Raman lines of benzene are 4686·74, 4682·11, 4659·30, 4618·36, 4554·87, 4525·0, and 4476·0 Å. It is concluded that the high resolving powers employed are not necessary owing to the considerable width of most of the lines. The range of frequencies covered by the benzene line 4554·87 Å., when translated into the range of the corresponding infra-red absorption band, gives one very much narrower than that observed by Coblentz close to 10 μ. A. E. Mitchell.

Raman effect with hydrogen chloride; the "missing line." R. W. Wood (Nature, 1929, 123, 279).—With hydrogen chloride at 100° and at atmospheric pressure a modified line of wave-length 4581 Å., presumably excited by the mercury line 4046 Å., was observed. The frequency difference corresponds with the frequency in the infra-red which would represent a line at 3·47 μ. The line thus appears to be the "missing line" corresponding with a vibration transition unaccompanied by change of rotation, which does not appear in the absorption spectrum of the gas. A. A. Eldridge.

Breadth of the spectral lines of the Raman scattered radiation of benzene. W. Gerlach (Ann. Physik, 1929, [v], 1, 301—308).—The Raman effect results in new diffuse lines and also in a definite broadening of some lines which are scattered without large change of frequency. This broadening occurs on both the long-wave and short-wave sides of the lines. The breadth and structure of scattered lines of both types have been determined for benzene. Different scattering processes are possible, an incident frequency ν_0 giving a Raman line $\Delta\nu'$ and differences $\pm\Delta\nu_1''$, $\Delta\nu_2''$ . . . accounting for the breadths of the modified and "unmodified" lines. The results permit the breadth of an infra-red band to be determined; *e.g.*, a benzene band near 3 μ would be 0·2 μ wide, in accordance with experience. Infra-red bands of benzene would appear not to be made up of unresolved neighbouring similar bands, but rather to be governed by a central frequency increased or decreased by a number of secondary frequencies. R. A. Morton.

Raman effect with alcohols. S. Venkateswaran and A. Karl (Z. physikal. Chem., 1928, B, 1, 466—474).—The radiation which is scattered when a beam of monochromatic light is passed through methyl, ethyl, amyl, or allyl alcohol or water has been examined. The secondary spectra have the usual characteristics of the Raman effect (A., 1928, 685), that of allyl alcohol consisting of lines only, and that of water of a band. Amyl alcohol gives a continuous spectrum, as well as lines, the presence of the former probably being connected with the relatively high viscosity of the liquid. From the difference in frequency between the primary lines and the lines to which they give rise the infra-red frequencies of the molecules have been calculated. In the scattered light the unmodified lines, the new lines, and the continuous spectrum are all polarised, but in different degrees. R. Cuthill.

Apparently anomalous Raman effect in water. J. W. Ellis (Nature, 1929, 123, 205—206).—The view that the band at 3·0 μ in the infra-red spectrum of water is composed of an overtone of the band at 6·1 μ and a fundamental of wave-length 2·9 μ does not require that the modified frequency afforded by Raman scattering by water molecules, corresponding with an infra-red band at 2·90 μ, should be regarded as anomalous. The width of the water band at 1·46 μ is 800 cm.$^{-1}$, a value which is somewhat greater even than that of the band at 2·9 μ of the Raman spectrum. A. A. Eldridge.

Raman effect in gases. F. Rasetti (Nature, 1929, 123, 205).—Carbon monoxide shows two Raman lines at 4432 and 4810 Å., respectively, evidently corresponding with the same quantum transition, excited by both 4046 and 4358 Å. of mercury; the differences in frequency between the Raman lines and the exciting lines correspond with an infra-red absorption band at 4·64 μ. In the Raman spectrum of carbon dioxide no lines corresponding with the infra-red absorption bands at 2·7, 4·25, and 14·7 μ were observed; two doublets, at 4639, 4616, and 4289, 4268 Å., excited respectively by 4358 and 4046 Å., were, however, observed. The corresponding transitions, 1284 and 1392 cm.$^{-1}$, coincide, within the limits of experimental error, with the differences in frequency between the two components of the double band at 2·7 μ and the band at 4·25 μ.

A. A. Eldridge.

Ionisation processes in methane interpreted by the mass spectrograph. T. R. Hogness and H. M. Kvalnes (Physical Rev., 1928, [ii], 32, 942—945).—The apparatus for ionisation by controlled electron impact and method of analysis were those of Hogness and Lunn (A., 1925, ii, 839). CH_4^+ and CH_3^+ are the only ions formed, and from their relative intensities under different conditions of pressure and voltage, were both found to be formed directly by electron impact. The ionisation processes are: $CH_4=CH_4^++e^-$ (14·5 volts); $CH_4=CH_3^++H+e^-$ (15·5 volts). Neon was used as a calibrating gas, and the existence of a third neon isotope of mass 21, in adddition to isotopes of mass 20 and 22, was definitely determined.

N. M. Bligh.

Ionisation of carbon monoxide by controlled electron impact, interpreted by the mass spectrograph. T. R. Hogness and R. W. Harkness (Physical Rev., 1928, [ii], 32, 936—941).—Ionisation processes may be accompanied by a dissociation of a gas molecule, either simultaneous with the ionisation by electron impact or resulting from the secondary collision of the ionised molecule with a neutral one as illustrated by the ionisation of nitrogen. The ionisation of CO molecules by electrons of definite energy was studied with the mass spectrograph (cf., this vol., 114). The variation of the relative intensities of the ions CO^+, C^+, and O^+ with changes of pressure and changes of the electric fields leads to the conclusion that the principal processes occurring are: (1) $CO=CO^++e^-$; (2) $CO=O^++C+e^-$ (3) $CO=C^++O+e^-$; (4) $CO+CO^+=CO_2+C^+$. No negative nor doubly-charged positive ions were found. Contrary to expectation, the ionisation processes were found not to resemble those of nitrogen.

N. M. Bligh.

Dependence of dielectric constant of liquid helium on temperature. M. Wolfke and W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 800—806).—A discontinuity in the values in the dielectric constant of liquid helium is found at 2·295° Abs. The helium molecule probably does not undergo any change in internal structure at this point. The results are in agreement with optical data.

C. W. Gibby.

Dielectric constant of supercooled sulphur and of some solutions of sulphur. S. Rosental (Bull. Acad. Polonaise, 1928, *A*, 1, 377—395).—The dielectric constant of sulphur, molten and supercooled between 150° and 95°, is found to obey the Clausius–Mossotti law. At the moment of solidification the dielectric constant suddenly increases. Solutions of sulphur in benzene and in carbon disulphide also obey the Clausius–Mossotti law.

W. E. Downey.

Dielectric constants of methylene chloride and bromide. P. C. Mahanti and D. N. Sen-Gupta (J. Indian Chem. Soc., 1928, 5, 673—681).—The dipole moments of methylene chloride and bromide, 1·621 and $1·914\times10^{-18}$ c.g.s.u., respectively, have been determined in the vapour state by the authors' heterodyne method (cf. this vol., 243). The higher value for the bromide is explained by assuming that the bromine atoms are more inclined to each other than the corresponding chlorine atoms: the resultant moment in the direction opposite to that developed in the CH_2^{++} ion is, therefore, smaller for the bromide. The bromide has a larger polarisation than the chloride owing to less distortion in the atomic orbits.

H. Burton.

Anomalous dispersion, absorption, and Kerr effect in viscous dielectrics. D. W. Kitchin and H. Müller (Physical Rev., 1928, [ii], 32, 979—987).—The temperature variation of the dielectric constant and power factor of castor oil and rosin, measured at different frequencies from 10^7 to 60 cycles, shows that, in accordance with Debye's theory of polar molecules, the region of anomalous dispersion shifts with decreasing temperatures into the long-wave radio region and even down to audio frequencies, whilst its existence in these regions explains the complicated dielectric behaviour of many insulating materials and makes it possible to observe an anomalous behaviour of the Kerr effect. As expected, the regions of anomalous Kerr effect and anomalous dispersion were found to coincide. The influence of viscosity in solutions of rosin in different oils which have no polar molecules was found to agree with Debye's theory.

N. M. Bligh.

Kerr constant for nitrobenzene. R. Möller (Physikal. Z., 1929, 30, 20—24).—The lack of agreement between the published values for the Kerr constant for nitrobenzene has been traced to instrumental defects and impurities. Nitrobenzene readily absorbs enough moisture from the air to increase greatly its conductivity. A special arrangement for filling the Kerr cell with dry liquid is described. Two different methods lead to the value $B=3·46\times10^{-5}$ at 20° for the line 546 μμ.

R. A. Morton.

Molecular refraction and non-polar linking. R. Samuel (Naturwiss., 1929, 17, 13—14).—In non-polar bound molecules there is a negative and a positive group or atom. It is, therefore, possible to give a group or an atom a different refraction constant according as it is positive or negative, instead of a single mean value as is usual. If this is done, many of the abnormalities in molecular refraction data vanish, exaltation and depression disappear, and the molecular refraction of the primary, secondary, and tertiary amines can be calculated by using one value for the atomic refraction of nitrogen instead of three. If this hypothesis is accepted it is possible, conversely, to arrive at the structure of non-polar molecules from observations of their molecular refraction.

A. J. Mee.

Formula for the optical rotatory dispersion of quartz. I. Bradshaw and G. H. Livens (Proc. Roy. Soc., 1929, A, 122, 245—250; cf. Lowry and Coode-Adams, A., 1927, 813).—Lowry's revised formula for the rotatory dispersion of quartz (*loc. cit.*) does not represent the experimental results obtained by Duclaux and Jeantet (A., 1926, 886), and accordingly a formula of a different type is suggested. In the case of a medium with three absorption bands at λ_1, λ_2, and λ_3, it takes the form $\alpha=\sum_{r=1}^{3}\{A_r/(\lambda^2-\lambda_r^2)+$

$B_r/(\lambda^2-\lambda_r^2)^2\}$. It is found by trial that with $\lambda_1^2=0{\cdot}01274912$, $\lambda_2^2=0{\cdot}01208$, $\lambda_3^2=80$, the values of the six constants A_r, B_r can be so chosen that the discrepancies between the calculated and observed values of α for quartz (including those of Duclaux and Jeantet) are practically within the limits of experimental error. This formula provides an explanation of the practically constant effect of the infra-red band. On comparison with that proposed by Lowry, it appears that the new formula is in general the more satisfactory. L. L. Bircumshaw.

Structure of cæsium and ammonium sulphates. W. Taylor and T. Bryer (Mem. Manchester Phil. Soc., 1927—1928, 72, 125—137).—These salts crystallise in the didigonal equatorial class of the orthorhombic system, being pseudo-hexagonal, the *c* axis the pseudo-hexagonal axis. A complete survey was made, in the case of ammonium sulphate, of the relative intensities of *X*-rays reflected from planes of the type (*hko*), (*hol*), (*okl*), and the space-group V_h^{16} assigned. This was confirmed in the case of cæsium sulphate, there being 4 mols. to the unit cell. The dimensions of the unit cell previously given by Ogg and Hopwood have been redetermined. The structure of the crystals is very similar, the positions of the constituent atoms having been allotted taking into consideration the determined and calculated values of the sum of the scattered amplitudes. G. E. Wentworth.

Heats of linking of C–H and N–H linkings from vibration spectra. J. W. Ellis (Physical Rev., 1929, [ii], 33, 27—36).—Theoretical. The frequency formula for an anharmonic vibrator is applied to visible and near infra-red absorption data for several molecules, previously obtained (this vol., 239), and the mechanical frequencies associated with each stationary state are evaluated and plotted. Assuming that these frequencies originate in oscillations between a hydrogen atom and the remainder of the molecule, the restoring force residing in the C–H and N–H linkings, the heats of linking, *i.e.* the heats of dissociation of these linkings are calculated, using the methods of the old quantum theory for non-polar, diatomic gaseous molecules. The values obtained for the C–H linking are, hexane, 97,000 (cf. 92,500, obtained thermochemically for methane); *cyclo*hexane, 94,000; benzene, 117,000; chloroform, 108,000; aniline, 117,000; aniline N–H linking, 113,000 g.-cal./mol. The last is believed to agree with 101,000 obtained thermochemically for an ammonia N–H linking. A possible explanation of the doubleness of the absorption bands of several substances, notably hexane and *cyclo*hexane, is sought in two types of carbon valency, the doubleness indicating a slight inequivalence in the energy content of two types of C–H linking (cf. Lonsdale, A., 1928, 1079). N. M. Bligh.

Chemical valency and spectral multiplicity. A. T. Williams (J. Chim. phys., 1928, 25, 722—726).—The valency V can be connected with the multiplicity r of the spectrum of an element by the relation $V=r\pm1$, the sign of which depends on connexions between x, the number of electrons in the outermost sub-group, N, the total number of electrons which can be present in that sub-group according to the rule of Stoner, and k, the azimuthal quantum number of that sub-group. The relationship holds for all elements except the rare earths, iron, cobalt, and iridium. Preliminary results are given of the application to elements of variable valency. R. N. Kerr.

Electric moments of methyl chloride, ethyl chloride, and chloroform. S. C. Sircar (Indian J. Physics, 1928, 3, 197—208).—The permanent moments of methyl chloride, ethyl chloride, and chloroform measured by the heterodyne null method were $1{\cdot}69\times10^{-18}$, $1{\cdot}98\times10^{-18}$, and $1{\cdot}05\times10^{-18}$, respectively, in complete agreement with Debye's dipole theory. Slight divergences from the values deduced from optical data and from the results of other investigators are attributed to the many sources of experimental error. N. M. Bligh.

Electric moment and its relation to chemical constitution. P. C. Mahanti and D. N. S. Gupta (Indian J. Physics, 1928, 3, 181—196).—The heterodyne beat method was used to determine the permanent dipole moments and polarisability of methyl iodide, ethyl bromide, and ethyl iodide. The values found for the moments were $1{\cdot}31\times10^{-18}$, $1{\cdot}78\times10^{-18}$, and $1{\cdot}62\times10^{-18}$, and for the polarisability 0·005761, 0·0022, and 0·007839, respectively. Such organic halides have gradually weakening dipole moment with increasing atomic weight of the halogens. It is suggested that the permanent dipole moment in compounds of this type is due to the deformation of the electron orbits of carbon and halogen which give rise to the permanent moment of the molecule, and that the polarisability of the molecule itself due to applied field increases with the increasing atomic weight of the halogen due to weakening of the linking of the shared electron. N. M. Bligh.

Dipole moments of some aliphatic ketones. K. L. Wolf and E. Lederle (Physikal. Z., 1928, 29, 948—950).—Determinations carried out on ten saturated aliphatic ketones show that the dipole moment is $\mu=2{\cdot}75\pm0{\cdot}05\times10^{-18}$, this value being independent of the length and structure of the side-chain. The carbonyl group thus shows a much greater dipole moment than gaseous carbon monoxide ($\mu=0{\cdot}108\times10^{-18}$). The difference is ascribed to different electronic structures. R. A. Morton.

Dipole moments of some mono- and di-substituted benzene derivatives. P. Walden and O. Werner (Z. physikal. Chem., 1929, B, 2, 10—26).—The dipole moments of fluoro- and iodo-benzene, *o*-, *m*-, and *p*-dibromobenzene, *o*-, *m*-, and *p*-bromoiodobenzene, *o*-, *m*-, and *p*-chlorotoluene, and *o*-, *m*-, and *p*-chloronitrobenzene were obtained from their dielectric constants in pure benzene solution, and their molecular refractions. There is a variation in the moment for isomeric compounds, the moment in some cases increasing, and in others decreasing in value from the *ortho*- to the *para*-compound, according to the nature of the substituent. It is to be expected that for compounds which have two electrically equivalent substituents, *e.g.*, dibromobenzene, the *p*-isomeride, possessing the greatest symmetry, will have the smallest moment, and the value actually obtained for *p*-dibromobenzene is zero. If both substituents are not electrically equivalent but are similar, there will be a decrease in the moment from the *o*- to the *p*-isomeride. This is found to be the case with bromoiodobenzene and chloronitrobenzene. Since bromine and iodine are very similar, the moment of *p*-bromoiodobenzene would be expected to be small; this is so. The introduction of the nitro-group seems to cause an extraordinary increase in the moment. The moments of *o*-, *m*-, and *p*-chloronitrobenzene are much greater than those of the corresponding chlorotoluenes. If the substituents have opposite electrical natures, the moment decreases from the *p*- to the *o*-compound. In chlorotoluene the methyl group is positive and the chlorine negative; it would be expected that in the *p*-compound where the two groups are diametrically opposite the greatest moment would be found. This was found to be so. The actual numerical values obtained for the moments are in good agreement with those arrived at from Thomson's theory. The values derived by Syrkin on the basis of the critical data are also compared with those obtained by experiment. A. J. Mee.

Dipole moments, association, and ultra-violet absorption of aliphatic ketones and their solutions. I. Influence of solvent and mechanism of reaction from the point of view of the dipole theory. K. L. Wolf (Z. physikal. Chem., 1929, **B**, **2**, 39—76).—The effect of various "indifferent" solvents on the structure and ease of reaction of dissolved molecules, and the effect of steric hindrance can be investigated by determinations of the ultra-violet absorption and the molecular polarisation of solutions. A characteristic homologous series of ketones was used and the relationship between these properties and concentration and temperature was determined, using solvents varying from neutral (dipole-less), such as hexane and benzene, up to strongly dipolar liquids. The relationship between molecular refraction, absorption, molecular polarisation, and the forces depending on solution is discussed, and various examples of non-ionic reactions which can be explained by the effect of the solvent are given. The value of the dipole moment of a saturated aliphatic ketone is independent of the length of the hydrocarbon chain, and is equal to $2{\cdot}74\times10^{-18}$. The ultra-violet absorption of the series of ketones was investigated, and the bands were found to be displaced owing to the influence of the solvent, the amount of displacement being dependent on the polar group. There is a parallelism between the displacement of the bands and the amount and type of association in the ketone itself. Both these phenomena, as well as the ease of formation of sulphite compounds and oximes, appear to be entirely or mainly determined by the size of the dipole moment and the amount of hindrance of the polar group by indifferent (electrosymmetric) CH_2 groups. The position of the carbonyl group in the hydrocarbon chain is discussed. A. J. Mee.

Electrical dipole moments of organic molecules. II. I. Estermann (Z. physikal. Chem., 1928, **B**, **1**, 422—426; cf. A., 1928, 1309).—The dipole moments of methyl phthalate and terephthalate are practically the same, but are greater than that of the benzoate. Lengthening the side-chain by a CH_2 group has no appreciable effect. Compared with benzophenone, *as*-diphenylethylene has only a very small moment, so that it appears that a double linking is not in itself sufficient to give rise to a high dipole moment. R. Cuthill.

Relation between polarisation and association. J. W. Williams (Proc. Nat. Acad. Sci., 1928, **14**, 932—936).—A short review of the theories of associated liquids and a criticism of the conclusion by Rolinski (cf. A., 1928, 1181) that the greater the dipole moment the larger is the degree of association of the substance in question. Certain substances, including phenol and benzoic acid, which on chemical evidence are associated, would show a zero degree of association according to Rolinski's treatment. Other factors in addition to the presence of a dipole moment influence the degree of association. N. M. Bligh.

Application to the allotropic varieties of phosphorus of Smits' theory. P. Jolibois (Compt. rend., 1929, **188**, 174—176).—Polemical against Smits' theory (this vol., 127; cf. A., 1916, ii, 317). The author considers that there are four varieties of solid phosphorus, white, red, black, and pyromorphic, all of which may coexist at the ordinary temperature and pressure, although only the pyromorphic and, possibly, the black varieties are stable. Smits' results may be explained by the slow transformation of one variety into another. J. Grant.

Intensity measurements on *X*-rays scattered by crystalline powders. J. Brentano (Physikal. Z., 1928, **29**, 893).—A preliminary account of work designed to yield quantitative data on the scattering of *X*-rays by very finely-divided crystalline powders. The importance of such data is indicated.

R. A. Morton.

Constitution of hydroxides and hydrates. III. Strontium hydroxide octahydrate. G. Natta (Gazzetta, 1928, **58**, 870—882; cf. this vol., 15).—An *X*-ray examination, by means of the Laue, rotating-crystal, and powder methods, of strontium hydroxide octahydrate was made in order to determine the exact position of the molecules of water of crystallisation in the lattice. The hydrate crystallises in the hexagonal system, with a unit cell containing 1 molecule of $Sr(OH)_2,8H_2O$ (a 6·41, c 5·807 Å., $d_{\text{calc.}}$ 1·85), defined by the following co-ordinates: Sr (0, 0, 0), O of hydroxide ($\frac{1}{2}$, 0, 0) (0, $\frac{1}{2}$, 0), and O of water molecules (u, u, v) (u, $-u$, v) ($-u$, u, v) ($-u$, $-u$, v) (u, u, $-v$) (u, $-u$, $-v$) ($-u$, u, $-v$) ($-u$, $-u$, $-v$), where u has a value of 0·29—0·30 and v is 0·25. The structure is also shown diagrammatically. O. J. Walker.

Determination of the orientation of crystal axes by *X*-rays. S. Takeyama (Mem. Coll. Sci. Kyoto, 1928, **11**, 469—479).—In a rotating-crystal spectrometer a V-shaped frame of lead wires is inserted between the crystal and the photographic plate, and rotated with the crystal. From the positions of the shadows cast by the lead wires on the spectral lines the angle through which the crystal must be rotated to reflect these spectral lines can be calculated. If *X*-rays of known wave-length are used the orientation of the crystal axes can be determined. The method is suitable for thick crystals, or crystals on the surface of thick specimens. A polished surface of copper examined by this method indicated a preferred orientation in which (111) or (100) planes were nearly parallel to the surface.

C. J. Smithells.

Form of the lattice of some monoclinic compounds of the magnesium tungstate type. E. Broch (Z. physikal. Chem., 1928, **B**, **1**, 409—421).—*X*-Ray examination shows ferrous, manganous, zinc, cobalt, nickel, and magnesium tungstates and also wolframite to form an isomorphous series. The lattice of magnesium tungstate is of the type $\begin{pmatrix} r_{11} r_{22} r_{33} \\ 0 \ 0 \ r_{12} \end{pmatrix}$, and has the dimensions $a=4{\cdot}67$, $b=5{\cdot}66$, $c=4{\cdot}92$ Å., $\beta'=89° \ 35'$, $\beta=90° \ 25'$, the unit cell containing 2 molecules. R. Cuthill.

Higher fatty acids. III. *X*-Ray measurements. G. T. Morgan and E. Holmes (J.S.C.I., 1928, **47**, 309—311T).—*X*-Ray measurements have been made on a series of pure saturated fatty acids, C_{17}—C_{26}, and on a number of fractions of acids obtained from hydrogenated whale oil, and also from arachis oil. The latter fractions have given anomalous results which suggest that the ester-distillation method of separation is to be preferred to the ordinary crystallisation methods. Normal hexacosoic acid has a main *X*-ray spacing $d_1=56{\cdot}6$ Å. for the bimolecular unit crystal cell, whilst examination of the so-called cluytinic acid suggests that it is of much higher mol. wt. than hitherto supposed.

Röntgen diagrams of cellulose. R. O. Herzog and W. Jancke (Z. physikal. Chem., 1928, **139**, 235—262).—From a survey of previous work and also from interference photographs of native and mercerised ramie, now reported, the following conclusions are reached. The cellulose crystals always take up positions with one and the same principal axis either in the axis of the fibre or for spiral fibres as a tangent to the spiral. The spiral angles determined from *X*-ray diagrams are, within the limit of experimental error, in agreement with those obtained from data on double refraction, striations, and directions of cleavage. All natural cellulose gives the diagram of native cellulose, but mercerised products or those strongly dispersed in solution give that of cellulose hydrate. The difference between the two types of diagrams can be explained by the existence of two modifications of cellulose of which one (native cellulose) crystallises as far as possible in a monoclinic and the other (cellulose hydrate) in a rhombic system. Native and mercerised fibres give fibre diagrams with the same identity periods in the direction of the fibre.

R. N. Kerr.

Structure of the crystalline part of cellulose. II. H. Mark and K. H. Meyer (Z. physikal. Chem., 1929, **B**, **2**, 115—145).—Work on the *X*-ray diagrams of cellulose has shown that it is made up of elementary cells, monoclinic in form. An atomic model is here put forward for the structure of cellulose which will give values for the intensities of the diagram in agreement with those observed. The size and form of the cellulose micelle are calculated. It has a length of about 500 and a width of about 50 Å. The mechanisms of reactions into which cellulose can enter are considered. The micellary structure of cellulose leads to two types of reaction, (*a*) the micellary surface reaction, and (*b*) the " permutoid " reaction. The latter is the more important. By the use of Hudson's rule, the rotations of various cellulose derivatives are calculated and found to agree with the observed values. An *X*-ray method for the comparison and identification of cellulose preparations is given and the question of small structural elements of cellulose is discussed. (See A., 1928, 621.) A. J. Mee.

***X*-Ray investigation of the mixed crystal system $BaSO_4+KMnO_4$.** G. Wagner (Z. physikal. Chem., 1929, **B**, **2**, 27—38).—Barium sulphate and potassium permanganate possess the properties necessary for the formation of mixed crystals. The Debye–Scherrer diagrams were obtained for ten preparations of varying permanganate content. Comparison of the lines obtained with those given by barium sulphate and potassium permanganate alone shows a displacement. By plotting the lattice space against the permanganate content it is shown that the displacement is proportional to the latter within experimental error. These facts are evidence for the mixed crystalline nature of the barium sulphate–potassium permanganate system. A photograph of barium sulphate with adsorbed barium nitrate gave no displacement of the barium sulphate lines.

A. J. Mee.

Nature of martensite. N. Seljakov (Nature, 1929, **123**, 204—205).—Honda and Sekito's result (A., 1928, 594; B., 1928, 753) that the ratio (1·07) of the axes of the lattice of tetragonal martensite is independent of the carbon content, is criticised; it is considered that the carbon content of the surface layers was the same in all cases. The presence of carbon atoms in the lattice will cause a decrease in the intensity, but not a broadening, of the spectral lines.

A. A. Eldridge.

Metallic filaments. R. Schenck, R. Fricke, and G. Brinkmann (Z. physikal. Chem., 1928, **139**, 32—46).—Artificially-prepared as well as naturally-occurring metallic filaments have been investigated by means of *X*-ray analysis. The artificial trichites of silver were prepared by means of the reaction between silver sulphate and sulphide and by the reduction of silver sulphide with hydrogen at 400—500°. The copper trichites were obtained in a similar manner by reduction with hydrogen at 500—600°. The silver threads show only isolated interference spots and those prepared by reduction are assumed to possess a uniform crystal orientation. When the material is heated at 900°, this uniformity disappears and simultaneous enlargement of the grains takes place. Natural silver trichites show no kind of orientation. With copper, the *X*-ray pattern changes from one preparation to another and heating is accompanied by re-orientation. The mode of formation of metallic trichites is discussed and the significance of the presence of sulphide is emphasised. In all probability, the former is to be ascribed to an electrolytic process arising from a short-circuited thermoelement between the metal and the sulphide. Photographs and data are reproduced. L. S. THEOBALD.

Crystal structure of anhydrous silicotungstic acid and related compounds, and their probable molecular formulæ. A. G. SCROGGIE and G. L. CLARK (Proc. Nat. Acad. Sci., 1929, **15**, 1—8).—An *X*-ray diffraction analysis was made of the crystal structure of the anhydrous acid obtained from the hydrated forms at 220°, and combined with chemical data to deduce the molecular structure. A series of modified acids with 7, 8, and 10 tungsten atoms was isolated by stepwise addition of alkali to the acid. The crystal form of the acid was shown by the *X*-ray examination to be a body-centred cube, with *a* 12·16 Å. This dimension applies to the acids with 8, 10, and 12 tungsten atoms, and to the modifications of the latter which contain 2 or 8 molecules of water, *i.e.*, $SiO_2,12WO_3,2H_2O$ or $(SiO_2,12WO_3,6H_2O)2H_2O$, but not to the anhydride, $SiO_2,12WO_3$. Phosphodecimolybdic acid similarly forms a body-centred cube with *a* 14·31 Å. A modified formula for the acid $(SiO_2,12WO_3,6H_2O)2H_2O$ or $H_4[SiO_4,W_{12}O_{30}(OH)_{12}]$ and a new spatial structure were deduced to correlate the *X*-ray and chemical data. N. M. BLIGH.

***X*-Ray analysis of cadmium arsenide and arsenious anhydride.** L. PASSERINI (Gazzetta, 1928, **58**, 775—781).—Cadmium arsenide, examined by the powder method, is shown to have a cubic structure with a non-ionic lattice of the zinc arsenide type (cf. A., 1928, 1313). The length of the unit cell is 6·29 Å., $d_{calc.}=6·495$ and the distance As–Cd is 2·723 Å. The structure of the cubic modification of arsenious oxide determined by Bozorth (A., 1923, ii, 632) is confirmed by the powder method. The length of the unit cell containing 16 molecules of As_2O_3 is 11·08 Å. ($d_{calc.}=3·851$). The distance As–O is calculated to be 2·016 Å., which gives a value of 0·696 Å. for the radius of the As^{+++} ion. O. J. WALKER.

Form of the central carbon atom in pentaerythritol tetra-acetate as shown by *X*-ray crystal analysis. (MISS) I. E. KNAGGS (Proc. Roy. Soc., 1929, **A**, **122**, 69—76).—*X*-Ray examination of pentaerythritol tetra-acetate by taking rotation, oscillation, and Laue photographs, indicates that it crystallises in the tetragonal bipyramidal class. There are two molecules in the unit cell, which has $a=11·98$, $c=5·47$ Å. The crystals are built on a simple tetragonal lattice, Γ_t, and the space-group is C_{4h}^4; this necessitates each molecule having a four-fold alternating axis of symmetry. The conclusions reached by Gerstäcker, Möller, and Reis (Z. Krist., 1928, **66**, 355), that the space-group is C_{4h}^3 and that the molecules possess a simple tetragonal axis of symmetry, are criticised. The evidence for the space-group C_{4h}^3 is very slight. A probable structure is suggested, from which it follows that the symmetry of the central carbon atom may be tetrahedral, although a slight departure from true tetrahedral symmetry is possible. L. L. BIRCUMSHAW.

Nature of interference lines in *X*-ray photographs of many crystalline materials. I. H. MÖLLER and A. REIS (Z. physikal. Chem., 1928, **139**, 425—438).—The influence exerted by the nature of the cross-section of the powder rod on the interference lines obtained in *X*-ray photographs taken by the Debye–Scherrer method is examined mathematically assuming that a parallel primary radiation is used. The shape, dimensions, and absorption of the rod are considered and results are given for three different shapes—flat slab, wedge, and cylinder. Weakening of intensity of the lines through increase in the coarseness of the particles is considered. R. N. KERR.

***X*-Ray diffraction of crystal powders and liquids in relation to their constitution.** P. KRISHNAMURTI (Indian J. Physics, 1928, **3**, 225—240).—Results for a number of organic liquids confirm those of a previous investigation (cf. A., 1928, 691). Geraniol and terpineol showed some differences, the former giving a broader and more diffuse halo, and a smaller inner ring due to double molecular spacing, indicating the existence of longer molecules than in the case of terpineol, for which, also, the halo was clearly defined. Some benzene derivatives with a long side-chain gave rings of about the same size as in a long-chain aliphatic derivative. Examination in both powder and liquid states was made of *o*- and *m*-nitrobenzaldehyde, *o*-nitrophenol, *o*-nitroaniline, and *p*-toluidine. In both states the *o*- and *m*-compounds showed two rings, the outer one contracted in the case of the liquid, for which both were broader and more diffuse at the edges. The outer ring is explained generally, with supporting evidence, as being due to the thickness of the molecule, and the inner to its length and breadth. The *p*-compound showed a number of rings close together in the powder, joining up into one broad ring in the liquid, when only the spacing due to the average thickness of the molecules is obtained. N. M. BLIGH.

New type of alum. W. R. C. CURJEL (Nature, 1929, **123**, 206).—The salt $K_2BeF_4,Al_2(SO_4)_3,24H_2O$ crystallises in the cubic system, normally as octahedra, and is a true alum; the salt $K_2ZnCl_4,Al_2(SO_4)_3,24H_2O$ is also an alum. Hence potassium sulphate and potassium beryllium fluoride are truly isomorphous. Rubidium beryllium fluoride is isomorphous with the potassium salt. A. A. ELDRIDGE.

Influence of traces of foreign ions on the absorption of alkali halide crystals. I. MASLAKOWEZ (Z. Physik, 1928, **51**, 696—706).—Measurements of the ultra-violet and infra-red absorption of crystals of potassium chloride, bromide, and iodide, and of sodium chloride, containing traces of potassium nitrate, or nitrite, show that nitrate and nitrite ions may be introduced in the alkali halide grating forming mixed crystals. Carbonate and sulphate ions cannot be introduced without producing very considerable distortion. R. W. LUNT.

Relationship between grain size and magnetic properties in pure iron. G. J. SIZOO (Z. Physik, 1928, **51**, 557—564).

Experimental study of the growth of zinc crystals by the Czochralski–Gomperz method. A. G. HOYEM and E. P. T. TYNDALL (Physical Rev., 1929, [ii], **33**, 81—89).—Conditions for the growth of single zinc crystals of any desired orientation were determined experimentally. For a constant rate of growth and given initial orientation the successful growth of a single-crystal rod 10 cm. or more in length was found to depend on the temperature gradient in the column of liquid zinc just below the growing crystal. The appropriate temperature gradient is plotted as a function of the orientation. Attempts to grow crystals outside the region of successful growth result in changes to new orientations.

N. M. Bligh.

Phase rule and Euler's law. O. Rüdel (Z. Elektrochem., 1929, 35, 54).—A parallelism exists between the phase-rule equation and Euler's equation relating the faces, edges, and corners of a crystal, and the number of phases, degrees of freedom, and components of the former equation may be identified with the number of faces (or corners), corners (or faces), and edges, respectively, of the latter.

L. L. Bircumshaw.

Form and potential energy of the isomorphous crystals ruby (Al_2O_3) and hæmatite (Fe_2O_3). J. Topping (Proc. Roy. Soc., 1929, A, **122**, 251—273; cf. Topping and Chapman, A., 1927, 96; Lennard-Jones and Dent, *ibid.*).—To determine the equilibrium configuration of a crystal, as given by the minimum value of the potential energy of the crystal, it is necessary to calculate the electrostatic potential energy of an infinite array of point-charges, arranged according to the crystal pattern, and the potential energy due to the intrinsic repulsive forces between the ions. From a consideration of these forces, a very good account can be given of the observed size and shape of the isomorphous crystals ruby and hæmatite, the structures of which involve three parameters. It is indicated that theoretically, in terms of the electrostatic and intrinsic repulsive ionic forces which have been considered, an exact hexagonal close-packed arrangement of the oxygen ions is not compatible with the observed size and shape of the crystals, and that there must be some slight distortion from the exact arrangement. This distortion is indicated by the mutual distances of the ions of the Al_2O_3 groups which surround the lattice-points—*i.e.*, by the value of the distance $2d$ between the aluminium ions and the distance $b\sqrt{3}$ between the oxygen ions of such an Al_2O_3 group. These results are in good agreement with experiment (cf. Bragg and Brown, A., 1926, 227). It is further found that, in order that the theoretical series of possible configurations of the crystal might include the observed configuration, it is necessary to adopt a value of $\mu_{22}=11{\cdot}0$ for O^{--}, which is considerably lower than the value 17·6 obtained by Lennard-Jones and Dent (A., 1926, 888). Using this revised value of μ_{22}, crystalline sodium nitrate has been reconsidered (cf. Topping and Chapman, *loc. cit.*) and fairly satisfactory results have been obtained.

L. L. Bircumshaw.

Molecular theory of crystals. K. Weissenberg (Z. physikal. Chem., 1928, **139**, 529—583).—Crystal structure is discussed from the point of view of the Schoenflies–Fedoran symmetry laws. It is shown that not only may morphological and physical properties thus be explained, but also the chemical constitution of crystals. From these laws a new hypothesis is deduced which is applicable to crystals in the same manner as Avogadro's law to gases and leads to a new type of space-lattice. A survey of different space-lattices has been made and examples of the new type are given. The hypothesis was tested for 459 substances; in 401 cases the mol. wt. of the crystal unit calculated from this hypothesis agrees with that of the simple chemical formula and in the remainder it is a simple multiple of that.

R. N. Kerr.

Quantum mechanics of electrons in a crystal lattice. F. Bloch (Z. Physik, 1928, **52**, 555—600).—Mathematical. The motion of an electron in a crystal lattice is discussed in relation to Fermi's statistics. An expression is deduced for the component part of the specific heat of crystals due to this motion. It is also shown that the order of magnitude of the electrical conductivity of metals and its dependence on temperature, as deduced from these considerations, are in qualitative agreement with experimental observations.

J. W. Smith.

Hall effect in steel–nickel alloys. U. Salerno (Rend. Accad. Sci. Fis. Mat. Napoli, 1928, [iii], **34**, 159—165).—The Hall effect is exhibited by steel–nickel alloys with the same characteristics as with ferromagnetic metals, invar showing a moderately high coefficient of rotation. The phenomenon is influenced to some extent by the nature of the secondary electrodes. Asymmetry, which is observed in all the alloys examined, is especially marked in that containing 22% of nickel (the least magnetic), but almost absent from the highly magnetic 49% alloy. The contribution of steel to the effect is greater than that of nickel, the presence of 80% of which is necessary to reverse the sign of the effect. Analogies are shown between the variation of the Hall effect and those of specific heat, thermo-electric power, electrical conductivity, and electrical resistance with the composition of the alloys.

T. H. Pope.

Comparison of the Corbino and Hall effects in silver and brass. K. K. Smith and H. M. O'Bryan (Physical Rev., 1929, [ii], **33**, 66—74).—An improved electromagnetic torque method was used to measure the Corbino effect, which was compared with the Hall effect, in rectangular silver sheets. To avoid magnetic impurities, navy brass was used for the suspended system and the two effects were measured also for this metal. The values obtained for the Corbino coefficient c, the Hall coefficient R, and the resistivity ρ, were, for silver $c=-5{\cdot}0\times10^{-7}$, $R=-8{\cdot}6\times10^{-4}$, $\rho=1{\cdot}72\times10^{3}$, and for the brass $c=-0{\cdot}14\times10^{-7}$, $R=-0{\cdot}96\times10^{-4}$, $\rho=6{\cdot}7\times10^{3}$ e.m.u. Probable causes of the differences of c for circular and rectangular plates and in previous experiments are discussed.

N. M. Bligh.

Magnetic susceptibility of alkali and alkaline-earth halides. K. Ikenmeyer (Ann. Physik, 1929, [v], **1**, 169—191).—The diamagnetic susceptibility of the halides of the alkali and alkaline-earth metals in aqueous solution has been determined by a differential method involving small rotating rods of material in an inhomogeneous field. Throughout the measurements the susceptibilities show a linear variation with respect to concentration, so that no apparent reciprocal action occurs between ions. The molecular susceptibility χ_m varies approximately linearly with the sum of the atomic numbers of atoms in the molecule Z_m, *i.e.*, $-\chi_m=c_1Z_m+c_2$, the constants having the values, $c_1=0{\cdot}80_3\times10^{-6}$ and $c_2=8{\cdot}30\times10^{-6}$. Using values of χ_m corrected to conform with this relation, the ionic susceptibilities have been calculated. The relation, $-\chi_{\text{ion}}=c_1Z+c'_2$ agrees well with the data if the following values of c'_2 are adopted: halogen ions 6·70, alkali ions 1·60, alkaline-earth ions $-51{\cdot}0\times10^{-6}$. The value of c_1 remains unchanged.

R. A. Morton.

Chromites and ferrites of nickel and of cobalt. (Mlle.) S. Veil (Compt. rend., 1929, **188**, 330—332).—The magnetisation coefficient–composition curves of mixtures of chromic or ferric oxide with nickelous or cobaltous oxide, prepared by calcination of the precipitate obtained on the addition of sodium hydroxide to solutions containing corresponding mixtures of the sulphates, show maxima at the points corresponding with the formation of the respective chromites and ferrites. The magnetisation coefficients of the ferrites are more than 1000 times as great as those of their pure constituents.

J. Grant.

Magnetic properties in relation to chemical constitution. L. C. Jackson (Nature, 1929, **123**, 279).—After allowance is made for the diamagnetic properties of the sulphur atoms in iron pyrites, the iron atom possesses a small residual positive magnetic moment, and the susceptibility is independent of the temperature. These properties are in agreement with what would be expected for a twofold co-ordination compound of ferrous iron, but differ from those associated with simple ferrous salts (cf. Lowry and Gilbert, this vol., 127). A. A. Eldridge.

Hall effect in galena and molybdenite. C. W. Heaps (Phil. Mag., 1928, [vii], 6, 1283—1286).—A specimen of galena from Missouri gave a Hall coefficient of −108·3 independent of the orientation of the crystal, whilst another specimen of unknown origin gave the value +4802. This great discrepancy in values for the same mineral is attributed to the presence of different proportions of different impurities. The average Hall coefficient for molybdenite was found to be −1907. The isothermal Hall coefficient for molybdenite is about 6% smaller than the adiabatic. In galena the two coefficients do not differ by more than 2%. A. E. Mitchell.

Magnetostriction of a single iron crystal. N. Akulov (Z. Physik, 1928, **52**, 389—405).—Mathematical. A general formula is deduced for the calculation of the energy of expansion of the dipole lattice and the electrostriction and magnetostriction of any crystal. The curve for the magnetostriction of an iron crystal, calculated from this formula, is compared with the experimental curve of Honda and Mashiyama (A., 1927, 299). The positions of the maxima and minima as well as the period of the effect coincide exactly with the experimental data, whilst the absolute values of the magnetostriction calculated by the formula are also of the same order as those found experimentally. It is concluded that the ions of iron have no perceptible electrical dipole moment, and that, for the calculation of the magnetic coupling force, the iron ion can be treated, as a first approximation, as a single magnetic dipole. J. W. Smith.

Resistance and thermo-electric phenomena in metal crystals. P. W. Bridgman (Proc. Nat. Acad. Sci., 1928, **14**, 943—946).—Some experimental results are summarised briefly. An improved method has been evolved for making single metal crystals and for measuring their thermal *E.M.F.*, some results being given. It is concluded that the Kelvin–Voigt law for thermal *E.M.F.* is approximate only. Some theoretical considerations are briefly discussed.

N. M. Bligh.

Pyro- and piezo-electricity. A. Meissner (Naturwiss., 1929, **17**, 25—31).—The pyro- and piezo-electric properties of quartz have been studied in detail. From the characteristic oscillations excited in a quartz disc it is possible to calculate the dimensions of the unit cell in the crystal lattice, and the structural dimensions obtained macroscopically agree closely with those obtained from *X*-ray data. The properties of quartz are connected with the orientation of the electric axes in the unit cell. At constant temperature the electric moment is constant, but increases with increasing shifts in the atoms, *i.e.*, with rise in temperature. The pyro-electric coefficient has been determined for quartz, sucrose, tartaric acid, sodium potassium tartrate, tourmaline, topaz, zinc blende, pyrites, and pentaerythritol. R. A. Morton.

Slip-bands produced when crystals of aluminium are stretched. II. Extension at high temperatures. K. Yamaguchi and S. Togino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 9, 277—292).—The deformation of single crystals of aluminium under tension, above the recrystallisation temperature, is studied. Slip takes place on the same planes and in the same crystallographic direction as at the ordinary temperature, but does not result in increased hardness. The distortion takes place by simple shear throughout the crystal, and not by a succession of slips on different planes. Instead of slip bands appearing on the surface, uneven wavy stripes having no relation to the direction of the crystal axes are produced. C. J. Smithells.

Recrystallisation of metals. II. R. Karnop and G. Sachs (Z. Physik, 1928, **52**, 301—313; cf. A., 1927, 504).—The influence of previous stretching and annealing on the temperature of crystallisation and the size of crystals formed in rods of commercial aluminium (99·3% Al, 0·4% Fe, and 0·2% Si) has been investigated. Comparisons have also been made between the effects of extension, compression, and a combination of these two on the recrystallisation. The application of a stress during the recrystallisation process is found to exert a marked effect on the product. J. W. Smith.

Molecular association and molar concentration. G. G. Longinescu and G. Chaborski (Bul. Chim. pura Appl., 1927, **30**, 3—29; Chem. Zentr., 1928, ii, 1175).—The number of g.-mols. of a liquid or solid contained in 1 litre (the " molar concentration," C_m) is determined for 350 organic compounds. In homologous series C_m diminishes with increasing mol. wt.; isomerides have similar values.

The values lie between 55·5 (water) and 0·09 (tristearin). All organic liquids which are considered to be associated have $C_m>10$, whilst normal liquids have $C_m=10$ (approx.). The difference between normal and "associated" liquids is not ascribed to an association of single molecules, but to an accumulation of single molecules in a given volume. The conception of molar concentration leads to an explanation of cryoscopic anomalies and of anomalous values of the temperature coefficient in Ramsay and Shields' formula. A. A. Eldridge.

Relations between physical constants of liquids. V. Perschke (Z. Elektrochem., 1929, **35**, 13—17).—See this vol., 21.

Magnetism of hydrated zirconia. F. Bourion and (Mlle.) O. Hun (Bull. Soc. chim., 1929, [iv], **45**, 49—60).—A more detailed account of work already published (this vol., 20).

Change in the intensity of magnetisation of an iron wire on stretching. J. B. Seth, C. Anand, and M. Dayal (Z. Physik, 1928, **52**, 382—388).—Application of stress to a piece of iron wire suspended in various weak magnetic fields caused a change in the intensity of its magnetisation, which was followed by a ballistic differential method. The curves obtained for the change with extension are analogous for different field strengths and are similar in form to the stress–strain curves for such a wire. J. W. Smith.

Anomaly in the diamagnetism of gases. H. Buchner (Ann. Physik, 1929, [v], **1**, 41—48).—Glaser's anomaly (A., 1925, ii, 82, 642) in the diamagnetism of gases at low pressures, namely, a triple increase in the susceptibility, is ascribed to an error in the temperature correction. R. A. Morton.

Electrical conductivities of dilute liquid amalgams of gold and copper at various temperatures. T. C. Williams and E. J. Evans (Phil. Mag., 1928, [vii], **6**, 1231—1253).—The electrical conductivities of liquid gold amalgams at concentrations up to the saturation at 11·5° have been determined at 11·5°, 100°, and 300°. Similar measurements have been made with copper amalgams, the concentrations being varied up to saturation at the temperature of experiment. In both cases the temperature coefficient of resistivity is less than that of pure mercury. The ratio of the increase of conductivity relative to mercury to the concentration has been determined at each temperature for each concentration, and at infinite dilution both series of amalgams gave the same values at the same temperatures. These values are equal to those obtained for silver amalgams by Johns and Evans (A., 1928, 244). The results show that, atom for atom, the effect on the conductivity of the different metals of group I(*b*) of the periodic table is the same. A. E. Mitchell.

Dissociation of pure mercury. E. S. Keeping (Nature, 1928, **122**, 728).—Bradley's results (A., 1928, 1302) are criticised. Values of p/q, where p and q are the average numbers of free electrons per atom of the metal X and mercury, respectively, are recorded for indium, magnesium, thallium, germanium, antimony, yttrium, cerium, gallium, copper, cadmium, and silver. A. A. Eldridge.

Tribo-electricity and friction. IV. Electricity due to air-blown particles. P. E. Shaw (Proc. Roy. Soc., 1929, **A**, **122**, 49—58; cf. A., 1928, 467).—An apparatus has been devised for studying the charges developed by the impact of two unlike metals, of two like metals, of sand on sand, or ice on ice. Particles of the materials are driven by means of a rapid stream of air on to surfaces of one material only, and the charges arising on the particles, on the surfaces, and on the issuing air are measured separately. Copper, iron, zinc, and brass are found always to receive charges of sign, and to some degree of amount, in accordance with the Volta effect, the photo-electric effect, and the thermionic effect. But the fact that considerable charges arise when the particles and surfaces are chemically identical, as with copper/copper, zinc/zinc, brass/brass, sand/sand, and ice/ice, indicates that the Volta effect alone will not account for all the charges developed. Physical differences of the surfaces—*i.e.*, strain differences—are suggested as contributory factors to tribo-electric charges. The effect of the cleanliness of the filings and of the temperature, speed, and direction of the air blast was studied. Fresh, clean filings yield as much as 30% more charge than old. On reducing the speed of the blast, the charges were reduced, whilst in some cases they were doubled by raising the temperature from 18° to 58°. The use of an oblique air blast also caused a considerable increase in the charges. The results for sand and ice provide a key to the meteorological effects observed in electric sand- and snow-storms. L. L. Bircumshaw.

Dependence of the susceptibilities of glasses on temperature. W. Gerlach and N. Little (Z. Physik, 1928, **52**, 464—465).—The magnetic susceptibility of glass is dependent to a remarkable extent on temperature. All the types of glass investigated had a temperature coefficient of the same order of magnitude, independently of the absolute value of the susceptibility. This temperature coefficient is ten times the order of magnitude found in the case of gases. The phenomenon is attributed to the paramagnetic components present in the glass. J. W. Smith.

Electrical resistance and magnetic permeability of iron wire at radio frequencies. G. R. Wait, F. G. Brickwedde, and E. L. Hall (Physical Rev., 1928, [ii], **32**, 967—973; cf. Wait, A., 1927, 505).—Further efforts to detect a reported anomalous change in the permeability of iron, and to observe a critical variation in the resistance of iron wire reported by Mitiaev (A., 1926, 1086), were unsuccessful. N. M. Bligh.

Changes in the resistance of nickel wire with stretching. J. B. Seth and C. Anand (Physikal. Z., 1928, **29**, 951—952).—In most cases metallic wires exhibit a steady increase of electrical resistance with stretching. Nickel, however, shows at first a decrease followed by the customary increase. The minimum occurs when the elongation is 15% of that observed just before the wire breaks. A detailed investigation of the elongation process up to the stage of minimum resistance shows that the change in resistance is not truly reversible since the curve obtained by plotting elongation against change in resistance is looped, one branch representing the change as the resistance is increased and the other branch representing the reverse process. The shape of the loop depends not only on the number of times the wire has been stretched, but also on the previous history of the specimen. R. A. Morton.

Measurements with the aid of liquid helium. III. Resistance of metals. Superconductivity of tantalum. Contribution to the explanation of superconductivity. Specific heat of gaseous helium. W. Meissner (Physikal. Z., 1928, **29**, 897—904).—The electrical resistances over the temperature range 1·29—273·20° Abs. have been determined for aluminium, beryllium, cobalt, molybdenum, rhodium, palladium, tantalum, tungsten, iridium, antimony, German silver, carbon, and various kinds of iron. Although some elements exhibit quite small resistances when highly purified, the only one among those listed which shows superconductivity is tantalum, the phenomenon commencing at 4·36° Abs. Attention is directed to the fact that all the known superconductors, including tantalum, occupy neighbouring places in the periodic table. German silver, like constantan and manganin, shows little decrease in resistance with fall in temperature, the value at 1·32° Abs. being 90% of that at 273·2° Abs. Carbon, on the other hand, shows an increase in resistance of 19% over the same temperature interval.

The superconductivity of tin at the temperature of liquid helium is not eliminated when the metal is enclosed in a tightly-fitting sheath of German silver, from which it is concluded that superconductivity is a volume- rather than a surface-effect. From other experiments it is concluded that the current is carried by electrons distributed at random, the disappearance of resistance being due to the failure of the electrons to give up their energy to the atoms, *i.e.*, to elastic reflexion of electrons. Experiments on the specific heat of gaseous helium show that at 5·5° Abs. and 0·75 atm., the molecular heat at constant volume is 1·94, *i.e.*, 65% of the normal classical value. R. A. Morton.

Disturbance of the superconductivity of thallium by magnetic fields. W. Tuyn (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 687—691).—The superconductivity of thallium has been measured at temperatures of 1·82—2·21° Abs., in fields of 22·3—67·8 gauss. Hysteresis is shown. C. W. Gibby.

New superconductors. W. J. de Haas (Naturwiss., 1929, **17**, 85—86).—Antimony and zinc, and bismuth and thallium yield superconducting alloys, the latter metal in each case being a superconductor. It is now found that the combination gold–bismuth is superconducting although neither metal is a superconductor *per se*. The resistance of the alloy at 2·2° Abs. is 0·7 of the resistance at the ordinary temperature, whilst 0·05° lower the alloy has no resistance. At 1·5° Abs. neither gold nor bismuth is superconducting. W. E. Downey.

Excitation of frictional electricity between metals and non-conductors in relation to the pressure of the surrounding gas and the outgassing of the metal. W. Kluge (Ann. Physik, 1929, [v], **1**, 1—39).—An experimental technique is described for the quantitative study of static electrification in a vacuum. It is shown that the polarity of the electrification produced by rubbing platinum, gold, and palladium in a high vacuum is reproducible. The magnitude of the charge depends on the condition of the metallic surface, outgassing by heating to redness causing an increased effect. When the metal is allowed to take up gas again, the original phenomena are reproduced. If platinum is heated to whiteness, friction against silk results in a marked positive polarity of the metal. This effect arises from the formation of a film of "sputtered" platinum, since a little volatilisation occurs with strong heating. The film is readily polished away by the silk, whereupon the normal negative polarity reappears on the metallic surface. The influence of the pressure of the surrounding air on the sign and magnitude of the electrification has been studied. R. A. Morton.

Excitation of frictional electricity. L. Wolf (Ann. Physik, 1929, [v], **1**, 260—288).—Frictional electricity arises largely from the transference of metallic ions in solution in the film of water on the insulator. Friction of an earthed metallic "needle" against a rotating plane surface of specially prepared shellac results, in the absence of an electric field, in an equilibrium between solution tension and the pressure of dissolved ions. Application of an electric field sets up a new equilibrium characterised by a smaller concentration of ions in the film, reversion to the first equilibrium being possible by reducing the field strength. The sign of the frictional electricity can be reversed by adjusting the field to neutralise the pressure of the ions. Artificially increasing the ionic concentration also reverses the sign. By increasing the surface of contact, the amount of electricity excited with constant capacity increases to a limiting value. It is also shown that the speed of the moving surface has no influence on the quantity of electricity excited. R. A. Morton.

Analogous properties and analogous radiometer curves of nitrogen and carbon monoxide, and of carbon dioxide and nitrous oxide. E. Brüche and W. Littwin (Z. Physik, 1928, **52**, 334—335; cf. this vol., 251).—It has been shown that, in common with the majority of the other physical properties of these pairs of gases, the radiometer curves of nitrogen and carbon monoxide are almost identical, as are those of carbon dioxide and nitrous oxide. J. W. Smith.

Dynamic allotropic state of selenium. G. Briegleb (Naturwiss., 1929, **17**, 51).—A preliminary account of experiments on the allotropic modifications of selenium, all of which have been shown by *X*-ray investigations, to contain two pseudo-components. Although the absolute solubilities of the constituents are almost identical, they dissolve at different rates in carbon disulphide, and use has been made of this property to effect some separation. By spectroscopic methods it has been shown that two forms of selenium exist in equilibrium in this solution, but that the equilibrium changes with temperature. The results are discussed in relation with the observations of previous investigators. J. W. Smith.

Radiometer question. E. Brüche and W. Littwin (Z. Physik, 1928, 52, 318—333).—With an improved form of measurement radiometer, the radiometer curves of twelve gases have been measured under various conditions. In low-pressure regions the radiometric effect appears to be a surface effect, independent of the type of gas and the geometrical relations of the instrument, being proportional only to the number of molecules in unit volume of the gas. With moderate pressures the effect attains a maximum in each gas which in pressure and magnitude is proportional to the free path of the molecules. In the regions of higher pressure it becomes an edge effect which is directly proportional to the square of the free path and inversely proportional to the pressure.

J. W. Smith.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. Cau (Compt. rend., 1929, 188, 57—58).—The component of the vibration parallel to the axis is less absorbed than the normal component by the birefringent, dichroic layers of iron obtained in the axial zone in the author's experiments (A., 1928, 695). In the middle of the visible spectrum the dispersion is normal for the ellipticity, and abnormal for the rotation of the emergent vibration. The effect, which increases with the thickness of the deposit and with decrease in distance between the wire and the deposition surface, was also studied by reflexion, a rectilinear incident vibration then being transformed into an elliptical vibration having a different azimuth. J. Grant.

Gaseous state of low-boiling substances. K. Wohl (Z. physikal. Chem., 1929, B, 2, 77—114).—The critical data for the permanent gases and normal substances are collected and compared. The two virial coefficients which express the deviations from the ideal gas state when reduced with the critical data correspond well with each other within the range neon, nitrogen, argon, and oxygen, whilst with normal substances there is a certain degree of correspondence above the critical temperature. This more or less close relationship holds in general up to the neighbourhood of the critical volume, although at the furthest extreme from the ideal gas state the compressibility of the permanent gases is markedly greater than that of normal substances. The dependence of the van der Waals constant *b* on temperature was investigated. The temperature coefficient of *b* is of the same order of magnitude for all permanent gases and decreases inversely with the critical temperature from helium to argon. The dependence of the van der Waals constant *a* on temperature is very small for all permanent gases above the critical temperature, and diminishes with falling temperature, so that no degeneration effect will be noticed in the rarefied gas. It is possible from the value of *b* to calculate the packing density of the molecules of the liquefied gases at 0° Abs. For neon and argon there is the closest packing, and there is a considerable decrease in packing density from neon, through hydrogen, to helium, which can be explained only by the existence of energy at 0° Abs. It can be shown that the ratio of this energy at 0° Abs. to the potential energy of the liquid for low-boiling substances must be large. For hydrogen and helium, and to a smaller extent neon, the values of the critical data are influenced by the energy at 0° Abs. By the use of "idealised" critical data it is possible to arrive at a value for the second virial coefficient which shows a good degree of correspondence for similar permanent gases. The difference between the permanent gases with the higher critical temperatures and normal substances lies in the fact that for the latter there is a somewhat larger temperature effect on the van der Waals attraction. Attempts to explain the van der Waals attraction on the basis of the old quantum theory lead to large deviations from practice. In particular the assumption that for polyatomic substances the attraction at medium and low temperatures rested ultimately on the orientation of the molecule is in contradiction with the good correspondence between monatomic and diatomic substances. A. J. Mee.

Multiplicative properties. M. Trautz (Z. angew. Chem., 1929, 42, 89—94).—A theoretical paper concerned with the physical properties of gases and based mainly on the results of the author's work on the specific heats, friction, and thermal conductivities of gases. J. S. Carter.

Heat capacity of methyl alcohol from 16° to 298° Abs. and the corresponding entropy and free energy. K. K. Kelley (J. Amer. Chem. Soc., 1929, 51, 180—187).—The method previously described was used (Giauque and Wiebe, A., 1928, 228). Methyl alcohol exists in two crystalline forms having a transition point at 157·4° Abs. and a heat of transition of 154·3 g.-cal./mol. The heat of fusion of the substance is 757 g.-cal./mol. at 157·22° Abs.; the molal entropy at 298° Abs. is 30·3 g.-cal./1° and the molal free energy of formation —44,000 g.-cal.

S. K. Tweedy.

Heat capacities at low temperatures of "ferrous oxide," magnetite, and cuprous and cupric oxides. R. W. Millar (J. Amer. Chem. Soc., 1929, 51, 215—222).—The molal heat capacities of "ferrous oxide" (83% FeO; 16% Fe_3O_4), magnetite, cuprous and cupric oxides are recorded for the range 70—300° Abs. Except in the case of cuprous oxide, the specific heat curves exhibit discontinuities. The smoothed curves are represented by the sum of Debye and Einstein functions, whence the respective molal entropies (g.-cal./1°) at 25° are calculated to be 12·7±2; 34·69; 21·7±1; 9·75. S. K. Tweedy.

Heat capacities at low temperatures of the oxides of tin and lead. R. W. Millar (J. Amer. Chem. Soc., 1929, 51, 207—214).—The molal heat capacities of stannous and stannic oxides, red lead, and lead dioxide are recorded for the range 70—300° Abs. (cf. Millar, A., 1928, 936). Except in the case of red lead the specific heats are represented as the sum of Debye and Einstein functions, whence the respective molal entropies at 25° are calculated to be (g.-cal./1°): 13·56, 12·51, 60·53, and 18·27. The molal free energies (ΔF) at 25° are —123540, —147270, —52010, and the heats of formation (g.-cal. evolved) 137800, 172440, and 65960, respectively, for the last three oxides. The molal entropies (g.-cal./1°), free energies (g.-cal.), and heats of formation (g.-cal. evolved) are, at 25°, 16·41, —44887, and 51960, respectively, for yellow litharge, and 15·62, —45050, and 52360, for the red modification. S. K. Tweedy.

Absolute zero of temperature ; specific heats of gases ; and deductions respecting quanta. F. H. Loring (Chem. News, 1928, **137**, 370 ; 1929, **138**, 18—22, 81).—Speculative. C. W. Gibby.

Specific heat of lead at the temperature of liquid helium. W. H. Keesom and J. N. van den Ende (Physikal. Z., 1928, **29**, 896—897).—The work of Keesom and Andrews (A., 1927, 1131) has been repeated using an improved technique. For the region 10—20° Abs. the earlier data are confirmed. The present work is in agreement with the Debye curve with $\theta=88$ even in the region 3—6·5° Abs. to which the T^3 law applies, so that discrepancies in the earlier work now disappear. At 7° Abs. a marked deviation persists, but since a similar deviation occurs when bismuth is studied instead of lead, the discrepancy may be due to an instrumental defect. R. A. Morton.

Supercooled water. L. Hawkes (Nature, 1929, **123**, 244).—Water remains liquid at $-9°$, but when suddenly cooled to $-12°$ or $-17°$ it solidifies without crystallisation. A. A. Eldridge.

Surface tension constants in an homologous series from the point of view of surface orientation. K. W. Hunten and O. Maass (J. Amer. Chem. Soc., 1929, **51**, 153—165).—The surface tensions (capillary-rise method) and densities of some fatty acids and of dicetyl were measured up to about 150° and, in the cases of hexoic and propionic acids, down to $-20°$ and $-36°$, respectively. The acids exhibit zero angle of contact with glass. The total surface energy of fatty acids rapidly reaches a series constant. The series constant for the paraffins is apparently reached much more slowly. These two series constants approach one another. The surface orientation of pure liquids, unlike that of water, is probably incomplete, and it is unlikely that abnormally high values of the Ramsay and Shields constant, K, can be accurately interpreted in terms of complete orientation. A partial orientation may be the cause both of the high values of K and of the regularities in the series constants. The value of K for a fatty acid containing n atoms of carbon is given by $n^{\frac{1}{2}}\times 2{\cdot}12/3{\cdot}95$. The deviations from the normal values both of K and of the parachor parallel one another in the case of the fatty acids and may be due to the same cause. S. K. Tweedy.

Determination of the density of liquids. J. Grindley (J.C.S., 1928, 3297—3298).—The method of Hartley and Barrett (*ibid.*, 1911, **99**, 1072) has been modified in order that the densities of more expansible liquids may be derived over a range of temperature. F. J. Wilkins.

Density and temperature. VII. W. Herz (Z. Elektrochem., 1928, **34**, 857—858 ; cf. A., 1927, 718, 927).—For 38 substances of widely different types, the ratios of the density of the liquid to the density of the saturated vapour at $\frac{9}{10}T_c$ and at $\frac{2}{3}T_c$ have been calculated from published data. In the first case the ratios are fairly concordant about an average value of 10, being highest for the alcohols (methyl alcohol 14·86) and lowest for gases (argon 6·88). At $\frac{2}{3}T_c$, the ratios are larger and become too divergent for a mean value to be given. The sequence also changes. L. S. Theobald.

Approximate prediction of vapour pressure. J. Chipman (J. Physical Chem., 1929, **33**, 131—135 ; cf. A., 1928, 1315).—Relationships between the heat of vaporisation, ΔH, the apparent heat of vaporisation, L', obtained from vapour-pressure data, and the heat of vaporisation ΔH_K derived from the Kistiakovski equation have been investigated. For a given class of liquids, the ratio between any two of these quantities at the b. p. is approximately constant. The ratio $L'/\Delta H_K$, called the "slope factor," g, can be estimated for most liquids from the tables which are given, and this factor and the normal b. p. suffice to establish an approximate vapour equation which is given as $\log P_{\text{atm.}}=-gT_b\log(82{\cdot}07T_b)/T+g\log(82{\cdot}07T_b)$. A method for correcting observed b. p. to normal pressure is also indicated. L. S. Theobald.

Vapour pressures of related compounds and the application of Dühring's rule. A. R. Carr and D. W. Murphy (J. Amer. Chem. Soc., 1929, **51**, 116—121).—The use of Dühring's rule for constructing vapour-pressure curves is discussed. The Dühring lines (the locus of points obtained by plotting the b. p. of a substance as ordinate against the b. p. of a reference substance at the same pressure) for a family of substances intersect in a common point. Graphs are given showing line families for aliphatic hydrocarbons, alcohols, anilines, esters, etc. In the case of organic acids the lines are parallel. S. K. Tweedy.

New equation of state. H. J. Brennen (Proc. Nat. Acad. Sci., 1929, **15**, 11—18).—Van der Waals' equation is criticised, and a parameter is shown to be missing. The equation is modified by substituting a/V^n for the term a/V^2 due to the cohesive pressure of the molecules, and n is regarded as the missing third parameter. It is shown that the reduced values a_r, b_r, and n are interconnected by simple relationships, and are definite single-valued functions of the critical ratio K. An exponential function is proposed for a, and it is shown that two substances will exactly obey the law of corresponding states only when they have the same values for both K and $\partial P_r/\partial T_r$ at the critical point. N. M. Bligh.

New equation of state for fluids. II. Application to helium, neon, argon, hydrogen, nitrogen, oxygen, air, and methane. III. Normal densities and compressibilities of several gases at 0°. J. A. Beattie and O. C. Bridgeman (J. Amer. Chem. Soc., 1928, **50**, 3133—3138, 3151—3157).—II. The equation of state previously proposed (A., 1927, 819) is applied to the above gases between $-252°$ and $+400°$ and up to 100—200 atm. The average deviation between the observed pressures and those calculated from the equation is 0·18%. A method of converting compressibility results in the form of isothermals into the form of isometrics is given, which smooths the results with respect to volume. A method of evaluating the constants in the equation is outlined.

III. The equation of state is used to calculate the compressibility coefficients of the above gases and of carbon dioxide at 0°, and thence their mol. wt. The results agree well with the accepted values. The agreement is also good in the cases of carbon monoxide and nitrous oxide when the mol. wt. of these gases are calculated using in the equation the constants of their isosteres, nitrogen and carbon dioxide, respectively (cf. Langmuir, A., 1919, ii, 506). S. K. Tweedy.

Allotropic modifications of phosphorus. A. Smits (Compt. rend., 1929, **188**, 390—391; cf. this vol., 127).—The possible forms of the vapour pressure–density curves of phosphorus are discussed on the assumption of the existence of four or three of the allotropic modifications proposed (cf. Nicolaïev, A., 1928, 827). J. Grant.

Compressibility of thallium, indium, and lead. T. W. Richards and J. D. White (J. Amer. Chem. Soc., 1928, **50**, 3290—3303).—The following compressibilities (in megabar$^{-1}\times 10^6$) are recorded for pressures between 100 and 500 megabars and at 24·84°: toluene, 70·9; lead, 2·40; thallium, 2·83; indium (*d* 7·296), 2·55; indium containing 3% of zinc (*d* 7·292), 2·51 (the value calculated by the mixture rule is 2·52). Details for the preparation of the metals in the pure state are given. The periodic variations of thermal pressure, internal pressure, and other properties of the elements, as calculated by Richards' equation of state, are discussed with particular reference to the gallium, indium, and thallium group. These elements seem to occupy sub-maximum points in the upward slope of the periodic curves previously given (A., 1915, ii, 518). S. K. Tweedy.

Compressibility of sodium, barium, and beryllium. T. W. Richards, L. P. Hall, and B. J. Mair (J. Amer. Chem. Soc., 1928, **50**, 3304—3310).—The following compressibilities (in megabar$^{-1}\times 10^6$) are recorded for 25° for the following very pure metals: barium (*d* 3·661) 10·48; beryllium (*d* 1·85) 0·927. The preliminary value of 7·22 is recorded for strontium (*d* 2·737), whilst the value previously recorded for sodium (15·6) is confirmed. Special methods of weighing barium and strontium, and of measuring their densities pycnometrically, are described. S. K. Tweedy.

Tube correction in measurements of the velocity of sound in gases. R. E. Cornish and E. D. Eastman (Physical Rev., 1929, [ii], **33**, 90—96).—The validity of the Helmholtz–Kirchoff equation for the velocity change of sound in a tube is examined, and it is concluded to be correct for fairly high frequencies and large tube diameters, but not wholly satisfactory for low frequencies and small tubes. An approximation is deduced for the variation of the correction with temperature. N. M. Bligh.

Internal friction of atomic hydrogen. P. Harteck (Z. physikal. Chem., 1928, **139**, 98—106).—An apparatus is described by which the internal friction of a mixture of atomic and molecular hydrogen and the concentration of atomic hydrogen in the mixture may be determined. Experiments have been carried out at −80°, 0°, and 100° with mixtures containing 58—67% of atomic hydrogen. The values found for the internal friction of atomic relative to that of molecular hydrogen are 0·925 at −80°, 0·792 at 0°, and 0·775 at 100°. From these the absolute value at 0° is calculated to be $(690\pm25)\times10^{-7}$. The temperature coefficient of the internal friction for atomic hydrogen is very small. The following values have been calculated for atomic hydrogen: the free path 130×10^{-7} cm., the active cross-section of the atoms present in 1 c.c. under normal conditions $1{\cdot}36\times10^4$ sq. cm. R. N. Kerr.

Viscosity and flow-orientation. S. Kyropulos (Physikal. Z., 1928, **29**, 942—947).—Viscosity–temperature curves have been determined for several saturated hydrocarbons. The curves show that in addition to the normal effect due to change in density the breakdown of complexes must be an important factor. The types of complexes and the influence they exert on viscosity are discussed. It is shown that the flow-orientation of the molecules of liquids is of importance to lubrication and other stream processes. R. A. Morton.

Variation with direction of the capillary constant of smectic substances. R. Gibrat (Compt. rend., 1929, **188**, 183—185).—Gauss' theory of capillarity is applied to smectic substances, and expressions are obtained for the capillary constant which indicate the existence of two minimum values, corresponding with planes passing through the axis and perpendicular to it. J. Grant.

Equation of state for gaseous mixtures. I. Application to mixtures of methane and nitrogen. J. A. Beattie (J. Amer. Chem. Soc., 1929, **51**, 19—30).—The equation of state previously proposed (cf. A., 1927, 819) applies to mixtures of methane and nitrogen, those constants in the equation containing the dimension of density to the first power being linearly combined in proportion to the relative amounts of each gas, *e.g.*, $b_{\text{mix}}=b_1(1-x)+b_2x$, where x is the mol. fraction of the second constituent, whilst the A constant is given by $A_{\text{mix}}=[\sqrt{A_1}(1-x)+\sqrt{A_2}x]^2$. A general algebraic equation in thus obtained for gaseous mixtures, and this can be thrown into the virial form (cf. A., 1928, 1315). S. K. Tweedy.

Pressures of gaseous mixtures. II. Helium and hydrogen, and their intermolecular forces. C. W. Gibby, C. C. Tanner, and I. Masson (Proc. Roy. Soc., 1929, **A**, **122**, 283—304; cf. Masson and Dolley, A., 1923, ii, 462).—Full details are given of measurements of the compressibilities, up to 125 atm., of helium, hydrogen, and ten mixtures of the two gases at 25°, and of both pure gases and an equimolecular mixture at seven temperatures from 25° to 175°. All the mixtures deviate from Dalton's partial pressure law, in the sense of yielding actual pressures higher than the additive figures. The deviation is at a maximum in equimolecular mixtures, where it reaches, at 25°, about 4% of the ideally additive pressure. Within a certain range of compositions, mixtures of the two gases are more incompressible than either constituent. The data may be expressed by $pv=a+bp$, and values of a and b are recorded for each gas and each temperature. Values of b are plotted against gas composition, and, applying Lennard-Jones' partial pressure equation (A., 1927, 727), the measurements are shown to support the assumption that the intermolecular forces in helium and hydrogen are spherically symmetrical about each molecule. The influence of temperature on the constants of the isotherms was studied, and the results confirm Lennard-Jones' theory of superposed forces of attraction and repulsion around each molecular centre in an encounter. The distance indices of these forces have been evaluated for encounters between 2He, between $2H_2$, and between He and H_2. If the distance index for the attractive component is -5, then the index for the repulsive component is found to be -10 or -11 in all three cases. The force constants are evaluated; regarding the constants for the attractive components of force, that between 2He is only about one fourth of that between $2H_2$, and that between He and H_2 is slightly larger than the value for 2He. The "cohesion energy" for each type of encounter is defined and tabulated, together with the kinetic diameter (the distance of closest approach) appropriate to various temperatures. The joint kinetic diameter when a helium atom meets a hydrogen molecule is practically the average of the respective kinetic diameters when each molecule meets its own kind.

L. L. BIRCUMSHAW.

Viscosity of mixtures of rare gases. I. A. NASINI and C. ROSSI (Gazzetta, 1928, 58, 898—912).—With the apparatus previously described (A., 1928, 1084) the viscosities of mixtures of helium and krypton containing 10·21—94·54% Kr have been measured at 16—27° and at 100° approx. A simple device for ensuring intimate mixture of the small quantities of gases used is described. The viscosity–composition curves show a maximum viscosity for 38% Kr at 16° and 43% at 100°. These are considered to be in fair agreement with the theoretical maxima at 30 and 35% Kr, respectively, calculated by means of Thomsen's modification of Puluj's formula (cf. following abstract). In the case of mixtures of helium and neon no maximum is possible from the formula, and preliminary measurements of the viscosities of such mixtures confirm this.

O. J. WALKER.

Viscosity of gaseous mixtures. A. NASINI and C. ROSSI (Gazzetta, 1928, 58, 912—921).—The relationship of Puluj connecting the viscosity of a gaseous mixture with those of the constituent gases has been critically examined with reference to the explanation of the gradual disappearance of the maxima in the viscosity–composition curves as the temperature is raised. The partial pressure (x) of the constituent with the higher mol. wt. (m_2) in the mixture of maximum viscosity is given by the expression derived from Puluj's formula $x=3/(c-1)-4/(a-1)$, where $a=m_2/m_1$ and $c=(\eta_1/\eta_2)^{3/2}(m_2/m_1)^{3/4}$ (cf. Thomsen, A., 1912, ii, 23). Since $1>x>0$ and $a>1$, the limits of η_1/η_2 between which a maximum is possible can be determined. The variation of η_1/η_2 with temperature is discussed. Using the Sutherland function connecting temperature and viscosity, the temperature limits between which a maximum viscosity is possible can be calculated. The maximum is restricted to definite temperature limits only in the case of certain mixtures. In other mixtures there is either a maximum at all temperatures or no maximum is possible. The experimental results bear out these conclusions.

O. J. WALKER.

Viscosity of supersaturated solutions. II. I. K. TAIMNI (J. Physical Chem., 1929, 33, 52—68; cf. A., 1928, 578).—The viscosities of supersaturated solutions of sucrose, carbamide, acetamide, citric acid, and sodium thiosulphate in water, of resorcinol, acetamide, and urethane in ethyl alcohol, and of phenanthrene and urethane in toluene have been measured by means of the apparatus previously employed (*loc. cit.*). The most pronounced supersaturation occurs with the solvent of greatest association. The curves viscosity–concentration, viscosity–temperature, $\log\eta$–temperature, and $\log\eta$–concentration and data for 10—50° are reproduced. The Arrhenius equation $\log\eta/\eta_0=\theta C$ is not applicable to these solutions, but either of the equations $\eta=mC+n$ or $\log\eta=\theta C+\phi$, where θ, ϕ, m, and n are constants depending on temperature, can be applied. The temperature coefficients of viscosity for all solutions increase with increasing concentration and with a fall in temperature. Under certain conditions, relative viscosity, concentration, and temperature can be connected by an equation of the type $\log\eta'=(kt+k')c$, which, in this instance, holds for solutions of sucrose in water.

L. S. THEOBALD.

Theory of concentrated solutions. VI. Application of thermal analysis to the determination of the f.-p. curves of binary mixtures of organic compounds of low m. p. J. TIMMERMANS (Bull. Soc. chim. Belg., 1928, 37, 409—423).—Using a thermo-couple the f.-p. curves of the binary mixtures of benzene with *n*-hexane and chloroform, *cyclo*hexane with methyl*cyclo*hexane, *n*-hexane, toluene, carbon tetrachloride, and chloroform, ethylene bromide with ethyl bromide and aniline, nitrobenzene with carbon disulphide and ethyl acetate, aniline with carbon tetrachloride, toluene, and acetone, carbon tetrachloride with chloroform, carbon disulphide, and acetone, and chloroform with *n*-hexane, toluene, and carbon disulphide have been investigated. Additive compounds are formed by chloroform with benzene and toluene, and by acetone with aniline. *cyclo*Hexane has a transition point at −91°.

J. S. CARTER.

Solutions. II. F.-p. diagrams and latent heats of evaporation of binary mixtures of volatile liquids. III. The transition point of carbon tetrachloride and compounds of carbon tetrachloride or chloroform with acetone, ether, and benzene. W. F. WYATT (Trans. Faraday Soc., 1929, 25, 43—48, 48—53; cf. A., 1928, 1085).—II. F.-p. curves have been determined for the systems methyl alcohol–chloroform, ethyl ether–carbon tetrachloride, ethyl acetate–carbon tetrachloride, and ethyl bromide–benzene. Cryoscopic evidence is found for the existence of the compounds MeOH,$CHCl_3$, Et_2O,CCl_4, CCl_4,$2Et_2O$, and CCl_4,2Me·CO_2Et. The f.-p. diagrams are considered in relation to the curves for the latent heats of vaporisation of the systems. The form of the latent heat curves for systems containing carbon tetrachloride indicates that compounds of this substance are not stable at elevated temperatures. The latent heat curve for the system MeOH–$CHCl_3$ shows two maxima and two minima.

III. The transition point at about −48·5° in the systems ethyl alcohol–carbon tetrachloride, ethyl ether–carbon tetrachloride, and ethyl acetate–carbon tetrachloride has been observed also in mixtures of acetone and of carbon disulphide with carbon tetrachloride. It is inferred from this and from the data of other workers that the break is due to the existence of two crystalline modifications of carbon tetrachloride, and it is suggested that observations of this transition point in a binary mixture would be preferable to the use of the pure substance as a fixed temperature in thermometry. The f.-p. curves for the systems benzene–carbon tetrachloride and ethyl ether–carbon tetrachloride have been determined, and in conjunction with curves for other systems evidence has been obtained for the existence of the following compounds: $C_6H_6,2CCl_4$, stable only in mixtures containing more than 71% of carbon tetrachloride; C_6H_6,CCl_4, stable only in the presence of more than 52% of carbon tetrachloride; $COMe_2,CCl_4$, stable only in the presence of more than 61% of acetone; $CHCl_3,3Et_2O$, unstable except in mixtures containing more than 84% of ether; $CHCl_3,2Et_2O$, more stable than the 1 : 3-compound, but only in the presence of more than 75% of ether; $CHCl_3,Et_2O$, stable, m. p. −99·5°; and $2CHCl_3,Et_2O$, stable at its m. p. −89·5°, and in excess of ether but not in excess of chloroform. The oxygen compounds are accounted for by supposing that a co-ordinate linking is formed by the oxygen atom of the one substance donating a lone pair of electrons to the chlorine atom of the halogen derivative. The etheric oxygen atom is seen to be a more powerful donator than a ketonic oxygen atom and the chlorine atoms of chloroform are more powerful acceptors than those of carbon tetrachloride. With benzene as a second component it is found that chloroform does not combine with it, although carbon tetrachloride is able to do so. F. G. Tryhorn.

Determination of vapour and liquid compositions in binary systems. I. Methyl alcohol–water. J. B. Ferguson and W. S. Funnell (J. Physical Chem., 1929, **33**, 1—8).—A description is given of a new type of apparatus by means of which the composition of the vapour in equilibrium with a binary liquid can be determined using only a small sample of liquid. Vapour is circulated over a weighed sample of liquid until equilibrium is obtained, the pressure is then measured, and finally a known volume of vapour is condensed and weighed. Data for the system methyl alcohol–water at 39·90° have been obtained and are critically examined, together with those of other investigators, by means of Miller's abacus (A., 1925, ii, 399). L. S. Theobald.

Vapour pressures in the systems ethyl phthalate with ethyl alcohol and with methyl alcohol. H. W. Foote and J. K. Dixon (Amer. J. Sci., 1929, [v], **17**, 146—152).—The vapour pressure–composition curves for these two systems have been determined at 25° by a static method. Both show wide deviations from the ideal and to approximately the same extent. As ethyl phthalate has a vapour pressure of approximately zero at 25°, the two systems give the partial pressures of alcohol vapour. R. N. Kerr.

Binary azeotropes. XII. M. Lecat (Ann. Soc. Sci. Bruxelles, 1928, **B 48**, i, 113—126; cf. A., 1928, 943).—A further list of binary organic mixtures is given containing 161 positive and 11 negative azeotropes, 27 eutectic mixtures, and a large number of euzotropes. The mixture of phenetole and *iso*amyl ether constitutes the first established case of azeotropy in which both the components are oxides. O. J. Walker.

New application of the differential ebullioscope. H. Swientoslawski (Compt. rend., 1929, **188**, 256—258).—The author's differential ebullioscope (A., 1927, 642), in which the b. p. of the solution (T_H) and pure solvent (T_B) are obtained simultaneously at a given pressure, has been used to distinguish between pure liquids and azeotropic mixtures. The pressure–temperature curves for these coincide when $T_H=T_B$, but at other pressures may be quite divergent. Mixtures of alcohol (32·41%) and benzene were studied. J. Grant.

Diffusion of hydrogen in iron. E. G. Mahin (Proc. Indiana Acad. Sci., 1927, **37**, 272—276).—Experiments support the view that hydrogen liberated by "pickling" oxide-coated iron diffuses into the metal in the atomic condition and is liberated at the surface as molecular hydrogen. Chemical Abstracts.

Diffusion in crystalline substances. C. Tubandt, H. Reinhold, and W. Jost (Z. anorg. Chem., 1928, **177**, 253—285).—A new method is described for measuring diffusion processes in solid salts. The rates of diffusion of the cations in silver sulphide, chloride, bromide, and iodide, and cuprous sulphide, bromide, and iodide have been determined. For the sulphides and for silver iodide the influence of temperature T on the diffusion rate D is given by $D=Ae^{-B/T}$, where A and B are constants. For the iodides D may be calculated from the equation $D=CT\mu$, where μ is the specific conductivity and C a constant. The self diffusion D_0 may be calculated from the observed diffusion rates by use of conductivity and transport data for the pure salt and for the mixed crystals; $D_0=D\mu_1(1-m)/\mu_2(1-n)$, where n and $1-n$ are the transport numbers and m and $1-m$ the fractional molar concentrations of the mobile ions in the mixed crystal. The self-diffusion of solid salts may be calculated approximately from the conductivity by means of the equation applicable to solutions, viz., $D=RTB/N$, where B is the mobility. H. F. Gillbe.

Binary solutions of consolute liquids. W. D. Bancroft and H. L. Davis (Proc. Nat. Acad. Sci., 1929, **15**, 8—10).—A generalised form of equation for Raoult's law is proposed, and this is shown to give satisfactory results when applied to ethyl alcohol and water, and to acetone and ethyl ether. A method is described which permits of the derivation of the distribution of a substance between two miscible liquids, and this is applied to the distribution of acetone between methyl alcohol and water. N. M. Bligh.

System *o*-cresol–methyl alcohol–water. G. von Szelényi (Z. Elektrochem., 1929, 35, 33—37).—Measurements have been made of the mutual solubility of *o*-cresol, methyl alcohol, and water, and a series of curves is constructed for ten mixtures of methyl alcohol and water (varying from 0 to 44·3% of methyl alcohol) showing the effect of adding increasing amounts of *o*-cresol on the mutual miscibility temperatures. The binodal curves of the system are also reproduced. It is found that the solubility of *o*-cresol in methyl alcohol–water mixtures decreases with decreasing concentration of alcohol, and that the critical solution temperature rises. A mixture of pure *o*-cresol (39·5%) and water (60·5%) has a critical solution temperature of 169·7°. L. L. Bircumshaw.

Influence [of alkali and alkaline-earth halides] on solubility. W. Herz and F. Hiebenthal (Z. anorg. Chem., 1928, 177, 363—380).—The effect of the halides of alkali and alkaline-earth metals on the solubility of potassium chromate, potassium permanganate, phenol, mercuric oxide, potassium dichromate, iodine, and several organic acids was determined. In the case of the three potassium salts the reverse effect was also investigated. The salts were added in varying concentrations. In most cases it was possible to represent the change in solubility by a simple linear equation, but sometimes the relationship was logarithmic in form. The effect on the solubility depends to a certain extent on the at. wt. of the added cation. A. J. Mee.

Solubility of complex cobalt and chromium precipitates. I. A. Benrath [with K. Mienes, H. Steinrath, and K. Andreas (Z. anorg. Chem., 1928, 177, 286—302).—The solubilities of hexammine-, pentammine-, tetrammine-, and diethylenediamine-chromic and -cobaltic complexes in solutions containing ammonia and in acid solutions which contain a common ion at varying concentrations have been determined at 25°, and the nature of the compounds which are stable in contact with these solutions has been established. H. F. Gillbe.

Distribution of ammonia between water and chloroform at 25°. H. G. Dietrich (J. Physical Chem., 1929, 33, 95—98).—The distribution coefficient in the system water–ammonia–chloroform has the value 35·8±0·1 at 25°, when expressed as the ratio number of g.-mol. ammonia per 1000 g. of water/number of g.-mol. ammonia per 1000 g. of chloroform. The value varies with the source of the chloroform, an effect attributed to traces of impurities used to inhibit hydrolysis of this reagent. An attempt to extend the study of this system to zinc hydroxide failed on account of the length of time required to attain equilibrium and the consequent hydrolysis of the chloroform. L. S. Theobald.

Adsorption from solution by ash-free adsorbent charcoal. E. J. Miller (Fifth Colloid Symposium Monograph, 1927, 55—80).—Pure sugar charcoal, and other pure charcoals, absorb acids, but not inorganic bases; only the anion of neutral salts of inorganic acids is adsorbed, whilst the absorption of salts of organic acids is partly hydrolytic and partly molecular. By the addition of certain impurities to the charcoals, adsorption anomalies as recorded in the literature could be observed. With hydroxy- and amino-benzoic acids absorption decreases in the order *o*-, *p*-, *m*-; chloro- and dichloro-acetic acids are more strongly adsorbed than acetic, whilst glycine is not adsorbed. With butyric, valeric, and hexoic acids the *iso*-compounds are less strongly adsorbed than the *n*-compounds. Adsorption increases in the order, ammonium, trimethylammonium, triethylammonium hydroxide. Acids adsorbed on charcoal are incapable of inverting sugar. The hydroxyl ion shows negative adsorption. Pure charcoal has no isoelectric point. Chemical Abstracts.

Adsorption of certain vapours by charcoal at various temperatures up to and above their critical temperatures. J. N. Pearce and C. M. Knudson (Proc. Iowa Acad. Sci., 1927, 34, 197—212).—The adsorption isotherms for water vapour differ from those for ethyl and methyl alcohol, ammonia, and methylamine, and indicate that retention of water is probably due merely to capillary action. Freundlich's relation applies, except near saturation, to the alcohols and ammonia, but not to water or methylamine. The applicability of other relations is investigated. Chemical Abstracts.

Adsorption of the fluorine ion. B. Tamamushi (Kolloid-Z., 1929, 47, 58—60).—Comparison of the adsorption of fluorine ions and of chlorine ions by pure sugar charcoal from solutions of potassium fluoride and potassium chloride respectively shows that, in spite of the greater hydration of the fluorine ion, it is adsorbed more strongly than the chlorine ion. This is explained as a hydrolytic adsorption, the solution becoming faintly alkaline, and by a displacement of the equilibrium at the carbon surface, favouring complex formation in the fluoride solution. In agreement with this view, sugar charcoal adsorbs two to three times as much fluorine ions as chlorine ions from pure solutions of the corresponding acids. E. S. Hedges.

Application of Langmuir's theory of the adsorption of gases on charcoal. M. Pólányi (Z. physikal. Chem., 1928, 138, 459—462).—A reply to Zeise's criticism (cf. A., 1928, 1182) of Pólányi's theory. For a number of systems to which the Langmuir adsorption isotherm is apparently applicable, further observations suggest that the agreement is fortuitous. A. J. Mee.

Adsorption of gases and vapours by different kinds of silica gels. E. Bosshard and E. Jaag (Helv. Chim. Acta, 1929, 12, 105—113).—Thirteen silica gels have been prepared by treatment of water-glass solutions of various concentrations with either hydrochloric or acetic acid or ferric chloride. Different methods of drying and activation have been used for the various gels. The adsorption of sulphur dioxide and bromine vapour has been measured and in both cases this is found to be dependent on the mode of preparation of the gel. Those produced from the more dilute water-glass solutions and subjected to the slowest activation have the greatest power of adsorption of sulphur dioxide. Adsorption of this gas causes a dark brown coloration of the gel. In the case of bromine vapour, adsorption is accompanied by condensation phenomena. The extent of the latter depends on the size of the pores of the gel, which is determined by the method of activation. The size of the particles of the gel has no influence on the power of adsorption of either sulphur dioxide or bromine. The heat produced on wetting the gel with alcohol has been measured and considerable differences have been found amongst the different kinds. The swelling powers of the gels have been measured by the method of Pavlov (A., 1927, 722). The weight of finely-powdered product obtained per c.c. of gel and the resistance to pressure have also been measured.

R. N. Kerr.

Siloxen as adsorbent. H. Kautsky and G. Blinoff (Z. physikal. Chem., 1928, **139**, 497—515).—The structure of siloxen is further discussed (cf. A., 1926, 924) and its simplicity compared with that of other adsorbents, especially carbon, is emphasised. Specific gravity determinations support this view. Siloxen is a good adsorbent for both gases and dissolved substances, although it is less active than specially-prepared carbon adsorbents. The addition of alcohols and fatty acids to siloxen during its preparation brings about, in many cases, a loosening of the structure and this effect increases with the higher members of an homologous series. It appears to be connected with adsorption of the substance by the siloxen to some extent, but it also depends on the polar nature of the substance. Acetone, which is markedly adsorbed, and ketones in general have no effect, however, on the physical structure of the siloxen. The adsorption isotherms of the first five members of the fatty acids in aqueous solution have been determined and are in good agreement with Traube's rule. Alcohols, benzoic acid, phenol, and phenylthiocarbamide also are adsorbed and certain dyes are decolorised, but this last effect may be due to reduction. Aniline hydrochloride is adsorbed only by oxidised siloxen; hydrolytic adsorption occurs, the positive ions only being fixed. Compared with other adsorbents, the simple and definite nature of the surface, which can be easily controlled, makes siloxen especially suitable for the study of adsorption phenomena.

L. S. Theobald.

Adsorption of carbon dioxide by ferric hydroxide. J. Tillmans, P. Hirsch, and K. Schilling (Kolloid-Z., 1929, **47**, 98—101).—In connexion with the question whether the corrosion of iron is related to an adsorption of carbon dioxide by ferric hydroxide, measurements have been made of the adsorption of carbon dioxide (both in the free state and as hydrogen carbonate) by precipitated ferric hydroxide. Adsorption was found to occur. The freshly-precipitated hydroxide did not differ from a preparation 8 days old, but ferric hydroxide precipitated from a hot solution adsorbed less than the precipitate formed in the cold. When the amount of sodium hydrogen carbonate was kept constant, the amount of carbon dioxide adsorbed increased with the concentration of carbon dioxide in the solution, and when the amount of carbon dioxide was kept constant, the carbon dioxide adsorbed increased with the concentration of sodium hydrogen carbonate. The adsorption is considered to be due to the formation of a complex of the type $Fe(OH)\cdot CO_3,xFe(OH)_3$.

E. S. Hedges.

Adsorption of the alkali metals on a mercury–vacuum interface. R. S. Bradley (Phil. Mag., 1928, [viii], 6, 775—779).—The results of Schmidt (A., 1913, ii, 190) and Oppenheimer (A., 1928, 702) for the surface tensions of alkali metal amalgams are used in conjunction with those of Bent and Hildebrand (A., 1928, 130) for the activities of the alkali metals dissolved in mercury to calculate the Gibbs surface excess $\Gamma.d\sigma/d(\log a_2)$=constant where σ=surface tension and a_2=activity of the dissolved metal. The results combined with those of Bragg (A., 1920, ii, 537) for the atomic radii of the metals indicate that the surface layer is characterised by compounds of mercury with sodium and potassium, the composition of which corresponds approximately with one alkali metal atom for six mercury atoms. In cæsium amalgams no such compounds are indicated.

A. E. Mitchell.

Adsorption of potassium chromate on zinc. R. F. Reed and S. C. Horning (J. Physical Chem., 1929, **33**, 136—137).—Aqueous solutions of potassium chromate react with a zinc surface, depositing on it a compound of chromium and making it less active towards methyl-violet. A 20% solution of potassium chromate yielded 0·003 mg./cm.^{2} of adsorbed chromate on the zinc. Treatment of zinc with potassium chromate solution lessens the amount of moisture which it can adsorb.

L. S. Theobald.

Adsorption of iodine on calcium fluoride. J. H. de Boer (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 906—914).—Adsorption isotherms for iodine on calcium fluoride have been determined. A theoretical explanation is offered.

C. W. Gibby.

Surface tension of solutions. I. Influence of salts on surface tension of aqueous solutions of urethane. The determinations. II. Calculation of surface tension from the drop-weight. III. Influence of salts on surface tension of aqueous solutions of urethane. Discussion of results. S. Palitzsch (Z. physikal. Chem., 1928, **138**, 379—398, 399—410, 411—431).—I. The drop-weight method was used to determine the influence of salts on the surface tension of aqueous solutions of urethane. Twenty-six salts of various kinds were used, and also hydrochloric acid. Tables are given showing the results of determinations on some four hundred solutions. The accuracy is about 1 in 500.

II. Modifications are made in the methods of Morgan and Harkins, making them simpler and more rapid. It is shown that the calculations of Iredale are not fundamentally different from those of Harkins. The radius of the dropping tube is calculated from the drop-weight of water, and the accuracy of the improved method of calculation is tested by determining the surface tension of benzene, for which a value is obtained in good agreement with that found by Sugden.

III. The results obtained in section I are re-grouped and discussed. The dependence of the influence of salts on their concentration can be investigated in two ways, first by using a solution with constant urethane concentration and variable salt concentration, and, secondly, by the reverse method of using solutions with variable urethane and constant salt concentrations. Curves are drawn for both methods. Those which are drawn for solutions containing the same salt concentration but different urethane concentrations are very similar. They cross the curve for the surface tension of salt-free urethane solutions. The maximum lowering of the surface tension by a given quantity of a salt is in a remarkable way characteristic for that salt. Salts can be divided up into two groups according to their influence on the surface tension. In the first group are salts with bivalent acid radicals. The second contains salts with univalent acid radicals. The influence of the first class is more than double that of the second. Phosphates seem to produce a large effect, but the salt which has the greatest influence is potassium ferrocyanide. A peculiarity was noted in the fact that different preparations of potassium chloride did not give the same results although all were chemically pure. The interfacial surface tension of solutions in equilibrium with urethane solution was determined. The action of hydrochloric acid was also investigated; it differs somewhat from the action of salts. A. J. MEE.

Rate of evaporation through surface films. R. BARTLETT and T. C. POULTER (Proc. Iowa Acad. Sci., 1927, **34**, 214—215).—Experiments with solutions of calcium and sodium chlorides show that the rate of evaporation is slightly influenced by the surface tension of the liquid. CHEMICAL ABSTRACTS.

Influence of adsorbed films on rates of evaporation. R. P. BELL (J. Physical Chem., 1929, **33**, 99—117; cf. A., 1928, 848).—The rate of evaporation of chlorine from solution in carbon tetrachloride has been measured at 25° with varying chlorine concentrations and velocity of air current; the results are compared with various equations for the kinetics of evaporation in a current of gas. Measurements have also been made of the reduction in the rate of evaporation which is brought about by dissolving trichloroacetic acid in the carbon tetrachloride. The reduction is attributed to surface adsorption of the acid, and it would seem that a saturated surface film of the acid is formed at concentrations greater than 1·4% by weight. The surface tension of solutions of trichloroacetic acid in carbon tetrachloride has been determined by the drop-weight method; by the application of Gibbs' adsorption equation the lower limit of concentration for the formation of a saturated film is found to be 1·0—1·6% by weight, in good agreement with the value given above. The measurement of rates of evaporation is suggested as a general method for the investigation of adsorption phenomena in solutions.
L. S. THEOBALD.

Osmosis of ternary liquids. General considerations. VI. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 811—822).—A theoretical discussion of the directions in which substances will diffuse through membranes. The effects have been investigated experimentally for the system sodium dithionate–barium dithionate–water, with membranes of collodion and of collodion containing copper ferrocyanide and for the system ammonium chloride–ammonium succinate–water, with membranes of collodion, pig's bladder, cellophane, collodion containing copper ferrocyanide, and parchment. C. W. GIBBY.

Mineral trees: their formation and significance. M. COPISAROW (Kolloid-Z., 1929, **47**, 60—65).—A description is given of arborescent forms of several slightly soluble inorganic compounds, mainly salts of calcium, strontium, barium, and cobalt. The formation of gas bubbles is not essential for the production of these structures. An analogy is drawn between the production of tree formations on the one hand, and Liesegang rings and spiral formations on the other. E. S. HEDGES.

Liesegang rings as a periodic coagulation phenomenon. J. R. I. HEPBURN (J.C.S., 1929, 213).—The formation of Liesegang rings of basic cupric carbonate is described. The theory of Henley and Hedges (A., 1928, 1323) concerning this phenomenon is essentially the same as the earlier one of Freundlich. F. W. WILKINS.

Relation between concentration and equivalent refractive power of strong electrolytes in solution. H. KOHNER (Z. physikal. Chem., 1928, **B**, **1**, 427—455).—In employing the mixture rule and the Lorentz–Lorenz formula to determine the variation with the concentration of the equivalent refractive power of a dissolved substance, the principal sources of error lie in the determination of the difference between the refractive index and the density of the solution and solvent. The refractive powers in aqueous solution of lithium, barium, and aluminium chlorides, sodium bromide, lithium, sodium, ammonium, and aluminium sulphates, and sodium and barium chlorates from concentrations of about 2 g.-equiv./1000 g. of water up to saturation have been measured, usually at 25°, and prove in every case to be a linear function of the concentration, increase in which causes a slight rise or slight fall in the refractive power. For a particular salt, the equivalent dispersion does not vary with the concentration. Extrapolating the refractive powers to infinite dilution, it appears that at this dilution the refractive powers of electrolytes are constituted additively of those of their ions. The variation in refractive power with concentration may be explained by supposing that with increasing concentration more and more ions with opposite charges unite without interposition of water molecules. R. CUTHILL.

Measurement of refraction of solutions. W. GEFFCKEN and H. KOHNER (Z. physikal. Chem., 1928, **B**, **1**, 456—465).—By fitting the Pulfrich refractometer with a divided circle having finer divisions than that usually supplied, and substituting a helium tube for the sodium light and a microscope with cross-wires for the reading-lens, the accuracy of the instrument has been very considerably improved. The trough has also been modified in such a way as to permit of liquid being introduced and withdrawn rapidly and without risk of evaporation, or coming in contact with air. A new form of pyknometer capable of an accuracy of about 0·001%, when 20 c.c. of liquid are used, is described.
R. CUTHILL.

Relation between specific rotation and refractive index of a solution. W. PERSCHKE (Z. Elektrochem., 1929, **35**, 17—18).—Using Gumprich's data (Physikal. Z., 1923, **24**, 434) for solutions of camphor in ethyl alcohol, camphor in benzene, and tartaric acid in water, it is shown that the relation between the specific rotatory power and refractive index of a solution may be expressed by means of the following formula, which is independent of the concentration: $\log [\alpha]=a+b \log n$, where a and b are coefficients which are approximately constant for a given optically active solute in a given solvent.

L. L. Bircumshaw.

Rotatory power of tartrates of organic bases; study of strong electrolytes. E. Darmois (Compt. rend., 1929, **188**, 388—390).—The $[\alpha]_J$–concentration curves of ammonium tartrate and its mono-, di-, tri-, and tetra-methyl or -ethyl derivatives follow the order mentioned, the decrease in $[\alpha]_J$ being very high for tetraethylammonium tartrate, whilst for benzylamine tartrate there is a considerable increase. If it is assumed that the solutions contain only dissociated molecules, there is evidence that the decrease and increase are due respectively to dehydration and deformation of the tartrate ion. J. Grant.

Molecular structure in solution. IV. Densities, viscosities, and electrical conductivities of aqueous solutions of cobalt chloride and hydrochloric acid at different temperatures. O. R. Howell (J.C.S., 1929, 162—172).—The densities, viscosities, and electrical conductivities of two aqueous solutions, one containing 120 g. of $CoCl_2,6H_2O$ per litre with 4*N*-hydrochloric acid and the other hydrochloric acid alone, have been determined every 5° over the temperature range 0—80°. The difference curves are quite smooth, differing from those previously obtained (A., 1927, 1136) for solutions of cobalt chloride containing varying concentrations of hydrochloric acid. Consequently, the changes involved in the two essentially similar colour changes are fundamentally different. It is suggested that the change in the number of groups round the cobalt atom takes place by addition or subtraction of 2 molecules of water to both cation and anion on cooling and heating respectively. F. J. Wilkins.

Chemical fogs. H. O. Askew (Trans. Proc. New Zealand Inst., 1928, **59**, 165—207).

Unsolved problems in the molecular-kinetic behaviour of colloidal suspensions. E. O. Kraemer (Fifth Colloid Symposium Monograph, 1927, 81—112).—A discussion of the limits of validity of the simple kinetic theory, the causes of departure from ideal relationships, and the extent to which the electric charge or volume of colloidal particles may modify their behaviour. Chemical Abstracts.

Stability of submicrons. I. Crystal disruption, crystal formation, and emulsion formation. J. Traube and W. von Behren (Z. physikal. Chem., 1928, **138**, 85—101).—Evidence is adduced for the formation of submicrons in the process of dissolution of a number of compounds among which are potassium dichromate, boric acid, aluminium citrate, mercuric chloride, and arsenic trioxide. Complex salts of nickel, iron, and cobalt are especially prone to form submicrons during the process of dissolution. Conversely, the formation of submicrons appears as an intermediate stage in the separation from solution of many crystals, especially those of lead chloride. The stages generally recognised in the process of dissolution of a crystal are, respectively, (*a*) homogeneous crystal, (*b*) aggregate of parallel pearl-like cells, (*c*) scission into individual cells, and (*d*) scission of the single cells into submicrons. These stages occur in reverse order in the process of crystallisation. Experiments on the emulsification of chloroform by means of various peptising agents indicate that these agents are capable of forming submicrons of exceptional stability, and the number of these increases with the dispersion of the emulsion.

F. G. Tryhorn.

Colloidal gold. H. Nicol (J.S.C.I., 1928, **47**, 343—344T).—Pure red sols are produced by adding hydrogen peroxide or "hyperol" in alcoholic solution to a dilute alkaline solution of a gold salt. Reduction by alcohol alone is possible, but is influenced by the nature of the container. Reduction is hastened by hydrogen peroxide, which tends to form a sol containing aurous oxide; alcohol reduces the latter to metal. The reaction proceeds in the absence of actinic light. The blue colour of gold sols is due to two causes: (*a*) presence of oxide, (*b*) presence of aggregates. The latter is unalterable if it occurs, as when sodium peroxide is used. Based on the principles studied, a method is given for preparing red sols of high sensitivity.

Tartaric acid method of preparing negatively-charged sols. II. Colloidal nature of Fehling's solution. H. Dumanski and A. A. Chalisev (Kolloid-Z., 1929, **47**, 121—131).—Colloid particles can always be detected in alkaline solutions of copper tartrate. In a solution containing 1 mol. of copper hydroxide to about 1·5 mols. of tartaric acid and not more than 1 mol. of sodium hydroxide, the basic salt $CuC_4H_4O_6,Cu(OH)_2$ is present. This salt may also be formed by shaking copper hydroxide with an excess of copper tartrate in water; it is decomposed by more concentrated alkali solution. A colloidal basic salt, $3CuC_4H_4O_6,5Cu(OH)_2$, can be produced by mixing copper tartrate with an excess of copper hydroxide in water. When the system is gently warmed, a copper oxide sol is produced, which is negatively charged and may be purified by dialysis. Concentrated solutions of alkali cause coagulation. Copper tartrate is considered to react with sodium hydroxide in the same way as any other salt, but the copper hydroxide or basic salt remains in colloidal solution in consequence of the protective effect of organic hydroxy-compounds on negative sols. Complex tartrates of copper and the alkali metals cannot be prepared, and those the preparation of which has been claimed are said to consist of mixtures or solid sols of cupric hydroxide or basic salts in sodium tartrate crystals. Sols of cupric sulphide and of copper ferrocyanide may readily be formed from solutions of copper tartrate in sodium hydroxide. The cupric oxide sol in alkaline Fehling's solution is a strong oxidising and catalytic agent in virtue of its high degree of dispersion, and its colloidal nature is used to explain the phenomena of ageing, oxidation of sugars, formation of cuprous oxide sols, and other properties. E. S. Hedges.

State of copper and iron in alkaline solution in presence of hydroxylic organic substances. W. Bachmann (Kolloid-Z., 1929, 47, 49—55).—An examination has been made of the solutions formed when sodium hydroxide is slowly added to solutions containing copper or iron salts in presence of glycol, glycerol, mannitol, dextrose, sucrose, dextrin, and starch. The investigation was made by fractional dialysis using different membranes, ultramicroscopic examination, ultra-filtration, measurement of sensitivity to electrolytes, cataphoresis, and electrolysis, and the conclusion was reached that the dissolved metal is present partly as a colloid and partly as a crystalloidal complex, the relative proportions of the two states depending on the conditions. The sensitivity of such systems to hydrolysis decreases with increasing number of hydroxyl groups in the organic substance. E. S. Hedges.

System colloidal ferric hydroxide–hydrochloric acid–water. E. Heymann (Kolloid-Z., 1929, 47, 48).—A preliminary account of a study of equilibrium in aqueous ferric chloride solutions which have been allowed to age until the content of colloidal ferric hydroxide has become constant. It is shown that the quotient $[HCl]^3/[FeCl_3]$ is not constant, but undergoes a steady change with a variation of about 30%. This indicates that the active mass of the colloidal ferric hydroxide cannot be regarded as constant. The size of the particles also influences the equilibrium, and the chlorine content of the colloid particles is greater when they have been formed by hydrolysis than when the system has been prepared by adding hydrochloric acid to colloidal ferric hydroxide. E. S. Hedges.

Micellar state of starch. M. Samec (Kolloid-Z., 1929, 47, 81—82).—The author summarises his views and shows that they are not completely at variance with those of Malfitano (cf. A., 1928, 1186). E. S. Hedges.

Structures of clear sodium oleate gels and number of nuclei in these gels. R. Zsigmondy (Kolloid-Z., 1929, 47, 97—98).—The structures of sodium oleate gels obtained under different conditions are discussed. In those clear gels that show the presence of nuclei, the number of nuclei depends on the degree of supercooling in a similar way to the relation found with undercooled melts. E. S. Hedges.

Theory of emulsions. Wa. Ostwald (Kolloid-Z., 1929, 47, 131—132).—The author's "phase-volume theory" of emulsions (A., 1910, ii, 194) can be applied only to the ideal case of pure, two-phase, unprotected, strictly monodisperse systems. The application of the theory to polydisperse and protected emulsions is due to a misunderstanding (cf. Bancroft, A., 1912, ii, 542). E. S. Hedges.

Emulsions. I. Influence of soap content of both phases on the [stability of] the emulsion. J. Weichherz (Kolloid-Z., 1929, 47, 133—136).—With small amounts of soap as the emulsifier, oil-in-water emulsions are readily prepared, but stable water-in-oil emulsions are formed only in presence of larger amounts of soap. When such a water-in-oil emulsion is diluted with water a phase reversal occurs at a critical phase-volume relation, with formation of an oil-in-water emulsion. This critical phase-volume relation is not connected with the phase-volume theory of Wa. Ostwald (A., 1910, ii, 194), for the critical point is a function of the soap content. E. S. Hedges.

Absorption of light in colloid systems as a function of the layer thickness. E. Galvez (Kolloidchem. Beih., 1929, 28, 148—154).—Theoretical. E. S. Hedges.

Scattering of light in colloidal solutions and gels. I. Agar sol and gel. K. Krishnamurti (Proc. Roy. Soc., 1929, A, 122, 76—103).—Previous work is summarised and methods are described for measuring the relative intensity and degree of depolarisation of the light scattered by agar sols and gels over the range 10—80°. In reference to these measurements the nature of gelatinisation is discussed. Agar sols are considered as colloids having as the intermicellary liquid a molecular solution of agar. On cooling to about 35°, the hydration of the colloid particles increases appreciably and the intermicellary solution becomes supersaturated. As a result, fresh colloid particles are formed, and when these are sufficiently numerous, further supersaturation is relieved by the condensation of the dissolved agar on the particles already present in the sol. This brings about an increase in the size of the particles, and tends to make them more spherical in shape. The phenomenon of gel-formation is essentially due to the union of the hydrated particles enmeshing the intermicellary liquid, and it is particularly emphasised that the precipitation tendency is not always the main factor which is responsible for gelatinisation. A comparison of the light-scattering capacity of agar sols and gels at the same temperature shows that gels are distinctly more opalescent, and that with rise of temperature the difference between the sol and gel tends to diminish. This suggests that the micelles present in gels are bigger than those in sols at the same temperature. The intensity (I) of the scattered light increases with the concentration of the sols and gels. The regular increase with concentrations of the ratio of I in the sol and gel states indicates that the micelles in the concentrated gels are bigger and more numerous than in the dilute gels. The intensity of the light scattered by agar sols increases with time at and below 35°, until finally a constant value is reached, and the lower the temperature the more rapid is the change. The effect of sudden cooling of agar sols on the light-scattering capacity of the gel was investigated, and in all cases gel-formation was accompanied by a distinct increase in the Tyndall number. The depolarisation factor θ of the light scattered by agar sols and gels was also found to vary with temperature and concentration. With concentrated sols (2·0%) θ increases regularly as the temperature is lowered below 33°, whilst in dilute sols (0·2%) θ decreases with fall of temperature, and with 0·5% sols θ decreases at first to a minimum and then rises. The light thrown by these results on the changes in size and shape of the gel particles is discussed. L. L. Bircumshaw.

Behaviour of cellulose nitrate gels in polarised light. A. J. Phillips (J. Physical Chem., 1929, 33, 118—130; cf. Tissot, B., 1926, 723).—Various commercial cellulose nitrates have been examined in polarised light. The colours exhibited by samples of varying nitrogen content depend on the degree of dispersion of the cellulose nitrate, which, in turn, is affected by the percentage of water in the nitrating bath, by the ratio of nitric to sulphuric acids, the time and temperature of nitration, viscosity, reduction processes, ultra-violet light, heat, and superheated water. The degree of dispersion effected by nitration to a definite nitrogen content is a more powerful factor in determining the colour exhibited with polarised light than is chemical constitution. The transmitted light ranges from red to blue as the degree of dispersion decreases. L. S. THEOBALD.

Silver nuclear sol and its derivatives. I. Action of light on these sols. A. GAŁECKI and R. SPYCHALSKI (Z. anorg. Chem., 1928, **177**, 337—344).—The sensitiveness to light of a number of silver sols and derivatives has been measured in terms of the time required for complete decolorisation to be produced under irradiation by a quartz mercury arc lamp. The sensitiveness is greatest for those sols which contain the smallest particles, and dilution of the sols reduces the time needed for decolorisation. Irradiation produces a decrease of the viscosity of the sols, which, however, is less for aged sols than for those recently prepared. The viscosity of the decolorised sols, although very small, is diminished by further irradiation. After decolorisation the conductivity of the sols increases, but on further irradiation a considerable decrease of conductivity ensues; parallel changes occur in the optical properties of the sols. It thus appears that on prolonged irradiation colloidal particles are again formed. H. F. GILLBE.

Dielectric constants of silver sols when diluted with varying amounts of ethyl alcohol. G. D. ROCK and S. KLOSKY (J. Physical Chem., 1929, **33**, 143—147).—The dielectric constants of silver sols prepared by heating suspensions of freshly-prepared silver oxide in water to boiling, filtering hot, cooling, and reheating to 80°, have been measured at 23±1° in aqueous solutions containing up to 41·6% of ethyl alcohol. In agreement with Errera (A., 1923, ii, 388), the dielectric constants of the sols are substantially equal to those of the pure dispersion media.

L. S. THEOBALD.

Ionic equilibrium in colloidal solutions. H. D. MURRAY (J. Physical Chem., 1929, **33**, 138—142).—The stability of sols as affected by electrolytes is discussed in reference to the view that the colloidal particle first adsorbs the electrolyte, which is then free to dissociate in such a manner that the ion remaining attached to the particle is that having the same chemical nature as the particle itself.

L. S. THEOBALD.

Variations of electrical charge of colloidal particles. III. The influence of non-electrolytes on the cataphoretic speed of colloidal particles and the adsorption of ions by colloidal particles as indicated by such measurements. J. MUKHERJEE, S. RAI-CHOUDHURY, and A. N. RAO (J. Indian Chem. Soc., 1928, 5, 697—713; cf. A., 1928, 15).—Migration velocity measurements, at 35°, have been made with arsenious sulphide sols in presence of methyl, ethyl, and *iso*butyl alcohols, carbamide, sucrose, and acetone. In all cases the rate of migration (sec. volt/cm.$\times 10^5$) decreases with added non-electrolyte, irrespective of an increase (carbamide) or decrease (sucrose) in the dielectric constant of the medium. The potential of the double layer is not determined by the change in dielectric constant alone (cf. Freundlich, "Kapillarchemie," 1922, 638), and the expression u_0/k (where v_0= cataphoretic speed after viscosity correction and k=dielectric constant) shows a steady decrease for methyl alcohol, sucrose, and carbamide. A tentative explanation of the results is advanced depending on the change of density of the charge and the thickness of the double layer. The effect of methyl and ethyl alcohols on arsenious sulphide sols containing varying amounts of potassium chloride and hydrochloric acid has also been studied. With varying concentration of potassium chloride the values for a fixed alcohol content decrease until the electrolyte concentration is 0·02*N*, and then increase; methyl alcohol shows a corresponding minimum at about 0·005*N*, and the subsequent increase is much greater. These results indicate that neither the cataphoretic speed nor the potential of the double layer has a critical value at the coagulating concentration. It is suggested that the cataphoretic speed is proportional to the product of the surface density and the thickness of the double layer, the thickness depending on the dielectric constant. The relation between the rate of migration and the adsorption of ions is also discussed.

H. BURTON.

Variation of electrical charge of colloidal particles. IV. Effect of dilution on charge of colloidal particles in presence and absence of electrolytes. J. N. MUKHERJEE, S. P. RAI-CHAUDHURI, and A. S. BHATTACHARYYA (J. Indian Chem. Soc., 1928, 5, 735—751).—A continuation of work previously described (A., 1928, 15) on the variation of the charges on arsenious sulphide sols on dilution. The rate of migration diminishes steadily on dilution with water, but in presence of potassium chloride the initial decrease is followed by an increase (in one case an increase followed by a decrease was observed). With ferric hydroxide sols the potential gradient does not remain constant during cataphoresis except when a mixture of ferric chloride and hydrochloric acid is used as the upper liquid. Five-fold dilution with water causes an increase in the rate of migration from 51·5 to 63·1, this value remaining nearly constant up to twenty-fold dilution. Coagulation of arsenious sulphide sols takes place at a much higher cataphoretic speed than that of the "pure" sol. The results previously obtained (*loc. cit.*) are ascribed to the different method of preparation, and to differences in the composition of the sol. The mechanism of coagulation and the relation between cataphoretic speed and adsorption of ions are discussed. H. BURTON.

[Electric] charge of carbon. H. R. KRUYT and G. S. DE KADT (Kolloid-Z., 1929, **47**, 44).—Experiments on ash-free carbon by a cataphoretic method and by precipitation with electrolytes have shown that the carbon particles have a negative charge in water. If the carbon is heated at 1000° in an atmosphere of carbon dioxide or in a vacuum, the product is positively charged in water. The positive carbon acquires a negative charge, however, when it is heated at 400° in a stream of oxygen. Whilst the positive carbon is not able to adsorb sodium hydroxide, the negative carbon has a high binding capacity for alkali. It is suggested that by treatment with oxygen at 400° a negative surface compound is produced, which gives carbonyl groups with water; this superficial compound may be decomposed at 1000°, leaving the carbon with a positive charge. E. S. Hedges.

Elastic properties of acid and alkaline silicic acid and their inner structure. M. Kröger and K. Fischer (Kolloid-Z., 1929, 47, 10—14).—Measurements of the velocity of gelatinisation of silicic acid in relation to the nature and hydrogen-ion concentration of the reacting acid are recorded. The more rapidly gelatinisation occurs, the sooner syneresis sets in. The shrinkage due to syneresis has been measured and was found to increase with rising alkalinity of the gel; at the neutral point a discontinuity was observed. Measurements were also made of the plastic and elastic properties of the acid, neutral, and alkaline gels. For gels of the same age, the elastic properties are not very different. The plastic properties increase in passing from acid to alkaline gels. The results are discussed in relation to the inner structure of the gels. E. S. Hedges.

Influence of mixtures of electrolytes on the viscosity of sols of gum arabic. H. J. C. Tendeloo (Rec. trav. chim., 1929, 48, 23—26).—The influence of mixtures of potassium, barium, and pentammine cobaltic chlorides in pairs on the viscosity of sols of gum arabic has been determined at 25°. A comparison of the influence of the separate electrolytes and their mixtures at equivalent concentrations seems to indicate that there is an influence which is proportional to the total amount of the electrolytes present. R. N. Kerr.

Mol. wt. of cellulose. D. Macgillavry (Rec. trav. chim., 1929, 48, 18—22).—A theoretical discussion of the theory of Hess (A., 1924, i, 142) that the rotatory power of a solution of cellulose in Schweitzer's reagent is due to a complex formed between copper and every glucose unit of the cellulose molecule. An alternative type of intermediate complex with a similar rotatory power is suggested in which only a fraction of the glucose units in the molecule combine with copper. On the assumption that each glucose unit reacts independently of the rest of the molecule a modified formula for the equilibrium is given. This formula may not be applied to determine the mol. wt. of cellulose as Hess has done. The method for calculating the equilibrium concentration of the intermediate product is described. R. N. Kerr.

Velocity function of viscosity of disperse systems. G. W. S. Blair (Kolloid-Z., 1929, 47, 76—81).—It is shown on theoretical grounds that a linear relation between the pressure acting on a system flowing through a capillary and the amount of liquid flowing in unit time is more probable than a parabolic relation. Two of the examples quoted by Ostwald (A., 1925, 291) give the same mean error, no matter which form of equation is applied. E. S. Hedges.

Mathematical representation of the structure region of viscosity. Wo. Ostwald (Kolloid-Z., 1929, 47, 176—187).—The equation given by Blair (cf. preceding abstract) is applicable only to systems showing little structure viscosity and breaks down when applied to many other cases, where structure viscosity is pronounced. At the same time, the possibility of applying Blair's equation to many practical, technical needs is recognised. E. S. Hedges.

Dual emulsions with examples of interest in the spraying of trees. R. M. Woodman (J. Physical Chem., 1929, 33, 88—94; cf. A., 1926, 676; B., 1926, 139).—Observations on dual systems at the same phase-volume ratio are recorded and discussed in relation to the preparation of spraying emulsions. Shaking 10 c.c. of light petroleum with an equal volume of 0·5% aqueous solution of potassium oleate at 25° gives an emulsion which creams upwards and is apparently of the oil-in-water type, but which actually is a water-in-oil emulsion as shown by the drop test. Re-shaking and keeping gives emulsions of both types, and finally, on further keeping inversion occurs. Experiments with aqueous solutions of potassium oleate of various concentrations and of phenol, *cyclo*hexanol, cresol, and methyl*cyclo*hexanol show that in the case of emulsions of the type hydroxyl compound-in-soap solution an increase in the concentration of the emulsifier causes easier emulsification when the phase-volume is kept constant. When this is altered, excess of one phase tends to make it the stable one, especially when the amount of emulsifier is low (cf. *loc. cit.*), although actually no stable emulsion of the type soap-in-hydroxyl compound is obtained. In some cases where inversion occurs with a change in phase-volume ratio, a critical value of this ratio is obtained where both types of emulsion are possible according to the method of shaking employed. Since an oil-in-water emulsion is essential for spraying, these systems are unsuitable for actual practice where a concentrated emulsion is often first made and then diluted. The danger of preparing an emulsion of the wrong type may be avoided by first making the emulsion so that the phase-volume ratio of aqueous to oil media is at least (2—4)/1, when the emulsion of the desired type is obtained. In the system cresol–gelatin–water (A., 1926, 676) previous wetting of the containing vessel does not affect the type of emulsion formed. L. S. Theobald.

Stability of emulsions, unimolecular and multimolecular films, thickness of the water film on salt solutions, and spreading of liquids. W. D. Harkins [with J. W. Morgan, N. Beeman, B. Guisberg, and B. B. Freud] (Fifth Colloid Symposium Monograph, 1928, 19—48).—Only di-β-naphthylamine and *s*-di-β-triphenylethyl give multimolecular films on water; other substances do so on calcium chloride solutions. Mixtures of stearic acid and phenanthrene give multimolecular films; the film strength and thickness have been investigated.

The stability of emulsions is determined from observations on the size distribution of the droplets at intervals. CHEMICAL ABSTRACTS.

Stability of submicrons. Disintegration and formation of crystals, and formation of emulsions. J. TRAUBE (Kolloid-Z., 1929, 47, 45—47).—When a drop of saturated potassium dichromate solution is allowed to crystallise on a microscope slide and a drop of water is then placed in contact with it, ultramicroscopic examination reveals the presence of numerous submicrons. These appear to be produced by disintegration of the crystals of potassium dichromate prior to their dissolution. The same phenomenon is observed with most other salts which are not too soluble, particularly with mercuric chloride, where the submicrons may have a life-period of 1 or 2 min. Complex compounds, such as potassium hexanitrocobaltate, show the effect best. The phenomenon is considered to be consistent with Smekal's theory of "lattice blocks" (Z. techn. Phys., 1927, 561; Naturwiss., 1922, 799), according to which crystals are built up of blocks of molecular units separated by pores or canals. The "lattice blocks" and the submicrons have the same order of magnitude, *i.e.*, 10^{-5} mm. The precipitation of zinc ammonium phosphate and of lead chloride by mixing solutions of reagents has been followed under the ultramicroscope, and similar submicrons, exhibiting the Brownian movement, were observed. Submicrons were also observed in the emulsions formed by shaking chloroform and water with saponin or other peptising agent.

E. S. HEDGES.

Mechanical coagulation as a coagulation at the surface of contact. H. FREUNDLICH and S. LOEBMANN (Z. physikal. Chem., 1928, 139, 368—374).—The coagulation by stirring of a FeO(OH) sol, prepared by the oxidation of iron carbonyl with hydrogen peroxide has been further investigated. This mechanical coagulation has many characteristics in common with that of the copper oxide sol previously investigated (Freundlich and Kroch, A., 1927, 18); it is independent of the concentration of the sol and of the quantity of liquid stirred, but is proportional to the square of the rate of stirring. It differs in the fact that only a definite fraction of the colloidal particles can be coagulated by stirring. Coagulation is also brought about by the passage of a current of air, and by shaking with quartz or with organic liquids such as benzene and nitrobenzene, the rate of coagulation increasing with a rise in the dielectric constant of the liquid. When coagulation is sufficiently slow, as is the case with stirring, coagula with regularly-ordered particles result. Mechanical coagulation appears to be the result of an enlargement of the surface of contact, and the present work is discussed in the light of Deutsch's (A., 1928, 1183) explanation of coagulation at an interface. L. S. THEOBALD.

Precipitation of gelatin by inorganic colloids. R. WINTGEN and H. ENGELMANN (Kolloid-Z., 1929, 47, 104—121).—The precipitation of gelatin by colloidal aluminium hydroxide has been studied on the same lines as a previous investigation by Wintgen and Löwenthal (A., 1924, ii, 739). The previous work indicated a value of about 30,000 for the equivalent aggregate weight of gelatin when precipitated by ferric hydroxide or by chromium hydroxide, and these experiments have been repeated and the results confirmed. The value agrees with that obtained from measurements of osmotic pressure. The experiments with colloidal aluminium hydroxide give a value of only 19,700 for the equivalent aggregate weight of gelatin, but, since the intermicellar liquid was found to contain basic aluminium chloride, it is believed that the latter has a dispersing effect on some of the gelatin, thus reducing its apparent mol. wt. The equivalent aggregate weight of gelatin is greater at the isoelectric point and alters with time, undergoing a fairly sharp rise to about 220,000, followed by a slow fall to about the original value. Increasing quantities of alkali progressively diminish the equivalent aggregate weight of gelatin.

E. S. HEDGES.

Effect of electrolytes on organic isocolloid systems. L. AUER (Kolloid-Z., 1929, 47, 38—43).—In an attempt to study the relation between the effect of gases on films of fatty oils and the effect of electrolytes on aqueous colloids, the influence of electrolytes on fatty oils has been investigated. The metallic salts were dissolved directly in the fatty oil (which is regarded as an isocolloid system) at temperatures between 280° and 310°. The general effect is the formation of a more viscous liquid, which when cooled produces gels of different degrees of rigidity. Examination of a large number of salts with linseed oil showed that both the cation and the anion influence the change, but the cation is predominant. Increasing concentration of the electrolyte causes greater increase in viscosity; in a few cases a lowering of viscosity is observed and then the lowering is greater for increasing concentration of the electrolyte. The nature and pressure of the atmosphere in which the experiment is conducted and the duration of heating also affect the product. The substances produced from wood oil, castor oil, linseed oil, rape oil, fish oil, sunflower oil, and olive oil are described.

E. S. HEDGES.

Unity in the theory of colloids. H. R. KRUYT (Fifth Colloid Symposium Monograph, 1928, 7—18).—A review.

Gel pseudomorphs. M. KRÖGER and K. FISCHER (Kolloid-Z., 1929, 47, 5—11).—A gel of magnesium hydroxide can be prepared by adding water to a 3% solution of magnesium ethoxide in methyl alcohol. Such a gel is not very stable and rapidly undergoes syneresis, the more readily the higher is the concentration. The gel may be stabilised by the addition of glycerol, glycol, and similar substances, but the effect does not appear to be connected with the viscous nature of these substances, but appears to be a peptising effect. By using water, glycerol, and alcohol in the proportions 5 : 10 : 10, a plastic, glass-clear gel which is stable for months can be obtained. The increased stability is probably due to the fact that the gel takes some minutes to form, thus facilitating complete mixing of the solutions. Small amounts of potassium hydroxide increase the rate of formation of the gel and larger amounts cause flocculation. Mixed gels containing about

$0{\cdot}2M$-magnesium hydroxide and about $0{\cdot}04M$-hydroxides of other metals have been prepared and their absorption of ultra-violet light has been studied. The gels are very transparent, the beginning of continuous absorption varying between 2200 and 3100 Å.
E. S. Hedges.

Plastic properties of gels, their dependence on temperature, and the formation of gelatinous lenses. M. Kröger and K. Fischer (Kolloid-Z., 1929, **47**, 14—19).—A method for measuring the plastic deformation of gels is described and has been applied to the study of gels of silicic acid, magnesium hydroxide, and gelatin. The plastic properties decrease with falling temperature and also with ageing. Gels may be obtained in the form of a lens by a method which is described in detail and involves the formation of a curvature by means of a mercury surface. The optical properties of some of these lenses have been investigated and good photographs may be taken by their means. E. S. Hedges.

Consistency and gel formation. H. Wagner (Kolloid-Z., 1929, **47**, 19—21).—The significance of consistency in gels is discussed and the following types of systems are defined. Sols of low viscosity are termed "liquosols" and those of high viscosity "viscosols." Similarly, gels are "liquogels" or "viscogels," according to the viscosity of the sol formed on melting the gel. Plastic or pasty substances are classified as "plastosols" and "plastogels" or "elastosols" and "elastogels," the latter being characterised by higher elasticity. E. S. Hedges.

Definite temperatures in gelatinising systems. S. Tsuda (Kolloid-Z., 1929, **47**, 28—36).—At high temperatures, gelatin sols exhibit neither structure viscosity nor ageing, but both these phenomena appear at a definite temperature. For 2—8% sols the critical temperature is 33—35°, agreeing with the temperature of gelatinisation. The phenomenon is not general for colloids; for example, mercury sulphosalicylic acid has no definite setting point up to 95°. Theories of the sol–gel transformation are discussed. The effect of addition of salts and of alcohol is small, thus resembling the effect on a phenol–water mixture. Agar sol behaves in a similar manner to gelatin, and the fact that the melting temperature lies far above the setting temperature indicates that an agar sol which has been cooled and again warmed does not easily lose its structure viscosity. E. S. Hedges.

Mechanism of the swelling of gels. K. Krishnamurti (Nature, 1929, **123**, 242—243).—The intensity of the light scattered by gelatin at first increases and then diminishes as swelling proceeds. Imbibition of two kinds is probably concerned in the swelling: (*a*) the solvent is taken up inside the structure of the gel micelles; this portion, which is held firmly, probably by chemical forces, increases the volume of the micelles, and hence the light-scattering capacity of the gel; (*b*) the solvent remains in the intermicellary space, diluting the gel, and diminishing its light-scattering capacity. A. A. Eldridge.

Electrolyte-free water-soluble proteins. VII. Hydration and sign of charge of the ions of proteins. W. Pauli (Biochem. Z., 1928, **202**, 337—364).—Viscosity measurements were made on solutions of various proteins with the addition of various acid or basic substances, the hydrogen-ion concentrations being determined. A table is given showing the maximum "binding power" for positive and negative groups of egg-albumin, serum-albumin, hæmoglobin, glutin, and ψ-globulin. The first two of these are predominantly acid, the last two predominantly alkaline. Hæmoglobin, on the other hand, is an almost ideally symmetrical ampholyte. The results lead to the conclusion that at the points of maximum charge there is increase of hydration with increase of charge and greater hydration with respect to the anion under otherwise equal conditions. In many cases, however, the viscosity increase gives place to a decrease before the point of maximum "binding" power is reached, whilst in other cases it increases almost continuously until the point of maximum charge of the protein ions is practically attained. Certain anomalies in the hydration phenomena are discussed. The effect of the addition of caffeine on the viscosity of the protein solutions is also discussed and the substances investigated are grouped according to their behaviour towards caffeine. The state of combination of the nitrogen in hæmoglobin and in serum-albumin has been deduced. In the latter somewhat more than two thirds, in the former only about one third is present as diamino-nitrogen. The possible significance of these facts is noted. W. McCartney.

Difference in osmotic concentration between yolk and white of egg. J. Straub [with M. J. J. Hoogerduyn] (Rec. trav. chim., 1929, **48**, 49—82).—The concentrations of the osmotically active components of the white and yolk have been determined analytically. Sodium, potassium, and chlorine ions are divided unequally and apparently independently between the yolk and white. The partial lowerings of the f. p. corresponding with each constituent have been calculated. If it is assumed that the skin of the live yolk is permeable to water, the difference of f. p. of the yolk and white requires, for an equilibrium state, a difference of pressure of 1·8 atm. across the skin. As the skin could not withstand such a pressure, it is concluded that the yolk and white cannot be in equilibrium. Stationary states other than equilibrium ones can be maintained only through the continual performance of work. That the maintenance of this work is dependent on the life of the egg is shown by experiments with eggs which have been (*a*) preserved, (*b*) frozen to −10°, and (*c*) poisoned; the difference of osmotic behaviour between the yolk and white after such treatments is much smaller than for fresh eggs. The rôle of the yolk skin and its permeability to water and dissolved substances in the processes performing this work are discussed. The work necessary during 24 hrs. is calculated from the gas laws to be 0·01 kg.-cal., and it is shown that this amount of energy may easily be acquired from oxidation of the dextrose in the egg by breathing. The method by which the energy of respiration may be used for the performance of work is discussed. R. N. Kerr.

Reversal of charge of collodion membranes in solutions of alkaloids. N. K. Harkevitsch

(Kolloid-Z., 1929, **47**, 101—104).—An electro-osmotic apparatus is described. This has been applied to the measurement of the charge on membranes in alkaloid solutions. Collodion membranes have hitherto been found to be uniformly negatively charged, but a reversal of charge is obtained in solutions of salts of quinine and cocaine, the charge becoming positive in very dilute solutions. Reversal of charge of agar was not found possible in solutions of quinine, but cellulose becomes positively charged in quinine dihydrochloride solution containing about 50 millimols. per litre. Collodion membranes also show reversal of charge in dilute solutions of the hydrochlorides of quinoline, pyridine, and piperidine.

E. S. Hedges.

Action of proteins on colloidal ferric hydroxide. H. Freundlich and G. Lindau (Biochem. Z., 1928, **202**, 236).—Sensitisation and protective action are not determined by capillary-chemical factors, but are an expression of a chemical reaction similar to that suggested by Heymann and Oppenheimer for albumin–ferric chloride mixtures (cf. A., 1928, 1388).

P. W. Clutterbuck.

Syneresis and hydration. Theory of syneresis. S. Liepatov (Kolloid-Z., 1929, **47**, 21—28).—By adding various amounts of alcohol to a solution of geranin in water, it is possible to prepare a series of colloidal solutions in which the ratio of molecularly dispersed to colloidally dispersed phase is graded. Dilute sols do not show any change of viscosity with time, but at concentrations above 0·25% of geranin a marked change of viscosity with time is observed and has been used to determine the degree of hydration of the particles. Gelatinisation of a sol is considered to take place when the particles of disperse phase come into such proximity that their mutually attractive forces come into operation. Syneresis is considered to be a continuation of this process, the particles growing together so as to squeeze out the liquid between them. The velocities of syneresis and of gelatinisation increase with the concentration of the colloid. Experiments with different concentrations of geranin gel indicate that the final stage of the gelatinisation–syneresis phenomenon is the production of a hydrate of geranin with 2043 mols. of water. In reversible emulsoids the equilibrium between gel and solution is regulated by temperature and pressure: this fact differentiates reversible emulsoids from irreversible emulsoids and suggests a similarity between reversible emulsoids and crystal hydrates.

E. S. Hedges.

Equilibrium between methyl alcohol, carbon monoxide, and hydrogen. D. F. Smith and B. F. Branting (J. Amer. Chem. Soc., 1929, **51**, 129—139).—A preliminary investigation of the above reaction at 304° and 1 atm., using a catalyst of zinc oxide, pure or promoted with chromic acid, gives a value $5{\cdot}57\times10^{-4}$ for the equilibrium constant $[MeOH]/[CO][H_2]^2$. The free energy of the reaction $CO+2H_2=MeOH$ is given by $\Delta F=-20857+41{\cdot}17T.\log T-0{\cdot}01423T^2-54{\cdot}42T$. The fugacities of the components are recorded graphically up to 400 atm. for 300°, 350°, and 400°. The results are not in accord with those of Kelley (B., 1926, 214) but approach more closely those of Christiansen (A., 1926, 358). The yields of methyl alcohol obtained in practice at high pressure compare favourably with those calculated from the thermodynamic data here recorded.

S. K. Tweedy.

Equilibrium constant of the esterification reaction in the gaseous phase. W. Swientoslawski and S. Poznanski (Rocz. Chem., 1928, **8**, 527—541).—See A., 1927, 204.

Modern development of the theory of solutions and its significance in biology. I. E. Benedicenti and G. B. Bonino (Arch. Sci. biol., 1927, **10**, 76—86; Chem. Zentr., 1928, ii, 1189).—A discussion. Weak electrolytes are probably completely dissociated in solution.

A. A. Eldridge.

Influence of neutral salts on acid–base equilibria. VII. Apparently anomalous behaviour of a mixture of a weak base and its salt on dilution and on the addition of a neutral salt. Dissociation constant of pyridine, pyramidone, and *p*-phenylenediamine. I. M. Kolthoff and W. Bosch (Rec. trav. chim., 1929, **48**, 37—48).—The following dissociation constants at 18° have been determined by measuring the p_H of mixtures of the bases and their chlorides at different dilutions and extrapolating for infinite dilution: pyridine $1{\cdot}4\times10^{-9}$, pyramidone $6{\cdot}9\times10^{-10}$, *p*-phenylenediamine $1{\cdot}1\times10^{-8}$, $3{\cdot}5\times10^{-12}$. Extrapolation for the first two bases is uncertain, as the dilution effect is less marked than required by the Debye–Hückel equation. The influence of adding the chlorides of potassium, sodium, and lithium and the bromide, nitrate, and iodide of potassium on the p_H of mixtures of the bases and their univalent salts and also of a mixture of the uni- and bi-valent salts of *p*-phenylenediamine has been investigated. The anion effect on the value of $\log f_1/f_0$ (f_1 and f_0 are the activity coefficients of the basic ion and the undissociated base, respectively) is approximately the same for the four anions used except with pyramidone; the pronounced anion effect with the latter is attributed to the formation of complex or undissociated salts. Potassium chloride exerts approximately the same influence on the above expression as it does in the case of a mixture of a weak acid and its salt (A., 1928, 1325). The cation effect decreases in the order K>Na>Li, which is the reverse of that observed in the acid systems. In order to account for this anomalous behaviour it is suggested that sodium and lithium chlorides increase the ionic product of water.

R. N. Kerr.

Behaviour of hydrogen peroxide in aqueous alkali phosphate solutions. S. Husain (Z. anorg. Chem., 1928, **177**, 215—226).—The partition of hydrogen peroxide between alkali phosphate solutions and amyl alcohol has been measured, and the f. p. of solutions containing phosphate and hydrogen peroxide in the ratios 1 : 2 and 1 : 4 have been determined. The results show that the tendency towards compound formation increases in the order primary, secondary, pyro-phosphate and is greater for the potassium salts than for those of sodium. Even in presence of a considerable excess of hydrogen peroxide the absolute quantity of compound formed is relatively small, in confirmation of the observation of previous workers that the solid complexes are largely broken down on dissolution in water.

H. F. Gillbe.

Dependence of the osmotic coefficients on the structure of the ions of the tetra-alkylammonium salts. L. Ebert and J. Lange (Z. physikal. Chem., 1928, **139**, 584—596).—F.-p. data are recorded for aqueous solutions of some of the chlorides, bromides, iodides, and nitrates of the tetra-alkylammonium bases over the concentration range 0·05—$1M$. Compared with other inorganic salts, these salts show a marked individual behaviour and the curves obtained by plotting concentration against the values of $1-\phi$, where ϕ is the osmotic coefficient, do not fall into groups as do those for the halides of an alkali metal. Tetraethylammonium iodide and tetrapropylammonium iodide show the smallest lowering of the f. p., and their curves lie above that for thallium nitrate. The anomalous behaviour of the tetra-alkylammonium salts is discussed.

L. S. Theobald.

Entropy and vibration number of elements. W. Herz (Z. anorg. Chem., 1928, **177**, 116—118).—The variation with at. wt. of the entropies S and the vibration numbers ν of the elements in each group of the periodic table is such that for each group the quantity $S\sqrt{\nu}$ remains approximately constant.

H. F. Gillbe.

Solubility. XII. Regular solutions. J. H. Hildebrand (J. Amer. Chem. Soc., 1929, **51**, 66—80).—A regular solution is defined as one which involves no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged. In such solutions association and chemical effects are absent. If a_2 is the activity of one component (mol. fraction N_2) of a solution, then (i) $RT \log_e a_2/N_2 = bN_1^2$, where b is a constant independent of temperature, although it often tends to diminish with rising temperature. A short discussion of this variation is given. If the system is unsymmetrical, then (ii) $RT \log_e a_2/N_2 = bN_1^2 + cN_1^3 + \ldots$ (cf. Heitler, A., 1926, 1006). The constancy of b in equation (i) is demonstrated for solutions of sulphur, iodine, naphthalene, and stannic iodide. The equations are also applied to two-phase liquid systems. If T_c is the critical mixing point, then $2RT_c = b$. The equations are also confirmed by *E.M.F.* measurements on molten alloy concentration cells (Taylor, A., 1924, ii, 89). The following topics are discussed with relation to the equation: heat of dissolution, heat of mixing, volume change on mixing. A correction term is introduced in Gibbs' adsorption equation, which takes into account the deviation from the ideal solution. The solubility of stannic iodide in *iso*octane is 0·342 mol.-% at 25°.

S. K. Tweedy.

Decomposition pressure of nitrides. R. Lorenz and J. Woolcock (Z. anorg. Chem., 1928, **177**, 380).—An addition to a previous paper (cf. this vol., 29). References are given to previous work on the formation and dissociation of zirconium nitride.

A. J. Mee.

System iron–water. G. Schikorr (Z. Elektrochem., 1929, **35**, 62—65).—On the assumption that certain electrochemical processes alone are involved in the reaction between iron and water, it is calculated from electrochemical data that no further evolution of hydrogen should occur above a limiting pressure of (very approximately) 0·25 atm. It is found by experiment, however, that very much higher pressures than this may be reached, and it is inferred that the evolution of hydrogen is due to the decomposition of water by ferrous hydroxide (cf. Traube and Lange, A., 1926, 257). Evidence is cited in support of this contention.

L. L. Bircumshaw.

Derivation of the solubility product law. W. C. Vosburgh (Proc. Iowa Acad. Sci., 1927, **34**, 213—214).—A thermodynamic derivation of the solubility product law is based on considerations of free energy and activity.

Chemical Abstracts.

Equilibria between metals and salts in melts. XII. Displacement of the equilibrium $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ by additions to the metal phase. R. Lorenz and M. Hering (Z. anorg. Chem., 1928, **177**, 1—12).—Addition of either antimony or bismuth to the system $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ causes a displacement from right to left which increases as the content of added metal increases. Antimony forms compounds with one of the components, viz., cadmium, but bismuth does not, and the added metal is therefore considered as increasing the "nobleness" of cadmium towards lead.

H. F. Gillbe.

Ionic equilibria. III. Equilibrium between cadmium sulphide and dilute hydrochloric acid. M. Auméras (J. Chim. phys., 1928, **25**, 727—742; cf. A., 1927, 312, 1141).—The method previously described has been applied to this system with special precautions against loss of hydrogen sulphide by evaporation and by atmospheric oxidation. On the assumption that cadmium chloride and hydrochloric acid are completely dissociated in dilute solution, an equation has been deduced from mass law considerations representing the solubility of cadmium sulphide in dilute hydrochloric acid with which the experimental results are in good agreement. The second dissociation constant of hydrogen sulphide at 16° has been calculated from the results with the addition of published data for the first dissociation constant and for the solubility product of cadmium sulphide; these give $[H'][S'']/[HS'] = 0{\cdot}59 \times 10^{-15}$ and $0{\cdot}37 \times 10^{-15}$.

R. N. Kerr.

Application of the law of mass action to the double decomposition of [solutions of] salts. Lemarchand and (Mme.) Lemarchand (Compt. rend., 1929, **188**, 254—256; cf. A., 1928, 1205).—The equilibrium constants for the reaction of barium sulphate with hydrochloric acid and with calcium chloride solutions at 100° have been calculated in reference to the activities of the reacting substances.

J. Grant.

Action of silica and alumina on sodium sulphate. (Mlle.) G. Marchal (Compt. rend., 1929, **188**, 258—260; cf. A., 1926, 924).—The decomposition of anhydrous sodium sulphate at temperatures up to 1300° is facilitated by the addition of powdered anhydrous silica or alumina, particularly the latter. The reaction does not proceed to completion. J. Grant.

Gibbs' theorem applied to heterogeneous equilibria. V. Polara (Atti R. Accad. Lincei, 1928, [vi], 8, 500—505).—Mathematical.

Saturation of sugar–lime solutions. III. A. H. W. Aten, P. J. H. van Ginneken, and E. Verweij (Rec. trav. chim., 1929, 48, 93—115).—The composition of the basic precipitates obtained by passing carbon dioxide into sugar–lime solutions (A., 1928, 21) has been determined. That of the precipitate obtained from solutions of fairly high concentration (*e.g.*, 0·7 mol. of sugar$+$1·7*N*-CaO) varies between 3sugar,6CaO,CO_2 and 3sugar,6CaO,2CO_2 according to the value of *R* (the degree of saturation of the solution) and the concentration of sugar. That of the precipitate formed at lower concentrations (*e.g.*, 0·35 mol. of sugar$+$1·0*N*-CaO) is 3CaO,2sugar,$x$$CaCO_2$, where x lies between 0·65 and 1·2. The solubility of calcium carbonate hexahydrate in sugar–lime solutions of varying concentrations has been determined. The effect of raising the temperature to 90° has been further investigated and the change in alkalinity on solution of the hexahydrate and on separation of the basic precipitates determined. Conductivity measurements of carbonated solutions have been carried out; a large decrease occurs after the absorption of the carbon dioxide whether a precipitate is formed or not. This decrease is much greater than can be accounted for merely on the formation of undissociated calcium carbonate. It appears that some of the free lime must be removed from the solution. This conclusion is supported by determination of the hydroxyl-ion concentration of the carbonated solutions. It is assumed therefore that complexes formed between the carbonate and hydroxide of calcium are present in solution. The approximate composition of these complexes has been calculated from the conductivity of the solutions during the transformation of the basic precipitate into the hexahydrate. It varies between $2CaCO_3,Ca(OH)_2$ and $CaCO_3,2Ca(OH)_2$. The presence of such complexes is confirmed by ultrafiltration experiments on freshly-carbonated solutions and also by periodic examination of the solutions under the ultramicroscope. R. N. Kerr.

Systems $KCl–FeCl_3–H_2O$ and $AlCl_3–FeCl_3–H_2O$ between 0 and 60°. G. Malquori (Gazzetta, 1928, 58, 891—898; cf. A., 1928, 20).—The isotherms for the system $KCl–FeCl_3–H_2O$ at 0°, 25°, 35°, and 60° show that the double chloride $FeCl_3,2KCl,H_2O$ is stable at all temperatures and separates only from solutions which are rich in ferric chloride. Data for the system $AlCl_3–FeCl_3–H_2O$ at 0° show that the two solids $AlCl_3,6H_2O$ and $FeCl_3,6H_2O$ may be present in the solid phase, but at 40° and 60° there is no ferric salt in the solid phase even when the co-existing solution contains 45% of ferric chloride.

O. J. Walker.

Reciprocal salt pair $MgSO_4–2NaNO_3–H_2O$. II. W. Schröder (Z. anorg. Chem., 1928, 177, 71—85).—Isotherms of the system $MgSO_4–Na_2SO_4–H_2O$ show that at 75° astrakanite alone is present. In the system $Mg(NO_3)_2–MgSO_4–H_2O$, at high nitrate concentrations, the transition from hexahydrate to monohydrate invariably takes place through an intermediate series of hydrates; at nitrate concentrations lower than about 50% no monohydrate is formed, but a series of metastable hydrates, of relatively high stability, is produced. The influence of temperature on the system $MgSO_4–2NaNO_3–H_2O$ is described. The space boundaries of the various phases in this system have been calculated, and the influence of temperature is described.

H. F. Gillbe.

Equilibria between water and the nitrates and sulphates of sodium [and potassium] at 50—90°. E. Cornec and H. Krombach (Caliche, 1928, 10, 396—401).—In contradiction to Hamid's results (A., 1926, 245, 246), potassium nitrate and sodium sulphate are capable of co-existence in contact with the saturated solution at 90°. On the addition of a solution of glaserite to a sodium nitrate solution the reaction $Na_2SO_4,3K_2SO_4+6NaNO_3 \longrightarrow 4Na_2SO_4+6KNO_3$ takes place, the reaction products being partly precipitated; the resulting solution, saturated with sodium and potassium nitrates and sodium sulphate, has *d* 1·761. On further addition of glaserite a point is reached at which the double salt co-exists with a solution, *d* 1·724, saturated with sodium sulphate, potassium nitrate, and glaserite. At 50° darapskite and potassium nitrate can co-exist, but this is not possible for sodium nitrate and sodium sulphate; the reverse obtains at 66·5°. At temperatures in the neighbourhood of 60° two types of solution exist, one saturated with sodium nitrate, sodium sulphate, and potassium nitrate, and the other with sodium and potassium nitrates and darapskite; above 60° the first is stable and the second labile, whilst below 60° these conditions are reversed. H. F. Gillbe.

Thallous double halides. A. Benrath and G. Ammer (Z. anorg. Chem., 1928, 177, 129—136).—Heterogeneous equilibria at 25° have been determined for three-component systems containing thallous chloride and water, together with cadmium, mercuric, zinc, magnesium, calcium, strontium, or barium chloride. The following double chlorides have been found to exist: $CdCl_2,TlCl$, $HgCl_2,TlCl$, $ZnCl_2,2TlCl$, $ZnCl_2,3TlCl$, and $MgCl_2,3TlCl$; the alkaline-earth metal chlorides do not form double salts with thallous chloride. The salts $CdBr_2,TlBr$, $ZnBr_2,2TlBr$, and $ZnI_2,3TlI$ also exist.

H. F. Gillbe.

Elimination of systematic errors occurring in the earlier thermochemical data. W. Swientoslawski (Rec. trav. chim., 1929, 48, 1—6).—Polemical. A reply to the criticism by Verkade and Coops (A., 1928, 845) of the author's previous work (A., 1920, ii, 470). R. N. Kerr.

Calorimetric researches. II. Heat of combustion of a proposed secondary calorimetric standard: salicylic acid. L. J. P. Keffler (J. Physical Chem., 1929, 33, 37—51; cf. A., 1927, 193).—Details are given of the determination of the heat of combustion of salicylic acid which, as a mean of nineteen combustions carried out adiabatically under varied conditions with eight different samples obtained by recrystallisation from three different preparations of the acid, has the value 5234·8 g.-cal.^{15}/g. (in a vacuum). This value holds for an isothermal reaction at 20° approximately, and may be compared with 6319 g.-cal.^{15}/g. for benzoic acid as standard. From an examination of the results of recent investigators, the value 5235±1 g.-cal.^{15}/g. (in a vacuum) is finally suggested.

L. S. Theobald.

Heat of formation of double chlorides of cadmium and potassium. P. Agostini (Atti R. Accad. Lincei, 1928, [vi], 8, 393—394).—From measurements of the heat of precipitation of cadmium hydroxide by potassium hydroxide from solutions of the double salts $KCl,CdCl_2$ and $4KCl,CdCl_2$ and from solutions of cadmium chloride, the heats of formation of the two double salts were calculated as 3·65 and 0·989 kg.-cal., respectively.

F. G. Tryhorn.

Thermochemical study in the furan series. P. Landrieu, F. Baylocq, and J. R. Johnson (Bull. Soc. chim., 1929, [iv], **45**, 36—49).—Measurements of the heats of combustion of furan, ethylenefuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, furfuraldehyde, furoic acid, and furylacrylic acid and of the corresponding benzene compounds are recorded. The molecular heats of formation have been calculated; those for the furan compounds are lower than those of the corresponding benzene compounds by a nearly constant amount of 26·4 g.-cal. The molecular heats of combustion at constant pressure of the furan compounds are likewise lower than those of the corresponding benzene compounds by a mean value of 284 g.-cal. per mol., the maximum variation being 0·5%. The only exception occurs with the hydrogenated alcohols, but if allowance be made for the additional hydrogen atoms present in the benzene compound the corrected value is in good agreement with the above mean. R. N. Kerr.

Calculation of the integral and differential heats of solution and dilution of potassium chloride and of the molecular heat of potassium chloride solutions at great dilution. E. Lange and J. Monheim (Z. Elektrochem., 1929, **35**, 29—33).—The experimental values obtained by Lange and Leighton (A., 1928, 1329) for the heats of dilution of dilute solutions of potassium chloride have been used to calculate the integral and differential heats of solution and dilution of potassium chloride at 12·5° and 25°, for concentrations ranging from 0·0007 to 0·9028 mols./100 mols. of water. The mean temperature coefficients of these quantities have also been calculated for the temperature range 12·5—25°, together with the specific and molecular heats of the solution over the whole concentration range. At great dilution, the specific heat is not a linear function of the concentration. L. L. Bircumshaw.

Transport numbers of lithium chloride and bromide, and sodium iodide dissolved in acetone and alcohol. W. Birkenstock (Z. physikal. Chem., 1928, **138**, 432—446).—It has been shown by Bruns and Thönnessen that the conductivity of concentrated aqueous solutions of cadmium iodide and alcoholic solutions of cadmium iodide, potassium iodide, etc. is increased by the addition of iodine. If a slowly moving I_3 ion is formed, the dissociation must have increased in order to account for this increase of conductivity. In order to find out whether complex aggregates exist in the solutions, the transport numbers of lithium chloride and bromide and sodium iodide in acetone and in mixtures of acetone and methyl alcohol were determined. Lithium chloride and bromide show strong association in acetone solution. The complexity is greatest with lithium chloride and decreases through lithium bromide to sodium iodide, which is not, or, at least, only a little, associated. The type of aggregate formed, *i.e.*, whether it is Li_2Cl_2, Li_3Cl_3, etc., cannot be determined by the experiments described. It is very probable that the acetone solution of lithium chloride contains very large aggregates of the form Li_nCl_n, on the one hand because of the low conductivity, and on the other because the great influence of dilution on the conductivity of this solution can be explained only in this way. The aggregates were in each case destroyed by the addition of methyl alcohol.

A. J. Mee.

Effect of addition of iodine on the conductivity of solutions of halogen salts of sodium, lithium, and potassium in mixtures of alcohol and acetone. F. Nies (Z. physikal. Chem., 1928, **138**, 447—458).—The addition of iodine to a solution of sodium iodide in acetone, or in a mixture of acetone and methyl alcohol, increases the conductivity. The effect diminishes as the proportion of methyl alcohol is increased. The conductivity of a solution of lithium bromide in acetone is also increased by the addition of iodine. For methyl alcohol solutions of lithium chloride and potassium iodide the increase in conductivity is confined to the more concentrated solutions. In acetone and in acetone–methyl alcohol mixtures, lithium chloride behaves like sodium iodide; the equivalent conductivity is increased on adding iodine, the increase being very much greater than for sodium iodide. The iodine not only affects the complex, but also the simple molecules, and also forms complex ions with the other halogens. The results of the experiments are not compatible with the theory of complete dissociation. A. J. Mee.

Effect of diffusion at a moving boundary between two solutions of electrolytes. D. A. MacInnes and I. A. Cowperthwaite (Proc. Nat. Acad. Sci., 1929, **15**, 18—21).—Since the method of moving boundaries affords an accurate means for determining the transference number of an electrolyte, experiments have been made to determine whether the movement of the boundary is affected by the diffusion of one electrolyte into the solution of the other. It was found that the diffuse zone between the two solutions moves at the same rate as the fully-formed boundary, and that the latter regains its original sharpness shortly after restarting the current. The probable action of the mechanism involved is outlined. N. M. Bligh.

Calculation of the [electrode] potentials of potassium and sodium. P. Drossbach (Z. Elektrochem., 1929, **35**, 95—96).—The values previously obtained for the electrode potentials of sodium and potassium (A., 1928, 481) are higher than the experimental values. It is now found that the influence of concentration is considerably greater than had been supposed, and on allowing for this and re-calculating, the values $\varepsilon_{Na}=-2\cdot72$ volts and $\varepsilon_{K}=-2\cdot97$ or $-2\cdot96$ volts are obtained, in good agreement with the experimental values $-2\cdot72$ and $-2\cdot92$ volts, respectively. L. L. Bircumshaw.

Concentration cells in ethyl alcohol : sodium and potassium iodides. G. F. Isaacs and J. R. Partington (Trans. Faraday Soc., 1929, **25**, 53—59).—The *E.M.F.* of the cells—$Ag|AgI,NaI(c_1)|NaI(c_2),AgI|Ag$, $Ag|AgI,KI(c_1)|KI(c_2),AgI|Ag$ with ethyl alcohol as the solvent have been measured between $0\cdot001N$ and $0\cdot5N$. Satisfactory results are not obtained at higher or lower concentrations, but within this range the *E.M.F.* are adequately represented by Nernst's equation in the form $E=2(1-n_a)RT/F \log_e \lambda_1 c_1/\lambda_2 c_2$, where n_a is the anion transport number and λ_1, λ_2 are the conductances at c_1, c_2, respectively. The values of n_a are constant except at the higher concentrations. Measurements of the *E.M.F.* at 25° agreed closely with those calculated from readings at the ordinary temperature on the assumption that the *E.M.F.* is proportional to the absolute temperature. F. G. Tryhorn.

Oxide cells of cadmium, copper, tin, and lead. C. G. Maier (J. Amer. Chem. Soc., 1929, **51**, 194—207).—From potential measurements of oxide electrodes containing barium hydroxide as electrolyte against standard electrodes (Maier, Parks, and Anderson, A., 1926, 1210) the molar free energies (g.-cal.) at 25° are calculated for cadmium monoxide (—55,064), cadmium hydroxide (—112,178), cuprous oxide (—34,672), cupric oxide (—30,800), stannous oxide (—61,332), and stannic oxide (—123,000). The heats of formation also are tabulated. Those calculated from the cell coefficients differ somewhat from those calculated from the free energy and entropy. Oxide electrodes are highly polarisable and very sensitive to traces of electronegative impurities. It is not possible to obtain permanently stable cells with such electrodes.

S. K. Tweedy.

Studies on the periodic system. I. Ionic potential as a periodic function. II. Ionic potential and related properties. G. H. Cartledge (J. Amer. Chem. Soc., 1928, **50**, 2855—2863, 2863—2872).—I. A periodic classification is put forward, based on the conception of an " ionic potential " (=charge/radius). Hydrogen occurs twice in the system, as an alkali-like ion and a halogen-like ion, respectively, although the former resemblance stops short with the valency. The triads of group eight fall logically into the scheme, as also do the rare earths, and all the valencies of multivalent elements are satisfactorily provided for. The ions fall into families which are characterised by the degree of completeness of their outer electron shells.

II. The relations between ionic potential, ϕ, and certain ionic properties are discussed. In aqueous solution, cations are basic, amphoteric, or acidic, according as $\sqrt{\phi}$ is less than 2·2, between 2·2 and 3·2, or greater than 3·2. Cations for which $\sqrt{\phi}$ exceeds 2·2 form volatile chlorides which, in the liquid state, are non-conductors. Binary crystals increase in hardness as the ϕ values of their constituents increase. The heat of hydration of gaseous ions increases with the ϕ value and the heat of solution of salts with a common anion increases with the ϕ-value of the cation, except in the case of fluorides, when the reverse holds. S. K. Tweedy.

Determination of the activity of one substance from that of another by a cell with a liquid junction. R. F. Nielsen and H. A. Liebhafsky J. Amer. Chem. Soc., 1929, **51**, 223—224).—It is contended that Schuhmann's experiments, instead of proving that the activity coefficients of hydrochloric and perchloric acids are the same at all concentrations, show that the hydrogen-ion activity in hydrochloric acid solutions is the same as that in perchloric acid solutions of the same molality. The method used by Schuhmann (cf. A., 1924, ii, 152) does not afford evidence for equal mean activity coefficients in equimolal solutions of two electrolytes with a common ion. S. K. Tweedy.

Study of complex formation by the polarographic method. (Mme.) N. Demassieux and J. Heyrovsky (Bull. Soc. chim., 1929, [iv], **45**, 30—35; cf. A., 1927, 1159).—Study of complex formation by an electrolytic method which makes use of the dropping mercury cathode has been extended to the salts of platinum, mercury, and copper. Experiments with potassium hexachloro- and hexabromo-platinates and tetrachloro- and tetrabromoplatinites show that the complexes in each case are dissociated in solution. Dissociation of the tetracyanoplatinite ion, on the other hand, cannot be detected. The metal can likewise not be deposited from the complex cyanides of iron, zinc, and copper, but with those of silver, gold, and cadmium the metal is deposited easily and reversibly at the cathode. The behaviour of mercuric cyanide to which potassium cyanide has been added is peculiar; a sharp-pointed maximum is obtained on the polarisation curve and this is attributed to adsorption of ions on the drops of mercury. The cyano-, tartrato-, oxalato-, and hyposulphito-complexes of copper have been examined. The cyano-complex is not dissociated at all in freshly-prepared solutions, but becomes so partly on keeping or on dilution of the solution; the other three complexes are all partly dissociated. The constant for the oxalato-complex has been determined, $K=[Cu(C_2O_4)_2{}'']/[Cu^{\cdot\cdot}]\times[C_2O_4{}'']^2=0\cdot25\times10^{13}$.

R. N. Kerr.

Current density–potential curves in the region of residual currents of various metals. W. J. Müller and K. Konopicky (Z. Elektrochem., 1928, **34**, 840—849).—The current densities at increasing potentials have been measured for copper, platinum, lead, iron, nickel, and aluminium in $0\cdot02N$-sulphuric acid, without and with the passage of hydrogen through the electrolyte, using zinc as the reference electrode. In the case of copper, the agitation of the electrolyte by the hydrogen was accompanied by an increase in the residual current from 2×10^{-5} to 13×10^{-5} amp. In the case of all the metals investigated, the residual current is strongly influenced by the gas content of the electrolyte. When oxygen is completely removed by hydrogen the residual current changes little and has a value less than 10^{-3} amp. in an undisturbed electrolyte, but when the electrolyte is saturated with oxygen the residual current reaches a constant value about ten times as large. Air produces a similar effect. The overvoltage, determined by breaks in the current–potential curves, is practically independent of the oxygen content of the electrolyte with copper, lead, aluminium, and nickel, but with platinum and iron it is changed by 0·14 and 0·1 volt, respectively. The apparent specific potentials of the electrodes, defined as the potential at which the current density–potential curve cuts the axis of zero current, are markedly influenced by the presence of oxygen in the electrolyte. The respective displacements towards the positive side are for copper and iron 0·05 volt, lead about 0·08 volt, aluminium 0·15 volt, and about 0·25 volt for nickel. They cannot be interpreted as passivity effects, for these are essentially associated with higher current densities. The hydrogen-overvoltage curves can be represented by a formula of the type established by Tafel and modified by Glasstone (A., 1925, ii, 133). For the metals, a formula of similar type holds. L. S. THEOBALD.

Periodic phenomena at the anode. W. J. MÜLLER (Z. Elektrochem., 1928, 34, 850—852).—Polemical. The explanation of the periodic passivity of chromium and other electrodes in terms of the oxygen-film theory of passivity advanced by Strauss and Hinnüber (A., 1928, 1098) is adversely criticised. Previous observations of the author and his co-workers (A., 1928, 713, 1319) render it untenable, and further, it is pointed out that the observations of Strauss and Hinnüber can be explained in terms of the metal transformation theory of passivity. L. S. THEOBALD.

Periodic phenomena at the anode. J. HINNÜBER (Z. Elektrochem., 1928, 34, 852—853).—A reply to Müller's criticism (preceding abstract). L. S. THEOBALD.

Experimental foundations of the passivity theory. W. J. MÜLLER (Z. Elektrochem., 1929, 35, 93—94).—Examination of the current density–potential curves for anodes exhibiting active and passive states, given in a previous paper (cf. A., 1928, 135, 713), shows that, although the oxygen content has a pronounced influence on the magnitude of the cathodic residual current, the presence of dissolved oxygen has no effect on the anodic part of the curve in the residual current region. On this evidence, Hinnüber's theory of the passivating action of oxygen dissolved in the electrolyte on the metal (A., 1928, 1098), which was advanced to explain the phenomenon of periodic passivity of chromium and chromium alloys, cannot be accepted. Various theories of passivity are discussed, and it is claimed that the phenomenon of anodic passivity is always due, primarily, to the formation of a non-conducting film (salt or basic salt), and secondarily, in the case of metals exhibiting true (chemical) passivity, to a change in the atoms of the metal caused by the high effective current density resulting from the deposition. L. L. BIRCUMSHAW.

Experimental foundations of the passivity theory. J. HINNÜBER (Z. Elektrochem., 1929, 35, 95).—In reply to Müller (cf. preceding abstract), it is emphasised that the author's investigations have been concerned only with those cases where no visible protective layer is formed on the passive metal (*i.e.*, chromium and chromium alloys). Reference is made to the fact, observed by Eggert (A., 1927, 423), that chromium remains active in dry hydrogen or nitrogen, but becomes passive on introduction of oxygen or exposure to the atmosphere. L. L. BIRCUMSHAW.

Corrosion, residual current, and passivity. III. F. TÖDT (Z. Elektrochem., 1928, 34, 853—857; cf. this vol., 145).—Measurements of the residual currents between iron and platinum, combined with observations on the corrosion of the iron, have been made in various solutions, and it is shown that the current strength between a noble and a non-noble metal immersed in the same solution is a measure of the corrosion of the latter. The corrosive properties of solutions and the corrosion of metals can thus be directly indicated by a method which is quicker and simpler than the classic method of analysis. Corrosion and passivity are discussed in relation to these residual currents. L. S. THEOBALD.

Electrical behaviour of surfaces of corroding iron. A. L. McAULAY and S. H. BASTOW (J.C.S., 1929, 85—92).—A study has been made of the change of potential with time when iron is introduced into 0·5*N*-potassium sulphate solution. It is found that iron, when corroding, is in a stable and reproducible state, and, provided that the electrodes are first aged by prolonged immersion in an electrolyte and the condition of aëration of the electrolyte is standardised, reproducible results can be obtained. Mild steel and cast iron give results similar to electrolytic iron, but stainless steel shows a completely different behaviour. The time–potential curves show that the film present on iron after exposure to air increases its resistance to destruction by the electrolyte with increasing time of exposure up to about 2 hrs. Anodic oxidation in alkali gives films more resistant to destruction than exposure to air. In all cases, however, prolonged immersion in the electrolyte produces the same final state. F. J. WILKINS.

Passivity of metals. II. Breakdown of the protective film and the origin of corrosion currents. U. R. EVANS (J.C.S., 1929, 92—110).—An attempt has been made to decide whether corrosion is due to the presence of invisible cavities in a metal, the interiors of which, being less accessible to dissolved oxygen, become anodic towards the area outside, or to breaks in a protective film where the exposed metal becomes anodic towards the surrounding film-covered surface. Breakdown of the protective film on iron, steel, or aluminium tends to occur where the surface has been bent or cut, or where rolling or casting defects occur at the surface. The phenomena can be explained satisfactorily only by assuming that the places of attack represent weak points in the invisible oxide film. Sometimes (as with zinc) corrosion starts at the site of pre-existing cavities.

Differential aëration currents are due to differences of potential existing between (1) the places where the film is kept in good repair by a supply of oxygen, and (2) those where it is not kept in repair. An *E.M.F.* of nearly 0·5 volt can be set up merely by differences in oxygen accessibility. The *E.M.F.* falls when a corrosion-current flows. The extension of breakdown, or the repair of the film, can be followed by changes in *P.D.* F. J. Wilkins.

Mechanism of corrosion. U. R. Evans (J.C.S., 1929, 111—129).—The corrosion of half-immersed specimens of zinc, aluminium, iron, steel, and copper in salt solutions commences at a limited number of weak points, mainly along the bottom and cut edges, but sometimes at defects occurring in the centre, or, in special circumstances, at the water line. The insoluble corrosion products are of four different types which depend on the way in which the anodic and cathodic products come together.

Under conditions of differential aëration, electrolytic iron is attacked nearly as fast as steel, whilst potassium sulphate and potassium chloride cause similar rates of corrosion, although the shapes of the corroding areas are different. In magnesium sulphate the rate of attack is slower. Zinc is attacked more quickly than iron, and aluminium much more slowly. The replacement of air by oxygen not only increases the rate of corrosion, but also restricts the corroded area to strips running along the bottom portion and the two edges. Doubling the breadth of half-immersed specimens nearly doubles the amount of corrosion, but increase of the length of the specimens has much less effect. The rate of corrosion is almost the same in $0{\cdot}05M$- and $0{\cdot}1M$-potassium chloride.

In the interpretation of the results it is suggested that the *E.M.F.* of the metal|oxygen cell, which determines the magnitude of the corrosion current and the rate of corrosion, is dependent on three factors: (*a*) anodic polarisation, (*b*) cathodic polarisation, and (*c*) the fall of potential across the liquid. For aluminium (*a*) is the important factor, but for zinc, iron, and steel (*b*) controls the rate of corrosion. F. J. Wilkins.

Ignition temperature of combustible gaseous mixtures. M. Prettre and P. Laffitte (Compt. rend., 1929, **188**, 397—399; cf. this vol., 33).—The ignition temperatures of mixtures of hydrogen and air, or hydrogen, oxygen, and carbon dioxide, are raised considerably in the presence of small quantities of the residual gases from a previous combustion, to an extent which increases with the initial pressure (10^{-4}—20 mm. of mercury) and with the hydrogen content. The presence of air has an analogous but less marked effect. The results explain the apparent divergence in the results of various workers. J. Grant.

Effect of compression on the explosive properties of explosive gas mixtures. A. Haid and A. Schmidt.—See B., 1929, 113.

Ignition of mixtures of air with natural gas and with methane by induction coil sparks. E. G. Meiter.—See B., 1929, 83.

Flame movement in gaseous explosive mixtures. O. C. de C. Ellis.—See B., 1929, 82.

Experiments with carefully dried substances. D. McIntosh (Proc. Nova Scotian Inst. Sci., 1928, **17**, 142—148).—A mixture of carbon monoxide (2 mols.) and oxygen (1 mol.), kept for 15 hrs. in a glass vessel, the lower part of which was immersed in carbon dioxide and ether in a Dewar flask, failed to explode when sparked. Even immersion for 5 hrs. in the low-temperature mixture usually prevented an explosion. At −50° to −60°, when 1 mol. of water is present to 40,000 mols. of gas, explosion can take place.

Sodium sulphate, carefully dried in air, or by connexion with a tube containing liquid air or phosphorus pentoxide, still caused immediate precipitation when introduced in minute fragments into a supersaturated solution of the same salt. No precipitation occurred, however, when the salt had previously been heated at 45° for 1 hr., indicating that crystallisation was due to the decahydrate.

Chlorine failed to react with mercury at −180° after both had been dried by suitable means, using liquid air. Below −65°, however, reaction took place. Freshly-distilled ammonia and hydrogen bromide, carefully dried by means of low temperatures, reacted at once when brought into contact. The vapour pressure of water must thus be reduced below 0·001 mm. to prevent their interaction.

Ether, twice re-distilled at −80°, boiled at its normal temperature. An unsuccessful attempt was made to dry ether in a special apparatus of Pyrex glass by distillation at low temperature followed by slow distillation through phosphorus pentoxide. B. W. Anderson.

Kinetics of the decomposition of solutions of sodium hypochlorite. F. Giordani and E. Matthias (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], **34**, 137—141).—To confirm that the decomposition of sodium hypochlorite solutions involves two simultaneous reactions, $NaOCl+2HClO \longrightarrow NaClO_3+2HCl$, $2NaOCl \longrightarrow 2NaCl+O_2$, measurements have been made of the temperature coefficient of the velocity of decomposition of hypochlorite solutions. If the decomposition proceeds according to the first equation alone the velocity coefficient should be proportional, not only to the coefficient for this reaction, but also to the square of the hydrolytic constant of the reaction giving rise to the hypochlorous acid, and thus should be abnormally high. On the other hand, the temperature coefficient of the second reaction should be normal. The velocity of decomposition of a solution containing 0·3 g.-mol./litre of sodium hypochlorite was increased 6·96 times by a temperature rise of 15° (31—46°), and that of a solution containing 0·381 g.-mol./litre 11·96 times by the same temperature rise. At 31° the influence of the alkalinity of the solution predominated, but at 46° this effect was negligible. F. G. Tryhorn.

Influence of non-electrolytes on the velocity of ionic reactions. A. von Kiss and (Frl.) L. Hatz (Rec. trav. chim., 1929, **48**, 7—17).—The study of the reaction between iodine and persulphate ions (A., 1928, 1332) has been extended to the influence of added non-electrolytes. Addition of methyl or ethyl alcohol or glycerol lowers the speed of the reaction, whilst that of sucrose or carbamide increases it. No simple relation was found between the velocity and the concentration of non-electrolyte; log k is not linearly proportional to the concentration, as was the case for the addition of electrolytes. Neutral salt action in solutions to which non-electrolytes have been added has also been studied. Addition of potassium nitrate or sulphate, ammonium nitrate, and hydrochloric acid increases the rate in an aqueous ethyl alcohol solution to a greater extent than in a pure aqueous solution, but with the sulphates of aluminium and magnesium and lithium chloride the reverse is the case. The effect of varying the concentration of salt in alcoholic solution has been determined for lithium chloride and ammonium nitrate; the curves correlating velocity and salt concentration follow the same course as in aqueous solution, but deviate more markedly from the latter as the concentration of salt increases. Variation of the concentration of the reacting components causes a more marked effect for solutions to which ethyl and methyl alcohol have been added than for pure aqueous solutions; this effect increases with the concentration of non-electrolyte. Increase of the iodide-ion concentration, that of the persulphate ion being kept constant, increases the rate of the reaction. The connexion between the reaction rate and the physicochemical properties of the solvent, particularly the dielectric constant, is briefly discussed but no simple relation is found. R. N. KERR.

Periodic law. P. PETRENKO-KRITSCHENKO (J. pr. Chem., 1929, [ii], **120**, 225—237).—Comparative reaction velocity measurements for the interactions of potassium hydroxide, tetramethyl- and tetraethylammonium hydroxides, barium hydroxide, thallium hydroxide, sodium ethoxide, metallic silver, ammonia, piperidine, water, ethyl alcohol, silver nitrate, potassium acetate, and potassium thiocyanate with halogeno- and halogenonitro-derivatives of methane and ethane, the chlorotoluenes, and halogenoacetic acids have revealed that the strengths of the linkings which, in each case, join the methane carbon atom to the first-removed halogen atom vary periodically from the mono-, through di-, to the tetra-halogenomethanes. R. J. W. LE FÈVRE.

Mutarotation of galactose. T. M. LOWRY and G. F. SMITH (J. Physical Chem., 1929, **33**, 9—21; cf. Worley and Andrews, A., 1928, 374).—Data relating to the mutarotation of galactose in water at 20° and at 0·8° are recorded, and a simplified, graphical method of analysing the complex mutarotation curves of α- and β-galactose is described. Assuming that only α-, β-, and μ-sugars are present in the equilibrium mixture, the percentage of α-galactose is found to be approximately 30% at 20° and at 0°. Solubility measurements of α-galactose in water at 0° confirm this to a certain extent by giving an uncorrected proportion of 37% of the α-sugar in the equilibrium mixture as against the value 6·6% found by Riiber and Minsaas (A., 1926, 1228). L. S. THEOBALD.

Velocities of nitration. F. H. COHEN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 692—700).—The velocity of nitration of benzene in acetic anhydride and in glacial acetic acid has been investigated at 0°, 18°, 25°, and 40°. Good bimolecular velocity coefficients were not obtained at the highest and lowest temperatures. Nitrous acid catalyses the reaction. The possibility of nitric acid reacting with the solvent is discussed. In the presence of concentrated sulphuric acid nitric acid reacts vigorously with acetic anhydride to give tetranitromethane. This reaction is greatly retarded by carbamide. No nitration takes place in glacial acetic acid.
C. W. GIBBY.

Stability maxima of some organic substances. II. I. BOLIN (Z. anorg. Chem., 1928, **177**, 227—252; cf. A., 1925, ii, 411).—The following values of the p_H of maximum stability at 25° have been determined: ethyl butyrate 5·65, methyl benzoate (80°) 4·0, ethyl benzoate (80°) 4·15, phenyl acetate 4·1, benzyl acetate 4·3, ethyl phenylacetate 4·9, ethyl acetoacetate 4·4, ethyl α-chloropropionate 4·0, ethyl hippurate 4·4, and methylacetanilide 6·0. Substances which are hydrolysed by both acids and alkalis may be classified in two groups; the members of the first group have their maximum stability at p_H less than 5, whilst those of the second group, consisting of secondary amines etc., are of maximum stability in the neighbourhood of the neutral point. For esters of the fatty acids the optimum p_H is for a weak acid lower than for a strong acid; for methyl esters the optimum p_H is somewhat less than for the corresponding ethyl esters. Introduction of a phenyl group lowers the optimum p_H and increases the velocity of decomposition of the ester. H. F. GILLBE.

Analogies between physiological rhythms and the rhythmical reactions in inorganic systems. R. S. LILLIE (Science, 1928, **67**, 593—598).—The conditions controlling a rhythmic reaction between iron and nitric acid are discussed. The rate of the rhythm depends on the extent of the active area, concentration of acid, temperature, polarisation, and length of the wire. Biological analogies are considered.
A. A. ELDRIDGE.

Kinetics of the combustion of carbon monoxide. W. FINKELSTEIN and W. MASCHOWETZ (Z. physikal. Chem., 1928, **138**, 369—378).—The kinetics of the combustion of carbon monoxide in the presence of glass is studied. The glass loses its catalytic activity in the presence of carbon dioxide. The combustion is a third order reaction. The mechanism of the reaction is explained in terms of adsorption. It would seem that reaction takes place between activated oxygen molecules adsorbed on the glass and carbon monoxide molecules. Two molecules of carbon monoxide must collide with each molecule of oxygen. Hence the reaction must be of the third order. The adsorption of oxygen on the glass must be small, as the catalytic effect is so low, and is physical in nature. On the other hand, since in glass a weak acid (silica) is combined with strong bases (sodium and calcium oxides) carbon dioxide will be attracted to the surface by chemical forces. The adsorption of carbon dioxide on the glass must therefore be of a chemical nature and practically irreversible. The poisoning of the glass surface by carbon dioxide therefore depends on the stability of the adsorbed carbon dioxide layer in comparison with that of the layers of carbon monoxide and oxygen. A. J. Mee.

Corrosion and rusting of alloyed and plain cast iron. P. Kötzschke and E. Pivovarski.—See B., 1929, 97.

Corrosion phenomena. XIII. Dissolution of metals with evolution of hydrogen, "catalytic" effect of foreign metals, and its connexion with the overvoltage series. A. Thiel and J. Eckell (Korrosion u. Metallschutz, 1928, 4, 121—133, 145—151; Chem. Zentr., 1928, ii, 1146).—See A., 1927, 1034.

Activator, promoter, or accelerator? A. Mittasch (Z. Elektrochem., 1929, 35, 96—97).—A question of nomenclature. L. L. Bircumshaw.

Acid catalysis in hydrolytic reactions. J. N. Brönsted and W. F. K. Wynne-Jones (Trans. Faraday Soc., 1929, 25, 59—76).—The conception of an acid or base as a substance with a tendency to dissociate or associate protons leads to the extended theory of acid and basic catalysis, which ascribes catalytic activity to acid or basic molecules in general and not solely to hydrogen and hydroxyl ions. It is shown that there is no *a priori* reason for excluding hydrolytic reactions from the scope of this theory, although there is a possibility of the effects escaping detection. From an analysis of the conditions obtaining in such reactions it is shown that if in a reaction catalysed by hydrogen or hydroxyl ions there is a detectable but not too large "spontaneous" reaction, then the conditions are favourable for the detection of effects of acids and bases in general. To verify this effect measurements were made by the dilatometric method of the acid catalysis of the hydrolysis of ethyl orthoformate, ethyl orthoacetate, ethyl orthopropionate, ethyl orthocarbonate, acetal, and ketal. These substances were chosen as being themselves neutral and giving hydrolysis products which also are neutral. Catalysis by acids other than the hydrogen ions was undetectable in the hydrolysis of acetal and ethyl orthoformate, a circumstance which renders these reactions suitable for the determination of hydrogen-ion concentration and for the investigation of salt effects. Catalytic effects due to water molecules, *m*- and *p*-nitrophenol, cacodylic and acetic acids, as well as to hydrogen ions were observed in the hydrolysis of the other substances investigated. The activities of these catalysts were found to be dependent on their strengths as acids. The "spontaneous" hydrolysis of the different substances employed was measured, and found in each case to be of small velocity (k_0^{20} of the order of 10^{-7}). Values are given for the dissociation constants of formic, acetic, and cacodylic acids, and for *m*- and *p*-nitrophenol, calculated from the data for the various reactions in different buffer solutions. The results afford definite evidence of the catalytic effects of uncharged acid molecules, and taken in conjunction with previous work on the decomposition of nitramide and the mutarotation of dextrose, support strongly the extended acid and basic theory of catalysis. F. G. Tryhorn.

Inhibitive action of alcohols on the oxidation of sodium sulphite. H. N. Alyea and H. L. J. Bäckström (J. Amer. Chem. Soc., 1929, 51, 90—109; cf. A., 1927, 737).—The thermal (21°) and also the photochemical oxidation of sodium sulphite solutions in presence of *iso*propyl, *sec.*-butyl, and benzyl alcohols was investigated. The oxidation of the sulphite induces an oxidation of the alcohol to an extent which increases with increasing alcohol concentration when the latter is low, but is independent of the concentration when the latter is high. When two alcohols are present, the same net amount of alcohol is oxidised, each one being oxidised in proportion to its inhibitory power. The chain length of the thermal reaction is equal to the photochemical quantum efficiency, or the induced oxidation obeys the Einstein photochemical equivalence law; in the process of breaking the reaction chain two molecules of alcohol seem to be oxidised instead of one (compare Cremer, A., 1927, 947). Copper sulphate accelerates the thermal reaction, but does not alter the ratio of oxidised sulphite to oxidised alcohol. Quinol exhibits anomalous behaviour as an inhibitor, possibly because it is directly oxidised and then reacts with the sulphite. Delicate colorimetric methods of determining traces (0·00005 mol./litre) of acetone, methyl ethyl ketone, and benzaldehyde are recorded. Minute traces of ketones may be removed from lower-boiling alcohols by refluxing the latter for several hours with a very small amount of *p*-nitrophenylhydrazine, nitrogen being simultaneously bubbled through the solution. S. K. Tweedy.

Use of iodine and iron as a chlorine carrier. H. E. Fierz-David (Naturwiss., 1929, 17, 13).—In the chlorination of benzene derivatives iodine together with iron is an extraordinarily active catalyst. By the use of 1% of iron and 0·1% of iodine, chlorinations which could be effected in the ordinary way only slowly and at high temperatures were carried out more rapidly and at lower temperatures. The chlorine derivatives obtained by this method are purer than those prepared with the use of iron or other carriers alone. Other combinations were tried, including iodine together with nickel, antimony, cobalt, bismuth, tin, phosphorus, and zinc, but these gave no satisfactory results. The catalyst goes into solution rapidly, producing a deep brown colour. A. J. Mee.

Decomposition of ammonia by iron. A. Mittasch, E. Kuss, and O. Emert (Z. Elektrochem., 1928, 34, 829—840; cf. A., 1928, 605).—The decomposition of ammonia by iron containing 0·035% of carbon and by iron containing before reduction potassium or aluminium oxide has been studied over the range 100—450° by a dynamic method. The catalysts were reduced in specially purified hydrogen at 400—480°. With the freshly-reduced iron, decomposition of the ammonia could be detected at 200°, with the formation of a nitride and the evolution of hydrogen. At 350°, appreciable amounts of nitrogen appear, and finally, at about 450°, a mixture of hydrogen and nitrogen in stoicheiometrical proportions is formed. In the case of iron activated by the addition of the oxides, the formation of nitrogen occurs first at a lower temperature, viz., 100°, as well as that of the stoicheiometric mixture. The velocity of the ammonia decomposition is determined by that of the formation of the nitrogen from the intermediate nitride which is produced, and the decomposition is shown to take place in the stages (i) iron+ammonia=iron nitride+hydrogen, and (ii) iron nitride=iron+nitrogen. The second stage is dependent on the temperature and on the addition of activators and it is generally the slower reaction, but under certain conditions it may become faster than (i). Decomposition, however, takes place exclusively at the metal independently of the individual effects of the added substances. At 360° and in the range 15—600 mm. pressure, the velocity of decomposition of the ammonia is independent of the total pressure and of the rate of passage of the gas over the metal.

Iron carbide, and mixtures of iron with other substances, especially the finely-divided carbide obtainable by reduction of the cyanide (*loc. cit.*), have also been investigated as catalysts. In all cases, the effective portion of an iron-containing catalyst is the metal itself. The carbide, both fine and coarse-grained, is not a catalyst for the synthesis or decomposition of ammonia. A method by which the effective portion of an iron-containing catalyst for ammonia can be determined is described together with a new gasometer for storage and exact analysis; the gasometer is especially suitable for use with highly-purified gases.

L. S. Theobald.

Copper catalysts prepared from precipitated hydroxide. I. Activity as a function of the temperature of precipitation. P. K. Frolich, M. R. Fenske, and D. Quiggle (J. Amer. Chem. Soc., 1929, **51**, 61—65).—The catalytic activity of copper catalysts prepared by reduction at 200° of the hydroxide obtained on precipitating copper nitrate solution with ammonia varies with the temperature of precipitation. The reaction studied was the catalytic decomposition of methyl alcohol vapour at 360° (cf. A., 1928, 1112); formaldehyde and methyl formate are produced simultaneously. A maximum activity occurs when the hydroxide is precipitated at 22°. *X*-Ray examination indicates that a small particle size of the dry hydroxide gel is associated with the more active catalysts. A minimum particle size at 22° may be produced as the result of two opposing factors, viz., the tendency for the initial particle size to decrease with falling temperature of precipitation, and the tendency for the initially formed particles to grow while the hydroxide is drying at 110°.

S. K. Tweedy.

Copper catalysts prepared from precipitated hydroxide. II. Comparison of sodium hydroxide and ammonia as a precipitating agent. P. K. Frolich, M. R. Fenske, L. R. Perry, and N. L. Hurd (J. Amer. Chem. Soc., 1929, **51**, 187—193).—When sodium hydroxide is the precipitating agent (cf. preceding abstract) the catalysts are much more active, due to promoter action of occluded sodium salts. Below 313° the activity of such catalysts is independent of time; at 380° the catalytic power is immediately destroyed. Thus fused occluded sodium salts appear to cover the active patches of the catalysts. Copper catalysts prepared by precipitating copper chloride or sulphate with sodium hydroxide are practically inactive. The promoted catalysts favour the formation of methyl formate in the thermal decomposition of methyl alcohol rather than that of formaldehyde. The conclusions are confirmed by experiments with catalysts containing known amounts of sodium nitrate. The results may explain some of the discordant observations recorded in the literature.

S. K. Tweedy.

Synthesis of water with a silver catalyst. II. Energy of activation and mechanism. A. F. Benton and J. C. Elgin (J. Amer. Chem. Soc., 1929, **51**, 7—18).—The synthesis of water in presence of a silver catalyst was investigated, the adsorption by the catalyst of oxygen and of water vapour (in presence of oxygen) being measured also. The oxygen adsorption is nearly independent of temperature and pressure (cf. A., 1927, 118). Water vapour is adsorbed much more strongly by a silver surface covered with adsorbed oxygen than by a bare surface. The reaction rate is independent of the oxygen pressure, but proportional to the hydrogen pressure and to the fraction of catalyst surface free from adsorbed water. The calculated energy of activation is 16,000 g.-cal. It is concluded that reaction occurs at every collision of hydrogen with " dry " adsorbed oxygen in which the energy available on collision exceeds the energy of activation. The results are probably not in disagreement with Taylor's theory of catalyst surfaces.

S. K. Tweedy.

[Catalytic] synthesis of methane from carbon dioxide and hydrogen. M. Randall and F. W. Gerard.—See B., 1929, 82.

[Catalytic] synthesis of higher hydrocarbons from water-gas [at atmospheric pressure]. II. D. F. Smith, C. O. Hawk, and D. A. Reynolds.—See B., 1929, 82.

Catalytic oxidation of naphthalene. T. Kusama.—See B., 1929, 88.

Effect of inhibitors on the acid dissolution of copper and copper alloys. H. O. Forrest, J. K. Roberts, and B. E. Roetheli.—See B., 1929, 98.

Theory of chemical action in electrical discharge. S. C. Lind (Science, 1928, 67, 565—569).—An address to the American Electrochemical Society, April 26, 1928.

Formation of ozone in the electrical discharge at pressures below 3 mm. J. K. Hunt (J. Amer. Chem. Soc., 1929, **51**, 30—38).—During the first half minute the quantity of ozone formed is approximately proportional to the input of electricity, but equilibrium is soon reached. The yield increases with increasing pressure, but at a decreasing rate; it is independent of the electrode material (small electrodes were used; aluminium gives abnormally high results) and increases with increasing cathode area. The number of ion pairs and of ozone molecules produced are both of the same order of magnitude. The following mechanism is suggested: $O_2=O^++O^-$; $O^++O_2=O_3^+$; $O^-+O_2=O_3^-$; $O_3^++O_3^-=2O_3$ or $O_3^++O^-=2O_2$ and $O_3^-+O^+=2O_2$.

S. K. Tweedy.

Electrolytic preparation of hydroxylamine. J. G. Stscherbakov and D. M. Libina (Z. Elektrochem., 1929, **35**, 70—83).—Different methods of determination of the hydroxylamine produced by the electrolytic reduction of nitric acid in sulphuric acid solution using a mercury cathode yield distinctly different results, and it is concluded that, besides hydroxylamine, considerable quantities of a second reducing agent are formed by the electrolysis. This is proved to be a compound of hydroxylamine*iso*-monosulphonic acid with sulphuric acid, $(NH_2{\cdot}O{\cdot}SO_3H)_2,H_2SO_4$. A low nitric acid concentration favours the formation of the *iso*-compound, which liberates iodine from potassium iodide, is oxidised to nitric acid by titration with permanganate in the cold, and is hydrolysed by heating to hydroxylamine. The combined sulphuric acid may be determined by titration with alkali, using phenolphthalein. An electrolyte containing the two compounds remains stable at the ordinary temperature for an indefinite period of time. An increase in the sulphuric and nitric acid concentrations up to certain limits (15—16*N*-sulphuric acid and *N*-nitric acid) causes an increase in the current yield of hydroxylamine, whilst below 3—4*N*-sulphuric acid a pronounced decrease takes place. For nitric acid concentrations above *N*, considerable quantities of oxides of nitrogen are formed. The most favourable acid concentrations, current densities, and temperatures are given, with which a mean current yield of 60—70% of hydroxylamine is obtainable. Under certain conditions (*e.g.*, the presence of foreign metals in the electrolyte, dissolved from the electrodes), the nitric acid is not reduced at the mercury cathode, but a hydrogen evolution of almost 100% takes place. At higher nitric acid concentrations, oxides of nitrogen are formed. In these circumstances, the cathode is found to be covered with a thin, scarcely visible film, which acts as a diaphragm and prevents reduction. The presence of the film increases the current yield of the *iso*-compound. At the end of the electrolysis, the free nitric acid may conveniently be removed by electrolysing with a copper cathode, since by this means the nitric acid is reduced to ammonia, whilst the hydroxylamine and *iso*-compound are unaffected.

L. L. Bircumshaw.

Influence of current density in the electrolytic preparation of sodium perborate. F. Giordani and R. Intonti (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], **34**, 30—36).—The yields of sodium perborate, obtained by electrolysing solutions of borax and sodium carbonate under conditions in which the current passing through the electrolyte was 10, 5, and 2·5 amp./litre, respectively, have been determined. Assuming that the perborate is formed according to the schemes $Na_2CO_3 \longrightarrow NaCO_3'+Na^{\cdot}$, $2NaCO_3'+2F \longrightarrow Na_2C_2O_6$, $Na_2C_2O_6+NaBO_2+2H_2O \longrightarrow 2NaHCO_3+NaBO_2,H_2O_2$, $Na_2B_4O_7+2NaOH \longrightarrow 4NaBO_2+H_2O$, it is shown that the effective instantaneous yield of perborate is given by $\rho=2F(V/I)k(Na_2C_2O_6)(NaBO_2)/\rho_1$, where ρ_1 is the current efficiency in the formation of sodium percarbonate, *V* the volume of the solution, and *I* the current intensity.

F. G. Tryhorn.

Electrolytic precipitation of metals. K. Arndt (Ber., 1929, **62**, [*B*], 80—84).—Study of the distribution of a metal on a cathodic surface frequently gives wave-like curves with distinct maxima and minima. Interposition of a non-conducting screen of mica or celluloid, pierced with a fine hole in the centre, between cathode and anode in the electrolysis of Öttel's solution (150 g. $CuSO_4,5H_2O$, 50 g. H_2SO_4, and 50 g. of alcohol per litre) causes the metal to be deposited in concentric rings which are more or less sharply defined. All the crystals have approximately the same size (5 μ). It is considered that the current initially causes an approximately uniform distribution of crystal nuclei and that subsequently the particles in unfavourable positions pass into solution whilst metal is deposited at the favourable positions. Study has also been made of the deposition of copper on a silvered cathode without a shield with a current density so small that the individual crystals can be measured and counted, Öttel's solution being used. Increased current density, cooling, or dilution increases the number of copper crystals, which is lessened by warming or decrease in current density. At the ordinary temperature with 8 milliamp. the size is about 1·5 μ, with 40 milliamp. about 0·5 μ. At 0° the size is also approximately 0·5 μ, whereas at 35° the few particles may attain 5 μ. From the warm bath crystals are obtained as much as 5 μ long. Addition of 0·1% of gelatin to the acid copper bath renders the copper particles so small that they cannot be distinguished under the microscope. A uniform copper deposit is also obtained from a copper bath containing potassium cyanide.

H. Wren.

Theory of electro-deposition of chromium from aqueous solutions of chromic acid. E. Müller and P. Ekwall (Z. Elektrochem., 1929, **35**, 84—89; cf. Schischkin and Gernet, A., 1928, 489).—A microscopical examination has been made of the deposits obtained under various conditions when 30% aqueous solutions of chromic acid are electrolysed, using smooth platinum electrodes. Photomicrographs are reproduced, showing the results with very carefully purified chromic acid, free from all traces of sulphate, with chromic acid 0·001, 0·01, 0·05, and 0·1*N* with respect to sulphuric acid, and chromic acid free from sulphate but containing tervalent chromium. The last-named solution was prepared by boiling chromic acid with hydrogen peroxide and contained about 0·13 g. of tervalent chromium to 1 g. of sexavalent chromium. The results confirm Müller's previous view (cf. A., 1926, 913), that a non-conducting diaphragm of chromic chromate is formed at the cathode, which hinders access of chromium ions but is permeable to hydrogen ions. At potentials lower than −1·1 volt, deposition of metallic chromium begins to take place, the first layer of metal deposited forming an alloy with the platinum. In the presence of sulphate ions, the chromic chromate diaphragm is considered to be mechanically imperfect and may be removed by the gaseous hydrogen evolved. For this reason, the presence of sulphates promotes deposition of chromium in a bright coherent form. Similar results are obtained if sulphate-free chromic acid containing tervalent chromium is used. A study was made of the cataphoretic behaviour of solid chromic chromate in the colloidal state, prepared by adding excess of alcohol to a concentrated solution of pure chromic acid, dissolving the brown gel, which formed after some time, in water, and dialysing the resulting solution. The chromic chromate migrates to the cathode, and is believed to be a basic compound with the composition $Cr_2(OH)_4CrO_4$.

L. L. Bircumshaw.

Electrolytic oxidation of methyl alcohol in alkaline solution. S. Tanaka (Z. Elektrochem., 1929, **35**, 38—42).—An investigation has been made of the relations between anode potential and current density in the electrolytic oxidation of methyl alcohol mixed with an equal volume of $8N$-sodium hydroxide, using as anode material smooth and spongy platinum, palladium, and rhodium, smooth gold, and silver. The current–potential curves for the smooth metals are all similar in form, but differ from those for the spongy metals, which resemble those obtained in the electrolytic oxidation of formaldehyde in alkaline solution (cf. Müller and Takegami, A., 1928, 1338). A current rise is observed in the low potential region, followed by a sudden fall, after which a second current rise occurs in the high potential region. In no case was any evolution of gas observed on the first rise, and with the smooth metals, the current rise at low potentials was absent. With rising temperature, the first rise becomes steeper and leads to higher current densities. The anolyte was analysed for formaldehyde and formic acid. No aldehyde appears to be produced, and it is considered that the reaction occurring in the low potential region may be represented by $CH_3O'+OH'-4$ faradays$=H{\cdot}CO_2H+2H^{\cdot}$ or $CH_3O'+3OH'-4$ faradays$=H{\cdot}CO_2H+2H_2O$. A theory developed to explain the observed phenomena is based on the supposed adsorption of the alcohol anions on the electrode surface.

L. L. Bircumshaw.

Regularity of the physical and chemical action of *X*-rays. R. Glocker (Z. tech. Phys., 1928, **9**, 201—207; Chem. Zentr., 1928, ii, 1063).—The law of photochemical equivalence is not applicable to *X*-rays, since the number of electrons liberated as a secondary process far exceeds that of the electrons primarily liberated by the absorption of the radiation. In photochemical reactions in solution, electrons liberated from all the molecules present, and not merely those of the solute, are active in the chemical change.

A. A. Eldridge.

Photo-expansion of chlorine. W. H. Martin, A. F. W. Cole, and E. E. Lent (J. Physical Chem., 1929, **33**, 148—153).—Contrary to the observation of Shenstone (J.C.S., 1897, **71**, 471), purified and dried chlorine still shows expansion when exposed to light. Chlorine fractionated by means of liquid air over purified phosphorus pentoxide showed practically no decrease in expansion, as compared with the undried chlorine, when insolated by the light from a carbon arc. Baking-out the expansion bulb at 425° under a pressure of less than 0·0001 mm. of mercury for 4 days before admission of the dried chlorine had no effect on the photo-expansion. The present experiments together with those previously reported (A., 1926, 559) show that dried chlorine at 1 atm. and at lower pressures exhibits no abnormal scattering nor any fluorescence which can be detected visually or photographically. The assumption that dry chlorine does not expand on insolation but re-radiates adsorbed energy is unwarranted.

L. S. Theobald.

Photochemical union of hydrogen and chlorine. A. J. Allmand and E. Beesley (Nature, 1929, **123**, 164).—The results of a study of the effect of the intensity of monochromatic light are in agreement with those of (Mrs.) Chapman, Kornfeld and Steiner, and Marshall. The effect of wave-length (Å.) on the quantum efficiency is as follows: 2600, 0·10; 3130, 0·49; 3650, 0·53; 4050, 1·00; 4360, 0·67; 5460, 0·22. The sensitivity of the gas used corresponded with a yield of the order of 2×10^5 mols. of hydrogen chloride per quantum of blue light absorbed; the mixture showed no induction period, but gave a marked Draper effect during the first instants of insolation. The relative temperature coefficients (between 19·7° and 25°) of the quantum efficiency increase slowly with wave-length between 3130 and 4360 Å. When acting simultaneously, two monochromatic beams gave a velocity equal to the sum of their separate effects.

A. A. Eldridge.

Budde effect in bromine. E. Matthews (Trans. Faraday Soc., 1929, **25**, 41—43).—A slight expansion on illumination by a 100-c.p. lamp was recorded for mixtures of dried bromine vapour and air at temperatures between 20° and 95°; a smaller expansion was shown by dry bromine vapour in the absence of air, and a somewhat greater one in the case of a mixture of bromine vapour and air which had not been dried over phosphorus pentoxide.

F. G. Tryhorn.

Further test of the radiation hypothesis. L. S. Kassel (J. Amer. Chem. Soc., 1929, **51**, 54—61).—The decomposition rate of nitrogen pentoxide, even at very low pressure, is not increased by radiation of wave-length less than 5 μ; not more than 3% of the total thermal reaction can be caused exclusively by radiation of wave-length less than 5 μ. The region between 5 and 10 μ may be all-important if the radiation theory is the true explanation (which is improbable) of the anomalous nitrogen pentoxide decomposition. If the diameter for intrinsic energy transfer of the nitrogen pentoxide molecule is approximately independent of the energy, and if it is larger than the kinetic theory diameter (which would supply an explanation of the anomalous decomposition rate), then the thermal conductivity of the gas should be abnormally large.

S. K. Tweedy.

Mechanism of the photochemical decomposition of nitrogen pentoxide. W. P. Baxter and R. C. Dickinson (J. Amer. Chem. Soc., 1929, **51**, 109—116).—From measurements of the relative rates of decomposition of nitrogen pentoxide at 0° by radiations of wave-lengths 4350, 4050, and 3660 Å., and comparison with the rates of decomposition of nitrogen dioxide, it is concluded that the mechanism of the pentoxide decomposition is essentially that suggested by Norrish (A., 1927, 119, 528).

S. K. Tweedy.

Herschel effect. Lüppo-Cramer (Z. wiss. Phot., 1928, **26**, 249—259).

Spectral distribution of the inner photo-effect in the silver halides. E. A. Kirillov (Z.

wiss. Phot., 1928, 26, 235—248).—The photo-electric conductivity of granular layers of silver halides has been investigated. New maxima in the longer waves have been found. In the case of silver bromide, the conductivity was less in the presence of light.

W. E. DOWNEY.

Photolysis of silver bromide. E. MUTTER (Z. wiss. Phot., 1928, 26, 193—234).—The bromine liberated by the photolysis of silver bromide in the presence of water exists as ions. Nitric acid dissolves the photolytic silver in small degree, the degree of regression being a function of the time and of the concentration of the solution. As a result of secondary reactions, hydrogen ions and free oxygen also appear. This behaviour is explained by the hypothesis that the hydroxyl ion behaves as an acceptor. The nitrite ion behaves similarly. The quantum yield in the presence of the nitrite ion is approximately 1. For equivalent substances the yield is only about 0·1 owing to the strong regression. Thus, the same amount of silver causes a much stronger blackening in the presence of nitrite than in that of equivalent substances. W. E. DOWNEY.

Photolysis of silver halides in the light of the quantum theory and the photo-electric effect. H. KIESER (Z. wiss. Phot., 1928, 26, 275—287).—Theoretical. Cf. Mutter (preceding abstract).

W. E. DOWNEY.

Sensitometry of desensitised films. H. ARENS and J. EGGERT (Z. wiss. Phot., 1928, 26, 111—126).—Three-dimensional models have been prepared showing the relationships between the darkening D and $\log i$ and $\log t$ for the Agfa "extra rapid" plate and for the same plate when desensitised before exposure by immersion in 1/2000 phenosafranine solution containing 2% of potassium bromide. The forms of surface obtained differ in both position and form. For the desensitised plate a section parallel to the $\log t$ axis exhibits maxima, which decrease as i decreases; at low values of i no darkening is produced. The intensity plane, parallel to the $\log i$ axis, is of the normal form, which, however, remains unaltered at high values of t. Although the desensitised plate has a rather steeper intensity curve, there is no typical difference in the time curves. The Schwarzschild exponent n assumes anomalous values for the desensitised plate; over a wide range $n=0$ and in the region of reversal $n=-2{\cdot}3$. No simple numerical expression can be obtained for the degree of desensitisation.

H. F. GILLBE.

Relation between the photo-electric and the photographic effect in silver bromide. L. W. BUTLER (Proc. Iowa Acad. Sci., 1927, 34, 277).—The results obtained by Toy, Edgerton, and Vick (A., 1927, 293) are confirmed. CHEMICAL ABSTRACTS.

Photometric and spectrophotometric studies. VI. Reflexion spectroscopy. K. SCHAUM (Z. wiss. Phot., 1928, 26, 97—110).—A method is described for the measurement of reflexion spectra, especially of opaque substances. The reflexion spectra of a number of aromatic azo-compounds have been determined, and in general the curves obtained resemble those of the absorption spectra. The influence of irradiation on films of a number of dyes has been investigated; the number of large particles increases, whilst the reflexion, and to a smaller extent the absorption, spectra are altered; this effect is dependent on the presence of oxygen, since it is at a maximum in pure oxygen but is not produced in a vacuum or in an atmosphere of hydrogen, and is probably partly photochemical and partly physical in nature. Analogous effects on the spectra are produced in some cases by treatment of the film with hydrogen peroxide, whilst coagulation of certain dye solutions by electrolytes results in similar effects.

H. F. GILLBE.

Influence of metallic magnesium on the formation of formaldehyde and sugars by the action of ultra-violet rays on calcium hydrogen carbonate solutions. G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1928, [vi], 8, 511—515).—The power to reduce iodine solution acquired by calcium hydrogen carbonate solutions on exposure to ultra-violet rays (cf. Mezzadroli and Gardano, A., 1928, 255) rises to a maximum after 30 min. when open basins, or after 1 hr. when closed transparent vessels, are used to contain the liquid, the reducing power being the higher in the latter case. The total amount of reducing substances formed is increased by the presence in the solutions of metallic magnesium, which also results in the formation of sugars which reduce Fehling's solution and form an osazone.

T. H. POPE.

Induction period and after-effect in photochemical reactions. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1928, 5, 721—732).—The induction period in the photo-bromination of cinnamic acid and stilbene (A., 1926, 366; 1928, 172) is diminished by any factor (*e.g.*, temperature, intensity of light) causing an increase in the velocity of the reaction. During the oxidation of tartaric acid by bromine (A., 1925, ii, 1179) the induction period increases with increased concentrations of tartaric acid, and to a certain point with bromine. Above this concentration of bromine a decrease is manifested owing to reaction being due to free bromine molecules. α-Hydroxy-β-phenylpropionic and mandelic acids are oxidised by bromine in the dark, the latter only slowly. The reactions are markedly accelerated by light, and then show both induction periods and after-effects. When potassium bromide is added to any of the above oxidation reactions in a concentration eight to ten times as great as that of the bromine the induction period either disappears or is reduced considerably. The period of gradually increasing velocity observed in these oxidations is not explained satisfactorily by Ghosh and Basu (A., 1928, 970), and it is assumed that the bromine molecules are hydrated. Whilst such molecules are active in the dark, on exposure to light they become activated, and this period of activation is, presumably, the induction period. In presence of bromide ions only a small percentage of the hydrated molecules exist as such owing to the change $Br'+Br_2 \rightleftharpoons Br_3'$, and reaction proceeds normally. The after-effect is probably due to the existence of chain-reactions. H. BURTON.

Photochemical studies. VIII. Photochemical decomposition of malonic acid both in the

presence and absence of uranyl sulphate. W. C. Pierce, A. Leviton, and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1929, **51**, 80—89).—The early stages of the decomposition lead almost exclusively to the formation of carbon dioxide and acetic acid, both in the presence and in the absence of the catalyst. The quantum efficiency of the catalysed reaction is smaller than that of the uncatalysed reaction and is not markedly influenced by the wave-length. In presence of radiation from a mercury arc lamp the decomposition rate increases with addition of uranyl sulphate and approaches a practically constant value, whereas with constant catalyst concentration the rate of decomposition of malonic acid is approximately proportional to the cube root of the acid concentration. The degree of ionisation of the acid seems to be without influence on the rate, since the addition of sulphuric acid is without effect. There is no evidence for the formation of a light-sensitive complex molecule, but the possible existence of such a complex is not eliminated. The results seem to indicate that there are two independent reactions, due to the light absorbed by the catalyst and by the malonic acid, respectively; it is possible, also, that with constant malonic acid concentration the rate of the catalysed reaction is proportional to the intensity of the light absorbed by the catalyst. The mechanism may involve the deactivation of uranyl sulphate molecules by collision with other uranyl sulphate molecules or with malonic acid molecules. Below 0·01*M*, uranyl sulphate behaves towards phenolphthalein as though it were an equivalent amount of sulphuric acid.

S. K. Tweedy.

Zinc oxide and chlorophyll as optical sensitisers. J. Böhi (Helv. Chim. Acta, 1929, **12**, 121—153).—An experimental investigation based on the theoretical views of Baur (A., 1928, 1338). The sensitising action of zinc oxide on the reduction of Prussian blue and of copper salts with and without the addition of anodic depolarisers (dextrose and glycerol) has been examined. Even in the presence of dextrose the reduction of Prussian blue by light reaches an equilibrium value of only 36%. On the other hand, if an anodic depolariser be present cupric salts are reduced by light to the cuprous state and finally to the metallic state and the amount of reduced copper obtained is linearly proportional to the duration of exposure to light. Without an anodic depolariser only cupric oxide is obtained, a fact which is attributed to oxidation of cuprous oxide formed at first. By the action of light on electrolytic gas in the presence of moist zinc oxide, water and hydrogen peroxide have been obtained.

Reduction of a large number of azo-dyes takes place by exposure to light in the presence of chlorophyll in methyl-alcoholic solution. The chlorophyll itself is destroyed, but this can be prevented by adding one of the following anodic depolarisers: oil of turpentine, piperidine, phenylhydrazine. Addition of the last-named was found to produce the most rapid photolysis. Some other vat, azine, and triphenylmethane dyes have also been studied. No reduction is obtained by exposure to light in the presence of chlorophyll alone, but by addition of phenylhydrazine reduction takes place. Experiments have also been carried out on systems in which the chlorophyll is in one liquid layer, *i.e.*, a solution in benzene or carbon tetrachloride, and the dye is in another aqueous layer; the sensitising action of chlorophyll in these systems is reduced.

R. N. Kerr.

Action of light on anthracene. E. Hibbert.—See B., 1929, 88.

Chain reactions. M. Bodenstein (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 490—497).

Ignition of detonating gas by hydrogen atoms. F. Haber and H. D. von Schweinitz (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 499—506).—According to Bonhœffer and Haber (cf. this vol., 11) the mechanism of the burning of detonating gas is a chain reaction of the form (*a*) $OH+H_2=H_2O+H$, (*b*) $2H+O_2=2OH$, so that the addition of a sufficient quantity of hydrogen atoms or hydroxyl radicals should bring about explosion at the ordinary temperature. This has been accomplished for hydrogen atoms. A stream of hydrogen was fed into an arc, a small concentration of hydrogen atoms being thereby produced, and their recombination prevented by rapid cooling. The stream of molecular and atomic (about 0·1%) hydrogen was then brought into contact with oxygen. A definite lag, varying in duration according to the strength of the arc current, was observed between switching on the arc and the commencement of the explosion. That the explosion was due to decomposition products of hydrogen was established by the fact that no explosion occurred when hydrogen was replaced by argon.

In other experiments arranged, *e.g.*, to eliminate the possibility that the explosion could be due to direct heating by the arc, similar results were obtained.

The explosion cannot be due to the heat developed by such reactions as $2H+0\cdot5O_2=H_2O+157$ kg.-cal., for this would require a 5% concentration of hydrogen atoms in order to produce the ignition temperature of 600°, as against the measured concentration of 0·1%.

S. J. Gregg.

Compounds of alkali phosphates with hydrogen peroxide. H. Menzel and C. Gäbler (Z. anorg. Chem., 1928, **177**, 187—214).—The solubilities have been determined of the salts $Na_4P_2O_7,10H_2O$, KH_2PO_4, and $Na_2HPO_4,12H_2O$ in water from about −3° to +25° and in aqueous hydrogen peroxide solutions of various concentrations at 0°. The formation of compounds between hydrogen peroxide and the phosphates is indicated by the rapid increase of solubility as the hydrogen peroxide concentration increases. Cryoscopic measurements with phosphate in hydrogen peroxide solution, and determination of the partition coefficients of hydrogen peroxide between these solutions and amyl alcohol, also indicate some combination between the hydrogen peroxide and the dissolved phosphate. By evaporation of the solutions at the ordinary temperature in a current of dry air the compounds $Na_2HPO_4,2H_2O_2$, $K_2HPO_4,2\cdot5H_2O_2$, and $KH_2PO_4,1—1\cdot25H_2O_2$ have been isolated; the sodium compound, although hygroscopic, is stable in dry air, and may be differentiated both microscopically and by its *X*-ray diagram from $Na_2HPO_4,2H_2O$; the compound $K_2HPO_4,2{\cdot}5H_2O_2$ is similar to the sodium salt. The monopotassium compound is considerably less stable, whilst the analogous sodium salt has not been prepared. By precipitation with alcohol an oily substance is obtained, of approximate composition $Na_2HPO_4,2H_2O_2,10H_2O$, which, however, on evaporation yields only $Na_2HPO_4,2H_2O_2$. The formulæ ascribed to these substances are supported by the observations that ether extracts hydrogen peroxide from the salts, and that at 130° in a vacuum hydrogen peroxide is evolved, leaving the anhydrous salts. These compounds are thus to be distinguished from the true perphosphates obtained electrolytically.

H. F. Gillbe.

Constitution of double salts. XV. Ammine iodides. G. Spacu and O. Voicu (Bul. Soc. Stiinte Cluj, 1928, **4**, 42—56; Chem. Zentr., 1928, ii, 1196).—The following *compounds* are described: $(NH_4)_2[ZnI_4(C_5H_5N)_2]$, from zinc ammonium iodide and pyridine in benzene, yellow, decomposed by light and air, and hydrolysed by water; $Na_2[ZnI_4(C_6H_5{\cdot}NH_2)_2]$, stable in air; $K[PbI_3(NH_3)_3]$; $[CdI_4][Ba(H_2O)_2(C_6H_5{\cdot}NH_2)_2]$; $[HgI_3][Cu(C_5H_5N)_4]$; $[HgI_3][Cu(C_5H_5N)_5]$. A. A. Eldridge.

Dehydration of $3CdSO_4,8H_2O$. L. Coniglio (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], **34**, 119—122).—The hydrate $3CdSO_4,5H_2O$, formed from $3CdSO_4,8H_2O$ at 41·5° (cf. Carpenter and Jette, A., 1923, ii, 292), exists over a range of more than 70°. At about 120° the hydrate $3CdSO_4,2H_2O$ is obtained, and at about 138° the hydrate $3CdSO_4,H_2O$. This last is converted into the anhydrous salt at 150°. The continued existence of the termolecular complex $3CdSO_4$ in the above hydrates is noteworthy.

E. W. Wignall.

Reaction of fusible and infusible white precipitates of mercury [mercuriammonium chlorides]. P. Rây and P. Banerji (J. Indian Chem. Soc., 1928, **5**, 715—719).—Ammoniacal hydrogen peroxide converts both the infusible (I) and fusible (II) white precipitates of mercury, $HgCl,NH_2$ and $HgCl_2,2NH_3$, respectively (cf. Franklin, A., 1905, ii, 581; 1907, ii, 264), into mercury and ammonium chloride. Mercuric oxide also gives mercury under the same conditions and is probably an intermediate product. Ethyl mercaptan reacts with I in alcoholic solution, yielding mainly mercuric mercaptide and smaller amounts of ethylthiolmercuric chloride, ammonium chloride, and ammonia. Under similar conditions II furnishes approximately equal amounts of the above mercaptides, indicating that dissociation of II occurs thus: $[Hg(NH_3)_2Cl_2] \rightleftharpoons HgCl_2+2NH_3$ or $[HgNH_2]Cl+NH_4Cl$. When I or II is treated with thiocarbamide in aqueous or alcoholic solution, ammonia is evolved and mercuric sulphide and the double compound of mercuric chloride and thiocarbamide are precipitated. The soluble residue contains ammonium chloride and gives on treatment with ammoniacal silver nitrate silver cyanamide. Thiocarbanilide and I give mercuric sulphide and diphenylguanidine hydrochloride, also formed together with ammonium chloride from II. It is concluded that I reacts as the equilibrium mixture $HgCl,NH_2 \rightleftharpoons [Hg{:}NH_2]Cl$. H. Burton.

Boron hydrides. XII. $B_{10}H_{14}$. A. Stock and E. Pohland (Ber., 1929, **62**, [*B*], 90—99; cf. A., 1926, 1217).—The initial material consisted of residues of boron hydrides remaining after heating B_4H_{10} and from which B_2H_6 and unchanged B_4H_{10} had been removed. The product after 4 years in a vacuum contained nothing volatile except $B_{10}H_{14}$, a little hydrogen, and some B_5H_9; the less stable $B_5H_{>9}$ had become decomposed. The non-volatile residue in the tubes consisted of the colourless hydride containing 12 atoms of boron, and the yellow hydride (B : H = about 5 : 4) insoluble in carbon disulphide. The hydride B_5H_9 combines with ammonia, giving the compound $B_5H_9,4NH_3$, which passes at 200° into hydrogen and $B_3N_3H_6$. The hydride $B_{10}H_{14}$ is separated from the small amounts of accompanying volatile hydrides by fractional condensation. The pure material has m. p. 99·6—99·7°. The vapour tensions between 55° and 156° are recorded and from these the b. p./760 mm. is calculated to be about 213°. The values $d^{\text{atm. temp.}}$ 0·94, $d^{99\cdot0}$ 0·92, and d^{100} 0·78 (molten) are given. The hydride is stable at the ordinary temperature, but decomposes slowly at 200°, extensively at 250°, giving hydrogen and a non-volatile, yellow material. Air and oxygen in the absence of moisture do not affect it at 50—60°. It is insoluble in water, by which it is quantitatively hydrolysed at 200° to boric acid and hydrogen; the action occurs moderately rapidly at 100°, but very slowly at the atmospheric temperature. Incomplete hydrolysis with an excess of water does not appear to yield any other hydride, but a boron compound with about the same volatility as water appears to be produced when the hydride is in excess. Sodium hydroxide dissolves $B_{10}H_{14}$ and the solution continuously evolves hydrogen; very stable, partly oxidised boron compounds appear to be produced. At low temperatures, $B_{10}H_{14}$ combines loosely with about $6NH_3$, which is evolved at the atmospheric temperature. When it is heated with ammonia a complex change occurs accompanied by evolution of hydrogen but without production of $B_3N_3H_6$. Electrolysis of solution of $B_{10}H_{14}$ in liquid ammonia follows a complicated course, but the electrolyte character of the additive compound is established. Hydrogen chloride does not react with $B_{10}H_{14}$ in presence of aluminium chloride at 100°. Apparently, the treatment of $B_{10}H_{14}$ with an excess of iodine leads to two groups of products, one of which is soluble in carbon disulphide and contains mainly the *di-iodo-compound* $B_{10}H_{12}I_2$, whereas the other is insoluble in carbon disulphide and contains 10—12 atoms of iodine in the molecule. The intermediate iodides are obviously unstable. Boron tri-iodide is not produced. $B_{10}H_{14}$ forms rhombic crystals, $a : b : c = 0{\cdot}6935 : 1 : 0{\cdot}2728$. Röntgenographic investigation affords little evidence of the structure of the molecule.

H. Wren.

Heterotri-salts. V. Heterotri-borates and their isomorphism with other heterotri-series. G. Canneri (Gazzetta, 1928, **58**, 840—844; cf. A., 1927, 220).—Since the radius of the boron atom is presumably not much different from those of silicon and phosphorus, it seemed likely that boron might be able to replace these two elements as the central atom in the complex anions of silico- and phosphotungstovanadates of the types $R_8[Si(W_2O_7)_x(V_2O_6)_y],nH_2O$ and $R_7[P(W_2O_7)_x(V_2O_6)_y],nH_2O$, respectively, where $x+y=6$. By allowing solutions containing commercial boric acid and alkali tungstates and vanadates to crystallise at the ordinary temperature small quantities of alkali polyborate separate at first. From the reddish-brown liquor which finally remains, small amounts of large brown crystals separate, which show the same crystallographic characteristics as the above-mentioned silico- and phospho-tri-salts. They are mixed crystals containing silicon and phosphorus, which were originally present as impurities in the boric acid, and they are not formed if the latter is purified by recrystallisation before use. Borotungstovanadates could not be obtained in the pure state, showing that boron is apparently incapable of co-ordinating the W_2O_7 and V_2O_6 groups simultaneously. O. J. Walker.

Hydrated aluminium silicates. I. Rehydration of metakaolin and synthesis of kaolin. C. J. Van Nieuwenburg and H. A. J. Pieters (Rec. trav. chim., 1929, **48**, 27—36).—Metakaolin (dehydrated kaolin) when treated with steam under a pressure of about 100 atm. for 2—6 days takes up water. This reaction is never wholly complete, the maximum amount of water present after rehydration being 14·5% (theory 15%). The amount taken up is dependent on the temperature of ignition of the original kaolin. If this is above 850°, the faculty of rehydration is gradually lost. Alumina takes up water when treated in a similar way: the amount taken up corresponds with the formula Al_2O_3,H_2O, but the product obtained is not identical with diaspore. The water taken up in this case also depends on the temperature of ignition of the alumina; if this be above 1000° a sharp break in the percentage of water taken up occurs. Under the same conditions amorphous silica takes up a quantity of water not exceeding 5·3%. It is shown that metakaolin cannot be simply a mixture of alumina and silica, since an artificial mixture of the two oxides in the correct ratio takes up only 11% of water. A product resembling kaolin has been synthesised by precipitating alumina and silica together in the correct proportions and treating the dried precipitate with steam for 12 days under a pressure of 200—260 atm. The water content is low, 9·1% (theor. 14·0%), but the solubility in dilute hydrochloric acid is of the right order and the physical properties are in good agreement with those of kaolin. R. N. Kerr.

Action of aluminium, ferrous and ferric iron, and manganese in base-exchange reactions. O. C. Magistad.—See B., 1929, 93.

Higher oxides of some rare-earth elements. H. A. Pagel and P. H. M.-P. Brinton (J. Amer. Chem. Soc., 1929, **51**, 42—54).—The composition of air-ignited praseodymium oxide varies with the conditions of ignition and especially of cooling, but with any specific set of conditions reasonably concordant compositions are obtained. By heating lower oxides at 370° for 11·5 hrs. in pure oxygen under a pressure of 215 lb. per sq. in., praseodymium dioxide of 99·2% purity is obtained. Higher purity could never be attained. The presence of ceria produces an abnormally high degree of oxidation of praseodymium only when the oxygen is under pressure. The oxide Pr_6O_{11} dissociates above 700°, but re-oxidises on cooling below 400° (cf. Prandtl and Huttner, A., 1926, 137). Lanthanum, neodymium, samarium, gadolinium, erbium, and ytterbium formed no higher oxides, and it is questioned whether these elements should occupy other than the third group of the periodic table. A method of adapting a balance for weighing hygroscopic substances is described, as well as a furnace applicable for the study of oxidation under pressure. S. K. Tweedy.

Silicic acids. W. Dilthey and E. Hölterhoff (Ber., 1929, **62**, [*B*], 24—31).—The difficulty of differentiating between combined and adsorbed water in silica gels has led the authors to attempt the union of the hydroxyl group with the silicon atom without the presence of water. For this purpose, silicon tetrachloride is allowed to react with about 4·5 mols. of triphenylcarbinol in anhydrous ether at the atmospheric temperature. The separated silicic acid is washed with anhydrous ether until the solvent is free from triphenylmethyl chloride as judged by the absence of halochromism on addition of concentrated sulphuric acid and exposed to the air for not more than ½ hr. The product then contains 29·6—26·2% of water and hence cannot consist of orthosilicic acid ($H_2O=37·5\%$). Variation in the temperature of the reaction between 2° and 35° shows the proportion of water to diminish somewhat with rising temperature, the extreme values being 28·1% and 26·6%, with a mean value of about 27·5%. If the proportion of triphenylcarbinol is reduced to 3 mols., hydrogen chloride is evolved and a chlorine-free silicic acid is produced containing only a slightly smaller percentage of water, which, in the most favourable case, is 1% greater than that required by metasilicic acid. The silicic acids thus obtained continuously lose water on exposure to air. Products dried until the water content is about 17% and then allowed to re-absorb moisture become constant in weight when 25% of the latter is present. Subsequent dehydration in a vacuum proceeds rapidly and rehydration of a product containing 13% of water leads to a material containing 25%. This amount is 1% in excess of that required for metasilicic acid, but 2% below that of the original material. The water in the hydrates is therefore regarded as constitutional, but so relatively loosely combined that a distinction cannot be made between adsorbed or united water by desiccation in air or in a vacuum.

Replacement of ether as solvent by carbon disulphide, chloroform, carbon tetrachloride, and benzene with consequent possibility of operating at a higher temperature shows that the proportion of water in the hydrates diminishes as the temperature rises and is also reduced by the use of 3 mols. instead of 4·5 mols. of triphenylcarbinol. The rules are not, however, without exception, since the nature of the solvent is not without influence. H. Wren.

Silicic acids. V. R. Schwarz and H. Richter (Ber., 1929, **62**, [*B*], 31—36; cf. A., 1927, 634).—

Silicic acid gels are obtained by the hydrolysis of silicon tetrachloride by water at 0°; the product is poured into much water and repeatedly washed with water until free from chlorine. It is subsequently dried by means of acetone, methyl or ethyl alcohol, or liquid ammonia, the temperature not being allowed to exceed 2° during the whole process. The products obtained with the three drying agents just named contain approximately 23% of water, corresponding thus with a polymetasilicic acid, $[SiO_2,H_2O]_x$. The probability that the material is a definite hydrate is established, not only by the stoicheiometric relationship, but also by its non-identity with the compound derived by subjecting gels from silicate solutions to a precisely similar treatment. Hydrolysis of titanium tetrachloride at 0° followed by desiccation of the product with acetone yields a product containing 32·4% of water, thus corresponding closely with the hydrate $TiO_2,2H_2O$.

Dehydration of silicic acid gels by liquid ammonia yields results not greatly dissimilar from those of Biltz and Rahlfs (cf. A., 1928, 854), the observed ratio being $SiO_2 : H_2O : NH_3 = 6 : 2{\cdot}95—3{\cdot}5 : 1{\cdot}7—2{\cdot}14$. Since the gels originally contain polymerised metasilicic acid, it appears that the ammonia causes a secondary change, the effect of which is a dehydration to the di-acid stage.

Hydrates poorer in water are obtained if the temperature is allowed to rise during hydrolysis of silicon tetrachloride; at 100°, the product formed has the composition $3SiO_2,2H_2O$. It is remarkable that almost identical substances result from the ammonia and acetone processes and that the amount of adsorbed ammonia is unusually small.

H. Wren.

Constitution of double salts. XVI, XVII. Ammine bromides. G. Spacu and J. Dick (Bul. Soc. Stiinte Cluj, 1928, 4, 84—103, 110—124; Chem. Zentr., 1928, ii, 1196—1197).—The following hexamethylenetetramine (*H*), pyridine, and piperazine (*P*), *compounds* have been prepared:

$[MnH_6][SnBr_6]$ (also $+2H_2O$); $[NiH_6][SnBr_6]$ (also $+2H_2O$); $[CoH_6][SnBr_6]$ (also $+4H_2O$); $[MnH_5,H_2O][SnBr_5OH],4H_2O$; $[Mn(C_5H_5N)_6][SnBr_6]$; $[Co(C_5H_5N)_6][SnBr_6]$; $[Ni(C_5H_5N)_6][SnBr_5OH]$; $[Ni(C_5H_5N)_6][SnBr_4(OH)_2]$; $[MnP_3][SnBr_6],6H_2O$; $[NiP_3][SnBr_6],8H_2O$; $[CoP_3][SnBr_6],8H_2O$; $[MnP_4][SnBr_6],6H_2O$; $[NiP_4][SnBr_6],8H_2O$; $[CoP_4][SnBr_6],8H_2O$; $[MnP_6][SnBr_6],6H_2O$; $[NiP_6][SnBr_6],8H_2O$; $[CoP_6][SnBr_6],8H_2O$.

A. A. Eldridge.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. VII. Effect on aqueous solutions of stannates of change of hydrogen-ion concentration by addition of hydrochloric acid. G. Jander, F. Busch, and T. Aden (Z. anorg. Chem., 1928, 177, 345—362).—Two methods are used to investigate the changes in solutions of alkali stannates on increasing the hydrogen-ion concentration. The first makes use of the fact that a knowledge of the diffusion coefficient of the stannate radical will give an approximate value for its mol. wt. The diffusion coefficient was determined for solutions of varying p_H, and a graph of the coefficient against the p_H was drawn. In strongly alkaline solutions the diffusion coefficient of the stannate radical is 0·44. With increasing p_H it decreases and reaches 0·36 at p_H 11·6. By applying the usual diffusion relationship $D_1\sqrt{M_1}=D_2\sqrt{M_2}$, where D_1, D_2 are the diffusion coefficients, M_1, M_2 are the mol. wts. of the radicals, to this case, it is found that the mol. wt. of the stannic acid radical in the least strongly alkaline solution (p_H 11·6) must be 1·5 times as great as that in the most strongly alkaline solution. The second method of investigation used was the absorption of visible and ultra-violet light. It has been shown that if with increasing hydrogen-ion concentration there is an association, then a displacement of the absorption band towards the longer waves will occur. On investigating solutions of alkali stannates of which the hydrogen-ion concentration was varied by addition of sodium hydroxide or hydrochloric acid, it was found that solutions which were made alkaline or were already alkaline by hydrolysis gave no appreciable absorption. On the other hand, addition of acid caused at a definite concentration a strong absorption in the ultra-violet, at a wave-length of about 300 $\mu\mu$. Further addition of acid caused no change in the characteristic absorption, but merely made it more intense. It is concluded that the change on acidifying a solution of an alkali stannate can scarcely be represented as the change of a normal into an acid stannate: $Na_2[Sn(OH)_6]+HCl=NaH[Sn(OH)_6]+NaCl$, but probably as $2[Sn(OH)_6]''+2H^{\cdot}\rightleftharpoons[Sn_2(OH)_{10}]''+2H_2O$. This reaction is comparable with the conversion of a chromate into a dichromate. At attempt was made to prepare salts of the second stannic acid, $H_2Sn_2(OH)_{10}$, but by the methods used only salts of the lower acid were obtained. This is not in contradiction to the physical results.

A. J. Mee.

Thermal decomposition of ammonia, with particular reference to the existence of active and inactive phases of ammonia. W. H. Stringfellow (J.C.S., 1929, 1—8).—An attempt has been made to substantiate the evidence brought forward by Baly and Duncan (*ibid.*, 1922, **121**, 1008) to demonstrate the existence of active and inactive phases of ammonia. Both synthetic and gas-works liquid ammonia have been used, but in no case has any indication of the phenomenon been obtained.

F. J. Wilkins.

Reaction between nitric oxide and hydrogen sulphide. J. Pierce (J. Physical Chem., 1929, **33**, 22—36).—Hydrogen sulphide and nitric oxide interact to form water, sulphur, and nitrogen, and the conditions of the reaction have been investigated between 28° and 100° in a modified Klemenc manometer. The effect of the addition of silica gel, alone and impregnated with 1% of ferric oxide, and of glass wool is to accelerate the reaction. No ammonium sulphide or nitrous oxide could be detected in the products of the reaction (cf. Thomson, Gmelin-Kraut's "Handbuch"), which is more complex than is represented by the equation $2NO+2H_2S=2H_2O+2S+N_2$. The mechanism proposed is that 2 mols. of nitric oxide condense to 1 mol. of N_2O_2, which is adsorbed and reacts with hydrogen sulphide to form sulphur, nitrogen, and water. Finally, hydrogen sulphide is adsorbed by the colloidal sulphur on the reacting surface and oriented so that its hydrogen ion extends outwards. The negative temperature coefficient found is attributed to decreased association of the nitric oxide to N_2O_2 molecules at higher temperatures. Sulphur, by forming a mechanically-coated surface, is the cause of the inhibitory effect observed.

L. S. THEOBALD.

Monochloroamine and hydrazine. II. M. BODENSTEIN (Z. physikal. Chem., 1928, **139**, 397—415; cf. A., 1928, 34).—The formation of hydrazine from aqueous solutions of ammonia and monochloroamine and the subsequent decomposition with evolution of nitrogen have been studied. Purification of the water used has an effect similar to the addition of gelatin in favouring increased yields of hydrazine, which increase with increasing purification of the water. The addition of very small amounts of cupric, ferrous, and cobaltous ions decreases the amount of hydrazine formed in the order given, copper having the greatest effect. Mannitol and gelatin increase the yields of hydrazine by counteracting the catalytic effects of the metallic ions; this is attributed to adsorption of these ions by the gelatin or mannitol.

[With TITSCHACK.]—Kinetic measurements show that the reaction between ammonia and monochloroamine to form hydrazine is proportional to the concentration of the reactants, that it has a high temperature coefficient, and that it is only slightly catalysed by the copper ion. Hydrazine is always the first product of the reaction between these two substances; the more or less extensive decomposition which follows is a dependent reaction, and it is this second reaction which is influenced by the various catalysts. The process is represented by the equations (i) $NH_2Cl+NH_3=NH_2{\cdot}NH_2+HCl$, and (ii) $NH_2{\cdot}NH_2+2NH_2Cl=N_2+2NH_4Cl$.

L. S. THEOBALD.

Concentrating hydrazine hydrate solutions. C. D. HURD and C. W. BENNETT (J. Amer. Chem. Soc., 1929, **51**, 265—269).—A solution containing a maximum concentration of 95—96% of hydrazine hydrate (12% of the original amount) remains when a 40—45% solution (5 parts) is heated with xylene (13 parts) until the latter has completely distilled. Larger yields of less concentrated solution are obtained by using less xylene. Most of the remaining hydrazine may be recovered from the distillate. Toluene has a smaller dehydrating effect and benzene practically none. Attempts to liberate hydrazine from its hydrochloride by means of sodamide, calcium carbide, or aluminium carbide were unsuccessful.

H. E. F. NOTTON.

Action of hydrogen sulphide on chromates. I. H. B. DUNNICLIFF and C. L. SONI (J. Physical Chem., 1929, **33**, 81—87).—The action of hydrogen sulphide on aqueous solutions of potassium chromate at the ordinary temperature and at 85° has been investigated. Chromium hydroxide contaminated by sulphur is precipitated, leaving a yellow, alkaline filtrate containing potassium sulphide, polysulphide, and thiosulphate and colloidal sulphur. At the ordinary temperature with a 2% solution the reaction is slow and is exothermic. The yellow crystals obtained by evaporation under reduced pressure from the filtrate resulting from the action of hydrogen sulphide at 85° on 2—15% solutions gave, on analysis, a polysulphide content corresponding with the formulæ $K_2S_{4\cdot67}$—$K_2S_{6\cdot61}$. The mechanism of the reaction, which may be conventionally represented by the equation $2H_2CrO_4+3H_2S=2Cr(OH)_3+2H_2O+3S$, is discussed.

L. S. THEOBALD.

Preparation of sulphuryl chloride. E. TERLINCK.—See B., 1929, 128.

Two ammonium molybdotellurates. V. W. MELOCHE and W. WOODSTOCK (J. Amer. Chem. Soc., 1929, **51**, 171—174).—*Ammonium mono-* and *di-molybdotellurates*, $3(NH_4)_2O,TeO_3,6MoO_3,7H_2O$ and $3(NH_4)_2O,2TeO_3,6MoO_3,10H_2O$, respectively, are obtained as clear white crystals by the interaction in suitable proportions of telluric acid, molybdic acid, and ammonia in aqueous solution. The crystals decompose at 550°, leaving a residue of tellurium dioxide admixed with a little molybdic oxide. Excess of ammonia converts the di-salt into the mono-compound. The compounds are unsuitable for the colorimetric determination of small quantities of tellurium.

S. K. TWEEDY.

Oxidation with fluorine. XI. Action of fluorine on solutions of the salts of thallium, manganese, copper, and lead. F. FICHTER and E. BRUNNER (Helv. Chim. Acta, 1929, **12**, 214—221; cf. A., 1927, 741).—Oxidation of thallous sulphate in neutral solution by fluorine is only partial on account of the simultaneous formation of hydrogen peroxide, but in moderately concentrated sulphuric acid solution it is almost complete. From these solutions crystals of the composition $TlH(SO_4)_2,4H_2O$ have been obtained. Oxidation of thallous nitrate even in acid solution is only partial, again due to the reducing action of hydrogen peroxide formed by the action of fluorine on nitric acid. By passing fluorine through a solution of manganous carbonate in orthophosphoric acid which is shown by analysis to contain $Mn(H_2PO_4)_2$, oxidation takes place to an extent not exceeding 66%. The incomplete oxidation is again attributed to the formation of hydrogen peroxide. As permonophosphoric acid has been shown previously to be formed by the action of fluorine on orthophosphoric acid, this oxidation may be explained on the theory that the oxidising agent is a peroxide or peracid derived from the anion such as sulphur tetroxide in the case of sulphates. It was not found possible to oxidise copper or lead salts by means of fluorine.

R. N. KERR.

Univalent iron, cobalt, and nickel. L. CAMBI (Atti R. Accad. Lincei, 1928, [vi], **8**, 535—536).—A reply to Manchot (A., 1928, 1344).

Reactivity of iron vapour with molecular nitrogen. A. MITTASCH and W. FRANKENBURGER (Z. physikal. Chem., 1928, **139**, 386—396).—Thin wires of electrolytic iron, previously melted and drawn out in a vacuum, were vaporised at 1240—1355° Abs. by electrical heating in an atmosphere of nitrogen at pressures of the order of 0·1 mm. No union of the iron and the nitrogen could be detected manometrically, the gas pressure at a given temperature remaining practically constant for several hours.

L. S. THEOBALD.

Reaction between ferric sulphate solution and cuprous sulphide. L. Whitby (J.C.S., 1929, 60—61).—The reaction between cuprous sulphide and ferric sulphate solution consists of two stages. The first may be represented: $Cu_2S+Fe_2(SO_4)_3=CuS+CuSO_4+2FeSO_4$. The second consists of a slower reaction between cupric sulphide formed in the first stage and more ferric sulphate, $CuS+Fe_2(SO_4)_3=CuSO_4+2FeSO_4+S$. At the ordinary temperature the first reaction predominates, the second being negligible except at higher temperatures.

F. J. Wilkins.

Reactions between iron, its hydroxides, and water. A. Schikorr (Z. Elektrochem., 1929, **35**, 65—70; cf. this vol., 266).—A detailed investigation has been made of the action of air-free water and ferric oxide (or meta-ferric hydroxide) on iron filings, whereby hydrogen is evolved and the oxide is blackened. The black oxide is shown to be mainly triferric tetroxide, formed by reduction of the hydroxide, whilst the evolution of hydrogen is due to the decomposition of water by dissolved ferrous hydroxide. Metallic iron and the solid hydroxide act as catalysts for the latter process. A series of experiments is described which indicates that the rate of hydrogen evolution (*a*) increases to a maximum value with increase in the amount of ferric hydroxide sol present; (*b*) is almost doubled by raising the temperature from 25° to 35°; and (*c*) is inversely proportional, at atmospheric pressure, to the cube root of the hydrogen pressure. The action of air-free water on compact rusted iron causes blackening of the iron, but no, or only an extremely slow, evolution of hydrogen.

L. L. Bircumshaw.

Oxidation of cobaltous sulphate and potassium cobaltous oxalate with ozone. E. Brunner (Helv. Chim. Acta, 1929, **12**, 208—213).—By passing ozonised oxygen into a well-cooled solution of cobaltous sulphate in sulphuric acid, crystals of $Co_2(SO_4)_3,18H_2O$ have been obtained. This is not a practicable method for the preparation of this salt, however, as only small quantities may be used in each experiment and it is necessary to pass the gas for long periods. On the other hand, oxidation of potassium cobaltous oxalate proceeds smoothly by this means and the method is suggested as practicable for the preparation of potassium cobaltioxalate.

R. N. Kerr.

Cobaltic monoammine. C. Duval (Compt. rend., 1929, **188**, 176).—Sodium amminocobaltiborate, $Na_2[Co(BO_2)_5,NH_3]$, has been prepared as a slightly water-soluble, violet-grey precipitate by heating 10 g. of triamminecobaltic nitrate, $[Co(NO_3)_3,(NH_3)_3]$, with 7·5 g. of sodium metaborate and 50 c.c. of water at 45° for 15 min. The solution is then cooled.

J. Grant.

Ruthenium hydroxytrichloride, ruthenum tetrachloride, and ruthenium trichloride. H. Remy and A. Lührs (Ber., 1929, **62**, [*B*], 200—209; cf. A., 1928, 722).—Fresh solutions of ruthenium tetroxide in concentrated hydrochloric acid contain ruthenium tetrachloride or the corresponding acid, $H_2[RuCl_6]$ as shown by the preparation of the alkali salts (Krauss, A., 1921, ii, 514). When the solutions are heated, the tetrachloride becomes hydrolysed to the compound $Ru(OH)Cl_3$, the change proceeding slowly even in solutions saturated with hydrogen chloride. In moderately dilute solution, the process is arrested when one chlorine atom is replaced by hydroxyl and proceeds beyond this stage only in solutions containing much less hydrochloric acid. In addition, reduction of ruthenium with evolution of chlorine, $RuCl_4=RuCl_3+Cl$, can occur, but, contrary to previous observers, this action is hindered rather than accelerated by rise in temperature unless a current of indifferent gas is passed through the solution. If carbon dioxide is passed until chlorine is no longer evolved, a partial reduction to tervalent ruthenium is observed unless the conditions for hydrolysis have been provided before driving out the chlorine. Solutions of ruthenium hydroxytrichloride do not evolve chlorine when treated with carbon dioxide and the valency of the metal does not alter. Solutions of ruthenium trichloride prepared according to Krauss and Kükenthal (A., 1924, ii, 196, 770) contain quadrivalent as well as tervalent ruthenium, the former frequently preponderating considerably. Quadrivalent ruthenium is also present in solutions prepared according to Gall and Lehmann (A., 1927, 123; 1928, 975). Evaporation to a syrupy consistency with concentrated hydrochloric acid has little influence on the valency of ruthenium unless repeated very frequently. A more marked effect is produced when the solutions are evaporated to dryness, but, in every case, the process comes to a conclusion when about half of the metal has passed into the tervalent state. Further reduction could not be effected by repeated evaporation to dryness extending over more than a week. It appears therefore impossible to obtain the pure trichloride by simply evaporating with hydrochloric acid a product containing large amounts of quadrivalent ruthenium. Ruthenium tetroxide reacts initially with concentrated hydrochloric acid, yielding the product RuO_2Cl_2, which is rapidly reduced further by excess of acid to ruthenium tetrachloride. This compound is unstable in solution, decomposing either into the trichloride or into the hydroxytrichloride. Pure solutions of the latter substance can be prepared readily and from them the "hydrated pentachlororuthenates" now recognised as hydroxypentachlororuthenates.

H. Wren.

Detection of active hydrogen atoms with zinc ethyl. F. Haurowitz (Mikrochem., 1929, **7**, 88—93).—Zinc ethyl dissolves readily in pyridine with the evolution of heat and the formation of a yellow liquid which fumes only slightly in contact with air. This solution forms a delicate test for the presence of active hydrogen in organic compounds in place of magnesium methyl iodide as recommended by Zerevitinov (A., 1907, ii, 509), but the test is not quantitative, as only 60—95% of the active hydrogen forms ethane. With benzoic acid about 66% of the theoretical yield of ethane is obtained, the remainder of the benzoic acid forming apparently a complex compound with zinc benzoate which is unaffected by excess of the zinc ethyl. A. R. Powell.

Potentiometric micro-titrations. F. L. Hahn (Z. anal. Chem., 1929, **76**, 146—149).—An amplification of the work of Zintl and Betz (A., 1928, 977). H. F. Gillbe.

p_H measurement with the glass electrode and vacuum tube potentiometer. L. W. Elder, jun., and W. H. Wright (Proc. Nat. Acad. Sci., 1928, **14**, 936—939).—The utility of the glass electrode for p_H measurements has been limited by difficulties attendant on the necessity of employing a quadrant electrometer. A method is described of using instead a vacuum tube potentiometer. The preparation of a special glass, which was used blown into small bulbs to form the electrodes, is described. In preliminary experiments the apparatus appeared to give satisfactory results. N. M. Bligh.

Amidosulphonic acid as primary standard in volumetric analysis. K. Misutsch (Pharm. J. [Russia], 1928, 310—313; Chem. Zentr., 1928, ii, 1129).—Amidosulphonic acid, $NH_2{\cdot}SO_2{\cdot}OH$, and hydrochloric acid give identical results when titrated with sodium hydroxide, carbonate, or borate. A. A. Eldridge.

Precipitation of group II acids (chloride group) in the presence of other acid radicals. L. J. Curtman and W. W. Plechner (Chem. News, 1929, **138**, 65—67).—The neutral solution is diluted to 50 c.c. and 1 c.c. of $0{\cdot}25N$-silver nitrate added. After addition of 5 c.c. of concentrated nitric acid the solution is warmed and stirred. A precipitate indicates the presence of one or more of the following : chloride, bromide, iodide, cyanide, thiocyanate, ferricyanide, ferrocyanide, sulphide. J. S. Carter.

Effect of sunlight on the determination of chlorine [in water] by the *o*-tolidine method. F. R. McCrumb and W. R. Kenny.—See B., 1929, 114.

Qualitative microanalysis. III. [Detection of thiocyanate, fluoride, and copper, two methods of distinguishing between tap water and distilled water, detection of alkali in water, and a drop reaction for ammonia.] F. Feigl [with G. Hirsch and I. Tamchyna] (Mikrochem., 1929, **7**, 10—20).—Addition of thiocyanate to a $0{\cdot}1N$-iodine solution containing 1·3 g./100 c.c. of sodium azide catalyses the reaction $2NaN_3+I_2=2NaI+3N_2$ and the solution becomes decolorised with evolution of nitrogen; as little as 0·03 mg. of thiocyanate is readily detected in the presence of most inorganic oxyacids and the common organic acids by this test, but sulphides and thiosulphates interfere and must be previously removed by mercuric chloride. For the detection of fluoride in insoluble substances the substance is treated with a hydrochloric acid solution of the violet zirconium alizarin compound (de Boer, A., 1924, ii, 705), which becomes yellow if fluorine is present. Traces of copper in solution may be detected by adding a few drops of dilute zinc nitrate solution followed by a solution of 8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 c.c. of water; with 0·00075 mg. of copper per c.c. a violet, crystalline precipitate is obtained. Tap water may be distinguished from distilled water by the reddish-violet colour it gives on the addition of a few drops of a blue ammoniacal solution of 2 : 3-dihydroxyanthraquinone or by the red, crystalline precipitate it produces with a solution of the sodium salt of 2 : 4 : 5 : 7-tetranitro-1 : 8-dihydroxyanthraquinone; both these reactions are due to the presence of calcium and magnesium in tap water. Addition of a solution of the compound $Hg(CN)_2{,}AgNO_3$ to water containing free alkali produces a turbidity due to the formation of silver cyanide. To detect ammonia in a neutral or slightly acid solution 1 drop of the liquid is mixed with 1 drop of a dilute solution of *p*-nitrodiazobenzene in hydrochloric acid on a small watch-glass and a small piece of quicklime is dropped into the mixture; if ammonia is present a red ring appears round the lime. A. R. Powell.

Detection of sulphurous acid with Bettendorf's reagent. S. Dunajeva (Pharm. J. [Russia], 1928, 379; Chem. Zentr., 1928, ii, 1129).—When Bettendorf's reagent is covered with a solution containing sulphite, reduction to sulphide produces a yellowish-brown ring of tin sulphides; 0·06% of sulphite can be detected. A. A. Eldridge.

Electrolytic analysis of nitrates. Apparatus for reduction with nascent hydrogen in presence of catalysts. M. Rabinovitsch and A. S. Fokin (Z. Elektrochem., 1929, **35**, 18—20).—The nitrate, in alkaline solution, is reduced to ammonia by means of nascent hydrogen, formed by the decomposition of sodium amalgam. Details are given of the apparatus, consisting of a small electrolytic cell with a mercury cathode. The presence of a catalyst (tungsten, vanadyl sulphate, or chloroplatinic acid) is recommended to accelerate the decomposition of the alloy, which is continuously produced during the electrolysis. The values obtained for a series of analyses of potassium nitrate are in satisfactory agreement with those found by Devarda's method. L. L. Bircumshaw.

Conductometric titration of phosphoric acid with sodium hydroxide. (Miss) J. C. Lanzing and L. J. van der Wolk (Rec. trav. chim., 1929, **48**, 83—92).—The neutralisation of phosphoric acid by sodium hydroxide has been investigated conductometrically at eight dilutions between 0·3 and $0{\cdot}005N$. Comparison with the theoretical curve for the titration of a tribasic acid shows that the first break at all dilutions agrees well with the theoretical, the second is displaced to the right, and the third is not found except for the two highest concentrations. The first branch of the curve shows a minimum with $0{\cdot}3N$-solution, but becomes straight at lower concentrations. The determination of phosphoric acid conductometrically should be restricted to the first end-point and the concentration of acid should not be above $0{\cdot}1N$. R. N. Kerr.

Standards for Gutzeit test [for arsenic]. A. T. Henley.—See B., 1929, 94.

Detection of the presence of reducing radicals in the systematic analysis for the acids. L. J. Curtman and W. W. Plechner (Chem. News, 1929, **138**, 50—51).—To 5 c.c. of solution are added 0·5 c.c. of $3N$-sulphuric acid and 2 drops of $0{\cdot}1N$-permanganate. If no bleaching occurs the amount of arsenite, thiosulphate, sulphite, sulphide, iodide, bromide, thiocyanate, ferrocyanide, or nitrite present does not exceed 1 mg. and the amount of tartrate or oxalate present does not exceed 10 mg. If no bleaching occurs on warming, oxalate and tartrate may be assumed to be absent and the amount of cyanide present does not exceed 10 mg. J. S. Carter.

Determination of arsenic in presence of organic substances, halogens, and heavy metals. E. Schulek and P. von Villecz (Z. anal. Chem., 1929, 76, 81—103).—The substance is treated with 30% hydrogen peroxide solution in presence of concentrated sulphuric acid. After reduction of the quinquevalent arsenic to the tervalent state by hydrazine sulphate, excess of which is destroyed by the hot sulphuric acid present, potassium bromide is added and the solution is titrated with 0·1*N*- or 0·01*N*-potassium bromate solution. H. F. Gillbe.

Determination of arsenic. E. G. Mahin and A. F. Doyle (Proc. Indiana Acad. Sci., 1929, 37, 269—272).—In the reduction of arsenic to the tervalent condition by means of potassium iodide, loss of arsenic as the tri-iodide is to be avoided. Limitation of the amount of potassium iodide employed is desirable. Chemical Abstracts.

Apparatus for the determination of carbon dioxide. R. C. Wiley (J. Amer. Chem. Soc., 1929, 51, 222—223).—A simple apparatus designed to minimise contamination with atmospheric carbon dioxide is described. S. K. Tweedy.

Microchemical separation of barium and calcium. R. Strebinger (Mikrochem., 1929, 7, 100—105).—The microchemical determination of barium by precipitation with ammonium dichromate in ammonium acetate solution followed by collection of the precipitate in a filter tube and weighing after drying at 140° yields slightly high results, but good results are obtained if the precipitate is dissolved in dilute nitric acid, the chromic acid reduced with alcohol, and the barium precipitated with ammonium sulphate. Calcium is determined in the filtrate from the barium chromate by precipitation with ammonium oxalate and weighing as CaC_2O_4,H_2O after drying at 110°. A. R. Powell.

Rapid determination of total hardness [of water] by separate determination of lime and magnesia hardness. K. V. Luck and H. J. Meyer. —See B., 1929, 114.

Separation of beryllium from aluminium, iron, and copper by 8-hydroxyquinoline. M. Niessner (Z. anal. Chem., 1929, 76, 135—145).—Since beryllium does not form a compound with 8-hydroxyquinoline, this reagent may be employed to obtain a rapid and complete separation of beryllium from iron, aluminium, and copper. H. F. Gillbe.

Determination of beryllium as pyrophosphate and as anhydrous sulphate. V. Čupr (Z. anal. Chem., 1929, 76, 173—191).—Direct precipitation of beryllium ammonium phosphate and subsequent ignition to pyrophosphate yields untrustworthy results. Beryllium should be precipitated from solutions containing ammonium salts with ammonia as hydroxide, or, if the solution contains phosphate, as the voluminous phosphate. If salts of the alkali metals are present beryllium should be reprecipitated. Ammonium phosphate is added and the solution made faintly acid (methyl-red). The solution is then diluted and made just alkaline with ammonia. Washing is effected with a 1%, faintly ammoniacal solution of ammonium nitrate. The resulting pyrophosphate is a white powder.

Beryllium sulphate is completely dehydrated at 400°, and if the period of heating does not exceed 2—3 hrs. there is no further decomposition. J. S. Carter.

Precipitation of zinc as sulphide from faintly acid solutions. J. Majdel (Z. anal. Chem., 1929, 76, 204—212).—Under the conditions described previously (A., 1928, 859) quantitative separation from iron, aluminium, chromium, nickel, cobalt, and manganese is effected. If metals of the copper and arsenic groups are present 5—7 c.c. of 1 : 1-sulphuric acid are added, and the solution is evaporated until fumes of sulphur trioxide are evolved. After dilution to 50 c.c., the hot solution is treated with hydrogen sulphide and the precipitated sulphides are washed with a solution containing 5 c.c. of concentrated sulphuric acid per 100 c.c., saturated with hydrogen sulphide. The filtrate and washings are boiled to expel hydrogen sulphide and zinc is determined as described. The precipitated zinc sulphide should be washed with a 1% solution of ammonium sulphate saturated with hydrogen sulphide. J. S. Carter.

Detection of zinc in presence of manganese, nickel, and cobalt. R. Ripan (Bul. Soc. Stiinte Cluj, 1928, 4, 80—83; Chem. Zentr., 1928, ii, 1239).—(*a*) In the absence of acids, *e.g.*, thiocyanic, which give a precipitate with pyridine, the solution is treated with 16% potassium iodide solution and excess of pyridine; the compound $[Zn(C_5H_5N)_2]I_2$ is precipitated quantitatively, whilst cobalt, nickel, and manganese do not react. (*b*) Precipitation with 10% sodium bromide solution and 0·5—1 c.c. of pyridine affords the corresponding bromide; 0·01 mg. of zinc can be detected. A. A. Eldridge.

Determination of cadmium in the metallic state in organic and inorganic compounds. H. ter Meulen and (Mlle.) H. J. Ravenswaay (Rec. trav. chim., 1929, 48, 198—200).—A method for the determination of cadmium similar to that for mercury and arsenic (A., 1926, 490, 492) is described. The compound is heated in a current of hydrogen and the cadmium formed by reduction is distilled into a quartz tube and weighed. If sulphur or halogens are present in the compound it must be mixed with calcium carbonate before heating and it is also advisable to add to the current of hydrogen a little ammonia. Good results have been obtained with both organic and inorganic compounds, the error not exceeding 0·1% in any case. An attempt has been made to apply the same method to the determination of zinc, but the results obtained are always too high, owing to a thin layer of oxide covering the metal. R. N. Kerr.

Reduction bead test as a simple preliminary test. H. Brintzinger (Z. anal. Chem., 1929, 76, 149—150).—The substance is mixed with about three times its weight of a reducing flux, such as 2 parts of sodium oxalate, 2 parts of potassium oxalate, and 1—1·5 parts of borax, and heated on magnesia in the reducing flame. Characteristic metallic beads are produced in many cases. H. F. Gillbe.

Gravimetric determination of lead. I. Soluble salts. P. N. Das-Gupta, G. C. Roy, and K. M. Sil (J. Indian Chem. Soc., 1928, **5**, 657—660).—The precipitation of the complex $Pb_5O_7,3H_2O$ (Brauner, J.C.S., 1894, **65**, 394) by the action of alkaline hydrogen peroxide on lead nitrate and acetate is quantitative when the alkali used is ammonia. The complex is unaffected by heating at 180°. It is insoluble in ammonia, but soluble in alkali hydroxides and ammonium salts. Hydrogen peroxide in excess converts it into lead hydroxide. In presence of ammonium acetate, ammonium nitrate, sodium acetate, and potassium nitrate precipitation of the complex is quantitative provided the concentrations of the salts do not exceed 1, 4, 8, and 15 g. per 100 c.c. of solution, respectively. The method appears to be most trustworthy in the determination of relatively large amounts of lead. H. Burton.

Electrolytic determination of small quantities of lead. A. Seiser, A. Necke, and H. Müller (Z. angew. Chem., 1929, **42**, 96—98).—Lead is deposited on a platinum gauze anode as dioxide. The blue coloration obtained on placing the washed anode in a solution of tetramethyldiaminodiphenylmethane in glacial acetic acid is made the basis of the colorimetric determination. The electrolyte should contain about 1% of nitric acid and about 10 mg. of copper. Iron does not interfere, but the amount of manganese or bismuth present should not exceed 0·2—0·5 mg. The method is primarily intended for the determination of small amounts (0·01—0·1 mg.) of lead in blood etc. Directions are given for the pre-treatment of the blood samples (cf. Arch. Hyg., 1928, **99**, 158). J. S. Carter.

Hexamethylenetetramine as a microchemical reagent. I. M. Korenman (Pharm. Zentr., 1929, **70**, 1—3).—Microchemical reactions with salts of silver, lead, mercury, cadmium, bismuth, tin, and antimony, and the appearances of the precipitates obtained, are described. S. I. Levy.

Rapid electrolytic determination and separation of some metals without mechanical agitation of the electrolyte. N. Vensovitch (Bull. Soc. chim. Belg., 1928, **37**, 353—376).—Results are given of numerous experiments on the determination and separation of metals by Sand's method, using electrodes of the Fischer type. The following determinations and separations are quantitatively possible by this method: copper from acid and ammoniacal solutions, silver, cadmium; copper from zinc, copper from zinc and tin, copper from tin, copper from nickel, zinc, and iron, copper from nickel and zinc, silver from copper; the simultaneous separation and determination of copper and silver.

F. G. Tryhorn.

Detection and identification of specific cations with sodium alizarinsulphonate. F. G. Germuth and C. Mitchell (Amer. J. Pharm., 1929, **101**, 46—52).—The reactions of sodium alizarinsulphonate with solutions of 36 different metallic salts are described. Characteristic precipitates are obtained with solutions of aluminium, titanous, chromic, ferric, uranium, cupric, platinic, bismuth, mercuric, and thallous salts. The formation of the precipitate is accelerated and made more sensitive by the previous addition of a small amount of ammonia. The degree of sensitivity of the reactions is in the above order, aluminium being the most sensitive, and detection of the metals was easily effected in aqueous solutions of concentration 1 in 10^6.

E. H. Sharples.

Electrometric titration of manganese by the Volhard method. B. F. Brann and M. H. Clapp (J. Amer. Chem. Soc., 1929, **51**, 39—41).—The Volhard method of titrating manganese may be satisfactorily carried out electrometrically at 90° by a modified "dead stop end-point" method (Foulk and Bawden, A., 1926, 927), a platinum cathode and silver anode being used. The latter is permanently depolarised by adding a trace of chloride ion to the solution. S. K. Tweedy.

Iodometric determination of iron. E. C. Grey (J.C.S., 1929, 35—39).—The causes of error in the iodometric titration of iron have been traced to the presence of copper, or of iron as oxide or colloidal hydroxide, and conditions affording accurate results are defined. The occurrence of iron in these forms can be prevented by carrying out the titration in a solution containing a suitable excess of acid. The copper is removed by dissolving out with ammonia solution. In the absence of colloidal ferric hydroxide the amount of copper present can be determined with fair accuracy by the rate of return of the blue colour after thiosulphate titration. By means of this effect it is possible to detect 1—2 parts of copper in 2,000,000 parts of water. F. J. Wilkins.

Determination and separation of metals using 8-hydroxyquinoline. VII. Determination of iron, manganese, nickel, and cobalt. Separation of iron from aluminium, manganese, and alkaline-earth metals. Separation of manganese from nickel, zinc, and alkaline-earth metals. R. Berg (Z. anal. Chem., 1929, **76**, 191—204).—Iron and nickel are precipitated from solutions containing acetate in presence of 10—20%, and 5—10% of acetic acid, respectively, whereas manganese and cobalt are precipitated from neutral or faintly acid solutions only. This dependence of solubility on acidity is made the basis of the separation of iron from manganese and metals of the alkaline-earth series, and the separation of manganese from nickel and zinc, which is precipitated from solutions containing about 6% of acetic acid. Manganese can be separated from alkaline-earth metals, which are not precipitated from faintly acid media. The separation of iron and aluminium is based on the fact that in presence of tartaric or malonic acid aluminium gives no precipitate with 8-hydroxyquinoline. The precipitates are most conveniently evaluated bromometrically. With iron the bromination etc. is effected in presence of phosphoric acid. J. S. Carter.

Diphenylamine as indicator in the titration of iron with dichromate. F. J. Watson (Chem.

Eng. Min. Rev., 1928, 20, 355—357).—Diphenylamine may be employed satisfactorily as an internal indicator provided that as the end-point is approached time be allowed for the colour changes to develop, and that not more than 1 c.c. of saturated mercuric chloride solution has been added to oxidise the excess of stannous chloride used for the reduction. Since the indicator change is reversible, the end-point, if overstepped, may be obtained by adding 1 c.c. of standard ferrous ammonium sulphate solution and re-titrating. It is not necessary to make an allowance for the quantity of dichromate used to oxidise the indicator if the first appearance of the purple colour be taken as the end-point. H. F. GILLBE.

Microchemical mineral analysis. [Detection of nickel, cobalt, copper, zinc, and cadmium.] A. MARTINI (Mikrochem., 1929, 7, 30—32).—Addition of ammonium thiocyanate and pyridine to a neutral cobalt solution produces a rose-coloured precipitate which becomes sky-blue and crystalline on addition of nitric acid. An ammoniacal copper solution to which ammonium thiocyanate has been added yields with pyridine green crystals of the *compound* $3(C_5H_5N,HSCN),Cu(NH_3)_4(SCN)_2$, and with quinoline sulphate green monoclinic crystals of the *compound* $3(C_9H_6N,HSCN),Cu(NH_3)_4(SCN)_2$. Zinc sulphate yields with a dilute acid solution of aniline hydrochloride colourless triclinic crystals of zinc aniline chloride, $C_6H_5{\cdot}NH_2,HCl,ZnCl_2$. Ammoniacal solutions of copper, nickel, and cadmium salts yield with ammonium thiocyanate and aniline characteristic crystalline *compounds* of the type $2(C_6H_5{\cdot}NH_2,HSCN),M(NH_3)_4(SCN)_2$; the copper compound separates in green, triclinic rosettes, the nickel compound in pale green, highly refracting, triclinic prisms, and the cadmium compound in monoclinic colourless prisms. Cobalt solutions give a rose-coloured crystalline precipitate with ammonium thiocyanate and aniline. A. R. POWELL.

Ceric sulphate as a volumetric oxidising agent. VIII. Determination of chromium in presence of manganese, iron, and vanadium. IX. Preparation and stability of solutions. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1929, 51, 139—149, 149—152).—VIII. The chromic salt is oxidised by excess of ceric sulphate solution, and then (i) the excess is titrated in presence of chromic acid with sodium nitrite or sodium oxalate; (ii) small excess of sodium nitrite is added, followed by carbamide, after which the chromic acid is titrated with standard ferrous sulphate; or (iii) sodium azide is added, followed by titration with standard ferrous sulphate. Iron and large amounts of manganese may be present; if vanadium is present, the method gives the sum of the chromium and vanadium, although the vanadium may be subsequently determined with the same solution. The titrations are carried out electrometrically, but in method (ii) an internal indicator, *e.g.*, diphenylamine, may be used.

IX. Ceric sulphate solution prepared from commercial hydrated oxide usually suffices for volumetric work. Ceric sulphate solutions are cheap, and when containing sulphuric acid exhibit a constant normality over a considerable period and are insensitive to the influence of light or air. The normality of solutions containing sulphuric acid remains unchanged after boiling for an hour or so, even if a little nitric or perchloric acid is present, although in presence of large quantities of the latter acids oxygen is lost.

S. K. TWEEDY.

Determination of vanadium in steel. K. SWOBODA.—See B., 1928, 131.

Micro-titration of bismuth. J. STRAUB (Z. anal. Chem., 1929, 76, 108—111).—A convenient volume of solution containing 0·1—1·0 mg. of bismuth is diluted to 5 c.c. and treated with small crystals of potassium iodide until it becomes faintly yellow. The whole of the bismuth is then precipitated as basic iodide by addition of 5 c.c. of water and heating on the water-bath. The precipitate, after collection and washing with alcohol and with water, is decomposed by 5% potassium hydroxide solution, and the resulting solution, containing all the iodine as potassium iodide, is rendered slightly acid with hydrogen chloride solution and treated with an excess of bromine water. After decolorisation by 5% phenol solution 0·1 g. of potassium iodide is added and the liberated iodine is titrated with 0·005*N*-sodium thiosulphate solution in presence of starch. At the end-point the colour of the solution changes from green to a faint yellow; a pure blue is not produced at any stage. H. F. GILLBE.

Fusion of rare metal ores. III. Determination of tantalum and niobium. G. W. SEARS (J. Amer. Chem. Soc., 1929, 51, 122—129; cf. B., 1926, 282).—Tantalic and niobic acids are insoluble in hot 3*N*-hydrochloric acid; if the pyrosulphate fusion has been carried out at about 650° the iron and titanium are completely soluble in this acid. If the fusion is carried out for 10—15 min. at 835—850°, only the niobium is rendered soluble in fuming sulphuric acid and it is not reprecipitated when the cold acid solution is poured into water which is kept cooled. Methods based on these results are given for the determination and separation of niobium and tantalum. Asbestos is not wholly resistant to the action of hot fuming sulphuric acid. S. K. TWEEDY.

Potentiometric determination of octavalent osmium. W. R. CROWELL and H. D. KIRSCHMAN (J. Amer. Chem. Soc., 1929, 51, 175—179).—Hydrazine reduces octavalent osmium to the quadrivalent state in acid solution, and the reaction can be followed potentiometrically. Hydrobromic acid is preferably used, the reaction probably being $N_2H_4,H_2SO_4+H_2OsO_5+6HBr=N_2+H_2SO_4+H_2OsBr_6+5H_2O$. The bulk of the reaction is carried out in sealed tubes kept at 100° for 30 min., the end-point being determined by subsequent potentiometric titration at 70°. The method, which serves to determine 10^{-5} g.-mol. of tetroxide, is accurate to about 0·2—0·3%.

S. K. TWEEDY.

Automatic pipette. M. HYMAN (J.S.C.I., 1928, 47, 368T).—A modification of an ordinary pipette which is filled by suction as usual, but in which the level of the liquid is brought automatically to the graduation mark, is described and figured.

Pneumatic regulator for manipulation of burettes without taps. E. SCHILOV (Z. anal. Chem., 1929, 76, 212—216).—The upper portion of the burette is connected to the air-space between an elastic membrane and a plate, the volume of which can be varied by means of a screw. J. S. Carter.

Precision valve for gases and liquids, especially liquid burettes, and a "tapless" burette. P. Fuchs (Z. anal. Chem., 1929, 76, 166—173).—The arrangement is essentially a narrow glass tube terminating in a hook, over which a piece of rubber tubing is pushed, so that the open end of the hook is sealed by the rubber. Contact is broken by pressing the rubber immediately above the hook. The device may conveniently replace the usual burette tap. J. S. Carter.

Vacuum tube potentiometer for rapid *E.M.F.* measurements. H. M. Partridge (J. Amer. Chem. Soc., 1929, 51, 1—7).—The Wheatstone bridge is replaced by an amplifier employing in conjunction a tetrode and a triode valve. A very stable balance is obtained. Calibration of the valves is obviated. Only one adjustment is required; the device, which virtually operates electrostatically, is direct reading and may be used with cells containing glass electrodes. p_H values, reproducible to 0·02 unit, may be rapidly determined with the apparatus. S. K. Tweedy.

Tantalum as a constructional material for chemical apparatus. F. Heinrich and F. Petzold.—See B., 1929, 99.

Steam drying oven with detachable base. H. J. S. Sand (J.C.S., 1929, 214). F. J. Wilkins.

Evaporation at low temperatures. E. Jantzen and H. Schmalfuss.—See B., 1929, 77.

[Apparatus for determining] heat of adsorption on charcoal of certain organic vapours. L. McKinley and J. N. Pearce (Proc. Iowa Acad. Sci., 1927, 34, 216).—Experiments were performed with an apparatus comprising a sensitive thermo-couple in a calorimeter system consisting of a known weight of oil of low specific heat in a Dewar flask. Chemical Abstracts.

Nephelometric and colorimetric measurements with a photo-electric current. E. Cuboni (Boll. Inst. Sieroterap. Milan., 1927, No. 6, 3 pp.; Chem. Zentr., 1928, ii, 919).—The observations are made by means of a photo-electric cell. A. A. Eldridge.

[Apparatus for] experimental structure analysis. A. Geller (Schweiz. Min. Petr. Mitt., 1927, 7, 219 Chem. Zentr., 1928, ii, 964).

Chemical reaction in the interferometer U-gauge. C. Barus (Proc. Nat. Acad. Sci., 1928, 14, 939—943).—To determine how far the course of a chemical process would be reproduced by the apparatus, the absorption of atmospheric oxygen by phosphorus was tested. Pressure and temperature changes in enclosed volumes of air connected with the U-gauge, one limb containing the phosphorus, are plotted against time, and the results obtained are discussed. N. M. Bligh.

Nomography. V. IX—XII. O. Liesche.—See B., 1929, 115.

Geochemistry.

Ratios of zirconium to hafnium and niobium to tantalum in minerals. G. von Hevesy and K. Würstlin (Z. physikal. Chem., 1928, 139, 605—614).—The ratio zirconium : hafnium in 16 minerals has been investigated and found to have the mean value 50 : 1. The ratio niobium : tantalum has the value 1 : 1 approximately. These values, together with the non-existence of a hafnium mineral or of a mineral in which the hafnium content exceeds that of zirconium, are discussed and an explanation is advanced. L. S. Theobald.

Chemical composition of the tectites, and in particular of those of Cambodia. A. Lacroix (Compt. rend., 1929, 188, 284—288; cf. *ibid.*, 117).—Chemical analyses and a number of physical and morphological properties of tectites have been collected, and a relation has been shown to exist between density and refractive index. Cambodia glass melts at 750—1200°. In general, tectites are rich in silica (particularly free silica), and free alumina, and contain alkali metals, of which the potassium is always in excess over the sodium. The lime, magnesia, and iron contents are relatively high, but phosphoric acid is absent, whilst traces of manganese and titanium are sometimes found. Three chemico-mineralogical types are distinguished: (1) Darwin glass (queenstownite), which is exceptional in that it contains little lime or alkali metals. (2) Moldavites. (3) Australites, billitonites, and Cambodia tectites. Explosive properties of tectites may be due to bubbles of occluded hydrogen, nitrogen, or oxides of carbon, and these serve to distinguish them from the obsidians, which may contain hydrogen chloride, sulphur dioxide, and sometimes chlorine. J. Grant.

Chemical composition of liparite. G. Carobbi (Gazzetta, 1928, 58, 801—808).—An investigation of the green mineral which along with malachite is found in lava incrustations in the Lipari Islands. It is suggested that the name "liparite" should be reserved for this mineral, which is a hydrated silicate of copper with the copper partly replaced by calcium and magnesium. The composition is SiO_2 33·08, Fe_2O_3 1·79, Al_2O_3 1·19, CaO 0·81, MgO 2·07, CuO 35·10, H_2O (loss on drying over calcium chloride) 9·52, H_2O (further loss on heating to a high temperature) 16·98, CO_2 traces (total 100·54). The mineral is birefringent (mean n 1·51) and has d^{25} 2·080. The crystal structure is undetermined. Liparite appears to be identical with chrysocolla, and the nearest formula is $H_2CuSiO_4,2H_2O$. O. J. Walker.

Microscopical study of the complex cupro-argentiferous minerals of Colquijirca (Peru). J. Orcel and G. R. Plaza (Compt. rend., 1929, 188, 181—183).—Two types of mineral of different origin are distinguished: (1) Hypogenic minerals, formed at a depth, consisting essentially of chalcopyrites, pyrargyrite, blende, galena, pyrites, enargite, panabase, and erubescite. (2) Supergenic minerals from the cementation zone, formed from the above minerals by metasomatic replacement, and containing native silver, stromeyerite, and pyrargyrite. The silver content is high in the cupro-argentiferous minerals, less when associated with lead and copper, and variable when zinc also is present. J. GRANT.

Presence of atacamite in the incrustation of the Vesuvian lava of [the eruption of] 1631. G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], **34**, 78—83).—The green portion of the incrustation on this lava consists essentially of atacamite, $CuCl_2,3Cu(OH)_2$, as was suggested by Scacchi (Mem. Soc. Ital. Sci., 1882, [iii], **4**, No. 8).

E. W. WIGNALL.

Klockmannite. P. RAMDOHR (Zentr. Min. Geol., 1928, **A**, 225—232; Chem. Zentr., 1928, ii, 868).—Klockmann's so-called umangite is a new mineral, klockmannite, CuSe. A. A. ELDRIDGE.

[Rhomboclase, szomolnokite, and berthierite.] J. KRENNER (Zentr. Min. Geol., 1928, **A**, 265—271; Chem. Zentr., 1928, ii, 1198).—Rhomboclase from Szomolnok, Hungary, $Fe_2O_3,4SO_3,9H_2O$, has *H* 2. Szomolnokite, $FeSO_4,H_2O$, has *d* 3·035, *a* : *b* : *c*= 0·9544 : 1 : 0·8999, β 86° 39′ 54″. Berthierite has *d* 4·622. A. A. ELDRIDGE.

Tikhvinite. J. M. ANSHELES and N. J. VLODAVETZ (Mem. Soc. Russe Min., 1927, **56**, 53—60; Chem. Zentr., 1928, ii, 976).—A new mineral, tikhvinite, from the bauxite deposits in the Tikhvin district contains SiO_2 0·56, TiO_2 0·16, Al_2O_3 31·14, Fe_2O_3 2·25, SrO 24·43, P_2O_5 18·05, SO_4 8·47, H_2O 12·54, corresponding with the formula $2SrO,3Al_2O_3,P_2O_5,SO_3,6$ or $7H_2O$; it has d^4 3·32, *H* 4½, *n* 1·62.

A. A. ELDRIDGE.

Iron ores of South Africa. E. KRENKEL (Naturwiss., 1929, **17**, 57—63).—*A résumé* of the Geological Survey Memoir (1928, **26**, 1—264) by P. A. Wagner. Some of the chemical analyses of the ores are quoted.

L. J. SPENCER.

Relations between refractivity, density, and chemical composition in the granite group. H. VON PHILIPSBORN (Ber. Sachs. Ges. Wiss. nat.-phys. Kl., 1928, **40**, No. 3, 1—42; Chem. Zentr., 1928, ii, 1197).—The above relations are discussed. Accurate refractivity and dispersion data were ascertained.

A. A. ELDRIDGE.

Origin of Mediterranean red earths (*Terra rossa*). A. REIFENBERG (Kolloidchem. Beih., 1929, **28**, 55—147).—The Mediterranean red earths are a product of the alternating rainy winter and dry summer characteristic of the Mediterranean climate. They are produced only in presence of limestone and have an alkaline reaction; they are rich in soluble salts, poor in humus, and have a high iron content. The humus is coagulated by the electrolytes present and is therefore incapable of protecting the iron, and the most important constituents from the colloid-chemical point of view are silicic acid, ferric oxide, and alumina. Experiments have been carried out on the inter-relations of these three colloids. Colloidal silicic acid peptises ignited ferric oxide, ferric hydroxide, and also ferrous oxide. The light green sol produced in the last case oxidises gradually in air and immediately on addition of hydrogen peroxide to a yellow ferric hydroxide–silicic acid sol. The three ferric hydroxide-silicic acid sols formed by these means are essentially different in optical, mechanical, and electrical properties and behave differently towards coagulation by electrolytes; they are regarded as artificial systems representing the factors involved in the formation of clays. It is considered that in the weathering of the earths the colloidal silicic acid formed by hydrolysis protects the iron and aluminium oxides, probably by replacement of part of the alkali in the colloidal micelle by molecules of the sesquioxides. This would explain the alkaline reaction of the earths. The protected ferric oxide sols are relatively more stable and are coagulated only by high concentrations of electrolytes.

E. S. HEDGES.

Geology and mineralogy of soils. I. Study of a region characterised by diverse rocks and partly covered with glacial drift. R. HART (J. Agric. Sci., 1929, **19**, 90—105).—Mineralogical details of the soils are recorded. The mineral contents of the glacial soils and alluvium are very similar and contain fresh ferrosilicates in considerable quantity. Soils on the screes and hillwash are characterised by their content of rock fragments and iron oxides. Drift soils contain potash, phosphate, and lime-bearing minerals. A. G. POLLARD.

Organic Chemistry.

Oxidation of methane with nitrogen peroxide. P. K. FROLICH, P. J. HARRINGTON, and A. H. WAITT (J. Amer. Chem. Soc., 1928, **50**, 3216—3221).—The oxidation commences at 430°, but the temperature rises after the reaction starts. Methyl alcohol could not be detected in the oxidation products, but it is probably formed and immediately decomposed into carbon monoxide and hydrogen. Large amounts of formaldehyde are produced; its formation is favoured by a low peroxide concentration, a slow rate of flow of the reactants, and absence of reacting surfaces. Liquid nitrogen peroxide seems capable of oxidising higher hydrocarbons to acetic acid. S. K. TWEEDY.

Intermediate products of the combustion of methane. E. H. RIESENFELD and D. GURIAN (Z. physikal. Chem., 1928, **139**, 169—197).—The combustion of methane in oxygen and of oxygen in excess of methane at various concentrations at the orifices of quartz capillaries has been investigated. The intermediate products detected were formaldehyde, carbon monoxide, hydrogen peroxide, and, in the first case, ozone. In the combustion of methane in oxygen the yields of hydrogen peroxide and formaldehyde decrease with an increase in the amount of excess oxygen, whilst that of ozone increases. When oxygen burns in methane, the yield of hydrogen peroxide again diminishes, whilst that of formaldehyde rises continually with an increasing excess of methane, but ozone is not formed. Maximal quantities are formed for (i) formaldehyde, with large excess of methane and the strongest cooling possible, (ii) hydrogen peroxide, at equivalent quantities of methane and oxygen (1 : 2 mols.) with strongest cooling, and (iii) ozone, with large excess of oxygen and slower cooling. Hydrogen peroxide does not arise, as has been previously assumed, from formaldehyde; the formation of these two products is independent. When equivalent quantities of methane and oxygen are used, the cone of the oxygen flame is more than double as high as that of the methane flame, which, however, is the hotter. The mechanisms are also different in the two cases. Other conditions being equal, substitution of the quartz capillaries by those of copper or silver is without influence on the quantities of the intermediate products formed. The mechanism of the formation of these products is concluded to be first the decomposition of methane into CH_2 and atomic hydrogen, which forms mainly molecular hydrogen and some hydrogen peroxide. The CH_2 then burns partly to carbon monoxide and partly to formaldehyde. The atomic oxygen arising from the decomposition of hydrogen peroxide forms ozone, which, on slow cooling, again decomposes. Finally, carbon dioxide and water result from the further oxidation of these products.

L. S. THEOBALD.

Action of aluminium chloride on olefinic hydrocarbons. A. SZAYNA.—See B., 1929, 117.

Ozonisation of gaseous unsaturated hydrocarbons. I. Ethylene. II. Propylene and a "cracking gas." E. BRINER and P. SCHNORF (Helv. Chim. Acta, 1929, **12**, 154—181, 181—186).—I. An apparatus is described for the ozonisation of a gas either in absence or in presence of water or water vapour. The liquid ozonide from ethylene is stable at 0°, becomes a vitreous mass at −80°, and at the ordinary temperature evolves hydrogen. The values of d and n_D vary slightly with the ratio of ethylene to ozone used. Mol.-wt. determinations on the ozonide in acetic acid or water give values which are too high, but diminish after some time, owing to decomposition. The ozonide is soluble in water in all proportions and such solutions decompose slowly at the ordinary temperature and more rapidly at 65°. In each case more formic acid than formaldehyde is produced and hydrogen is always evolved. This is due to the presence in the ozonide of formaldehyde peroxide, shown to be identical with dihydroxymethyl peroxide (Wieland and Wingler, A., 1923, i, 650). The production of this is formulated $CH_2{:}CH_2+O_3+H_2O \longrightarrow [OH{\cdot}CH_2{\cdot}O]_2$, the water either being present because of incomplete drying or formed by oxidation of some ethylene. Decomposition of the peroxide occurs : $[OH{\cdot}CH_2{\cdot}O] \longrightarrow 2CH_2O_2+H_2$, and explains the preponderance of formic acid. The ozonide contains only traces of hydrogen peroxide; the peroxide cannot be formed by the action of hydrogen peroxide on formaldehyde (cf. Wieland and Wingler, *loc. cit.*). The free ozonide is isolated by vacuum distillation as a highly explosive liquid, b. p. 20°/16—17 mm. Ozonisation in presence of water gives similar results, but if the ozonide is decomposed by sodium hydrogen sulphite formaldehyde is the chief decomposition product, and is isolated as the additive compound. Addition of an ammoniacal solution of the ozonide to ammonium chloride solution gives hexamethylenetetramine, a small amount of ammonium formate, and oxygen.

II. Ozonisation of propylene proceeds in much the same manner as of ethylene. The stable products are formaldehyde, acetaldehyde, and formic and acetic acids. The evolution of hydrogen is not so marked as in the case of ethylene, although peroxides are again produced. Ozonisation of a "cracking gas" containing ethylene (15%), propylene (12%), butylene (8%), and other hydrocarbons proceeded similarly to the above examples.

H. BURTON.

Electron displacement in carbon compounds. V. Addition of hydrogen chloride to γ-ethyl-Δ^{β}-pentene. H. J. LUCAS (J. Amer. Chem. Soc., 1929, **51**, 248—253).—γ-Ethyl-Δ^{β}-pentene (cf. Brooks and Humphrey, A., 1918, i, 286) and hydrogen chloride in glacial acetic acid yield almost quantitatively γ-chloro-γ-ethylpentane. This is in accordance with the hypothesis of electron displacement (cf. A., 1926, 943), but contrary to that of alternating polarity. γ-Ethylpentan-β-ol, obtained together with a little *δε-dimethyl-γζ-diethyloctane-δε-diol*, m. p. 100·7—101·2°, from γ-ethylpentan-β-one and sodium in alcohol, is converted by concentrated hydrochloric acid in presence of zinc chloride at the ordinary temperature into *β-chloro-γ-ethylpentane*, b. p. 62·0—62·5°/50 mm., d_{25}^{25} 0·8911, n_D^{25} 1·4295. γ-Ethylpentan-γ-ol is similarly converted into *γ-chloro-γ-ethylpentane*, b. p. 83—83·5°/100 mm., n_D^{25} 1·4311. The product from γ-ethyl-Δ^{β}-pentene and hydrogen chloride had b. p. 78—79°/90 mm., d_{25}^{25} 0·8951, n_D^{25} 1·4311.

H. E. F. NOTTON.

Action of acetylene on selenium. F. P. MAZZA and L. SOLAZZO (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 236—239).—The action of acetylene on selenium at 250—300° yields selenophen, b. p. 207—209° (cf. Foà, A., 1910, i, 187), and the selenium analogue of thionaphthene, *selenonaphthene*, C_8H_6Se, m. p. 53—54°, which gives a sparingly soluble *picrate*.

T. H. POPE.

[Conjugated] diacetylenic hydrocarbons. V. GRIGNARD and TCHÉOUFAKI (Compt. rend., 1929, **188**, 357—361).—The interaction of reagents, $CR\vdots CMgX$ (2 mols.), and iodine (2 atoms) yields diacetylenic hydrocarbons through the probable intermediate formation of the α-iodoacetylene (1 mol.; cf. Grignard and Perrichon, A., 1926, 381). In this way the following are prepared : *$\Delta^{\delta\zeta}$-decadi-inene*, b. p. 88°/12 mm.; *$\Delta^{\epsilon\eta}$-dodecadi-inene*, b. p. 103°/8 mm.; *$\Delta^{\zeta\theta}$-tetradecadi-inene*, b. p. 118—119°/4 mm.; αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadi-inene, m. p. 86·5—87°; αδ-di-2 : 4-dimethylphenyl-$\Delta^{\alpha\gamma}$-butadi-inene, m. p. 145·5—146°; *αζ-diphenyl-$\Delta^{\beta\delta}$-hexadi-inene*, m. p. 101°; αθ-diphenyl-$\Delta^{\gamma\epsilon}$-octadi-inene, m. p. 118°; iodoacetylene, b. p. 32°; *α-iodo-$\Delta^{\alpha\gamma\epsilon}$-hexatri-inene*, m. p. 52°; di-iododiacetylene, m. p. 101—105°; $\Delta^{\alpha\gamma}$-butadi-inene, b. p. 8·5—9°; and *phenyltriacetylene*, b. p. 52°/18 mm., d_4^{18} 0·9708, n_D^{18} 1·534. Hydrolysis of the product of the reaction of iodine (1·5 mol.) and the dimagnesium derivative of acetylene yields a dark-coloured powder part of which sinks in ethyl iodide but does not scratch glass. This last-named product contains 98% of carbon and no hydrogen; it may be a condensed form of carbon (C_6). G. A. C. Gough.

Action of sulphuric acid in preparing alkyl halides. R. McCullough and F. Cortese (J. Amer. Chem. Soc., 1929, **51**, 225—228).—Sulphuric acid acts both on alcohols and on alkyl halides, particularly *iso*propyl, *sec.*-butyl, *iso*butyl, and *iso*amyl bromides, forming unsaturated products, the polymerides of which form unstable coloured additive products with acids. Accordingly, when alcohols are both distilled and washed with hydrobromic acid alone (cf. Michael and others, A., 1916, i, 361; Norris, *ibid.*, 461), the products are of greater purity and deteriorate much less rapidly on keeping than when sulphuric acid is used, although the yields are smaller. Stable samples of allyl halides are prepared by treating allyl alcohol (1 vol.) for several days at the ordinary temperature with hydrochloric acid (*d* 1·19; 8 vols.), hydrobromic acid (*d* 1·4; 7 vols.), or hydriodic acid (*d* 1·7; 6 vols.) and washing the product with alkali before distillation. H. E. F. Notton.

Action of alkyl chlorides in the Würtz reaction. H. F. Lewis (Proc. Iowa Acad. Sci., 1927, **34**, 222).—The replacement of butyl bromide by chloride in the preparation of octane gives yields up to 20% (based on the chloride), but the reaction is difficult to control, and a highly inflammable by-product is produced. Chemical Abstracts.

Manufacture of ααβ-trichloroethane. I. G. Farbenind. A.-G.—See B., 1929, 122.

Molecular compounds of organic iodides with sulphur. H. Rheinboldt and K. Schneider (J. pr. Chem., 1929, [ii], **120**, 238—248).—A study of the phase-diagrams of the binary systems organic iodide–sulphur has been made. Iodoform gave two eutectics (42% and 69% S) at 85° and 91°. Tetra-iodoethylene gave two eutectics (54% and 68% S) at 95·5° and 101°. The following mixtures gave eutectics: αβ-di-iodoethane–sulphur, 28% S at 65°; di-iodoethylene–sulphur, 29% S at 54°; tri-iodonitroethylene–sulphur, 35% S at 80°; di-iodoacetylene–sulphur, 29% S at 48°; *p*-di-iodobenzene–sulphur, 58·5% S at 91°; iodoform–antimony tribromide, 63% $SbBr_3$ at 62°; tetrabromoethylene–sulphur, 13% S at 44°; diphenyliodinium tri-iodide–sulphur, 94% S at 117°. The following gave neither maxima nor minima: methylene iodide–sulphur; bromoform–sulphur. The compounds of sulphur with iodoform and tetraiodoethylene (Anger, A., 1908, i, 241) were isolated. R. J. W. Le Fèvre.

Relationship of constitution of alkyl halides to the formation of nitroparaffins and alkyl nitrites. R. B. Reynolds and H. Adkins (J. Amer. Chem. Soc., 1929, **51**, 279—287; cf. Meyer and Stuber, A., 1872, 682, 804; Neogi and others, J.C.S., 1906, **89**, 1905; 1916, **109**, 701).—Alkyl halides are treated with silver nitrite, first in the cold and then under reflux, until the halogen-free distillate gives correct analyses for a mixture of alkyl nitrite and nitroparaffin. The proportion of the latter is determined by hydrolysing a weighed sample with alcoholic sodium hydroxide and analysing the residue, after removal of alcohol, for carbon by a wet combustion method. This method is not applicable to *tert.*-alkyl derivatives. *n*-Butyl chloride does not react with silver nitrite under these conditions, whilst *iso*amyl chloride, *tert.*-butyl and *cyclo*hexyl iodides, and benzyl and phenylethyl bromides do not give a simple mixture of isomerides. The percentage yield and the percentage of nitroparaffin in the products from the following bromides are allyl: 74·0, 79·8; *n*-propyl: 86·1, 77·4; *iso*propyl: 78·5, 40·3; *n*-butyl: 88·2, 77·0; *iso*butyl: 77·2, 57·8; *sec.*-butyl: 68·3, 30·0; *tert.*-butyl: 60·0, 48·3; *iso*amyl: 78·2, 67·5; *n*-heptyl: 94·3, 71·0, and *sec.*-octyl: 82·1, 34·3; and from the following iodides: *n*-propyl: 85·9, 66·9; *iso*propyl: 71·7, 31·8; *n*-butyl: 85·1, 60·7; *iso*butyl: 74·9, 40·0, and *sec.*-butyl: 70·0, 31·9. The results show that, except with *sec.*-butyl bromide, a larger yield and a larger proportion of nitroparaffin are obtained from an alkyl bromide than from the corresponding chloride or iodide. Among isomeric derivatives, *n*-alkyl halides give a larger yield and a larger proportion of nitroparaffin than do *iso*alkyl, and *tert.*- give more than *sec.*-alkyl halides. The proportion of nitroparaffin formed is not greatly affected by the size or unsaturation of the alkyl radical. The reactivity of the alkyl halides increases in the order: allyl, *tert.*-butyl, *sec.*-alkyl, *iso*alkyl, *n*-alkyl- and the iodides are more reactive than the bromides. H. E. F. Notton.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. II. Synthesis of methyl alcohol with catalysts composed of copper and zinc. P. K. Frolich and others.—See this vol., 153.

Determination of the configuration of poly-alcohols by means of boric acid. J. Böeseken (Bull. Soc. chim. Belg., 1928, **37**, 385—402).—A lecture. J. W. Baker.

Cyclic acetals. J. D. van Roon (Rec. trav. chim., 1929, **48**, 173—190; cf. Hill, Hibbert, and others, A., 1928, 1114, 1213).—The separation of the two isomeric ethylideneglycerols from the mixture obtained by Hill and Hibbert's method (A., 1924, i, 133) or by the action of acetaldehyde or paracetaldehyde on glycerol, is not possible by careful fractional distillation. Benzoylation of the mixture in quinoline (Fischer, Bergmann, and Bärwind, A., 1920, i, 805) gives αγ-ethylideneglyceryl β-benzoate, b. p. 183°/20 mm., m. p. 85°, monoclinic, also obtained by the action of paracetaldehyde and hydrogen bromide or chloride on β-benzoylglycerol αγ-ditriphenylmethyl ether (Helferich and Sieber, A., 1928, 44), and αβ-ethylideneglyceryl γ-benzoate, b. p. 173°/20 mm., d_4^{25} 1·1663, n_D^{25} 1·5100, also prepared from paracetaldehyde and glyceryl α-benzoate in presence of 1% of dry hydrogen chloride. Both ethylideneglyceryl benzoates yield glyceryl α-benzoate when hydrolysed with 0·5*N*-hydrochloric acid in acetone solution (cf. Fischer, A., 1920, i, 808). αγ-Ethylideneglycerol (phenylcarbimide derivative, m. p. 134°) and αβ-ethylideneglycerol (phenylcarbimide derivative, m. p. 129°) have b. p. 176° and 187°, respectively. Small amounts of dry hydrogen chloride have an equilibration action on mixtures of the ethylideneglycerols, and subsequent benzoylation of mixtures equilibrated by 1% of dry hydrogen chloride at 0—180° shows that the αβ-form predominates at all temperatures, and increases with rise of temperature.

Paraformaldehyde and glycerol react in presence of 1% of dry hydrogen chloride at 130°, yielding a product (50%), b. p. 193—194°, which when benzoylated in quinoline affords αγ-methyleneglyceryl β-benzoate, b. p. 181°/20 mm., m. p. 74·6°, and αβ-methyleneglyceryl γ-benzoate, b. p. 173°/20 mm., d_4^{25} 1·2011, n_D^{25} 1·5184, obtained also from glyceryl α-benzoate or αβ-*iso*propylideneglyceryl γ-benzoate and formaldehyde. Hydrolysis of these esters with 4*N*-sodium hydroxide solution gives αγ-methyleneglycerol, b. p. 193·8°, 94°/20 mm., d_4^{25} 1·220, n_D^{25} 1·4527 (phenylcarbimide derivative, m. p. 133°), and αβ-methyleneglycerol, b. p. 192·5°, 93°/20 mm., d_4^{25} 1·2008, n_D^{25} 1·4469 (phenylcarbimide derivative, m. p. 72°). These ethers are also affected by small amounts of dry hydrogen chloride, but appreciable amounts of undistillable condensation products are formed.

H. Burton.

Partial esterification of polyhydric alcohols. VII. Unreliability of proofs of the structure of disubstituted glycerols. A. Fairbourne and G. W. Cowdrey (J.C.S., 1929, 129—135; cf. Fairbourne and Foster, A., 1927, 131).—The "αβ"-diphthalimidoglycerol of Philippi and Seka (A., 1923, i, 1185) is identical with the "αγ"-isomeride of Gödeckmeyer (A., 1888, 1294) and Gabriel (A., 1889, 486). The corresponding "αβ"- and "αγ"-diphthalimido-acetates and -benzoates have been synthesised and are also identical. It is considered that the only absolute proof of αβ-structure is resolution, and that this cannot be extended to derivatives. *Diphthalimidoacetoxypropane* was synthesised by three methods: (*a*) $OH\cdot CH_2\cdot CHBr\cdot CH_2Br \xrightarrow{AcCl} OAc\cdot CH_2\cdot CHBr\cdot CH_2Br \xrightarrow{KX} OAc\cdot CH_2\cdot CHX\cdot CH_2X$ ($X=$ phthalimido-group); (*b*) $CH(OH)(CH_2Cl)_2 \xrightarrow{AcCl} CH(OAc)(CH_2Cl)_2 \xrightarrow{KX} CH(OAc)(CH_2X)_2$; (*c*) $CH(OH)(CH_2X)_2 \xrightarrow{AcCl} CH(OAc)(CH_2X)_2$, all of which yielded the same product, m. p. 194°. Specimens of *diphthalimidobenzoyloxypropane* similarly synthesised by methods (*a*) and (*c*) were identical, m. p. 194—195°. αβ-*Dibromohydrin palmitate*, m. p. 34°, was prepared by method (*a*), using palmityl chloride and also by dibromination of *allyl palmitate*, m. p. 20—25°. αγ-*Dibromohydrin palmitate*, m. p. 35·5°, was similarly obtained, using method (*a*), and depressed the m. p. of the αβ-isomeride to 28°. *Monopalmitin di*-p-*nitrobenzoate*, m. p. 102°, was prepared by heating silver *p*-nitrobenzoate and either αβ- or αγ-dibromohydrin palmitate. αγ-*Dichlorohydrin* β-*triphenylmethyl ether*, m. p. 108—109°, obtained from αγ-dichlorohydrin and triphenylmethyl chloride in pyridine solution is also described.

C. W. Shoppee.

Additive compounds of hydrogen chloride with ethyl ether and acetone. D. McIntosh (Proc. Nova Scotian Inst. Sci., 1928, 17, 112—113).—The existence of the three ether–hydrogen chloride compounds Et_2O,HCl, $Et_2O,2HCl$, and $Et_2O,5HCl$ found by Maass and McIntosh (A., 1913, i, 584), two of which Hirai (A., 1926, 908) was unable to obtain, was confirmed by the method of thermal analysis. Crystallisation of the first two compounds was induced by inoculation; the last-named compound separated only after cooling and prolonged stirring. The existence of the acetone–hydrogen chloride compounds, $COMe_2,HCl$ (Hirai, *loc. cit.*) and $2COMe_2,5HCl$ (Archibald and McIntosh, J.C.S., 1904, 85, 919), was also confirmed.

B. W. Anderson.

Isomorphism in oxonium compounds. D. McIntosh (Proc. Nova Scotian Inst. Sci., 1928, 17, 116—117).—Relationships between the chemical constitutions of various oxonium compounds were investigated by determining which compounds formed an isomorphous series, the method being to inoculate supercooled solutions of the various compounds with compounds of supposedly similar nature. Systems examined were: ethyl ether with hydrogen chloride, bromide, and iodide; ethyl alcohol, acetone, and ethyl acetate with hydrogen bromide; ethyl ether, ethyl alcohol, ethyl acetate, and acetone with chlorine and bromine; and methyl ether with hydrogen bromide and iodide. Supercooled ethyl ether–hydrogen chloride is precipitated at once by its own crystals and by the corresponding hydrobromide, and, more slowly, by the hydriodide, but not by the corresponding salts of methyl ether, by acetone–hydrobromide, or by ether–chlorine. The compound $Et_2O,2HCl$ is precipitated by its own crystals and by $Et_2O,2HBr$, but not by ether–hydriodide, whilst $Et_2O,5HCl$ is unaffected by any oxonium compound. The oxonium–chloride compounds are precipitated by the corresponding bromides, not by other halogen compounds. Thus compounds of each class made with the same organic substances are isomorphous, whilst corresponding compounds with closely related organic substances are not.

B. W. Anderson.

Carbohydrates and polysaccharides. XX. β-Methyl glyceryl ether. H. Hibbert, M. S. Whelen, and N. M. Carter (J. Amer. Chem. Soc., 1929, 51, 302—306).—The α- and β-methyl glyceryl ethers, important for the identification of glycerides, are most conveniently characterised as the *p*-nitrobenzylidene acetals (cf. this vol., 47, 170). α-Methyl glyceryl ether also gives a *di*-p-*nitrobenzoate*, m. p. 108°, and a *diphenylurethane*, m. p. 118—119°, and β-methyl glyceryl ether a *di*-p-*nitrobenzoate*, m. p. 155°, and a *diphenylurethane*, m. p. 102°.

H. E. F. Notton.

Alkyl peroxides. II. Methyl ethyl peroxide and refractometric investigations on alkyl peroxides. A. Rieche [with F. Hitz] (Ber., 1929, 62, [*B*], 218—225; cf. A., 1928, 734).—*Methyl ethyl peroxide* is obtained only in traces by the action of diazomethane on ethyl hydroperoxide, readily by means of methyl sulphate. It has b. p. 40°/740 mm., d_4^{17} 0·8337, n_D^{15} 1·35987; the vapour density is normal. Like the other alkyl peroxides, it is only a feeble oxidising agent, liberating iodine from acidified potassium iodide only slowly and in traces. There is therefore a fundamental difference between the alkyl peroxides and hydrogen peroxide or ethyl hydroperoxide, which liberate iodine quantitatively. The peroxidic oxygen can be determined by titanium trichloride. In stability and other properties methyl ethyl peroxide is intermediate between the dimethyl and diethyl compounds. For dimethyl peroxide the constants d^0 0·868, f. p. $-100°$ to $-105°$, are recorded. Diethyl peroxide, d^{17} 0·8266, m. p. about $-70°$, from hydrogen peroxide, ethyl sulphate, and potassium hydroxide, has b. p. 64°/740 mm.; fractions collected close to the true b. p. contain considerable quantities of ether. Refractometric determinations on dimethyl, methyl ethyl, and diethyl peroxides show that the peroxidic oxygen cannot be present in purely ether-like linking. The refractions and dispersions of the compounds differ by definite amounts from the values calculated for ethereal oxygen. The formulation R·O·O·R expresses badly the union of peroxidic oxygen in alkyl peroxides and the structure RO:OR is preferred. Decomposition into radicals with univalent oxygen is excluded, since all alkyl peroxides have normal vapour densities. H. WREN.

***iso*Propyl and *n*-propyl sulphates.** R. LEVAILLANT (Compt. rend., 1929, 188, 261—263).—Anhydrous *iso*propyl alcohol is added slowly to sulphuryl chloride in carbon tetrachloride at 0°, the whole is washed with ice-water, and the lower layer is distilled in a vacuum below 90°, giving in 34% yield *iso*propyl sulphate, b. p. 78—80°/3·7 mm., d_0^0 1·118, n_D^{17} 1·409. The preparation of phenyl *iso*propyl ether, b. p. 63—65°/11 mm., d_0^0 0·959, $n_D^{17.5}$ 1·4983, and of phenyl *n*-propyl ether, b. p. 81°/17 mm., d_0^0 0·969, n_D^{15} 1·503, is described. *n*-Propyl sulphite, b. p. 82°/15 mm., d_0^0 1·042, n_D^{16} 1·426, is oxidised to the sulphate by permanganate. C. HOLLINS.

β-Hydroxyethyl allyl sulphide and its derivatives. S. M. SCHERLIN and V. V. VASILEVSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1629—1632).—Treatment of allyl mercaptide with ethylene chlorohydrin yields β-*hydroxyethyl allyl sulphide*, b. p. 90—92°/12 mm., d_{15}^{15} 1·0325, which with phosphorus trichloride gives β-*chloroethyl allyl sulphide*, b. p. 68°/12 mm., d_{20}^{20} 1·0768, and with acetic anhydride the corresponding *acetate*, b. p. 95°/12 mm., d_{20}^{20} 1·0469.
M. ZVEGINTZOV.

Stereoisomerism of disulphoxides and related substances. IV. Di- and tri-sulphoxides of trimethylene trisulphide. E. V. BELL and G. M. BENNETT (J.C.S., 1929, 15—19).—Hydrogen peroxide in acetone yields *trimethylene trisulphide monoxide*, m. p. 187°, converted by further treatment with hydrogen peroxide in glacial acetic acid into a mixture of α-*trimethylene trisulphide dioxide*, decomp. 220—280° (*labile* form, square plates, extinction angle 16°; *stable* form, monoclinic prisms, extinction angle 35°), and β-trimethylene trisulphide dioxide, decomp. 200—215°, pointed needles, extinction angle 32° (cf. Hinsberg, A., 1913, i, 818). The α-dioxide when further oxidised yields a single α-trimethylene trisulphoxide, decomp. 230—280° (cf. Hinsberg, A., 1912, i, 546; 1914, i, 797), and the β-dioxide similarly yields this α-trioxide together with β-*trimethylene trisulphoxide*, decomp. 220—260°, extinction angle 32°. The above oxides all yield trimethylene trisulphide when gently reduced, and the solubilities of the stable α-dioxide, the β-dioxide, and the isomeric trioxides in water at 25° are recorded.

The isomeric form of trimethylene trisulphide reported by Hinsberg has been examined; trimethylene trisulphide was heated with hydriodic acid (*d* 1·7) at 100°, and a substance, m. p. 247° (decomp.), isolated. It is reconverted into the ordinary trisulphide, m. p. 216°, by crystallisation, and its composition differs slightly from that of $[CH_2S]_n$. C. W. SHOPPEE.

Oxidation of unsaturated compounds. I. Oxidation of crotonic and *iso*crotonic acids, of γ-*iso*crotonolactone, and of maleic anhydride. G. BRAUN (J. Amer. Chem. Soc., 1929, 51, 228—248).—Crotonic and *iso*crotonic acids are oxidised by perbenzoic acid in chloroform in presence of water, yielding 63% of the theoretical of *dl*-erythro- (I), m. p. 81·5°, and *dl*-threo- (II), m. p. 74—75°, -αβ-dihydroxybutyric acids, respectively (cf. Melikoff, A., 1888, 1056; Milas and Terry, A., 1925, i, 780). The same products are formed in aqueous solution. Crotonic acid is oxidised by potassium and barium chlorates in presence of osmic acid to II (80% and 38% yields, respectively) together with about 20% of a *chlorohydroxybutyric acid*, m. p. 76°. The formation of the latter indicates that, contrary to the statement of Hofmann (A., 1913, ii, 609), hypochlorous acid is formed during chlorate oxidations. Addition of hypochlorous acid also occurs when barium crotonate is oxidised with chlorate in neutral solution, but it is reduced to a minimum when crotonic and *iso*crotonic acids are oxidised by adding silver chlorate during some weeks to an aqueous solution at 0° (82% yields of II and I, respectively). The prefixes assigned to the acids I and II indicate their relationship to erythronic and threonic acids, assuming the usually accepted structure for crotonic acid and the occurrence of *cis*-addition in chlorate oxidations (cf. Glattfeld and Woodruff, A., 1927, 1054). Oxidations of γ-*iso*crotonolactone (Lespieau, A., 1905, i, 566) with silver, barium, or alkali chlorates give good yields of erythronolactone, but no chloro-derivative. Maleic anhydride is also oxidised without chlorination by barium chlorate to 90% and by silver chlorate to 70% of mesotartaric acid. H. E. F. NOTTON.

Determination of higher unsaturated fatty acids. H. H. ESCHER (Helv. Chim. Acta, 1929, 12, 27—49).—Saturated, unsaturated, and brominated fatty acids are converted by an excess of thionyl chloride into the corresponding acid chlorides and then treated with excess of *p*-aminoazobenzene in an indifferent solvent. After removal of solvent and excess of base by washing with aqueous-alcoholic hydrochloric acid, the resulting anilide is dried. The yields are from 87·5 to 98%. For full details of the method the original must be consulted. A scheme for the analysis of a fat is appended which gives the usual constants from the same specimen.

Condensation *products* of *p*-aminoazobenzene with the following acids are described: *palmitic*, m. p. 121·5—122·5°; *stearic*, m. p. 123—124°; *oleic*, m. p. 93—94°; *elaidic*, m. p. 111·5—112·5°; *oleic acid dibromide*, m. p. 90—91·5°; *elaidic acid dibromide*, m. p. 131—132°; *linoleic acid tetrabromide*, m. p. 137—138°, and *linolenic acid hexabromide*, m. p. 193—194°. The *compound* from oleic acid dibromide and aminoazo-*p*-xylene has m. p. 155°. H. BURTON.

Attempt to remove hydrogen from higher fatty acids. T. Suzuki and T. Kurita (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 5—6).—Attempts to dehydrogenate palmitic, stearic, and oleic acids and their esters under diminished pressure (10—0·1 mm.) and at temperatures ranging from atmospheric to 300°, in the presence of various catalysts, were unsuccessful. A. I. Vogel.

Pityrol. VI. Distillation of palmitic acid. S. Shoyama (Mem. Coll. Sci. Kyoto, 1928, **11**, 533—542).—Dry sodium palmitate was distilled from a Fischer retort at 380—540°, and yielded tar 70%, coke 24%, and gas 6%. The gas contained carbon monoxide 11·8%, carbon dioxide 12·2%, ethylene 1·7%, paraffins and hydrogen 27·4%. Fractionation of the part of the tar volatile with steam revealed the presence of the paraffins from C_9H_{20} to $C_{13}H_{28}$, confirmed by their physical constants and analysis. Olefinic hydrocarbons in the same portion of the tar were separated by means of liquid sulphur dioxide, and fractionated; the series from C_7H_{14} to $C_{13}H_{26}$ were identified. From the non-volatile portion of the tar, consisting mainly of unsaturated hydrocarbons C_{15}, C_{19}, C_{20}, C_{30}, palmitone was isolated; $C_{14}H_{30}$, $C_{18}H_{38}$, and $C_{20}H_{42}$ were also identified in this portion. B. W. Anderson.

Conversion of higher fatty acids into barium salts. H. H. Escher (Helv. Chim. Acta, 1929, **12**, 103—105).—Solutions of higher fatty acids in methyl or ethyl alcohol, ether, chloroform, carbon tetrachloride, or dichloroethane can be conveniently titrated with a solution (about 2*N*) of barium hydroxide in methyl alcohol. The resulting barium salt is usually precipitated in a pure condition. H. Burton.

Distillation of higher unsaturated fatty acids. H. H. Escher (Helv. Chim. Acta, 1929, **12**, 99—102).—Oleic and similar acids are much more sensitive to heat (up to 150°) than is usually supposed. This sensitivity is more apparent in the oleic than in the elaidic series. Distillation of the acids is best carried out in a high vacuum and even then only an apparent purification occurs. Even with one distillation through a glass column partial rearrangement is unavoidable. H. Burton.

Pityrol. VII. Distillation of oleic acid. H. Ogata (Mem. Coll. Sci. Kyoto, 1928, **11**, 543—547).—Sodium oleate, when distilled from a Fischer retort at 390—550°, yielded tar 65%, coke 17%, and gas 18%. More than 80% of the tar consisted of unsaturated hydrocarbons. By repeated distillation the part of the tar volatile with steam was divided into 18 fractions, examination of which showed the presence of a series of olefines from C_7H_{14} to $C_{16}H_{32}$. Similarly the non-volatile portion, after separation of 10% of unchanged sodium oleate, was found to contain the olefines from $C_{14}H_{28}$ to $C_{18}H_{36}$. B. W. Anderson.

So-called "arachidic acid" and other acids of high mol. wt. from arachis oil. D. Holde, W. Bleyberg, and I. Rabinowitsch (Ber., 1929, **62**, [*B*], 177—183; cf. Ehrenstein and Stuewer, A., 1923, i, 1057; Cohen, B., 1926, 98).—The technical fatty acids from arachis oil were worked up by a combination of distillation in a high vacuum, crystallisation of the acids and their esters, and fractional precipitation of the lithium salts (cf. Holde and Godbole, A., 1926, 268, 498). The presence of *n*-docosoic acid, $C_{22}H_{44}O_{21}$, doubted by Cohen (*loc. cit.*), is placed beyond doubt. The acid is shown by the mixed m. p. method to be *n*- instead of *iso*-behenic acid (cf. Ehrenstein and Stuewer, *loc. cit.*). In addition, small quantities of an acid, $C_{26}H_{42}O_2$, m. p. 69—70°, mol. wt. 323—324, were separated which appears homogeneous, since the m. p. remains constant after lithium precipitation and repeated crystallisation; further characterisation appears, however, to be required, since the m. p. is considerably lower than that recorded by Levene and Taylor (A., 1924, i, 827) for the synthetic acid. *n*-Eicosoic acid, detected by Cohen in arachis oil, was absent or present only in traces in the "crude arachidic acid" of m. p. 73°, but is probably contained in the separated lower acids. The acid $C_{26}H_{52}O_2$, m. p. 79°, isolated by Holde and Godbole (*loc. cit.*) from Indian arachis oil, was isolated from the fraction of highest mol. wt. The m. p., 78—78·8°, agrees closely with that recorded previously, but the mol. wt., 381—384, corresponds more closely with $C_{25}H_{50}O_2$ than with $C_{26}H_{52}O_2$. Although fractional precipitation with lithium acetate did not lead to recognisable separation, cautious distillation in a high vacuum gave a residue which, after crystallisation from acetone, had m. p. 81—82·4°, mol. wt. 390. It appears therefore that the lithium method alone does not afford certain evidence of homogeneity with very sparingly soluble fatty acids of high mol. wt.

Tetracosoic acid, m. p. 83—84° (presumably the *n*-acid), has been isolated from the portions of lowest b. p. of the free acids of beeswax. H. Wren.

Constitution of clupanodonic acid. M. Tsujimoto (Bull. Chem. Soc. Japan, 1928, **3**, 299—307).—Clupanodonic acid, $C_{22}H_{34}O_2$, was isolated from Japanese sardine oil by the author's lithium-salt–acetone method (cf. Armstrong and Hilditch, A., 1925, i, 778; McGregor and Beal, A., 1927, 145) and had d_4^{15} 0·9410, n_D^{15} 1·5057, neutralisation value 170·7, iodine value 388·5. Ozonolysis of the acid followed by decomposition of the ozonide with water afforded acetaldehyde, propaldehyde, carbon dioxide, and a comparatively large amount of succinic acid, but no azelaic acid (cf. Armstrong and Hilditch), whereas *amyl clupanodonate* (saponification value 139·5) similarly treated furnished a product insoluble in water which gave a 49% yield of succinic acid on hydrolysis. The latter fact is regarded as evidence for the first ethylenic linking being situated between the fourth and fifth carbon atoms; acetaldehyde and carbon dioxide are considered to be secondary decomposition products of malon-aldehyde or -semialdehyde. The absence of glyoxal or glyoxylic acid and of oxalic acid from the decomposition products together with the constancy of the iodine value after reduction with sodium and alcohol point to the absence of conjugated double linkings. The following two formulæ for the acid are provisionally suggested:

$Et{\cdot}\{CH{:}CH{\cdot}[CH_2]_2\}_3{\cdot}[CH{:}CH{\cdot}CH_2]_2{\cdot}CH_2{\cdot}CO_2H$,

$Et{\cdot}\{CH{:}CH{\cdot}[CH_2]_2\}_2{\cdot}[CH{:}CH{\cdot}CH_2]_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$. A. I. Vogel.

Oxidation of lignoceric acid. F. A. Taylor and P. A. Levene (J. Biol. Chem., 1928, **80**, 609—613).—Repetition of the work of Meyer and others (A., 1913, i, 1151) and of Levene and Taylor (A., 1922, i, 714) has given α-bromolignoceric acid, m. p. 69·5—70·5°, α-hydroxylignoceric acid, m. p. 94—95°, and *iso*-tricosoic acid, m. p. 76·5—77·5°.

C. R. Harington.

Sodium salts of ω-hydroxy-butyric, -valeric, and -hexoic acids. C. S. Marvel and E. R. Birkheimer (J. Amer. Chem. Soc., 1929, **51**, 260—262).—Details are given of the conversion of γ-phenoxybutyronitrile into γ-phenoxybutyric acid, γ-bromobutyric acid, γ-butyrolactone, and sodium γ-hydroxybutyrate, of δ-valerolactone into sodium δ-hydroxyvalerate, and of ε-bromohexoic acid into a mixture of ε-hexolactone and a polymeric product, both of which are hydrolysed by alkali to sodium ε-hydroxyhexoate.

H. E. F. Notton.

Formation of methyl sodiochloromalonate and its reaction with iodine. Stability of halogeno-ethanes. A. Eccles (Proc. Leeds Phil. Soc., 1929, 1, 356—359).—The lability of halogen atoms in halogeno-ethanes is discussed on the basis of the relative displaceability of the unshared electrons in the four halogen atoms (I>Br>Cl>F; cf. Ingold and others, A., 1928, 164, 402). In the hexahalogenoethane molecule two opposing factors are in operation: (1) the intrinsic tendency of the halogen atom to assume anionic condition, and (2) the cationising effect of the halogen atoms on each other. On heating, the amplitude of the oscillations of the shared electrons increases with resulting extremes of negative and positive polarisation, so that in molecules above a certain critical energy separation of negative and positive ions occurs with thermal decomposition into the corresponding tetrahalogenoethylene and free halogen. Attachment of a powerful electron sink such as the carbomethoxy-group (Cooper and Ingold, A., 1927, 558) to a carbon atom bearing an atom of strong anionic tendency (halogens) will cause an increase in the amplitude of oscillation of the carbon–halogen shared electrons and a correspondingly increased tendency towards elimination of halogen. In agreement with this view the action of iodine on *methyl chlorosodiomalonate* yields only methyl ethylenetetracarboxylate (identical with a specimen prepared by the action of iodine on methyl disodioethanetetracarboxylate), the intermediate methyl αβ-dichloroethanetetracarboxylate produced momentarily eliminating chlorine with the formation of the unsaturated compound (cf. Bischoff and Rach, A., 1885, 244).

J. W. Baker.

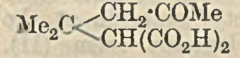
Reaction of alkali molybdates with malic and tartaric esters. E. Darmois (Bull. Soc. chim., 1928, [iv], **43**, 1214—1229; cf. A., 1926, 457).—Further evidence is adduced in support of the two-stage hydrolysis of ethyl malate. Although molybdotartrates have not been actually isolated, measurements of the mutarotation of mixtures of tartaric esters and molybdates indicate that such substances exist and that hydrolysis of the esters occurs in two stages.

J. S. Carter.

Influence of the solvent on the optical rotation of ethyl tartrate. T. J. Hebert and J. N. Pearce (Proc. Iowa Acad. Sci., 1927, **34**, 218—219).—Values of [α] depend on the composition of the solvent (ethyl alcohol, methyl alcohol, benzene, and toluene, and binary mixtures thereof), on the concentration of ester, and on the temperature. Chemical Abstracts.

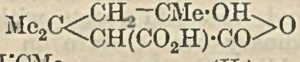
Replacement of hydroxyl group in hydroxy-acid esters by chlorine with phosphoryl chloride and pyridine. (Steric course of substitution.) T. Wagner-Jauregg (Helv. Chim. Acta, 1929, **12**, 61—63).—Methyl *l*(—)-malate is converted by treatment with phosphoryl chloride in cold pyridine into methyl *d*(+)-chlorosuccinate, b. p. 106—107°/10—11 mm., $[\alpha]_D^{20}$ +36·6°. Similarly, methyl (+)-mandelate gives methyl (—)-phenylchloroacetate, b. p. 130—131°(corr.)/15·5—16 mm., $[\alpha]_D^{18}$ —62·2°. *Methyl* r-*phenylchloroacetate* has b. p. 129—130°(corr.)/13—15 mm. Partial racemisation occurs during the formation of methyl (—)-phenylchloroacetate. Substitution is of the same order as with phosphorus pentachloride (cf. A., 1928, 506). H. Burton.

Keto–lactol tautomerism. I. Ring–chain tautomerism in α-carboxy-γ-acetyl-ββ-dimethylbutyric acid and a synthesis of γ-acetyl-ββ-dimethylbutyric acid. M. Qudrat-i-Khuda (J.C.S., 1929, 201—209).—Evidence is adduced to show that both the forms I and II are necessary to explain all reactions of α-carboxy-γ-acetyl-ββ-dimethylbutyric acid.



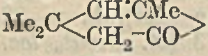
$$Me_2C{<}\begin{matrix}CH_2\cdot COMe\\ CH(CO_2H)_2\end{matrix}$$

(I.)



$$Me_2C{<}\begin{matrix}CH_2{-}CMe\cdot OH\\ CH(CO_2H)\cdot CO\end{matrix}{>}O$$

(II.)



$$Me_2C{<}\begin{matrix}CH{:}CMe\\ CH_2{-}CO\end{matrix}{>}O$$

(III.)

Condensation of mesityl oxide and cyanoacetamide with sodium ethoxide yields 6-*hydroxy*-2-*keto*-3-*cyano*-4 : 4 : 6-*trimethylpiperidine*, m. p. 272° (decomp.), also obtained by synthesis from mesityl oxide and ethyl cyanoacetate, which condense to give *ethyl α-cyano-γ-acetyl*-ββ-*dimethylbutyrate*, b. p. 160°/16 mm., $d_4^{20·3}$ 1·03705, $n_D^{20·3}$ 1·44652 (*semicarbazone*, m. p. 166·5°), yielding with aqueous ammonia δ-*amino*-δ-*hydroxy*-α-*cyano*-ββ-*dimethylhexoamide* [*trihydrate*, m. p. 87° (decomp.)], which is converted by alcoholic sodium ethoxide into the above trimethylpiperidine. It is dehydrated by phosphoryl chloride to 2-*keto*-3-*cyano*-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m. p. 253°, but is unaffected by dilute sodium hydroxide; hydrolysis with concentrated potassium hydroxide yields only α-*carboxy*-γ-*acetyl*-ββ-*dimethylbutyric acid*, m. p. 95° (*semicarbazone*, m. p. 177°); the *ethyl* ester, b. p. 153°/12 mm., $d_4^{20·2}$ 1·03921, $n_D^{20·2}$ 1·4413 (*semicarbazone*, m. p. 76°), is converted by alcoholic sodium ethoxide into ethyl 5 : 5-dimethyl-5 : 6-dihydroresorcinol-4-carboxylate. When hydrolysed with concentrated hydrochloric acid, the above trimethylpiperidine yields the *dilactone* of α-carboxy-γ-acetyl-ββ-dimethylbutyric acid, m. p. 137°, also obtained by hydrolysis with concentrated hydrochloric acid of ethyl α-cyano-γ-acetyl-ββ-dimethylbutyrate or of the tetrahydropyridine described above (cf. Vorländer and Gartner, A., 1899, i, 259). The dilactone is converted by hot dilute sodium hydroxide into α-carboxy-γ-acetyl-ββ-dimethylbutyric acid; at 200° it loses carbon dioxide, giving the unsaturated lactone (III).

Oxidation of α-carboxy-γ-acetyl-ββ-dimethylbutyric acid with sodium hypobromite gives α-carboxy-ββ-dimethylglutaric acid, m. p. 173° (decomp.) (cf. lit.), which passes into ββ-dimethylglutaric acid when heated. It decomposes at 130—140°, yielding a mixture of the dilactone and γ-acetyl-ββ-dimethylbutyric acid (cf. Bredt, A., 1898, i, 264), b. p. 162°/25 mm., $d_4^{19\cdot5}$ 1·03646, $n_D^{19\cdot5}$ 1·44652 [semicarbazone, m. p. 172° (decomp.) : cf. Vorländer and Gartner, *loc. cit.*], in relative quantities which suggest that the parent acid is a mixture of the forms I and II in the ratio of about 3 : 1. Ethyl γ-acetyl-ββ-dimethylbutyrate, b. p. 112°/17 mm., $d_4^{9\cdot8}$ 0·96248, $n_D^{19\cdot3}$ 1·43047 (semicarbazone, m. p. 114°), is obtained directly from the acid and has also been synthesised as follows : ββ-dimethylglutaric anhydride is converted by absolute alcohol into *ethyl hydrogen* ββ-*dimethylglutarate*, b. p. 164°/16 mm., $d_4^{18\cdot1}$ 1·05774, $n_D^{18\cdot1}$ 1·4403, which with thionyl chloride yields the corresponding *chloride*, b. p. 117°/16 mm. ; this with zinc methyl iodide in benzene yields the ester, which, after purification through the semicarbazone, m. p. 114°, has b. p. 113°/18 mm., $d_4^{20\cdot9}$ 0·96323, $n_D^{20\cdot9}$ 1·43067. The synthetic ester is completely converted by alcoholic sodium ethoxide into dimethyldihydroresorcinol and is hydrolysed to the γ-acetyl-ββ-dimethylbutyric acid, b. p. 162°/25 mm. [semicarbazone, m. p. 172° (decomp.)], described above. Thus the free acid appears to possess the normal ketonic structure I. On the other hand, the acid reacts with acetyl chloride at the ordinary temperature in the lactonic form (II), yielding the lactone (III), b. p. 82°/10 mm., $d_4^{22\cdot2}$ 0·98658, $n_D^{22\cdot2}$ 1·45573 (cf. Bredt, *loc. cit.*), which is re-converted into the keto-acid by alcoholic potassium hydroxide. Reduction of γ-acetyl-ββ-dimethylbutyric acid with sodium and alcohol yields ββδ-*trimethylvalerolactone*, b. p. 120°/18 mm., d_4^{17} 0·98039, n_D^{17} 1·47743. C. W. SHOPPEE.

Dimethyldihydroresorcinol as reagent for aldehyde, and carbon assimilation. D. VORLÄNDER (Z. angew. Chem., 1929, 42, 46—47. P. MAYER (*ibid*, 48). C. NEUBERG (*ibid.*, 48).—A question of priority. C. HOLLINS.

Condensation products of formaldehyde and urea. POLLOPAS, LTD., E. C. C. BALY, and E. J. BALY.—See B., 1929, 138.

Oxygen-compound formation with acetaldehyde at low temperature. D. LEB. COOPER (Proc. Nova Scotian Inst. Sci., 1928, 17, 140—141).—When oxygen was bubbled through a mixture of acetaldehyde and manganese acetate at the low temperature of a carbon dioxide–ether bath, the solution became dark pink, possibly owing to the formation of some complex, but no peroxide stable at the ordinary temperature was formed. Absorption reached a maximum after a few hours, which probably represented the solubility of oxygen in the mixture. By warming to the ordinary temperature, some oxidation of the acetaldehyde to acetic acid occurs. B. W. ANDERSON.

Preparation of aldehydes and ketones by degradation of quaternary ammonium bases. J. VON BRAUN and W. TEUFFERT [and, in part, G. MANZ] (Ber., 1929, 62, [*B*], 235—241 ; cf. von Braun and Heymons, this vol., 62).—Dihydrocitronellol, d_4^{16} 0·835, $[\alpha]_D^{16}$ +3·85°, prepared by hydrogenation of *d*-citronellol in the presence of platinum, is converted into βζ-dimethyloctyl bromide, which, with trimethylamine in benzene at 100°, affords the quaternary *bromide*, $C_{10}H_{12}\cdot NMe_3Br$, m. p. 255°. Treatment of this with silver oxide followed by addition of potassium hydroxide to the concentrated solution and distillation under atmospheric pressure yields *dimethyl-γη-dimethyloctylamine*, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_2\cdot NMe_2$, b. p. 95—98°/13 mm., d_4^{20} 0·7757, n_D^{20} 1·4302, $[\alpha]_D^{20}$ −4·79° (*methiodide*, m. p. 243°), and γη-*dimethyl*-Δ^{α}-*octene*, b. p. 45—46°/13 mm., 154°/atm., d_4^{20} 0·7321, n_D^{20} 1·4176, $[\alpha]_D^{20}$ −12·38°. The hydrocarbon is converted by ozonisation in chloroform and subsequent decomposition of the ozonide into iso*nonaldehyde*, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot CHO$, b. p. 72—74°/15 mm., 185—186°/752 mm., d_4^{19} 0·819, n_D^{15} 1·4203, $[\alpha]_D^{20}$ −9·1°, which reacts very slowly with hydroxylamine and semicarbazide, but is very easily oxidised to αε-*dimethylheptoic acid*, b. p. 127—130°/13 mm., d_4^{20} 0·8975, n_D^{19} 1·4287, $[\alpha]_D^{20}$ −14·1°.

Ethyl ethylmalonate is transformed by sodium and *n*-octyl bromide in presence of ether into *ethyl ethyl*-n-*octylmalonate*, b. p. 171—180°/13 mm. The corresponding *acid*, m. p. 72°, loses carbon dioxide with formation of *ethyloctylacetic acid*, b. p. 186°/12 mm. *Ethyl ethyloctylacetate*, b. p. 135—137°/12 mm., is reduced by sodium and alcohol to β-*ethyl*-β-*octylethyl alcohol*, b. p. 135—137°/12 mm., which is converted successively into β-*ethyl*-β-*octylethyl bromide*, b. p. 135—137°/12 mm., and the quaternary *bromide*, $C_8H_{17}\cdot CHEt\cdot CH_2\cdot NMe_3Br$, m. p. 225—227°. The salt is transformed in the usual manner into a mixture of *dimethyl*-β-*ethyl*-β-*octylethylamine*, $C_8H_{17}\cdot CHEt\cdot CH_2\cdot NMe_2$, b. p. 124°/13 mm., d_4^{20} 0·7913 (*picrate*), and as-*ethyloctylethylene*, b. p. 91—93°/11 mm., d_4^{22} 0·7703. The hydrocarbon is converted through its ozonide into ethyl octyl ketone, which, after purification through its semicarbazone, m. p. 91—92°, has b. p. 112°/12 mm., m. p. 12·5°. Its odour is considerably less pronounced than that of methyl nonyl ketone. The non-crystalline *oxime* has b. p. about 146°/13 mm.

Ethyl sodiomalonate and γ-phenylpropyl bromide afford ethyl γ-phenylpropylmalonate, b. p. 202°/11 mm., and small amounts of *ethyl di-γ-phenylpropylmalonate*, b. p. about 230°/1 mm. With β-phenylethyl bromide, ethyl γ-phenylpropylmalonate gives *ethyl* β-*phenylethyl-γ-phenylpropylmalonate*, b. p. 215—217°/1 mm. The corresponding *acid*, m. p. 124°, decomposes into β-*phenylethyl-γ-phenylpropylacetic acid*, b. p. 263—265°/18 mm., the *ethyl* ester, b. p. about 253—255°/18 mm., of which is reduced by sodium and alcohol to β-β′-*phenylethyl*-β-γ′-*phenylpropylethyl alcohol*, b. p. 242—245°/13 mm. The corresponding *bromide*, which has almost exactly the same b. p., is transformed into the extremely hygroscopic quaternary *bromide* (I), which yields *di*-$CH_2Ph\cdot CH_2\cdot CH_2\cdot CH(CH_2\cdot CH_2Ph)\cdot CH_2\cdot NMe_3Br$, (I), *methyl*-β-β-*phenylethyl*-β-γ-*phenylpropylethylamine*, b. p. about 200°/0·7 mm. (*picrate*, m. p. 109°), and as-β-*phenylethyl-γ-phenylpropylethylene*, b. p. 199—200°/14 mm., d_4^{18} 0·915, n_D^{18} 1·5517. Ozonisation of the hydrocarbon followed by treatment of the product with zinc dust gives *β-phenylethyl γ-phenylpropyl ketone*, b. p. 213—215°/11 mm., m. p. 31° after softening at 30° (non-crystalline *semicarbazone*).

H. WREN.

Catalytic reduction of geraniol and citronellal by means of nickel. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 3—4).—The first molecule of hydrogen was attached much more rapidly to citronellal than to geraniol. At this stage the product was, in both cases, citronellol with some dihydrocitronellol. The second molecule of hydrogen was introduced much more slowly in each case.

B. W. ANDERSON.

α-Bromo- and α-hydroxy-aldehydes. II. Bromination of valeraldehyde. R. DWORZAK and A. ENENKEL (Monatsh., 1928, **50**, 449—458).—Catalytic dehydrogenation of a sample of amyl alcohol, $[\alpha]_D$ −2·47° (whence 42% of α-methylbutyl alcohol), with a brass catalyst (details to be published later) gives a mixture of valeraldehydes, b. p. 90—92°, $[\alpha]_D$ +0·35°. This is polymerised by treatment with concentrated sulphuric acid into paravaleraldehyde, b. p. 122—124°/10 mm., which on bromination at −10 to −5° and subsequent treatment with alcohol (cf. A., 1927, 1055) affords *α-bromo-α-methylbutaldehyde ethylacetal*, b. p. 83°/10 mm., d_{18}^{18} 1·29, $[\alpha]_D$ +0·12°, and *αα-dibromo-β-methylbutaldehyde ethylacetal*, b. p. 121°/10 mm., d_{18}^{18} 1·37°. The former acetal is hydrolysed by boiling with water to the corresponding *hydroxy-aldehyde*, b. p. about 120°/high vacuum, which with *p*-nitrophenylhydrazine gives a homogeneous, dark red precipitate.

H. BURTON.

α-Bromo- and α-hydroxy-aldehydes. III. Crystalline lactaldehyde and its behaviour towards dilute aqueous alkalis. R. DWORZAK and W. PRODINGER (Monatsh., 1928, **50**, 459—475).—Crystalline, dimeric α-hydroxypropaldehyde (I) [*p*-nitrophenylhydrazone, m. p. 126·5° (corr.)], has been obtained in 35% yield by the hydrolysis of α-bromopropaldehyde ethylacetal, b. p. 69°/9 mm. (A., 1927, 1055), with water and prolonged extraction with ether of the resulting solution after neutralisation and saturation with sodium sulphate. The residue from this is distilled in a vacuum, when a mixture of I and unimolecular lactaldehyde is obtained. Cryoscopic determinations of I in aqueous solution show that after keeping for 24 hrs. the solution contains the unimolecular aldehyde only. When I is treated with 1% sodium hydroxide solution during several days oxidation occurs: this is minimised by working in an atmosphere of nitrogen. With 4% sodium hydroxide solution for 5 days a chloroform-soluble syrup is obtained which appears to be a condensation product of 3 mols. of lactaldehyde with loss of 1 mol. of water. The product reduces Fehling's solution slightly in the cold. Lactaldehyde is oxidised by aqueous copper acetate to pyruvaldehyde.

H. BURTON.

Inosinic acid. IV. Ribophosphoric acid. P. A. LEVENE and T. MORI (J. Biol. Chem., 1929, **81**, 215—219).—Ribophosphoric acid undergoes lactone formation slowly, indicating the formation of an αδ-lactone and the attachment of the phosphoric acid residue in the ε-position; the suggestion of Robinson (A., 1927, 960, 1225) is therefore not accepted.

C. R. HARINGTON.

Precipitation of carbohydrates and glucosides by alkaloid precipitants. L. ROSENTHALER (Pharm. Acta Helv., 1928, **3**, 93—96; Chem. Zentr., 1928, ii, 374).—Under the conditions employed, potato, wheat, maize, rice, barley, arrowroot, and sago starches gave with bromine and hydrobromic acid, silicotungstic acid, and phosphomolybdic acid more or less precipitate, and with tannin a turbidity. Aloin, convallamarin, digitalin, gitalin, and strophanthin gave a positive test with silicotungstic and phosphomolybdic acids; *Gypsophila* saponin reacted similarly, but was not precipitated by tannin or by bromine and hydrobromic acid. Thus precipitation of carbohydrates and glucosides can occur if the basicity due to the bridge oxygen atom is not too much weakened by hydroxyl or other acid groups.

A. A. ELDRIDGE.

Influence of sugars on the stability of hydrogen sulphite solutions. E. HÄGGLUND (Ber., 1929, **62**, [*B*], 84—90).—The action of dextrose on the stability of sodium hydrogen sulphite solutions at 135° has been investigated. About 4—5 hrs. after the maximal temperature has been attained, the sulphur dioxide content suddenly diminishes and the amount of sulphuric acid increases rapidly. At this period, a rapid increase in the amount of "loosely combined" sulphurous acid is observed but this subsequently diminishes greatly. At this stage, considerable amounts of dithionic and, possibly, polythionic acids are present which are transition products in the conversion of sulphurous into sulphuric acid. Under similar conditions in the absence of dextrose the sulphur dioxide content diminishes at a slower rate and the amount of sulphuric acid increases very slowly. The sugar content, as judged by the behaviour towards Fehling's solution, diminishes considerably, probably owing to oxidation. Instability of the hydrogen sulphite solutions increases with increasing sulphite concentration exactly as would be expected with solutions free from sugar. The catalytic effect of mannose, xylose, and arabinose is approximately the same as that of dextrose, whereas lævulose is less, but distinctly, effective. The acceleration of the decomposition of sulphite by sugars depends on the reactive carbonyl group of the latter. It is certain that the production of sulphuric acid is not due to reduction of the sugar by sulphur dioxide. The catalytic effect is due in the main to the facilitated formation of such intermediate products of the sulphite reaction, particularly thiosulphate ions, which cause and accelerate the decomposition.

H. WREN.

Oxidative decomposition of sugar. I. Action of "chloramine-*T*" on dextrose. K. BERNHAUER and K. SCHÖN (Biochem. Z., 1928, **202**, 159—163).—The oxidation of dextrose (1 mol.) using sodium *p*-toluenesulphonchloroamide by eight equivalents of oxygen giving rise to 2 mols of acetic acid and 2 mols. of carbon dioxide (Bleyer and Braun, A., 1927, 341) could not be quantitatively confirmed. Acetic acid cannot be detected and considerable amounts of formic acid are obtained. Gluconic acid is not formed initially, since this substance is not attacked by "chloramine-*T*." P. W. Clutterbuck.

Oxidation of dextrose in alkaline solution with formation of carbon monoxide. M. Nicloux (Compt. rend. Soc. Biol., 1928, **99**, 226—228; Chem. Zentr., 1928, ii, 1077).—The consumption of oxygen and the yield of carbon monoxide are maximal at 85°. Lævulose, lactose, galactose, and maltose, but not sucrose until inverted, are similarly attacked. The effect of various salts is examined.

A. A. Eldridge.

Colorimetric determination of dextrose. A. B. Schachkeldian (J. Russ. Phys. Chem. Soc., 1928, **60**, 1517—1520).—The method is based on the red coloration, due to the formation of picramic acid, which is developed when a solution of dextrose is treated with picric acid in the presence of alkali. The intensity of the colour depends on the concentration of dextrose, and can be compared with a standard scale. Disaccharides do not give the reaction, whilst lævo-hexoses produce a more intense colour. If chlorine ions are present, the coloration is fainter, and a special solution containing chlorides must be used as a standard of comparison.

M. Zvegintzov.

Hexosediphosphate. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1928, **80**, 633—638).—Hydrolysis of the methylglucoside of hexosediphosphate (cf. Morgan, A., 1927, 749) at 100° with 0·1*N*-hydrochloric acid consisted of initial rapid rupture of the glucosidic linking followed by much slower liberation of 1 mol. of phosphoric acid; the hexosediphosphate is therefore a γ-derivative, and the stable monophosphate of Neuberg (A., 1913, i, 423) is ζ-lævulosephosphate. C. R. Harington.

Pityrol. VIII. Distillation of sucrose. Y. Hidaka (Mem. Coll. Sci. Kyoto, 1928, **11**, 549—551).—Pure sucrose when distilled from an iron retort at 240—610° gave a distillate consisting of water 75%, neutral portion 4·5%, acidic substance 1·5%, and humus 8·5%. Furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde were identified as the neutral constituents, and formic and lævulic acids in the acidic portion.

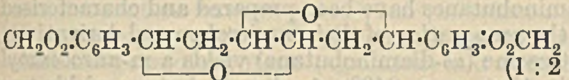
B. W. Anderson.

Constitution of daphnin. F. Wessely and K. Sturm (Ber., 1929, **62**, [*B*], 115—119).—The glucodaphnetin obtained by Leone (A., 1925, i, 1283) from β-acetobromoglucose and 7 : 8-dihydroxycoumarin is considered to have the glucose residue substituted in the 8- rather than in the 7-hydroxyl group of 7 : 8-dihydroxycoumarin. Until direct comparison can be made, the identity of this synthetic with the natural glucoside is not regarded as established and the present work refers to the synthetic material. Tetra-acetyldaphnin, m. p. 217°, $[\alpha]_D^{17}$ $-31·64°$ in methyl alcohol, and daphnin, m. p. 216—217°, $[\alpha]_D^{17}$ $+29·36°$ in methyl alcohol, are prepared by Leone's method. Treatment of tetra-acetyldaphnin with diazomethane followed by hydrolysis of the product affords 8-*hydroxy*-7-*methoxycoumarin*, m. p. 175° (corr.) after slight previous softening, which is similarly prepared from daphnin. 8-*Hydroxy*-7-*ethoxycoumarin*, m. p. 145 (corr.) after slight softening, is obtained analogously. Treatment of 8-hydroxy-7-methoxycoumarin with diazoethane in absolute alcohol gives an 80—90% yield of 7-*methoxy*-8-*ethoxycoumarin*, m. p. 85·5° (corr.) [8-methoxy-7-ethoxycoumarin has m. p. 80·5° (corr.)], which is converted by successive treatment with sodium methoxide and ethyl alcohol and with ethyl iodide into 4-methoxy-2 : 3-diethoxycinnamic ester, hydrolysed to 4-*methoxy*-2 : 3-*diethoxycinnamic acid*, m. p. 157—158°. Oxidation of the acid by permanganate yields 4-*methoxy*-2 : 3-*diethoxybenzoic acid*, identical with the acid, m. p. 75° (corr.) after softening, obtained by treatment of methyl 4-methylpyrogallolcarboxylate with ethereal diazoethane and hydrolysis of the product. H. Wren.

Constitution and properties of fraxin. F. Wessely and E. Demmer (Ber., 1929, **62**, [*B*], 120—126).—Fraxin, obtained by extraction of the young bark of *Fraxinus excelsior* with boiling water, precipitation of the extract with lead acetate, decomposition of the precipitate by hydrogen sulphide, and crystallisation of the glucoside from alcohol, forms pale yellow, hydrated crystals, m. p. 205° (corr.) when slowly heated. It is readily hydrolysed by hot, dilute sulphuric acid to fraxetin and dextrose and belongs to the β-series, since it is attacked by emulsin. Since the constitution of fraxetin has been elucidated (Wessely and Demmer, A., 1928, 893) the possible positions of the glucose residue and the methyl group in the 6 : 7 : 8-trihydroxycoumarin structure of fraxin are 8 : 6 or 7 : 6; the decision in favour of the former is reached as follows. Fraxin is converted by successive treatment with ethereal diazomethane and hydrolysis into 8-*hydroxy*-6 : 7-*dimethoxycoumarin*, m. p. 195° (corr.; decomp.), which with diazoethane affords 6 : 7-*dimethoxy*-8-*ethoxycoumarin*, m. p. 108·5° (corr.). By a similar series of changes fraxin is converted into 8-*hydroxy*-6-*methoxy*-7-*ethoxycoumarin*, m. p. 153—154° (corr.; decomp.), and 6 : 8-*dimethoxy*-7-*ethoxycoumarin*, m. p. 82° (corr.). Dimethyldaphnetin is oxidised by potassium persulphate in alkaline solution in the presence of ferrous sulphate to a hydroxydimethoxycoumarin (cf. Bargellini, A., 1916, i, 490) which must be 6-hydroxy-7 : 8-dimethoxycoumarin, since it is methylated by diazomethane to 6 : 7 : 8-trimethoxycoumarin, m. p. 103—104° (corr.), identical with dimethylfraxetin. *Diethyldaphnetin*, b. p. 160°/0·2 mm., m. p. 67—78° (corr.), prepared by treating daphnetin with diazoethane, is oxidised to 6-*hydroxy*-7 : 8-*diethoxycoumarin*, b. p. 170°/0·2—0·4 mm., m. p. 149—150° (corr.), which is methylated to 6-methoxy-7 : 8-diethoxycoumarin, m. p. 80—81° (corr.), identical with diethylfraxetin (A., 1928, 893). Oxidation of 7-methoxy-8-ethoxycoumarin affords 6-*hydroxy*-7-*methoxy*-8-*ethoxycoumarin*, m. p. 156—157° (corr.), methylated to 6 : 7-dimethoxy-8-ethoxycoumarin, m. p. 108·5° (corr.), identical with the compound obtained from fraxin. H. Wren.

Sesamin. J. Böeseken and W. D. Cohen (Biochem. Z., 1928, **201**, 454—463).—*Sesamin*, m. p. 122·5°, $[\alpha]_D^{18}$ $+68·6°$ in chloroform, is shown to have the composition $C_{20}H_{18}O_6$. It is not reduced at 250°/100 atm. by hydrogen, and on oxidation no intermediate stages could be detected. The six oxygen atoms are held in ether linkings, and it contains the methylenedioxy-group attached to a benzene nucleus. Nitration with a mixture of nitric and acetic acids yields *dinitrosesamin*, $C_{20}H_{16}O_{10}N_2$, m. p. 235—245° (*tin* salt of reduction product, $C_{20}H_{22}O_6N_2Cl_6Sn$, has $[\alpha]_D^{18}$ +60·0°), 4-nitro-1 : 2-methylenedioxybenzene, and a little nitropiperonal (cf. Salway, J.C.S., 1909, **95**, 1163).

The action of magnesium ethyl iodide on sesamin gives a product with two ethyl groups, showing that sesamin has two methylenedioxy-groups. Alcoholic hydrogen chloride produces an *isomeride*, m. p. 95—98° $[\alpha]_D^{18}$ +86·6° (in chloroform), probably by a kind of Walden inversion. Acetic acid in presence of sulphuric acid at 60° gives a third *isomeride* of sesamin, m. p. 118—120°, $[\alpha]_D^{18}$ +73·3°. The following constitution is suggested :



$$CH_2O_2{:}C_6H_3{\cdot}CH{\cdot}CH_2{\cdot}CH{\cdot}CH{\cdot}CH_2{\cdot}CH{\cdot}C_6H_3{:}O_2CH_2$$

(1 : 2 : 4)

J. H. Birkinshaw.

Solanine. G. Oddo (Ber., 1929, **62**, [*B*], 267—271; cf. Oddo and others, A., 1905, i, 455; 1906, i, 527, 980; 1911, i, 671; Colombano, A., 1908, i, 99; 1912, i, 798).—In their criticisms of the work of Oddo and co-workers, Zemplén and Gerecs (this vol., 51) have overlooked the established difference between the glucosides extracted from *Solanum sodomœum* (with which Oddo has worked) and *S. tuberosum* (investigated by Colombano). Zemplén has used a technical variety of solanine of unknown origin, but usually derived from *S. tuberosum*. H. Wren.

Methyl salicylate glucoside of *Gaultheria procumbens*, L., identical with monotropin. M. Bridel and (Mlle.) S. Grillon (Bull. Soc. Chim. biol., 1928, **10**, 1326—1335).—See A., 1928, 1224.

Formulæ of *Digitalis* glucosides. II. A. Windaus (Nachr. Ges. Wiss. Göttingen, 1927, 422—426; Chem. Zentr., 1928, ii, 669—670).—The formula $C_{24}H_{32}O_3$ previously ascribed to digitaligenin is replaced by the formula $C_{23}H_{30}O_3$, which is supported by the fact that oxidation of hexahydrodigitaligenin affords a dicarboxylic *acid*, $C_{23}H_{34}O_6$, m. p. 286—287° (*dimethyl* ester, m. p. 174°), but this conclusion is rendered uncertain by the observation that pure digitaligenin on oxidation yields no toxigenone, but a *product*, $C_{23}H_{28}O_3$, m. p. 197°. A. A. Eldridge.

Carbohydrates. VII. Starch acetate. P. Brigl and R. Schinle (Ber., 1929, **62**, [*B*], 99—103).—Rice starch, swollen with hot water, precipitated by alcohol, and dried with alcohol and ether, is heated with pyridine and acetic anhydride at 80° until a transparent jelly is produced which yields starch triacetate, $[\alpha]_D^{18}$ +162·40° in chloroform. The product is soluble in chloroform, *s*-tetrachloroethane, and glacial acetic acid, giving solutions which are very viscous even when dilute. Hydrolysis with alcoholic potassium hydroxide yields starch which appears more freely soluble in water than the original material, but gives the blue coloration with iodine and normal hydrolysis by diastase. The acetate has a high mol. wt., since it does not appreciably increase the b. p. of chloroform. The constant cannot be determined by Rast's method. In glacial acetic acid the acetate does not suffer dialysis under conditions whereby the acetates of dextrose, sucrose, and maltose readily pass through the membrane.

Repetition of the work of Friese and Smith (A., 1928, 1225) on rice and potato starch affords a starch acetate which, contrary to these authors, is soluble in chloroform or glacial acetic acid, yielding colloidal solutions which slowly pass through a Jena glass filter, size <7. Intensive desiccation appears to render the acetate less soluble.

Many of the conclusions of Peiser (A., 1927, 753) with regard to the composition of starch acetate and the constitution of starch are invalid, since acetylation by acetic anhydride in presence of sulphuric acid yields a partly changed product in which free reducing groups are present. H. Wren.

Disruption of the corn [maize] starch granule and its relation to the constituent amyloses. T. C. Taylor and C. O. Beckmann (J. Amer. Chem. Soc., 1929, **51**, 294—302).—The discrepancies in the values obtained by previous workers for the proportions of α- and β-amylose in starch (cf. Sherman and Baker, A., 1916, i, 767; Ling and Nanji, J.C.S., 1923, **123**, 2666) are due to the fact that starch pastes prepared with boiling water at 1 or 2 atm. pressure contain, even after passage through a ball mill or homogeniser, a large proportion of swollen but unruptured granules. The high viscosity of the paste is mainly due to the presence of these gelatinised particles. When dry maize starch is ground in a quartz ball mill the viscosity and apparent α-amylose content of 1% pastes prepared from it gradually decrease until, when unbroken granules can no longer be detected microscopically, these values are identical with those previously obtained for a 1% paste in which the granules had been ruptured by chemical means (cf. B., 1926, 717). This proves that the latter treatment does not alter the relative proportions of α- and β-amylose in the product. The viscosity of a paste from untreated starch is approximately equal to that of a β-amylose solution of ten times the concentration. H. E. F. Notton.

Allylcellulose. I. Sakurada (J. Soc. Chem. Ind. Japan, 1928, **31**, 638—642).—By treating tissue paper with 40—50% sodium hydroxide solution and allyl bromide, the higher cellulose allyl ethers (tri- and di-ether of C_6 unit) were directly obtained. The halogen-absorbing power of the resulting ether was concordant with the result of elementary analysis, and the double linking remained intact by etherification. The tetrabromide of cellulose diallyl ether was isolated almost pure. The higher allyl ether is partly soluble in alcohol, benzene, and carbon tetrachloride, but its solubility is not so great as expected. Y. Tomoda.

Manufacture of mixed acid esters of cellulose or esters of cellulose ethers. I. G. Farbenind. A.-G.—See B., 1929, 126.

Action of fatty acids on cellulose. C. J. Malm and H. T. Clarke (J. Amer. Chem. Soc., 1929, **51**, 274—278).—Prolonged refluxing of native cellulose with acetic acid effects esterification up to a limit (6—7% Ac) which is independent of the source and molecular complexity (cuprammonium viscosity) of the fibre, and corresponds with the formula $C_{24}H_{39}O_{20}Ac$. The same product is obtained more rapidly at higher temperatures. The corresponding *propionate* and *butyrate* are obtained similarly. Cellulose which has been mercerised or regenerated from its nitrate, from viscose, from cuprammonium solution, or from a solution of its acetate yields on similar treatment *acetates* of the limiting composition $C_6H_9O_5Ac$ (21—22% Ac). These differ from cellulose in their capacity to retain basic dyes. Cellulose regenerated from cellulose acetate which has retained its original fibrous structure is esterified to a much smaller extent (about 10·8% Ac). These results are regarded as evidence that native cellulose has the unit molecule $C_{24}H_{40}O_{20}$. H. E. F. NOTTON

Cellulose xanthamides. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1928, **31**, 629—633).—Cellulose xanthamides were obtained by the interaction of sodium cellulose xanthoacetic acid and ammonia or amines. Y. TOMODA.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. I. Prototropy and anionotropy in trialkylpropenylammonium derivatives. C. K. INGOLD and E. ROTHSTEIN (J.C.S., 1929, 8—14).—Prototropic and anionotropic changes are recorded in the system C·C:C, the facilitating group being the trialkylammonium ion. *Diethyl-γ-chloroallylamine*, b. p. 55°/9 mm. (*hydrochloride*, m. p. 221°; *picrate*, m. p. 78°), obtained in 57% yield from γ-chloroallyl chloride and diethylamine, when treated with ozone yields hydrochloric acid, carbon monoxide, and probably diethylaminoacetaldehyde; with ethyl iodide it yields *triethyl-γ-chloroallylammonium iodide*, m. p. 210° (*picrate*, m. p. 125°), also prepared directly from γ-chloroallyl chloride and triethylamine through the quaternary hydroxide. These salts do not react with triethylamine at 100°. When triethyl-γ-chloroallylammonium chloride or iodide is warmed with alcoholic sodium ethoxide and the product treated with picric acid *triethyl-α-ethoxyallylammonium picrate*, m. p. 122—123°, is obtained; the corresponding acetate when treated with ozone and then with picric acid yields formaldehyde and *triethylethoxyaldehydomethylammonium picrate*, m. p. 110—111°, hydrolysed by hydrochloric acid to *triethylhydroxyaldehydomethylammonium picrate*, m. p. 195—196°; triethyl-α-ethoxyallylammonium chloride when warmed with concentrated hydrochloric acid yields *triethyl-α-hydroxyallylammonium chloride*, oily (*picrate*, m. p. 145°; *chloroplatinate*), and the corresponding acetate when treated with ozone and then with picric acid gives the preceding hydroxyaldehydo-picrate, m. p. 195—196°.

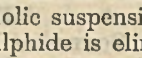
γ-Chloroallyl chloride with alcoholic trimethylamine yields *trimethyl-γ-chloroallylammonium chloride*, m. p. 193° (*picrate*, m. p. 141°), which with ozone gives hydrochloric acid, carbon monoxide, and betaine; neither the chloride nor the picrate reacts with diethyl- or triethyl-amine at 100°. The chloride is converted into *trimethyl-α-ethoxyallylammonium picrate*, m. p. 111—112°, and the acetate of this base yields formaldehyde and *trimethylethoxyaldehydomethylammonium picrate*, m. p. 168°, hydrolysed to *trimethylhydroxyaldehydomethylammonium picrate*, m. p. 182—184°. Trimethyl-α-ethoxyallylammonium chloride when treated with warm hydrochloric acid yields non-crystalline *trimethyl-α-hydroxyallylammonium chloride* (*picrate*, m. p. 149°), and the acetate of the latter base gives the preceding hydroxyaldehydo-picrate, m. p. 182—184°.

The ease of hydrolysis by acids of the ethoxy-compounds described above (which resemble esters rather than ethers) suggests that this effect, as also failure to replace the ethoxy-group by bromine, is due to the electron-affinity of the $\cdot NR_3^{\oplus}$ group.

C. W. SHOPPEE.

Diaminobutanes. E. STRACK and H. FANSELOW (Z. physiol. Chem., 1929, **180**, 153—160).—Various diaminobutanes have been prepared and characterised by the preparation of their *m*-nitrobenzoyl derivatives. Putrescine (αδ-diaminobutane) yields a m-*nitrobenzoyl* derivative, m. p. 240°; βγ-diaminobutane yields two m-*nitrobenzoyl* derivatives, m. p. 238° (soluble in methyl alcohol) and 320° (insoluble); αγ-diaminobutane m-*nitrobenzoyl* derivative, m. p. 199°. αβ-Diaminobutane (m-*nitrobenzoyl* derivative, m. p. 197°) could not be obtained by Demjanoff's method (A., 1907, i, 174) and is best prepared by the action of saturated alcoholic ammonia on propaldehyde cyanohydrin for 3 hrs. at 100° and reduction of the aminonitrile with sodium and alcohol, or, in small yield, by the action of saturated methyl-alcoholic ammonia for 24 hrs. at 100° on αβ-dibromobutane. αγ-Diamino-β-methylpropane (Johnson and Joyce, A., 1916, i, 755) (m-*nitrobenzoyl* derivative, m. p. 182°) is obtained by similar reduction of methylmalononitrile. αβ-Diamino-β-methylpropane (not obtained by Sidorenko's method, A., 1907, i, 270) is prepared by reduction of α-amino*iso*butyronitrile and yields two m-*nitrobenzoyl* derivatives, m. p. 145° and 174°, the former being converted into the latter by heating with alcohol. J. W. BAKER.

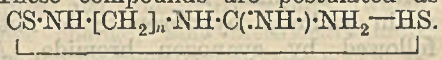
Reaction between carbon disulphide and some diamines and guanidines. E. STRACK (Z. physiol. Chem., 1929, **180**, 198—211).—When an alcoholic solution of tetramethylenediamine is treated with carbon disulphide δ-*aminobutyldithiocarbamic acid*, $NH_2\cdot[CH_2]_4\cdot NH\cdot CS_2H$, m. p. 173° (all m. p. are uncorr.; decomp.), is obtained (cf. von Braun and Lemke, A., 1923, i, 6). When an alcoholic suspension of this is heated at 100° hydrogen sulphide is eliminated and *tetramethylenethiocarbamide*,



$\underbrace{NH\cdot[CH_2]_4\cdot NH}_{CS}$

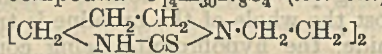
m. p. 177°, results. Pentamethylenediamine and carbon disulphide afford ε-*aminoamyldithiocarbamic acid* (*cadmium*, *barium*, and *silver* salts).

Ethyl-ψ-thiocarbamide hydrobromide reacts with tri-, tetra-, and penta-methylenediamines in alcoholic solution, forming α-*amino-γ-guanidinopropane hydrobromide*, m. p. 116° (*sulphate*, m. p. 265°), and αγ-*diguanidinopropane*, m. p. 135° (*hydrobromide*, m. p. 218°; *sulphate*, m. p. 270° after sintering at 260°); αδ-*diguanidinobutane hydrobromide*, m. p. 212°, after sintering at 205° [sulphate, m. p. 297° (lit. 291°)] (cf. Kiesel, A., 1922, i, 531); α-*amino-ε-guanidinopentane hydrobromide*, m. p. 105° (*sulphate*, m. p. 284°), and *αε-diguanidinopentane*, m. p. 173° (decomp.; *hydrobromide*, m. p. 217° after sintering at 212°; *sulphate*, m. p. 317°), respectively. Guanidine reacts with carbon disulphide in alcoholic solution at 100° yielding *guanidine trithiocarbonate*, $CS[SH,NH_2{\cdot}C(:NH){\cdot}NH_2]_2$, m. p. 133—135° after sintering at 125°, also obtained from guanidine sulphate and sodium trithiocarbonate. The production of this salt demonstrates the following changes: $CS_2+2H_2O=CO_2+2H_2S$; $CS_2+H_2S=CS(SH)_2$. The above trithiocarbonate is decomposed by dilute acids, including carbonic acid, into hydrogen sulphide, and when it is treated with aqueous lead acetate lead trithiocarbonate is obtained. The *trithiocarbonates* obtained from methyl- and ethyl-guanidines, αγ-diguanidinopropane, αδ-diguanidinobutane, and αε-diguanidinopentane have m. p. 153°, 165°, 95° (decomp.), 193° (decomp.), and 190° (decomp.), respectively. α-Amino-δ-guanidinobutane (agmatine) and α-amino-ε-guanidinopentane react with carbon disulphide forming the corresponding *dithiocarbamates*, m. p. 210° (decomp.) after sintering at 200° and 201°, respectively. These compounds are postulated as internal salts



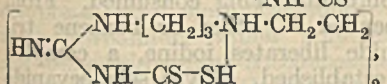
$CS{\cdot}NH{\cdot}[CH_2]_n{\cdot}NH{\cdot}C(:NH{\cdot}){\cdot}NH_2—HS.$

The compound $C_{12}H_{22}N_4S_2$, previously abstracted as $C_{12}H_{22}N_4S_3$ (Wrede, Strack, and Hettche, A., 1928, 511), and the compound $C_{14}H_{30}N_8S_4$ (*loc. cit.*) are postulated as



$[CH_2{<}{}^{CH_2\cdot CH_2}_{NH-CS}{>}N{\cdot}CH_2{\cdot}CH_2{\cdot}]_2$

and

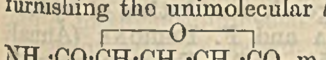


$\left[HN{:}C{<}{}^{NH\cdot[CH_2]_3\cdot NH\cdot CH_2\cdot CH_2}_{NH-CS-SH}\right]_2$

, respectively.

H. BURTON.

Glutaric series. C. RAVENNA and R. NUCCORINI (Gazzetta, 1928, **58**, 853—864).—The formation of a dipeptide of aspartic acid from asparagine (A., 1920, i, 150) has no analogy in the glutaric series. Beetroot glutamine, m. p. 178—186°, according to conditions of preparation, when boiled with water for 10 days lost ammonia, but yielded glutamic acid, with pyrrolidonecarboxylic acid, which substances also formed some labile compounds of undefined character. *Ammonium hydroxyglutamate* was prepared by precipitation from an ethereal solution of the acid. It was converted when heated into the *diamide*, m. p. 181—182° (decomp.), of glutamic acid, which on further heating at its m. p. lost a molecule of water, furnishing the unimolecular *lactone amide*,



$NH_2{\cdot}CO{\cdot}\overset{}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}CO$ (ring through O), m. p. 87—89°.

E. W. WIGNALL.

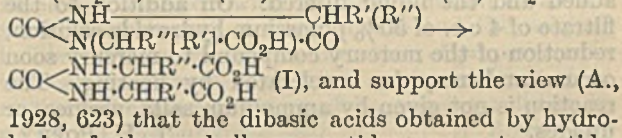
Ammonium creatinine picrate. I. GREENWALD (J. Biol. Chem., 1929, **81**, 73—75).—Addition of excess of picric acid to a concentrated ammoniacal solution of creatinine yields *ammonium creatinine picrate*, m. p. 241°, which, on successive recrystallisations from water, dissociates, yielding eventually creatinine picrate; the ammonium creatinine picrate may be utilised for the recovery of creatinine from ammoniacal mother-liquors containing the latter.

C. R. HARINGTON.

Structure and rate of hydrolysis of peptides. P. A. LEVENE, L. W. BASS, and R. E. STEIGER (J. Biol. Chem., 1929, **81**, 221—230).—The hydrolysis of dipeptides by erepsin followed the course of a unimolecular reaction, the reaction constant being of the same order of magnitude with all those peptides which were attacked by the enzyme except the alanyl peptides, which gave anomalous results. The hydrolysis of glycylglycine was retarded by the presence of free glycine; the action of the enzyme was confined to peptides containing the naturally occurring optical modification of the amino-acids; glycyl-*d*-*iso*valine was not attacked. *Chloroacetyl*-l-*valine* had m. p. 112—113°, $[\alpha]_D^{25}$ −15° in alcohol, and yielded *glycyl*-l-*valine*, $[\alpha]_D^{25}$ +20·3° in water.

C. R. HARINGTON.

Polypeptide *N*-carboxylic acids. F. WESSELY, E. KEMM, and J. MAYER (Z. physiol. Chem., 1929, **180**, 64—74).—Hydrolysis of either methyl (or ethyl) alanylglycine-*N*-carboxylate or methyl glycylalanine-*N*-carboxylate yields the same product, *carbonylglycinealanine* (I; R′=H, R″=Me), m. p. 182° (*methyl* ester, m. p. 106°). Similarly, a repetition of Leuchs and Sander's work (A., 1925, i, 1248) shows that the product of hydrolysis of (unpurified) ethyl carbomethoxyglycyl-β-aminobutyrate or of carbomethoxy-β-aminobutyrylglycine ethyl ester is not an *N*-carboxylic acid, but is the *diethyl* ester, m. p. 103—104°, of carbonylglycine-β-aminobutyric acid (I; R′=H, CHR″=CHMe·CH₂). These changes are explained by the scheme



$$NH(CO_2Me){\cdot}CHR'(R''){\cdot}CO{\cdot}NH{\cdot}CHR''(R'){\cdot}CO_2H\longrightarrow CO{<}{}^{NH\text{———}CHR'(R'')}_{N(CHR''[R']\cdot CO_2H)\cdot CO}\longrightarrow CO{<}{}^{NH\cdot CHR''\cdot CO_2H}_{NH\cdot CHR'\cdot CO_2H}$$

(I), and support the view (A., 1928, 623) that the dibasic acids obtained by hydrolysis of the carbalkoxy-peptides are not peptide-*N*-carboxylic acids but carbonylbisamino-acids. Similarly, hydrolysis of the *carbomethoxy*-derivative, m. p. 179·5°, of phenylalaninephenylalanine yields two *acids*, m. p. 203° and 176°, respectively, both of which yield *ethyl* esters, m. p. 142—143° and 138°, which are identical with the corresponding esters of carbonylbisphenylalanine (m. p. 145° and 141·5°), identification being complicated in this case by optical isomerism.

J. W. BAKER.

Aminoacetals and aminoaldehydes containing three carbon atoms. R. VOET (Bull. Soc. chim., 1929, [iv], **45**, 61—69).—γ-Chloropropaldehyde dimethylacetal (A., 1927, 1172) reacts readily with amines at 100°, affording with 1 mol. of tertiary amines the hydrochloride of the aminoacetal, and with primary and secondary amines (2 mols.) the free aminoacetal and the amine hydrochloride and some tertiary amide $NR[CH_2{\cdot}CH_2{\cdot}CH(OMe)_2]_2$. Concentrated hydrochloric acid converts the aminoacetals into the corresponding aminoaldehydes, obtained in crystalline monomeric and non-crystalline polymeric forms, the latter possessing no reducing properties and reacting slowly to give the same semicarbazones as the crystalline form. The aminoaldehydes are non-toxic and possess no physiological activity. The following are described: *γ-methylaminopropaldehyde dimethylacetal*, b. p. 164·5°/760 mm. (yield 80%) (*hydrochloride*), and *γ-methyliminodipropaldehyde tetramethylacetal*, b. p. 130°/20 mm., d^{20} 0·9759; *γ-ethylaminopropaldehyde dimethylacetal* (yield 70%), b. p. 177·3°/760 mm., d^{20} 0·9095 (*hydrochloride*), and *γ-ethyliminodipropaldehyde tetramethylacetal* (yield 10%), b. p. 133°/20 mm., d^{20} 0·9608. *γ-Propylaminopropaldehyde dimethylacetal* (yield 60%), b. p. 195·5°/760 mm., d^{20} 0·9002 (*hydrochloride*), and *γ-propyliminodipropaldehyde tetramethylacetal* (yield 9%), b. p. 140°/20 mm., d^{20} 0·9483; *γ-diethylaminopropaldehyde dimethylacetal* (yield 95%), b. p. 194·2°/760 mm., d^{20} 0·8846 (*hydrochloride*); *γ-dipropylaminopropaldehyde dimethylacetal* (yield 82%), b. p. 223·4°/760 mm., d^{20} 0·8715 (*hydrochloride*); *γ-methylaminopropaldehyde hydrochloride* (*acetosemicarbazone*, $C_7H_{16}O_3N_4$, m. p. 300°); *γ-ethylaminopropaldehyde hydrochloride* (*semicarbazone*, $C_8H_{18}O_3N$, m. p. 301·5°) (cf. Wohl and Losanitsch, A., 1906, i, 107); *γ-propylaminopropaldehyde hydrochloride* (*semicarbazone*, $C_9H_{20}O_3N_4$, m. p. 303)°, and *γ-diethylaminopropaldehyde hydrochloride* (*semicarbazone*, $C_{10}H_{22}O_3N_4$, m. p. 309·5°, *chloroaurate*, decomp. at 100°). R. Brightman.

Reaction for carbamide. F. Pisani (Annali Chim. Appl., 1928, 18, 555—556).—This reaction depends on the conversion of carbamide into hydrazine by hypochlorite or hypobromite in alkaline solution. The hypobromite solution is added dropwise to an alkaline carbamide solution, total oxidation of the carbamide being avoided; 1 drop of hypobromite solution suffices for 0·002—0·003 g. of carbamide. Slight excess of 5% mercuric chloride solution is then added and the liquid filtered. On addition to the filtrate of 4 c.c. of 50% potassium hydroxide solution, reduction of the mercury compound to mercury soon occurs and may be accelerated by heating. The reaction is not given by ammonium salts, ureines, or ureides. T. H. Pope.

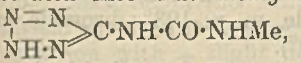
Iodometric determination of thiosemicarbazide. A. Gaffre (J. Pharm. Chim., 1929, [viii], 9, 19—23).—In presence of sodium hydrogen carbonate, iodine and thiosemicarbazide require contact for 8 hrs. for complete reaction to occur. After acidification, which decomposes the cyanogen iodide formed, 10 atoms of iodine are found to react with 1 mol. of thiosemicarbazide. In presence of sodium hydroxide, only 30 min. contact is necessary and 12 atoms of iodine are absorbed by 1 mol. of thiosemicarbazide. E. H. Sharples.

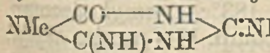
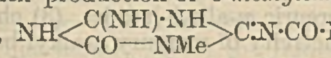
Pseudohalogens. III. The pseudohalogen tricyanomethyl and the mixed halogen tricyanomethyl bromide. L. Birckenbach and K. Huttner (Ber., 1929, 62, [*B*], 153—163; cf. A., 1926, 30).—The validity of the previous hypothesis that the halogen character of an atomic complex is attributable to the presence of an outer ring of seven electrons is further established by experiments with the tricyanomethyl group. With regard to the nomenclature of compounds such as $Br{\cdot}C(CN)_3$, $K{\cdot}C(CN)_3$, the terminology bromotricyanomethane is considered unsatisfactory, since the union of the two parts is not aliphatic as in bromomethane and the terms "tricyanomethyl bromide," "potassium tricyanomethylide," etc. are adopted.

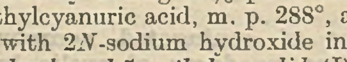
Malononitrile and cyanogen bromide are added successively to a solution of sodium ethoxide in absolute alcohol and the sodium tricyanomethylide is transformed into the corresponding silver salt, the yield being about 90%. Treatment of a suspension of an excess of silver tricyanomethylide in anhydrous ether with bromine at −10° gives *tricyanomethyl bromide*, colourless rhombic crystals, m. p. 72° (decomp.) after becoming yellowish-red at 68°. The compound is very sensitive to moisture. A crystal first reddens and then bleaches moist blue litmus paper. Iodine is liberated from alcoholic ammonium iodide and aqueous potassium iodide, $Br{\cdot}C(CN)_3+2KI=K{\cdot}C(CN)_3+KBr+I_2$,reaction in the latter case proceeding more rapidly than hydrolysis and being quantitative. With aqueous potassium bromide bromine is liberated. Aqueous sulphurous acid dissolves tricyanomethyl bromide with reduction to $CH(CN)_3$ and hydrogen bromide; the bromide ion can be titrated potentiometrically with 0·1*N*-silver nitrate, thus giving a ready method of determining bromine in the compound. Tricyanomethyl bromide and aqueous potassium cyanide afford potassium tricyanomethylide and cyanogen bromide; evidence of the production of tetracyanomethane is not produced. Water slowly dissolves tricyanomethyl bromide, the solution becoming first yellow, then colourless, and again yellow; hypobromite is initially produced, followed by cyanogen bromide. Aqueous alkali hydroxide rapidly dissolves tricyanomethyl bromide, 1 mol. of which neutralises 2 mols. of alkali; the oxidising power of the solution diminishes rapidly. Almost the whole of the bromine is transformed into bromide, the hypobromite being consumed. From silver iodide suspended in ether or benzene tricyanomethyl bromide liberates iodine, a complex equilibrium being established. Silver selenocyanide in benzene liberates bromine. Dry ethylene appears to react with tricyanomethyl bromide in the molar ratio 1 : 1, giving a red, presumably polymerised, compound of unknown structure. The decomposition tension of potassium tricyanomethylide in 0·1*N*-solution is 2·08 volts, whereas for bromine under similar conditions the value is 1·68 volts. In absolute alcoholic solution the value is 1·38 volts. Tricyanomethyl is therefore more electronegative than bromine and is placed next to chlorine in the affinity series of the halogens.

Treatment of iodine chloride with potassium cyanide gives potassium chloride and cyanogen iodide; occasionally iodine is liberated in small amount. H. Wren.

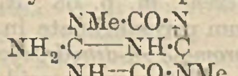
Formation of cyanogen by oxidation of hydrocyanic acid. B. Ricca and F. Pirrone (Annali Chim. Appl., 1928, 18, 550—555).—Experiments with hydrocyanic acid, potassium cyanide, and ferro- and ferri-cyanides show that, in a medium rendered acid with sulphuric acid, hydrocyanic acid is oxidised, in nearly all cases, to cyanogen by sodium persulphate, hydrogen peroxide, potassium permanganate, potassium dichromate, and manganese, lead, and tin dioxides; the proportions of the latter vary widely with the experimental conditions and with the nature of the oxidising agent (cf. Bellucci and Ricca, A., 1924, ii, 672, 791; A., 1926, 489). T. H. Pope.

Carbimides. VI. Condensations of methylcarbimide with cyanamide under the influence of triethylphosphine. K. H. Slotta and R. Tschesche (Ber., 1929, **62**, [*B*], 137—145; cf. A., 1927, 346, 548, 578).—Cyanamide reacts with methylcarbimide in anhydrous ether in the presence of triethylphosphine, giving *dimethylcarbamylcyanamide*, $(\mathrm{NHMe{\cdot}CO})_2\mathrm{N{\cdot}CN}$, decomp. 124°, in 80% yield. The compound is decomposed by ethereal diazomethane with production of N-*cyano*-NN′-*dimethylcarbamide*, m. p. 114°, in small amount. In methyl-alcoholic suspension, it is converted by hydrogen sulphide at the atmospheric temperature into N-*cyano*-N′-*methylcarbamide*, decomp. 122° (*silver* salt), whereas if the solution is subsequently boiled and the passage of hydrogen sulphide is continued N^{ω}-*methylthiobiuret*, $\mathrm{NHMe{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2}$, decomp. 198°, is produced. Dimethylcarbamylcyanamide is transformed by ammonia into N′-*guanyl*-N-*methylcarbamide*, decomp. 165° (*silver* salt), and by sodium azide and dilute acetic acid into 4-N^{ω}-*methylureido*-1 : 2 : 3 : 5-*tetrazole*,  $\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{NH{\cdot}N}\end{array}\!\!>\!\mathrm{C{\cdot}NH{\cdot}CO{\cdot}NHMe}$, decomp. above 300° after softening at 265°, converted by boiling water into methylcarbimide and *C*-aminotetrazole, m. p. 203°. In all these changes the primary action is decomposition into cyanomethylcarbamide (which undergoes further change) and methylcarbimide. The latter compound is identified in the action of hydrazine hydrate on dimethylcarbamylcyanamide, whereby NN′-*dimethylcarbamylhydrazine*, decomp. 270°, is produced. When dimethylcarbamylcyanamide is treated with boiling ethyl acetate, it decomposes into methylcarbimide and *N*-cyano-*N*′-methylcarbamide, which polymerises normally to NN′-*dimethylcarbamyl*-N-*cyanoguanidine*, $\mathrm{NHMe{\cdot}CO{\cdot}N(CN){\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}NHMe}$, m. p. 280—285° (decomp.) after softening at 190°. The last substance is transformed by boiling water into N-*methylcarbamyl*-N′-*cyanoguanidine*, decomp. 320—325°, and by boiling hydrochloric acid or sodium hydroxide into N-*methylammelin*,


$\mathrm{NMe}\!<\!\begin{array}{l}\mathrm{CO{-\!\!-}NH}\\ \mathrm{C(NH){\cdot}NH}\end{array}\!\!>\!\mathrm{C{:}NH}$, decomp. 242—245°. If, however, dimethylcarbamylcyanamide is boiled with ethyl acetate containing a little triethylphosphine, abnormal polymerisation of cyanomethylcarbamide occurs with production of 6-*methylcarbamyl*-5-*methylammelin*,  $\mathrm{NH}\!<\!\begin{array}{l}\mathrm{C(NH){\cdot}NH}\\ \mathrm{CO{-\!\!-}NMe}\end{array}\!\!>\!\mathrm{C{:}N{\cdot}CO{\cdot}NHMe}$, decomp. 290° (*diacetyl* derivative, m. p. 214°). The compound is transformed by boiling 30% potassium hydroxide into *N*-methylcyanuric acid, m. p. 288°, and by short treatment with 2*N*-sodium hydroxide into ammonia and 6-*methylcarbamyl*-5-*methylammelide* (I), gradual de-


$$\mathrm{NH}\!<\!\begin{array}{l}\mathrm{CO{-}NH}\\ \mathrm{CO{\cdot}NMe}\end{array}\!\!>\!\mathrm{C{:}N{\cdot}CO{\cdot}NHMe},\qquad \text{(I.)}$$

comp. above 300°. Treatment of 6-methylcarbamyl-5-methylammelin with concentrated sulphuric acid at 80—100° followed by addition of perchloric acid to the


$$\begin{array}{c}\mathrm{NMe{\cdot}CO{\cdot}N}\\ \mathrm{NH_2{\cdot}C{-\!\!-}NH{\cdot}C}\\ \mathrm{NH{-\!\!-}CO{\cdot}NMe}\end{array}\qquad \text{(II.)}$$

diluted solution yields a *substance*, decomp. 250°, from which boiling sodium carbonate solution liberates the dicyclic *isomeride* of 6-methylcarbamyl-5-methylammelin (II), decomp. 320°. H. Wren.

Tertiary phosphines containing the *n*-butyl radical. W. C. Davies and W. J. Jones (J.C.S., 1929, 33—35).—By the action of magnesium *n*-butyl bromide on phosphorus trichloride, phenyldichlorophosphine, and *p*-tolyldichlorophosphine, the corresponding tertiary phosphines are obtained. They are colourless liquids, unimolecular in freezing benzene and stable in air. The following are described: *tri*-n-*butylphosphine*, b. p. 149·5°/50 mm., d_4^{25} 0·8118 (*carbon disulphide additive compound*, m. p. 65·5°); *methyltri*-n-*butylphosphonium iodide*, m. p. 133·5°; *ethyltri*-n-*butylphosphonium iodide*, m. p. 153°; *phenyldi*-n-*butylphosphine*, b. p. 184·5—185·5°/50 mm., d_4^{25} 0·9115 (*mercuric chloride* compound, m. p. 160·5°); *phenylmethyldi*-n-*butylphosphonium iodide*, m. p. 168°; *phenylethyldi*-n-*butylphosphonium iodide*, m. p. 147°; p-*tolyldi*-n-*butylphosphine*, b. p. 197°/50 mm., d_4^{25} 0·9076 (*mercuric chloride* compound, m. p. 112°); p-*tolylmethyldi*-n-*butylphosphonium iodide*, m. p. 130·5°.

Tri-n-*butylphosphine oxide*, b. p. 300°, is prepared by the action of magnesium *n*-butyl bromide on phosphoryl chloride, or by boiling tri-*n*-butylphosphine in a current of air, and by oxidising it with warm 40% nitric acid. C. W. Shoppee.

Tetraethylphosphonium nitrite. P. C. Rây and N. Ray (J. Indian Chem. Soc., 1928, **5**, 733—734).—When tetraethylphosphonium iodide is treated with silver nitrite a poor yield of *tetraethylphosphonium nitrite* is obtained owing to the formation of an insoluble double salt of silver iodide and the original iodide. The most convenient method of preparation is to treat tetraethylphosphonium sulphate with barium nitrite and evaporate the resulting aqueous solution in a vacuum over sulphuric acid. H. Burton.

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

Factors affecting starting of Grignard reagents. H. Gilman and R. J. Vanderwal (Rec. trav. chim., 1929, **48**, 160—162).—A study has been made of the effect of (*a*) moisture, (*b*) addition of rubber, powdered glass, mercury, small amounts of decomposed Grignard reagents, and magnesium bromide etherate, (*c*) presence of dry nitrogen, carbon dioxide, hydrogen chloride, carbon dioxide-free air, and oxygen, (*d*) solvents, and (*e*) temperature on the time necessary for a mixture of magnesium (0·5 g.), butyl bromide (2 c.c.), and dry ether (5 c.c.) to give the positive colour test previously described (A., 1925, ii, 1011; 1928, 160). Magnesium bromide etherate is a positive catalyst; water, oxygen, carbon dioxide, hydrogen chloride, benzene, light petroleum, and the outside surface of new rubber stoppers are all negative catalysts; at low temperatures the action is delayed. The other substances have no appreciable action.

H. Burton.

Qualitative colour test for reactive organometallic compounds. H. Gilman and L. L. Heck (Rec. trav. chim., 1929, **48**, 193—197).—The colour test previously described (A., 1925, ii, 1011; 1928, 160) is more sensitive when a hot, saturated solution of Michler's ketone in benzene is used. Positive results can be obtained for low concentrations of the Grignard reagent by using 5—10 c.c. The minimal concentration for a positive test varies from 0·01 to 0·05*M* for 14 typical Grignard reagents.

H. BURTON.

Preparation of magnesium allyl bromide. H. GILMAN and J. H. McGLUMPHY (Bull. Soc. chim., 1928, [iv], **43**, 1322—1328).—Yields of 90—95% of magnesium allyl bromide are obtained by Gilman and McCracken's method (A., 1924, i, 23; 1927, 865), using 0·5 mol. of allyl bromide, 3 atoms of finely-divided magnesium (cf. Gilman and Zoellner, A., 1928, 401, 875), and 7·5 mols. of ether. By filtering off the excess of magnesium yields of 90·5% of δ-phenyl-Δ^{α}-butene are obtained by treatment with benzyl chloride; in presence of excess of magnesium the yield is reduced by formation of magnesium benzyl chloride and subsequent decomposition to dibenzyl. Benzophenone similarly affords 74·9% of diphenylallylcarbinol, and acetophenone 80·2% of phenylmethylallylcarbinol. Carbon dioxide, however, gives only 21·7% of vinylacetic acid, oily non-acid products being formed in considerable amount.

R. BRIGHTMAN.

Reaction between organomagnesium halides and some salts. H. GILMAN and J. E. KIRBY (Rec. trav. chim., 1929, **48**, 155—159).—The action of cuprous cyanide on magnesium phenyl bromide in ether, benzene, and toluene gives 6·5, 64, and 100% of diphenyl, respectively. Silver and nickel cyanides, silver cyanate, cuprous and silver thiocyanates, silver carbonate, chromate, phosphate, and citrate afford varying amounts (traces to 90%) of diphenyl. Mercuric cyanide produces mercuric phenyl bromide. Silver cyanide converts magnesium benzyl chloride into dibenzyl, whilst mercuric acetate gives 49% of mercuric benzyl chloride. No addition of the Grignard reagent to any group attached to a metal takes place.

H. BURTON.

Preparation of mercury di*iso*butyl by the reaction of Frankland and Duppa. H. F. LEWIS and E. CHAMBERLIN (J. Amer. Chem. Soc., 1929, **51**, 291—294; cf. J.C.S., 1863, **16**, 415).—The following optimum procedure has been developed for this reaction: sodium (2 mols.) in the form of 0·25% amalgam is added to a mixture of *iso*butyl iodide (1 mol.) and ethyl acetate (0·5 mol.) or acetone (1 mol.), which is kept at 0—5°. Water is then added and the product extracted with ether and distilled (yield, 0·282 mol.). Other carbonyl compounds such as *iso*valeraldehyde and acetic anhydride also act as catalysts. *iso*Butyl bromide yields only traces of mercury di*iso*butyl when substituted for the iodide. The by-products consist mainly of di*iso*butyl.

H. E. F. NOTTON.

Organic mercury bases and their salts. K. H. SLOTTA and K. R. JACOBI (J. pr. Chem., 1929, [ii], **120**, 249—300).—Interaction of ethereal solutions of the appropriate magnesium alkyl bromide with mercuric bromide gave the mercuric alkyl bromides: *methyl*, m. p. 172°; ethyl, m. p. 198° (lit. 193·5°), *n*-propyl, m. p. 140°, *n*-butyl, m. p. 136°, *n*-amyl, m. p. 127°, *n*-hexyl, m. p. 127·5°, *n*-heptyl, m. p. 118·5°, and n-*cetyl*, m. p. 101·5°. Treatment of the foregoing compounds with methyl-alcoholic potassium hydroxide followed by the corresponding halogen acid gave: mercuric methyl chloride, m. p. 167°, and iodide, m. p. 152° (lit. 145°), mercuric ethyl chloride, m. p. 192°, and *iodide*, m. p. 186°, mercuric *n*-propyl chloride, m. p. 147°, and iodide, m. p. 113°, *mercuric* n-*butyl chloride*, m. p. 130°, and iodide, m. p. 117°, *mercuric* n-*amyl chloride*, m. p. 110°, and *iodide*, m. p. 110°, *mercuric* n-*hexyl chloride*, m. p. 125°, and *iodide*, m. p. 110°, *mercuric* n-*heptyl chloride*, m. p. 119·5°, and *iodide*, m. p. 103°, *mercuric* n-*cetyl chloride*, m. p. 102°, and *iodide*, m. p. 82°.

The following mercuric alkyl hydroxides were obtained from the corresponding bromides: methyl, m. p. 137°; *ethyl*, m. p. 37°; n-*propyl*, m. p. 78°; n-*butyl*, m. p. 68°; n-*amyl*, m. p. 50°; n-*hexyl*, m. p. 54·5°; n-*heptyl*, m. p. 54°; n-*cetyl*, m. p. 78°; *phenyl*, sinters at 195°, froths at 200° (chloride, m. p. 271°; bromide, m. p. 280°; iodide, m. p. 269°); α-*naphthyl*, sinters at 228° (chloride, m. p. 193°; bromide, m. p. 201°; iodide, m. p. 219°).

Neutralisation of these mercuric *n*-alkyl hydroxides in methyl-alcoholic solution with anhydrous hydrocyanic acid followed by absorption of the water and methyl alcohol by calcium chloride under reduced pressure gave the mercuric alkyl cyanides: methyl, m. p. 93°; *ethyl*, m. p. 77°; n-*propyl*, m. p. 28°; n-*butyl*, m. p. 42°; n-*amyl*, m. p. 39°; n-*hexyl*, m. p. 38°; and n-*heptyl*, m. p. 53°.

In a similar manner acetic acid gave mercuric alkyl acetates: methyl, m. p. 101°; ethyl, m. p. 54°; n-*propyl*, m. p. 57°; n-*butyl*, m. p. 56°; n-*amyl*, m. p. 52°; n-*hexyl*, m. p. 50°; and n-*heptyl*, m. p. 45°; nitric acid gave the mercuric alkyl nitrates: methyl, decomp. 168° after softening at 100°, becoming green at 135°; ethyl; n-*propyl*, m. p. 75°; n-*butyl*, m. p. 75°; n-*amyl*, m. p. 78°; n-*hexyl*, m. p. 75°; and n-*heptyl*, m. p. 66°; whilst analogous use of sulphuric acid led to the mercuric alkyl sulphate: methyl, decomp. 255°; ethyl, decomp. 199°; n-*propyl*, decomp. 196°; n-*butyl*, m. p. 181°, decomp. 183°; n-*amyl*, decomp. 188°; n-*hexyl*, m. p. 173°, decomp. 174°, and n-*heptyl*, m. p. 180° (decomp.).

Tables and curves are included to show (1) solubilities of mercuric *n*-alkyl halides in ethyl alcohol at 18° and 78°, in chloroform at 18°, and in water at 100°, (2) m. p. of mercuric *n*-alkyl halides, (3) changes in molecular conductivity of mercury *n*-alkyl bases with increase of alkyl radical, and (4) m. p. of mercuric *n*-alkyl cyanides.

R. J. W. LE FÈVRE.

Properties of conjugated compounds. VI. Dibromination products of cyclic butadienes. E. H. FARMER and W. D. SCOTT (J.C.S., 1929, 172—180).—$\Delta^{1:3}$-*cyclo*Hexadiene, b. p. 80°, d_4^{16} 0·8421, n_D^{16} 1·4760, on bromination in chloroform, or preferably *n*-hexane, below −15°, and immediate removal of the solvent in a vacuum yields: (*a*) 1 : 2-*dibromo*-Δ^3-cyclo*hexene*, m. p. 68°, easily oxidised by neutral potassium permanganate in aqueous acetone at 0° to 1 : 2-*dibromo*-3 : 4-*dihydroxy*cyclo*hexane*, m. p. 96—98°, which yields succinic acid on further oxidation; (*b*) a stereoisomeric 1 : 2-*dibromo*-Δ^3-cyclo*hexene*, liquid, yielding an isomeric 1 : 2-*dibromo*-3 : 4-*dihydroxy*cyclo*hexane*, oily, and succinic acid. Both these 1 : 2-dibromides pass readily into 1 : 4-dibromo-Δ^2-*cyclo*hexene, b. p. 110—120°/2 mm., m. p. 108° (cf. Crossley and Haas, J.C.S., 1903, **83**, 498; 1904, **85**, 1403; Zelinski and Gorsky, A., 1908, i, 619), which is converted into succinic acid by hot aqueous chromic acid. This 1 : 4-dibromide is the sole product of bromination if there is prolonged delay in working up the reaction mixture, or if heat is used in the removal of the solvent. The possibility of reversing the 1 : 2 ⟶ 1 : 4-change could not be gauged owing to the decomposition of the 1 : 4-dibromide when maintained at 100°. The proportion in which the original bromides appear varies little with the nature of the solvent or the degree of dilution.

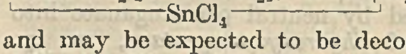
*cyclo*Pentadiene, b. p. 42°, was prepared from the dimeride, some specimens of which had m. p. 19° and others m. p. 32° (cf. Staudinger and Rheiner, A., 1924, i, 274; Wieland and Bergel, A., 1926, 56); both modifications have the same b. p., 56°/13 mm., and yield *cyclo*pentadiene on depolymerisation. On bromination with a slight deficiency of bromine in *n*-hexane at –15°, it yields: (*a*) *trans*-1 : 4-dibromo-Δ^2-*cyclo*pentene, m. p. 45—46° (cf. Thiele, A., 1901, i, 181), oxidised by neutral permanganate in aqueous acetone to trans-1 : 4-*dibromo*-2 : 3-*dihydroxy*cyclo*pentane*, m. p. 75° (yield 52%), further oxidised by cold aqueous chromic acid to *r*-αα′-dibromoglutaric acid, m. p. 142° (yield 85%; cf. Thiele, *loc. cit.*); (*b*) *cis*-1 : 4-dibromo-Δ^2-*cyclo*pentene, b. p. 72°/5 mm., 82°/15 mm., d^{20} 1·9198 (cf. Thiele, *loc. cit.*), in small quantity, converted by neutral permanganate into cis-1 : 4-*dibromo*-2 : 3-*dihydroxy*cyclo*pentane*, m. p. 76° (mixed m. p. with *trans*-glycol about 45°), yielding *meso*-αα′-dibromoglutaric acid, m. p. 170° (cf. Thiele, *loc. cit.*), by further oxidation with cold aqueous chromic acid; (*c*) 1 : 2-*dibromo*-Δ^3-cyclo*pentene*, d^{20} 1·8867, yielding with neutral permanganate a syrupy *dibromoglycol* from which none of the isomeric 1 : 4-dibromoglycols could be separated, and this on oxidation with aqueous chromic acid gave a syrupy *dibromo-acid* together with a trace of *meso*-αα′-dibromoglutaric acid. The syrupy acid on treatment with zinc and acetic acid yields glutaconic acid; both the αα′-dibromoglutaric acids yield glutaric acid on debromination with zinc and acetic acid (cf. Thiele, *loc. cit.*). The 1 : 2-dibromide is converted (with decomposition) by distillation into the solid 1 : 4-form to a small extent, but mainly yields the liquid 1 : 4-form. In hexane solution, with increasing dilution the proportion of solid 1 : 4-dibromide formed falls steadily; the effect of substituting chloroform for hexane is to reduce largely the proportion of solid 1 : 4-form, and to increase the total proportion of 1 : 4-dibromide in the product. C. W. Shoppee.

Manufacture of *o*- and *p*-xylenes. I. G. Farbenind. A.-G.—See B., 1929, 123.

Alkyl esters of aromatic sulphonic acids as alkylating agents. W. M. Rodionov [with Romankov and (Mlles.) Vvedenskaja, Viaskov, Vedernikov, Federov, and Tourkowskaja] (Bull. Soc. chim., 1929, [iv], **45**, 109—121).—The action of ammonia on the arylsulphonyl esters previously described (A., 1926, 532) gives alkylamines in low yields, especially of ethylamine, methyl *p*-toluenesulphonate giving 30% of methylamine. Hydroxyaldehydes are readily alkylated with these reagents, monohydroxy-aldehydes giving higher yields than the dihydroxy-aldehydes. Phenyltrimethylammonium *p*-toluenesulphonate in methyl alcohol with sodium methoxide, after removal of sodium *p*-toluenesulphonate, when heated at 120° with vanillin, yields 88% of veratraldehyde, and with protocatechualdehyde 58·3%. Salicylaldehyde yields 72% of anisaldehyde, the *m*- and *p*-methoxyaldehydes being similarly obtained in 88% and 70% yields, respectively. Aliphatic alcohols did not react (cf. Schöpf, A., 1927, 472) and with hydrazine, methyl *p*-toluenesulphonate reacts violently. *Hydrastine benzenemethylsulphonate*, m. p. 218° (yield quantitative), is converted quantitatively into methylhydrastine with 1% sodium hydroxide. Narceine and methyl *p*-toluenesulphonate when treated successively with potassium iodide and hydroxide yield *narceonic acid*, m. p. 207—208°. Allyl *p*-toluenesulphonate and aqueous potassium thiocyanate give about 40—43% of allylthiocarbimide.

Methyl β-naphthalenesulphonate, m. p. 56° (yield 82%), and *methyl α-naphthalenesulphonate*, m. p. 72—73° (yield 68—70%), are readily converted by dimethylaniline into the compounds, $C_{19}H_{22}O_3NS$, β- and α-*naphthylphenyltrimethylammonium sulphonate*, m. p. 206—208° and 161°, respectively. The corresponding *ethyl* α- and β-*naphthalenesulphonates* (yield 65—66%) and their compounds with dimethylaniline are oils. 1-Phenyl-3-methyl-5-pyrazolone and methyl naphthalenesulphonate give a similar oily additive product. All four sulphonates are effective alkylating agents. The compound derived from ethyl α-naphthalenesulphonate and dimethylaniline converts phenol into phenetole (88%), but not anisole. Morphine yields 75% of codeine. Naphthalene-1 : 5-disulphonyl chloride with methyl alcohol and sodium hydroxide is converted into *methyl* 1 : 5-*naphthalenedisulphonate*, m. p. 205°, which with dimethylaniline gives the additive *compound*, m. p. 262° (yield 70%), which converts morphine into codeine in 73—74% yield. Phenylbenzyldimethylammonium chloride, analogous to these ammonium sulphonates, acts exclusively as a benzylating agent, converting morphine into peronine (yield 50%). The alkyl *p*-toluenesulphinates cannot be used as alkylating agents and give no quaternary compounds with tertiary bases. R. Brightman.

Highly polymerised compounds. XIV. Polystyrene, a model of caoutchouc. H. Staudinger, M. Brunner, K. Frey, P. Garbsch, R. Signer, and S. Wehrli (Ber., 1929, 62, [*B*], 241—263; cf. this vol., 51).—Caoutchouc and polystyrene (formerly "metastyrene") must possess a similar structure, since both hydrocarbons yield very viscous, colloidal solutions in organic media. Investigation of the former compound is rendered difficult by its ready auto-oxidation, the uncertainty of the removal of impurities from the natural material without alteration of the structure of the product, and the incomplete identity of natural and synthetic caoutchoucs. Polystyrene represents a pure hydrocarbon in which the colloidal character cannot depend on impurities. The large molecules can be formed only by the linking of individual molecules to long chains; since the chains are saturated, their union by normal valencies to three-dimensional molecules is excluded. The union occurs symmetrically, $\cdots CHPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2\cdots$. The molecules are not auto-oxidisable. Contrary to the views of Stobbe (A., 1910, i, 235; 1915, i, 660), the polystyrenes are mixtures of molecules of similar structure but varying length of chain. Styrene polymerises very slowly in the cold, increasingly rapidly as the temperature rises to 250°; above 300°, depolymerisation occurs. The product obtained without the aid of heat is a very viscous, glassy mass which can scarcely be pulverised. It swells with organic solvents in which it dissolves very slowly. Its solubility is small, 2% solutions being very viscous. Polystyrenes prepared at higher temperatures are glasses which increase in brittleness with rise of temperature of preparation. At 240°, a readily powdered product is obtained. The solubility increases with rise of temperature of preparation, the easily-powdered products dissolving freely in ether without previous swelling. Cryoscopic determinations in benzene show that the mean mol. wt. of polystyrene mixtures diminishes with rise of temperature of preparation. The values 8000—10,000 have an accuracy of about 15%, whereas higher values are estimated and those above 15,000 cannot be determined. The relatively simpler products which do not exhibit characteristic colloidal properties are termed "hemicolloids," whereas those which swell and yield highly viscous solutions are designated "eucolloids." Hemicolloids similar to the mixtures obtained at 240° are also prepared by the polymerisation of styrene in dilute solution under the influence of tin tetrachloride and other halides. The product, mean mol. wt. 3000—4000, can be separated by suitable treatment with solvents into fractions, the most soluble of which have the lowest mol. wt. and temperature of liquefaction and give the least viscous solutions. In comparison with the paraffins, the free solubility of polystyrenes, mol. wt. 3000—10,000, in benzene or chloroform is very striking, but is attributed to their amorphous nature. Polymerisation of styrene at atmospheric temperature leads to very large molecules of estimated mean mol. wt. 10,000—200,000. It is assumed that these "macromolecules" are identical with the primary, colloidal particles. The large intermolecular forces of such macromolecules explain the sparing solubility, swelling power, and high viscosity in solution of the eucolloidal polystyrenes. When heated at temperatures up to 240° in an atmosphere of carbon dioxide, the complex polstyrenes are transformed into products giving solutions in benzene which have greatly diminished viscosity (η 370—1·8). Solutions of eucolloidal polystyrene diminish in viscosity as the temperature is raised; since the process is irreversible, a degradation of the molecules must be assumed. The less viscous solutions of hemicolloidal polystyrenes do not show any change in viscosity, since their molecules are relatively stable. The viscosity increases proportionally with the concentration, showing the single molecules to be mobile in solution. With polystyrenes of mean mol. wt. 10,000 and more the increase of viscosity is more than proportional to the concentration. With increase in mol. wt., solubility in the polystyrenes gradually gives place to swelling, showing that there is probably no essential difference between the two processes. In the former, the smaller molecules become detached, solvatised, and dissolved. In the latter, the solvent first penetrates between the molecules and the single molecules only pass into solution when the process of solvatisation is complete. Swelling is therefore an intermolecular, not an intermicellary phenomenon (except with regard to substances like cellulose). Since polystyrenes which swell have a mean mol. wt. of about 100,000, it must be assumed that other complex compounds such as caoutchouc, albumin, cellulose derivatives, and starch, which also show this property, have very large molecules; substances of mol. wt. 3000—15,000 do not swell. The tenacity of hemicolloidal polystyrenes, mol. wt. 3000—10,000, is very slight, but increases with increasing mol. wt. The marked tenacity of eucolloidal polystyrenes must therefore be connected with the presence of very long molecules which are irregularly oriented, since the effect is the same in all directions. Polymerisation of styrene cannot occur in such a manner as to leave two terminal tervalent carbon atoms, for indications of their presence are not obtained in the relatively simple hemicolloids and the intermediate production of derivatives of α-methylstyrene is improbable, since it is less readily polymerised than styrene. The additive products formed under the influence of stannic chloride are formulated



$$\underbrace{CHPh{\cdot}CH_2{\cdot}[CHPh{\cdot}CH_2]_x{\cdot}CHPh{\cdot}CH_2}_{SnCl_4} \qquad (x = 30\text{—}100)$$

and may be expected to be decomposed by water giving products with two terminal hydroxy-groups, the presence of which would not be easily detected in such large molecules. If, however, decomposition is effected by hydrogen chloride, methyl alcohol, or acetic acid, the presence of the readily characterised residues cannot be established. The terminal valencies, therefore, probably satisfy one another with production of many-membered rings. This accounts for their lack of ability to crystallise, since the molecules cannot arrange themselves in a lattice. As eucolloidal polystyrene is the terminal member of a polymeric–homologous series, so is caoutchouc the ultimate product of a polymeric–homologous series of polyprenes with a very high mean mol. wt. Pummerer's view that it is formed by association of a basal molecule, $(C_5H_8)_8$, is improbable. Meyer's view that caoutchouc is composed of micelles formed by the union of main valency chains of 50—100 isoprene groups is untenable in this form, since polystyrene chains of 50—100 units form hemicolloidal substances. Eucolloidal polystyrenes probably consist of about 1000 basal molecules united in a long chain by normal co-valencies, and the molecules of caoutchouc are of a similar order of magnitude. The macromolecules are identical with the primary colloidal particles. The size of the latter in benzene solution has been shown to be about 200,000 and this is regarded as a determination of mean mol. wt.

H. WREN.

Highly polymerised compounds. XV. Reduction of polystyrene. H. STAUDINGER, E. GEIGER, and E. HUBER (Ber., 1929, 62, [*B*], 263—267; cf. preceding abstract).—Polystyrene is reduced in the presence of nickel at 270° (under the same conditions as caoutchouc) to *hexahydropolystyrene*. The primary action is a degradation of the larger to smaller molecules which are sufficiently active to permit reduction. At the ordinary temperature polystyrene is not reduced in presence of platinum, whereas styrene affords ethyl*cyclo*hexane. Hexahydropolystyrene is a colourless powder which is not attacked by concentrated sulphuric acid and does not give a coloration with tetranitromethane. It decomposes at 350—400°, giving a little hexahydrostyrene, but mainly di-, tri-, and tetra-meric hydrocarbons, whereas polystyrene at 300° gives styrene with a little distyrene. Cracking of hexahydropolystyrene is analogous to that of hydrocaoutchouc. Determinations in benzene show hexahydropolystyrene to be a hemicolloid of mean mol. wt. 3000—4000. It can be separated into more and less soluble portions distinguished by mol. wt. and viscosity. The reduction of polystyrene to hexahydropolystyrene is considered to place beyond doubt that in polystyrene the individual molecules are united in a long chain by normal co-valencies.

H. WREN.

Compounds of antimony trichloride and stannic chloride with unsaturated hydrocarbons. H. VON EULER and H. HELLSTRÖM (Svensk Kem. Tidskr., 1929, **41**, 11—15; cf. A., 1928, 1405).—Mainly a discussion of the colour reactions of compounds of the carotin type with metallic chlorides. The coloured solution obtained by mixing 1 c.c. of a 20% chloroform solution of stilbene with 0·1 c.c. of a 20% stannic chloride solution shows an absorption band at 535—495 μμ (max. 515 μμ) and at 405 μμ. The 95% alcoholic extract of cod-liver oil (lipoid fraction) gives the colour reaction with antimony trichloride twice as intensely as the original oil, the latter showing correspondingly diminished absorption. Diergosteryl phosphate gives a characteristic colour with antimony chloride (A., 1928, 1406) and with stannic chloride, the latter being intensely red with a green fluorescence, with an absorption band at 434 μμ. On dilution the colour changes to violet and then green (band at 620—640 μμ) and finally a new band at 505—485 μμ appears.

J. W. BAKER.

Diphenyl and its derivatives. III. Stereoisomerism of monophenylnaphthalene and dinaphthyl derivatives. IV. Considerations on the great number of optical antipodes without asymmetric atoms which can be derived [from diphenyl]. L. MASCARELLI (Gazzetta, 1928, **58**, 791—800, 865—869; cf. this vol., 181).—Theoretical. Assuming that α- and β-phenylnaphthalenes may be regarded respectively as 2 : 3- and 3 : 4-disubstituted diphenyls, the nature of the further substitution necessary to impede free rotation of the phenyl group and thus give rise to stereoisomerism is discussed, together with the similar conditions for stereoisomerism in αα-, ββ-, and αβ-dinaphthyls.

E. W. WIGNALL.

Symmetry of naphthalene. K. LONSDALE (Proc. Leeds Phil. Soc., 1929, **1**, 346—348).—A naphthalene molecule which, in agreement with *X*-ray investigations (Bragg, A., 1922, ii, 128), has a centre of symmetry only and accounts satisfactorily for the observed differences in the absorption spectra of the ten dichloronaphthalenes (de Laszlo, A., 1928, 514) can be built up on the author's assumption (A., 1928, 1079) of an anisotropic carbon atom having two A and two B valencies. Such a molecule may have either a double linking in the 9 : 10-position, or a centric configuration. In this molecule all the four α-positions are identical, $\beta_2 \equiv \beta_6$, $\beta_3 \equiv \beta_7$, but $\beta_2 \not\equiv \beta_3$.

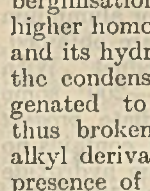
J. W. BAKER.

Hydrogenation of fluorene under pressure with nickel or osmium as catalysts, together with traces of cerium and thorium oxides. V. S. SADIKOV and A. K. MICHAILOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 1567—1573).—See A., 1928, 1235.

Pyrogenic dissociation of condensed ring systems. N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 1447—1458).—Tetrahydrophenanthrene when treated with hydrogen at 450—470°/70—170 atm. with an iron oxide catalyst gave a mixture of phenanthrene, tetrahydronaphthalene and its homologues, and benzene and its homologues. Similar products, together with free carbon, were obtained by heating tetrahydrophenanthrene with aluminium chloride at atmospheric pressure. Berginisation of retene gave small quantities of benzene hydrocarbons, naphthalene and its homologues, and methylphenanthrene. Coal-tar oil, under the same conditions, yielded a mixture of benzene and naphthalene hydrocarbons, together with some phenanthrene derivatives. Anthracene and aluminium chloride gave free carbon, hydrogenated products of anthracene, naphthalene, and its homologues. Fluorene, on berginisation, yielded much benzene, toluene, and higher homologues, together with unchanged fluorene and its hydrogenated products. It is concluded that the condensed nuclei hydrocarbons are first hydrogenated to the tetrahydro-derivatives, which are thus broken by the further action of hydrogen to alkyl derivatives of naphthalene and benzene. The presence of a catalyst, such as aluminium chloride, causes the reactions to take place at atmospheric pressure, the hydrogen being formed by the complete dehydrogenation of part of the hydrocarbons, with separation of free carbon. It is suggested that the formation of naphthalene and its derivatives in high-temperature coal tar is due to the cracking in the presence of hydrogen of the primary tars formed, which always contain the tetrahydro-derivatives of the condensed nuclei hydrocarbons.

M. ZVEGINTZOV.

Benzopolymethylene compounds. XV. Composition, constitution, and synthesis of fluoranthene. J. VON BRAUN and E. ANTON (Ber., 1929, **62**, [*B*], 145—151; cf. A., 1926, 1139; 1927, 666).—The conception of fluoranthene as a derivative of indene is not in harmony with the authors' experiments on the stability of ring systems. Since, however, the presence of an additional carbon atom to the molecule of fluoranthene or its quinone makes little difference in the analytical results, the possibility is suggested that it is actually a naphthalene derivative (I); this is shown to be the case by direct synthesis.



(I.)

[With H. WAGNER.]—Ethyl dibenzofulvenecarboxylate, from fluorenone, zinc, and ethyl bromoacetate, is very readily hydrogenated in the presence of nickel under pressure at 230° to ethyl 9-fluorenylacetate, b. p. 193—194°/12 mm., from which 9-fluorenylacetic acid, b.p. 218—220°/11 mm., is derived. 9-*Fluorenylacetyl chloride*, b.p. 194—196°/13 mm., from the acid and thionyl chloride, does not react with aluminium chloride in light petroleum at 60°. Ethyl fluorenylacetate is reduced by Ladenburg's method to fluorene and β-9-*fluorenylethyl alcohol*, b. p. 190—195°/13 mm., but the conversion of the alcohol through the corresponding bromide and cyanide into fluorenylpropionic acid does not occur readily. The sodio-derivative of ethyl 9-fluorenecarboxylate is smoothly converted by ethyl β-chloropropionate into the *ester*, $C_{12}H_8{>}C(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 247°/14 mm., which is almost quantitatively hydrolysed and decarboxylated to β-9-fluorenylpropionic acid. The acid is transformed by thionyl chloride into the corresponding *chloride*, b. p. 180—185°/0·8 mm., m. p. 58—59°, which, when heated with aluminium chloride in light petroleum, affords 4-*keto*-1 : 2 : 3 : 4-*tetrahydrofluoranthene*, m. p. 98° (*semicarbazone*, m. p. 250—251°; *oxime*, m. p. 170—171°). Reduction of the ketone by Clemmensen's method yields 1 : 2 : 3 : 4-*tetrahydrofluoranthene*, b. p. 155°/0·7 mm., m. p. 69°, dehydrogenated by lead oxide to fluoranthene (9 : 10-benzoacenaphthene), m. p. 110°. H. WREN.

Preparation of perylene. C. MARSCHALK (Bull. Soc. chim., 1928, [iv], 43, 1388—1402).—When 2 : 2′-dinaphthol is heated with zinc, zinc chloride, or a mixture of these or with ferric chloride or aluminium chloride, yields of 2—12% of perylene are obtained, β-dinaphthylene oxide being the main product. With phosphoryl chloride and zinc at 100—200° some phosphine is evolved and an intermediate *product* is obtained which is insoluble in toluene, contains no chlorine, and is decomposed by potassium hydroxide into 2 : 2′-dinaphthol and phosphate. On distillation in presence of a little lime it affords perylene in yields up to 46·5%. The action of 1 mol. of phosphoryl chloride on 1 mol. of 2 : 2′-dinaphthol yields 2 : 2′-dinaphthol chlorophosphate, $(C_{20}H_{12}O_2){:}POCl$, 2 mols. of hydrogen chloride being evolved, from which the corresponding sodium phosphate and hydrogen phosphate, $(C_{20}H_{12}O_2){:}PO\cdot OH$, are obtained by hydrolysis with dilute sodium carbonate: the cyclic structure of these products is indicated by their stability towards boiling sodium hydroxide solution. When heated alone the dinaphthol chlorophosphate yields 12% of perylene, but on distilling with zinc and zinc chloride after previous heating at 270° for 1½—2 hrs., yields of 46—55% of perylene are obtained. Similarly, when heated with zinc and zinc chloride the hydrogen phosphate gives 21% of perylene, only traces being formed on heating alone. With aluminium chloride in carbon tetrachloride, but not in nitrobenzene (cf. Scholl, A., 1922, i, 336) at the ordinary temperature or when heated at 100° in absence of solvent, the sodium dinaphthol phosphate yields 1 : 12-dihydroxyperylene phosphate (cf. Zincke and Dengg, A., 1922, i, 1013), converted by alkaline fusion into 1 : 12-dihydroxyperylene. With phosphorus trichloride 2 : 2′-dinaphthol gives a similar condensation *product*, $C_{20}H_{12}O_2PCl_3$, which is converted by sodium carbonate into a chlorine-free phosphate, and with zinc and zinc chloride affords 33% of perylene. R. BRIGHTMAN.

Relationship between constitution and taste among some derivatives of carbamide. H. THATE (Rec. trav. chim., 1929, 48, 116—120).—The following substituted carbamides are obtained by the action of potassium cyanate on the requisite aniline hydrochloride: phenyl-, α-phenyl-α-methyl-, *p*-tolyl-, m. p. 176° (lit. 158° and 180°), α-*p*-*tolyl-α-methyl*-, m. p. 103°. α-*Phenyl-α-methyl*-, m. p. 156°, and α-*p*-*tolyl-α-methyl-biurets*, m. p. 167°, are formed as by-products with the corresponding carbamides. Whilst phenylcarbamide is bitter, the remainder are sweet, showing that substitution of the imido-hydrogen atom by a methyl group has a sweetening influence (cf. Lorang, A., 1928, 285). H. BURTON.

Existence of dihydro- and octahydro-*p*-indole. E. FERBER (Ber., 1929, 62, [*B*], 183—195).—Repetition of the work of von Braun and Gavrilov (A., 1912, i, 497) fails to confirm the production of dihydro-*p*-indole. β-Phenylethyl chloride, b. p. 96°/23 mm., conveniently prepared by heating β-phenylethyl alcohol saturated with hydrogen chloride in sealed tubes at 140—160°, is converted by nitric acid (*d* 1·5) at −15° into a mixture of β-*p*-nitrophenylethyl chloride, m. p. 48—49°, β-*o*-nitrophenylethyl chloride, and small amounts of β-2:4-*dinitrophenylethyl chloride*, m. p. 136°. The *p*-nitro-compound is reduced by stannous chloride and hydrochloric acid to β-*p*-aminophenylethyl chloride hydrochloride, m. p. 209—210°, decomp. about 212° (corresponding *chlorostannate* and chloroplatinate, m. p. 192—193° after blackening). Contrary to von Braun (*loc. cit.*), the slow distillation of an ethereal solution of the base leaves the compound almost quantitatively unchanged, as does protracted treatment with boiling ethyl alcohol. When heated at 100—115°, the base affords products of high mol. wt. formed by external condensation. The liquid products obtained by nitration of β-phenylethyl chloride and consisting largely of the *o*-nitro-compound (see above) are reduced to β-*o*-aminophenylethyl chloride hydrochloride, m. p. 205°; the corresponding free base passes when its ethereal solution is distilled (more simply when the base is distilled with steam) into *o*-dihydroindole, b. p. 228—230° [nitroso-derivative, m. p. 81—82°; *picrate*, m. p. 172°; *hydrochloride*, m. p. 219° (subl.); *benzenesulphonyl* compound, m. p. 130—132°].

β-Phenylethyl acetate is converted by treatment with nitric acid (*d* 1·5) at −15° to −12° and subsequent hydrolysis of the product with methyl-alcoholic hydrogen chloride into β-*p*-nitrophenylethyl alcohol, m. p. 60—61° (*benzoate*, m. p. 105·5°), the constitution of which is confirmed by its formation from β-*p*-nitrophenylethyl chloride. The alcohol is reduced by zinc dust in presence of calcium chloride to β-*p*-aminophenylethyl alcohol, m. p. 108° (*dibenzoyl* derivative, $C_8H_9ONBz_2$, m. p. 136°; *hydrochloride*, m. p. 163°), converted by nitrous acid in presence of aqueous copper sulphate at 90° into β-*p*-hydroxyphenylethyl alcohol, m. p. 92—93° (dibenzoyl derivative, m. p. 111°), in 65% yield. The phytochemical conversion of *p*-aminophenylethyl alcohol into the corresponding phenol could not be effected.

Hydrogenation of *p*-amino- or *p*-nitro-phenylethyl chloride by Skita's method in strongly acid solution affords β-p-*amino*cyclo*hexylethyl chloride*, b. p. about 136°, d_4^{20} 1·0332, n_D^{20} 1·5036 [non-crystalline *hydrochloride* and *picrate*; *chloroplatinate*, m. p. 231° (decomp.)], with small amounts of *αδ-di*-p-*amino*cyclo*hexyl*-n-*butane*, b. p. about 312°/720 mm. (decomp.), d_4^{19} 0·9774, n_D^{19} 1·5077 (*hydrochloride*, m. p. 207°), and tertiary base. Intramolecular condensation to a perhydro-*p*-indole could not be effected. At 180—200° the compound is converted into a *substance*, $C_{21}H_{45}N_3$ [*picrate*, m. p. (indef.) 143°; p-*toluenesulphonyl* derivative, m. p. 143° (indef., decomp.)], which appears to be a secondary amine. Hydrogenation of β-*p*-aminophenylethyl alcohol hydrochloride affords β-p-*amino*cyclo*hexylethyl alcohol*, m. p. 77—85°, probably a mixture of *cis*- and *trans*-isomerides; the non-crystalline *picrate* and *hydrochloride* are described. H. Wren.

Sulphonic acids of 6-chloro-*o*-toluidine. I. G. Farbenind. A.-G.—See B., 1929, 123.

Compounds of the higher oxy-acids of the halogens with benzidine. A. E. Kretov (J. Russ. Phys. Chem. Soc., 1928, **60**, 1427—1433).—Chloric acid and benzidine in alcoholic solution give two *compounds* with 1 and 2 mols. of the acid to 1 mol. of benzidine, respectively. Bromic acid yields only one compound, with 2 mols. of the acid. Both the benzidine chlorate and the bromate can be titrated quantitatively with phenolphthalein as indicator, and explode on rapid heating. The *iodate* can be obtained by treating iodic acid with benzidine in acetic or hydrochloric acid solutions, and the reaction can be employed for the quantitative precipitation of iodic acid. All the salts are colourless, but darken on keeping. Perchloric acid and benzidine in equimolecular proportions in alcoholic solution give a blue *salt*, whilst if an excess of perchloric acid is present, a white *salt* is obtained. M. Zvegintzov.

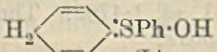
Bis-semidine inversion in aromatic dihydrazo-compounds. B. C. Guha and H. K. Banerjee (J. Indian Inst. Sci., 1928, **11 A**, 231—239).—The semidine inversion of several aromatic dihydrazo-compounds has been studied and the resulting diamines have been diazotised and coupled with various amines and phenols. *s*-Diphenylthiocarbohydrazide, prepared in greatly improved yield by heating phenylhydrazine phenyldithiocarbazinate at 80° for 3—4 hrs., is converted by 3% hydrochloric acid at 60—65° into *diaminodiphenylthiocarbamide* (which could not be isolated either as the free base or its hydrochloride), giving a bisdiazo-compound which couples with the appropriate second component to yield *thiocarbamidobisbenzeneazo*-β-*naphthol* (sodium salt), m. p. 131—132°, *-dimethylaniline*, m. p. 164—166°, *-resorcinol*, m. p. 158° (explosively), and reacts with phenylthiocarbimide, phenylcarbimide, and formaldehyde to yield, respectively, *diphenylthiocarbamidodiphenylthiocarbamide*, $CS(NH{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHPh)_2$, m. p. 182—183°, *diphenylcarbamidodiphenylthiocarbamide*, m. p. 238—240°, and *dimethyleneaminodiphenylthiocarbamide*, not melting below 300°. Similarly, inversion of diphenylcarbohydrazide (Skinner and Ruhrmann, A., 1888, 274) yields diaminodiphenylcarbamide (unstable) which is not identical with the *pp′*- or (stable) *oo′*-diamino-compound, since it diazotises and couples to yield *carbamidobisbenzeneazo*-β-*naphthol* (*sodium* salt, m. p. 131—132°), *-dimethylaniline*, m. p. 160—161°, *-resorcinol*, m. p. 157° (decomp.); and yields *diphenylcarbamidodiphenylcarbamide*, m. p. 236—238°, and *dimethyleneaminodiphenylcarbamide*, not melting at 300°, whilst the *pp′*-diaminodiphenylcarbamide couples with β-naphthol to give an azo *dye*, m. p. 263°, and reacts with phenylthiocarbimide to yield a *diphenylthiocarbamidodiphenylcarbamide*, different from those obtained from the inversion compound. Reduction of *pp′*-dinitrodiphenylthiocarbamide does not yield the corresponding *pp′*-diamino-derivative, since this seems to lose 1 mol. of hydrogen sulphide, the product being p-*aminophenyl*-p-*phenyleneguanidine*, $C_6H_4{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C{:}N{\cdot}C_6H_4{\cdot}NH_2$, m. p. 295° (decomp.) (isolated as its *hydrochloride*), identical with the product obtained by the loss of ammonia from the base obtained by hydrolysis of *pp′*-diacetamidodiphenylthiocarbamide (obtained by heating acetyl-*p*-phenylenediamine with carbon disulphide). By the usual methods it is converted into the *sodium* salt of p-*phenyleneguanidinobenzeneazo*-β-*naphthol* and *phenylthiocarbamidophenyl*-p-*phenyleneguanidine*, both m. p. above 300°. J. W. Baker.

Azo-triarylmethane and azo-pyronine dyestuffs (*meta* series). P. N. Sen and B. Ghosh.—See B., 1929, 89.

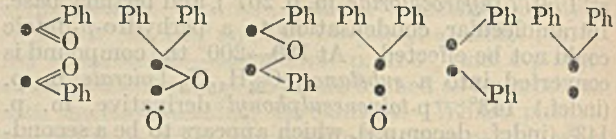
Formals and mixed carbonic esters. S. Sabetay and P. Schving (Bull. Soc. chim., 1928, [iv], **43**, 1341—1345).—Chloromethyl ethers, obtained by saturating an alcoholic suspension of trioxymethylene with hydrogen chloride, with sodium derivatives of alcohols or phenols in ether, alcohol, or in benzene afford mixed formals. In some cases, *e.g.*, benzyl alcohol and β-phenylethyl chloromethyl ether, heating without sodium or solvent is sufficient. β-*Phenylethyl chloromethyl ether* has b. p. 119—121·5°/16 mm., n_D^{18} 1·5227; β-*phenylethyl cyanomethyl ether*, b. p. 96—98°/15 mm., n_D^{19} 1·5416, d^{19} 1·067; benzyl chloromethyl ether, b. p. 102—102·5°/14·5 mm., d_D^{17} 1·5270 (cf. Hill and Keach, A., 1926, 271), and *di*cyclo*hexylformal*, b. p. 139—140°/14 mm., d^{21} 0·9741, n_D^{21} 1·4702. The following β-*phenylethyl methylene ethers*, $CH_2Ph{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}OR$, are described; *methyl*, b. p. 102—103°/13 mm., n_D^{19} 1·4951, d^{19} 1·002; *ethyl*, b. p. 113—113·5°/14 mm., n_D^{21} 1·4846, d^{21} 0·9757; *acetyl*, b. p. 136—137°/13 mm., n_D^{20} 1·4950; iso*butyl*, b. p. 131—132°/14 mm., n_D^{21} 1·4793, d^{21} 0·9504; *phenyl*, b. p. 181—182°/14 mm., d^{18} 1·074, n_D^{18} 1·5501; o-*tolyl*, b. p. 190°/14 mm., n_D^{21} 1·5472, d^{21} 1·061, m-4-*xylyl*, b. p. 203—204°/17 mm., d^{21} 1·045; *α-naphthyl*, b. p. 213—215°/2 mm.; *benzyl*, b. p. 192—194°/14 mm., d^{20} 1·012, n_D^{20} 1·5436; *guaiacyl*, b. p. 207°/12 mm., n_D^{18} 1·5562; *linolyl*, b. p. 198—199°/15 mm., n_D^{18} 1·5120. *Phenyl-γ-phenylpropyl methylene ether* has b. p. 166°/2 mm., d^{19} 1·059, n_D^{19} 1·5451; *phenyl benzyl methylene ether*, b. p. 172°/14 mm., d^{21} 1·090, n_D^{21} 1·5560; *benzyl methyl methylene ether*, b. p. 95—97°/16 mm., n_D^{20} 1·4941, d^{20} 1·013. β-Phenylethyl chloroformate and phenol in chloroform in presence of pyridine afford *phenyl β-phenylethyl carbonate*, m. p. 89°, b. p. 203°/15 mm. *α-Phenylpropyl ethyl carbonate*, b. p. 131—133°/14 mm., n_D^{21} 1·4858, is similarly prepared from α-phenyl-*n*-propyl alcohol. β-Phenylethyl bromide, phenol, and potassium hydroxide in presence of copper at 160° yield phenyl β-phenylethyl ether, b. p. 162—163°/14 mm., d^{16} 1·054, n_D^{16} 1·5706 (cf. Schorigin, A., 1925, i, 1404). R. BRIGHTMAN.

Nitration of methane- and ethane-sulphon-*p*-phenetidides. F. REVERDIN (Helv. Chim. Acta, 1929, 12, 113—121).—Methanesulphonyl chloride reacts with an aqueous suspension of *p*-phenetidine in presence of sodium carbonate, forming *methanesulphon-*p*-phenetidide*, m. p. 127° (*acetyl* derivative, m. p. 112°), which is nitrated in hot alcoholic solution by nitric acid (*d* 1·185) to 3-*nitro-4-methanesulphonamidophenetole*, m. p. 100°. This is hydrolysed by cold concentrated sulphuric acid to 2-nitro-*p*-phenetidine. Similar nitration with nitric acid, *d* 1·4, gives 3 : 5-*dinitro-4-methanesulphonamidophenetole*, m. p. 176—177°. When nitration is effected by cold nitric acid (*d* 1·52) alone a small amount of 2 : 3 : 5-*trinitro-4-methanesulphonamidophenetole*, m. p. 235° (not sharp, crystallographic data given), is obtained. Corresponding nitrations of 4-*ethanesulphonamidophenetole*, m. p. 83° (*acetyl* derivative, m. p. 81°), yield 3-*nitro-*, m. p. 91—92°, 3 : 5-*dinitro-*, m. p. 182°, and 2 : 3 : 5-*trinitro-4-ethanesulphonamidophenetole*, m. p. 229°, respectively. 2 : 5-*Dinitro-4-ethanesulphonamidophenetole*, m. p. 166—167°, is obtained by the action of nitric acid (*d* 1·52) at −5° to 2°. H. BURTON.

***iso*Phenyl sulphide and its derivatives.** O. HINSBERG (Ber., 1929, 62, [*B*], 127—135).—Phenyl sulphide reacts moderately violently with hot 70% perchloric acid containing a little glacial acetic acid, yielding the basic *perchlorate* of *iso*diphenylsulphonium hydroxide, $(C_{12}H_{10}S)_2,HClO_4,H_2O$, which usually contains a small proportion of more highly oxygenated and chlorinated compounds. It is converted by potassium iodide in presence of methyl alcohol into the basic *hydriodide*, $(C_{12}H_{10}S)_2I,H_2O$; the *chloroplatinate*, $C_{48}H_{46}O_2S_4Cl_6Pt$, is described. The basic perchlorate is converted by methyl-alcoholic potassium hydroxide into the amorphous iso*diphenylsulphonium hydroxide* (I), which is unusually stable towards reducing agents. The base decomposes when heated at 280—350°, giving a yellow oil oxidised by hydrogen peroxide to a substance, m. p. 225° (see later), mainly diphenyl sulphone, m. p. 127°, and *iso*phenyl sulphone; it consists therefore mainly of diphenyl sulphide. Distillation of the basic hydriodide proceeds similarly. The sulphonium base is converted by potassium hydroxide in boiling methyl alcohol into iso*phenyl sulphide*, b. p. 300—340°/atmos. pressure (partial decomp.), which is isomerised to diphenyl sulphide when repeatedly distilled and transformed, apparently smoothly, by perchloric acid into *iso*diphenylsulphonium perchlorate. The *iso*sulphide is transformed by an excess of hydrogen peroxide into the corresponding *sulphone*, Ph·SO₂·Ph,0·5H₂O, m. p. 81° [also (?) +0·25MeOH, m. p. 83°], and by moderated oxidation into the non-crystalline *sulphoxide*, $C_{12}H_{10}OS$. The compound, m. p. 225°, is regarded as (?) iso*phenoxthin sulphone*, $C_{12}H_8O_3S,0{\cdot}5H_2O$. Since the usual structural and spatial formulæ are inadequate for the full explanation of the observed isomerism, recourse is had to the atomic formulæ of sulphur containing two valency centres, thus leading to the following expressions :



(I.)



Sulphone and *iso*sulphone. Sulphoxide and *iso*sulphoxide. Sulphide and *iso*sulphide.

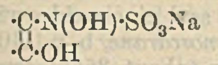
H. WREN.

Halogen derivatives of β-naphthol unsubstituted in position 1. C. MARSCHALK (Bull. Soc. chim., 1928, [iv], 43, 1361—1367).—Halogen derivatives of β-naphthol with the 1-position unsubstituted are obtained by elimination of the α-amino-group from 1-amino-2-naphthol derivatives. Thus, 3-bromo-1-nitroso-β-naphthol (Brömme, A., 1888, 490) is converted by sodium hyposulphite at 30—35° into 3-*bromo-1-amino-β-naphthol*, which yields an insoluble *diazo-oxide*, reduced by sodium stannite to 3-*bromo-β-naphthol*, m. p. 84—85°. 3-Chloro-1-nitroso-β-naphthol (Zincke and Schmunck, A., 1890, 1146), obtained by the action of sulphuryl chloride on nitroso-β-naphthol in tetrachloroethane, and 3 : 4-dichloro-1-nitroso-β-naphthol similarly yield 3-*chloro-1-amino-β-naphthol*, 3-*chloronaphthalene*-1 : 2-*diazo-oxide*, 3-chloro-β-naphthol, 3 : 4-*dichloro-1-amino-β-naphthol*, 3 : 4-*dichloronaphthalene*-1 : 2-*diazo-oxide*, and 3 : 4-dichloro-β-naphthol (cf. B., 1926, 869). The last-named is reconverted into 3 : 4-dichloro-1-nitroso-β-naphthol by nitrous acid. R. BRIGHTMAN.

Naphthalene series. I. Mechanism of the reaction of naphthol derivatives with hydrogen sulphite. N. N. VOROSHCOV [with A. G. KASSATIN] (Ber., 1929, 62, [*B*], 57—68).—Previous investigations of the interaction of hydrogen sulphites with phenols have usually involved such drastic treatment that no guarantee is afforded of the isolation of primary products (cf. Bucherer, A., 1904, i, 309; 1905, i, 48; Fuchs and Pirak, A., 1927, 53; Voroshcov, A., 1917, i, 300). An instance of reaction under mild conditions is now recorded. β-Naphthol is treated with sulphuric acid (*d* 1·84) at a temperature which is finally raised to 42—45° and the product is diluted with ice and neutralised by chalk. The solution of calcium salts is saturated with sodium chloride, which causes an immediate separation of a mixture of sodium β-naphthol-1- and -6-sulphonates, whereas the -8-sulphonate separates more slowly. The mixed salts are treated with boiling 96% alcohol in which the -6-sulphonate is insoluble, whereas the -1-sulphonate dissolves. Addition of 50% sodium hydroxide to the alcoholic solution causes the precipitation of the *disodium* salt of β-naphthol-1-sulphonic acid. Saturation of a cold, aqueous solution of the salt with sulphur dioxide causes the precipitation of the additive *compound*, $C_{10}H_8O_7S_2Na$, for which the sulphurous ester formula suggested by Bucherer for analogous cases is shown to be untenable. The hydrogen sulphite compound decomposes into its components in aqueous solution in a degree which increases with increasing dilution. Decomposition increases rapidly under the influence of hydroxyl ions even in the presence of alkalis as weak as sodium hydrogen carbonate. Addition of hydrogen ions increases the stability of the hydrogen sulphite compound in aqueous solution, even minimal quantities of acid retarding the decomposition. The graphs representing the equilibria of the hydrogen sulphite compound under the influence of dilution and on addition of hydroxyl and hydrogen ions are closely analogous to those of the similarly constituted compounds from benzene-azo-β-naphthol. Since, further, a series of analogies in chemical character between the hydrogen sulphite compounds of azonaphthol dyes and the colourless naphthol derivatives has been established (Voroshcov, *loc. cit.*) it appears that in both cases the reactive hydroxyl group is particularly important for the production of hydrogen sulphite compounds. Treatment of saturated solutions of the hydrogen sulphite compound of the sodium salt of β-naphthol-1-sulphonic acid with the chlorides of barium, copper, zinc, or mercury gives crystalline precipitates of new salts; in dilute solution, the sulphites of the heavy metals are precipitated. The *barium*, $C_{10}H_8O_7S_2Ba$, and the corresponding *copper* salt have been analysed.

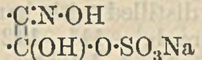
H. WREN.

Naphthalene series. II. Action of sodium hydrogen sulphite on nitrosonaphthols. N. N. VOROSHCOV and S. W. BOGDANOV (Ber., 1929, 62, [*B*], 68—80).—1-Nitroso-β-naphthol unites with sodium hydrogen sulphite giving the additive compound, $C_{10}H_8O_5NSNa$, thus excluding Bucherer's ester formula and indicating the structure I or II.



$$\begin{array}{l}\cdot C\cdot N(OH)\cdot SO_3Na \\ \quad \| \\ \cdot C\cdot OH\end{array}$$

(I.)



$$\begin{array}{l}\cdot C{:}N\cdot OH \\ \quad \| \\ \cdot C(OH)\cdot O\cdot SO_3Na\end{array}$$

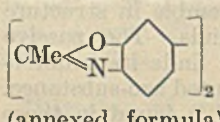
(II.)

The properties of the compound agree with those recorded in the literature except that it does not appear to be decomposed into its components by acid, but converted into a brown compound soluble in alkali (cf. G.P. 82097). Since the action of sodium hydrogen sulphite on the methyl ether of 1-nitroso-β-naphthol, $O{:}C_{10}H_6{:}N\cdot OMe$, gives an additive *product*, $C_{11}H_{10}O_5NSNa$, which is closely analogous in properties to that derived from 1-nitroso-β-naphthol, it may be assumed that the last compound reacts in the quinoneoxime form. Addition of sodium hydrogen sulphite to a solution of sodium 1-nitroso-β-naphthol-6-sulphonate followed by sodium hydroxide gives the pale green disodium salt of nitrosonaphtholsulphonic acid; the isolation of the hydrogen sulphite compound is difficult on account of its ready solubility, but its additive nature is placed beyond doubt by examination of the corresponding *barium* compound. Treatment of the mixture of 4- and 2-nitroso-α-naphthols with sodium hydrogen sulphite shows that only the 4-nitroso-compound is able to form an unstable hydrogen sulphite compound which has not been obtained homogeneous. A ready means of separating these nitrosonaphthols from one another is thus afforded. Isolation of the 4-derivative from its hydrogen sulphite compound, after separation of the insoluble 2-nitroso-α-naphthol, is effected by addition of alkali hydroxide and subsequently of acid. Only those nitrosonaphthols react with hydrogen sulphite which resemble in structure the similarly active azo-compounds. The passive behaviour of 2-nitroso-α-naphthol finds its counterpart in that of the similarly constituted azo-substance. Ability to add hydrogen sulphite is found in those azo-, nitroso-, and sulphonic acid derivatives of naphthols in which these groups occupy the position 1, whilst the hydroxyl group is in the position 2 or 4. Naphthol derivatives in which the azo-, nitroso-, or sulphonic acid groups are in position 2 and the hydroxyl group in position 1 do not add hydrogen sulphite. The hydrogen sulphite compounds of the azo-compounds must therefore possess the same structure as those of the nitroso-derivatives and, since the ketone hydrogen sulphite formula has been established for the former, it must also be applied to the latter. The hydrogen sulphite compound of 1-nitroso-β-naphthol, therefore, has the constitution II.

H. WREN.

Nitroarylsulphuric acids and their reduction products. G. N. BURKHARDT and H. WOOD (J.C.S., 1929, 141—152).—The preparation of arylsulphuric acids from *o*-, *m*-, and *p*-nitrophenols and 1 : 4- and 1 : 2-nitronaphthols is described (cf. Burkhardt and Lapworth, A., 1926, 511). The arylsulphuric acids are prepared by addition of the appropriate phenol to a mixture of chlorosulphonic acid and dimethylaniline; the following *potassium* salts were prepared: *potassium* o-*nitrophenyl sulphate*, p-*nitrophenyl sulphate*, 1-*nitro*-2-*naphthyl sulphate*, and 4-*nitro*-1-*naphthyl sulphate*. Reduction of these by warm ferrous sulphate solution in the presence of precipitated calcium carbonate or barium carbonate gives the corresponding amino-compounds. The following are described: *potassium* o-*aminophenyl sulphate*, *potassium* p-*aminophenyl sulphate* (acids precipitate from aqueous solution the corresponding *hydrogen* p-*aminophenyl sulphate*), *potassium* p-*benzylideneaminophenyl sulphate*, $C_{13}H_{10}O_4NSK,0{\cdot}5H_2O$, *potassium* p-*acetamidophenyl sulphate*, *potassium* 1-*amino*-2-*naphthyl sulphate*, $C_{10}H_8O_4NSK,0{\cdot}5H_2O$; potassium 4-amino-1-naphthyl sulphate; *hydrogen* 4-*amino*-1-*naphthyl sulphate*. The potassium aminoaryl sulphates are all hydrolysed less readily by mineral acid than is potassium phenyl sulphate itself. By diazotisation and coupling are obtained: from hydrogen *p*-aminophenyl sulphate and resorcinol, *potassium dihydroxybenzeneazophenyl sulphate*, $C_{12}H_9O_6N_2SK,1{\cdot}5H_2O$; from the same base and potassium β-naphthoxide *potassium* 2-*hydroxynaphthaleneazophenyl sulphate*, $C_{16}H_{11}O_5N_2SK,0{\cdot}5H_2O$; from potassium *o*-aminophenylsulphate and potassium β-naphthoxide *o*-hydroxybenzeneazo-β-naphthol.

Alkaline reduction of potassium *o*-nitrophenyl sulphate (either zinc dust and potassium hydroxide solution or sodium amalgam and water) gives *potassium azobenzene* 2 : 2′-*disulphate*, $(KO{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}N{:})_2,0{\cdot}5H_2O$ and potassium hydrazobenzene 2 : 2′-disulphate. The last-named compound, by treatment with hydrogen chloride, yields 4 : 4′-*diaminodiphenylene dihydrogen* 3 : 3′-*disulphate*, $C_{12}H_{10}N_2(SO_4H)_2,2{\cdot}5H_2O$ (*potassium* salt), which, by hydrolysis gives 3 : 3′-dihydroxybenzidine identical with the demethylation product of dianisidine. *Diacetyl*-3 : 3′-*dihydroxybenzidine*, m. p. 292° (decomp.), is dehydrated by heating at 300°, giving the *dianhydro*-derivative (annexed formula), m. p. 164—165°. 4-Hydroxynaphthaleneazo-β-naphthol has m. p. 236° (lit. 228—229°).



R. J. W. Le Fèvre.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. V. E. de B. Barnett and N. F. Goodway (J.C.S., 1929, 20—23).—1 : 5-*Dichloro*-9-*benzhydrylanthrone*, m. p. 191° (prepared by boiling 1 : 5-dichloroanthrone with benzhydryl chloride and aqueous potassium hydroxide), gave, by reduction with either zinc dust and alcoholic potassium hydroxide or zinc dust and hydrogen chloride in acetic acid, 1 : 5-dichloroanthracene. Interaction, in ethereal solutions, with Grignard compounds gave (in low yield) the corresponding crystalline dihydroanthranols in the cases where halides of Et, Pr^{α}, Pr^{β}, Bu, *iso*-Bu, and *iso*amyl were employed. Higher yields were obtained from magnesium methyl, benzyl, and phenyl halides. These dihydroanthranols undergo facile transannular loss of benzhydrol rather than water with resultant formation of the corresponding 1 : 5-dichloro-9-alkylanthracene.

The following m. p. of 10-substituted 1 : 5-*dichloro*-9-*benzhydryldihydroanthranols* are given: 10-*methyl*, 160°; *ethyl*, 140°; *propyl*, 185°; iso*propyl*, 170°; n-*butyl*, 182°; iso*butyl*, 212°; iso*amyl*, 193°; *benzyl*, 206°; *phenyl*, 259°. The last compound underwent change in boiling xylene solution to an isomeric *compound*, m. p. 271°; both isomerides lose benzhydrol with formation of 1 : 5-dichloro-9-phenylanthracene. The isomerism may be due to a non-coplanar arrangement of the anthracene ring system such as suggested by Schlenk (A., 1928, 1031).

R. J. W. Le Fèvre.

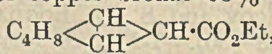
Cholesterol. V. E. Montignie (Bull. Soc. chim., 1928, [iv], 43, 1403—1405).—When treated with an acetic acid solution of mercuric oxide, cholesterol yields α-hydroxycholestenol, m. p. 180° (Mauthner and Suida, A., 1896, i, 425), and resinous products. Only the acetate is obtained when cholesterol is heated with 10 mols. of acetic anhydride at 150°; with 1 mol. of camphoric acid at 190—200°, *cholesteryl camphorate*, $C_8H_{14}(CO_2C_{27}H_{45})_2$, m. p. 133—134°, is obtained. Perchloric acid at 100° acts as a dehydrating agent, giving β-cholesterylene, m. p. 193°, and α-cholesterylene, m. p. 79—80° (cf. A., 1927, 556, 969).

R. Brightman.

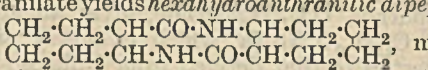
Specific colour reaction for ergosterol and its transformation products. E. P. Häussler and E. Brauchli (Helv. Chim. Acta, 1929, 12, 187—193).—The Tortelli and Jaffe colour reaction (A., 1914, ii, 822) appears to be specific for ergosterol and its derivatives. A positive reaction can be obtained with 1—1·5 mg. even in presence of cholesterol or phytosterol. Zymosterol (Maclean, A., 1928, 329) after further purification from ether, or removal of admixed ergosterol by irradiation, has m. p. 105—107°, $[\alpha]_D^{20}$ +44·0° in chloroform. It also gives the above colour reaction, but not so strongly as ergosterol, indicating that it might be an isomeride or a rearrangement product. Definite positive reactions are given by *iso*ergosteryl acetate, dehydroergosterol, and dehydroergosteryl acetate. From one attempt to prepare *iso*ergosteryl acetate a substance, m. p. 132—134°, $[\alpha]_D^{20}$ −170·9° in chloroform, was obtained. This depresses the m. p. (133—135°) of *iso*ergosteryl acetate, and gives a positive colour reaction. Irradiation of a solution of ergosterol in olive oil for 3·5 hrs. causes a 50% diminution in the intensity of the colour; the decrease in colour of an irradiated benzene solution is of the same order after 4 hrs., but after 16 hrs. the original intensity is almost reached. Positive reactions were also given by the lipoid from calf's bone-marrow, two specimens of linseed oil, poppy-seed and chaulmoogra oils, and the ether extract from *Meconium*.

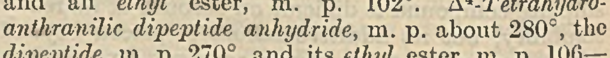
The reaction is not given by cholesterol from various sources, or its derivatives, phytosterol, plant and animal lipoids, olive, cotton-seed, sesamé, nut, walnut, peach, sweet almond, soya-bean, castor, croton, hydnocarpus, and rapeseed oils, the sterols from gallstones, cholic, glycocholic, and taurocholic acids, and the bile acids from ox, pig, and human bile.

H. Burton.

Norcarane. F. Ebel, R. Brunner, and P. Mangelli (Helv. Chim. Acta, 1929, 12, 19—26).—When *cyclo*hexene is treated at 88° with ethyl diazoacetate in presence of copper bronze 53% of *ethyl norcaranecarboxylate*,  $C_4H_8{<}^{CH}_{CH}{>}CH{\cdot}CO_2Et$, b. p. 109—110°/18 mm., is obtained. This is hydrolysed by alcoholic potassium hydroxide to *norcaranecarboxylic acid*, m. p. 97°, the barium salt of which when distilled with barium and zinc oxides yields a mixture, b. p. 111—112°, of *norcarane*, b. p. 110°, and an unsaturated hydrocarbon (about 35%), separable by treatment with benzoyl peroxide.

H. Burton.

Products of the auto-condensation of ethyl hexahydroanthranilate and ethyl Δ^4-tetrahydroanthranilate. F. P. Mazza [with M. Ferrajolo] (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 229—236).—Gradual auto-condensation of ethyl hexahydroanthranilate yields *hexahydroanthranilic dipeptide anhydride*,  $\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CH{\cdot}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}NH{\cdot}CO{\cdot}CH{\cdot}CH_2{\cdot}CH_2\end{matrix}$, m. p. 300—305° (decomp.), which forms a *diacetyl* derivative, m. p. 210—211°, and is hydrolysed by aqueous potassium hydroxide to the *dipeptide*,



$$CH_2{<}\begin{matrix}CH_2\text{——}CH_2\\ CH_2{\cdot}CH(NH_2)\end{matrix}{>}CH{\cdot}CO{\cdot}NH{\cdot}CH{<}\begin{matrix}CH_2\text{———}CH_2\\ CH(CO_2H){\cdot}CH_2\end{matrix}{>}CH_2,$$

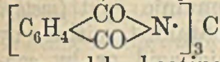
decomp. about 250°; this gives a *copper* salt (+$2H_2O$) and an *ethyl* ester, m. p. 102°. Δ^4-*Tetrahydroanthranilic dipeptide anhydride*, m. p. about 280°, the *dipeptide*, m. p. 270°, and its *ethyl* ester, m. p. 106—108°, were also prepared.

T. H. Pope.

Salts of aromatic nitriles. II. Potassiophenylacetonitrile. M. M. Rising, I. E. Muskat, and E. W. Lowe (J. Amer. Chem. Soc., 1929, 51, 262—265; cf. A., 1928, 881).—Sodiophenylacetonitrile has been previously described (Upson and Thompson, A., 1922, i, 343). Potassium powder and phenylacetonitrile in dry ether in an atmosphere of nitrogen yield yellow *potassiophenylacetonitrile*, which, like the sodio-derivative, reacts in tautomeric forms.

H. E. F. Notton.

Action of phthalic anhydride on triaminoresorcinol. M. Covello [with P. L. Scatola] (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 240—243).—*Triphthalylstyphnamine*,



$\left[C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N\cdot\right]_3C_6H(OH)_2$[1 : 3], m. p. above 300°, prepared by heating triaminoresorcinol hydrochloride with phthalic anhydride in an atmosphere of carbon dioxide, gives, when treated with aqueous potassium hydroxide, *styphnaminotriphthalic acid*, $(CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot)_3C_6H(OH)_2$, m. p. 235°, which forms a *silver* salt, an *acetyl* derivative, m. p. above 300°, and a *benzoyl* derivative, m. p. 275°, and yields phthalimide when oxidised by nitric acid.

T. H. Pope.

Resolution of *dl*-thyroxine. C. R. Harington (Biochem. J., 1928, 22, 1429—1435).—*Formyl*-3 : 5-*di-iodothyronine* (the term thyronine is used for de-iodothyroxine), m. p. 207°, is prepared by treating the racemic di-iodothyronine with formic acid. The racemic formyl derivative was boiled with *l*-phenylethylamine and on cooling an optically impure salt separated, but the mother-liquor yielded fairly pure *formyl*-l-3 : 5-*di-iodothyronine*, $C_{24}H_{21}O_5N_2I_2$, m. p. 214° (decomp.), $[\alpha]_{5461}^{21}$ +27·8°. This was converted by hydrobromic acid into l-3 : 5-*di-iodothyronine*, m. p. 256° (decomp.), $[\alpha]_{5461}^{20}$ −1·3°, from which *l*-thyroxine, m. p. 235—236°, $[\alpha]_{5461}^{21}$ −3·2°, was obtained by iodination (cf. Harington and Barger, A., 1927, 358). The preparation of *d*-thyroxine, m. p. 237° (decomp.), $[\alpha]_{5461}^{21}$ +2·97°, was carried out on similar lines. The *d*-α-phenylethylamine salt of the racemic formyl derivative of di-iodothyronine, m. p. 187—188°, $[\alpha]_{5461}^{19\cdot5}$ −21·9°, was converted into *formyl*-d-3 : 5-*di-iodothyronine*, m. p. 210°, $[\alpha]_{5461}^{21}$ −26·9°, from which d-3 : 5-*di-iodothyronine*, m. p. 256° (decomp.), $[\alpha]_{5461}^{18}$ +1·15°, was obtained and the latter was iodinated.

l-Tyrosine on iodination in ammonia yielded 3 : 5-di-iodotyrosine, $[\alpha]_{5461}^{23}$ +2·6°. *l*-Tyrosine does not suffer racemisation when reduced. *l*-Thyroxine is about three times as active physiologically as its *d*-isomeride.

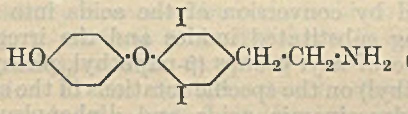
S. S. Zilva.

Derivatives of thyroxine. J. N. Ashley and C. R. Harington (Biochem. J., 1928, 22, 1436—1445).—Glycyl- and *dl*-alanyl-thyroxine have been prepared (*a*) by condensing chloroacetyl chloride and α-bromopropionyl chloride respectively with the methyl ester of 3 : 5-di-iodothyronine followed by hydrolysis of the ester group and iodination, and (*b*) by condensing the acid chlorides with thyroxine methyl ester followed by hydrolysis of the ester group and treatment with ammonia. 3 : 5-*Di-iodothyronine methyl ester hydrochloride*, m. p. 230° (decomp.), is prepared by treating the amino-acid in methyl alcohol with dry hydrogen chloride. From this compound the *methyl* ester, $C_{16}H_{15}O_4NI_2$, m. p. 174—175°, is obtained by neutralisation with sodium hydroxide. By condensing the ester with chloroacetyl chloride in anisole, *chloroacetyl*-3 : 5-*di-iodothyronine methyl* ester, m. p. 160°, was prepared, which by hydrolysis with sodium hydroxide yielded *chloroacetyl*-3 : 5-*di-iodothyronine*, m. p. 166—168°. The latter compound when treated with ammonia gave *glycyl*-3 : 5-*di-iodothyronine*, $C_{17}H_{16}O_5N_2I_2$ (not melted definitely below 290°), which on iodination yielded *glycylthyroxine*, $C_{17}H_{14}O_5N_2I_4$. The following were the stages in the attempted synthesis of the alanyl derivative. α-*Bromopropionyl*-3 : 5-*di-iodothyronine methyl* ester, $C_{19}H_{18}O_5NBrI_2$, m. p. 161—162°, prepared in the same way as the corresponding chloroacetyl compound, by hydrolysis gave α-*bromopropionyl*-3 : 5-*di-iodothyronine*, m. p. 194—195°, which on treatment with ammonia gave dl-*alanyl*-3 : 5-*di-iodothyronine*, m. p. 207°. The iodination of the *dl*-alanyl derivative was not successful.

The second method of synthesis was carried out as follows. *Thyroxine methyl ester hydrochloride*, m. p. 221·5° (decomp.), obtained by treating thyroxine in methyl alcohol with dry hydrogen chloride, on hydrolysis gave *thyroxine methyl* ester, m. p. 156°; this was condensed with chloroacetyl chloride in anisole, giving *chloroacetylthyroxine methyl* ester, m. p. 159—160°, and, by hydrolysis, *chloroacetylthyroxine*, m. p. 201—202° (decomp.). *Glycylthyroxine*, m. p. 188—190° (decomp.), identical with the product obtained by the first method, was prepared by heating the last with ammonia. Similarly, in the synthesis of the alanyl derivative the following compounds were prepared: α-*bromopropionylthyroxine methyl* ester, m. p. 199—201° (decomp.); α-*bromopropionylthyroxine*, m. p. 193—194° (decomp.); *alanylthyroxine*, m. p. 195—200° (decomp.).

N-*Lactylthyroxine*, m. p. 199—200° (decomp.), was prepared by treating with sodium hydroxide N-*acetyllactylthyroxine methyl* ester, $C_{21}H_{19}O_7NI_4$, obtained from acetyl-lactyl chloride and thyroxine methyl ester, in anisole.

The following amines were prepared: by heating 3 : 5-di-iodothyronine with diphenylamine in a current of dry hydrogen, 3 : 5-*di-iodothyronamine* (I), m. p.



(I).

243—245° (*hydrochloride*, m. p. 285—290°), and *thyroxamine*, $C_{14}H_{11}O_2NI_4$, m. p. 207° (decomp.) (*chloroacetate*, $C_{16}H_{14}O_4NCl$, m. p. 152°), by similar decarboxylation of thyroxine, as in the preceding preparation.

Glycyl-, *dl*-alanyl-, and *N*-lactyl-thyroxine are not more soluble in water than thyroxine and consequently do not possess a higher therapeutic value than the parent compound.

S. S. Zilva.

Synthesis of esters of αγ-dicyano-β-benzylglutaconic acid. Y. Urushibara (Bull. Chem. Soc. Japan, 1928, 3, 316—320).—Phenylacetyl chloride condenses with ethyl sodiocyanoacetate in benzene solution with the formation of ethyl α-cyano-γ-phenylacetoacetate, which on ethylation with ethyl iodide afforded ethyl α-cyano-β-ethoxy-γ-phenylcrotonate (cf. Smith and Thorpe, J.C.S., 1907, **91**, 1905). The condensation of the latter with ethyl sodiocyanoacetate in ethyl-alcoholic solution gave the *monohydrate* of *diethyl αγ-dicyano-β-benzylglutaconate*, $CO_2Et\cdot C(CN)\colon C(CH_2Ph)\cdot CH(CN)\cdot CO_2Et$, m. p. 131°, whilst methyl sodiocyanoacetate yielded the *monohydrate* of *methyl ethyl αγ-dicyano-β-benzylglutaconate*, m. p. about 115°. An *isomeride* of the last-named, m. p. about 115°, was produced by the condensation of methyl α-cyano-β-ethoxy-γ-phenylcrotonate and ethyl sodiocyanoacetate. In the above monohydrates, it is supposed that a cyano-group is hydrated to a carbamyl group. A. I. VOGEL.

Phenylsuccinic acid series. IX. Resolution of *r*-diphenylsuccin-α- and -β-naphthylamic acids into their optical antipodes. X. Racemisation phenomena observed during the action of water and bases on optically active diphenylsuccinic anhydrides. H. WREN and E. WRIGHT (J.C.S., 1929, 136—138, 138—141).—IX. r-*Diphenylsuccin-α-naphthylamic acid*, m. p. 217—219° (decomp.) (obtained by interaction of equivalent quantities of *r*-diphenylsuccinic anhydride and α-naphthylamine), was resolved into its optical antipodes by quinine in alcoholic solution, the salt of the *d*-acid being the more sparingly soluble. α-*Diphenylsuccin-α-naphthylamic acid* has m. p. 206—207°, $[\alpha]_D^{16}$ +205·8° in acetone. l-*Diphenylsuccin-α-naphthylamic acid*, m. p. 206—207°, $[\alpha]_D^{17}$ −206·6° in acetone, was separated by means of cinchonidine in alcohol from the crude *l*-acid obtained during resolution of the *r*-acid by quinine. α-*Diphenylsuccin-α-naphthil*, m. p. 145°, $[\alpha]_D^{16}$ +139·2° in acetone, $[\alpha]_D^{17}$ +123·3° in chloroform (prepared by action of 3% ethyl-alcoholic hydrogen chloride on the corresponding acid), was readily racemised by alkali.

α-*Diphenylsuccin-β-naphthylamic acid*, m. p. 188°, $[\alpha]_D^{15.5}$ +386·9° in acetone, was obtained by resolution of the corresponding r-*acid*, m. p. 201—202°, by quinine in alcoholic solution. α-*Diphenylsuccin-β-naphthil*, m. p. 178—179°, $[\alpha]_D^{18}$ ±104·9° in acetone, is described.

The marked diminution in specific rotation occasioned by conversion of the acids into the corresponding substituted imides and the irregularity of influence of aryl groups (β-naphthyl, phenyl, *p*-tolyl, α-naphthyl) on the specific rotations of the substituted diphenylsuccinamic acids and diphenylsuccinimides are pointed out.

X. The conversion of the active diphenylsuccinic anhydrides into the corresponding substituted amic acids by aniline, *p*-toluidine, α- or β-naphthylamine in cold benzene solution was not accompanied by any marked racemisation. The optical activity of the diphenylsuccinic acids which resulted from the action of water on the active anhydrides was found to be greatly influenced by the presence of a mutual solvent; thus from aqueous acetic acid, aqueous ether, aqueous acetone, and aqueous pyridine, acids were derived with the respective specific rotations −364·7° (from *l*-anhydride), +232·7°, +116·7°, and +22·4° (from *d*-anhydride) whereas the homogeneous acids had $[\alpha]_D$ ±383°. The partly racemised products always contained some *meso*diphenylsuccinic acid. This was true also for the mixtures derived from *r*-diphenylsuccinic acid, although, in certain cases, the proportion of *meso*-acid obtained from the *r*-anhydride greatly exceeded that derived from the active anhydrides under identical conditions. The authors consider, therefore, that even in dilute solution the *r*-compound does not behave as a simple mixture of *d*- and *l*-forms. l-*Diphenylsuccin-β-naphthylamic acid*, m. p. 188—188·5°, $[\alpha]_D^{17.5}$ −388·2°, is described.

R. J. W. LE FÈVRE.

Synthesis of *iso*opianic acid. S. N. CHAKRAVARTI and W. H. PERKIN, jun. (J.C.S., 1929, 193—196).—5-Nitro-2 : 3-dimethoxycinnamic acid (*methyl ester*, m. p. 154—155°) is obtained either by nitrating 2 : 3-dimethoxycinnamic acid or by condensing malonic acid and 5-nitro-2 : 3-dimethoxybenzaldehyde in the presence of piperidine. It is smoothly reduced by ferrous sulphate and ammonia to 5-*amino*-2 : 3-*dimethoxycinnamic acid*, m. p. 233° (decomp.), which is converted through the diazo-compound into 5-*cyano*-2 : 3-*dimethoxycinnamic acid*, m. p. 251°. The cyano-acid is oxidised by potassium permanganate in presence of benzene to 5-*cyano*-2 : 3-*dimethoxybenzaldehyde*, m. p. 135°, which when heated with hydrochloric acid is converted into *iso*opianic acid. R. J. W. LE FÈVRE.

Aldehydes from acetylenic carbinols. IV. 3-Methyl-6-*iso*propyl*cyclo*hexylideneacetaldehyde. H. RUPE and A. GASSMANN (Helv. Chim. Acta, 1929, **12**, 193—204).—The action of acetylene on *d*-menthone in presence of benzene and sodamide yields 3-*methyl*-6-iso*propyl*-1-*ethinyl*cyclo*hexan*-1-*ol*, b. p. 101·5—102·5°/12·5 mm., d_4^{20} 0·9257, $[\alpha]_D^{20}$ +5·08° (*silver* derivative), which when heated with 5 parts of 71% formic acid changes to 3-*methyl*-6-iso*propyl*cyclo*hexylideneacetaldehyde* (I), b. p. 111°/12·5 mm., d_4^{20} 0·9115, $[\alpha]_D^{20}$ +82·9° (*semicarbazone*, m. p. 146—147°), the *oxime*, m. p. 101°, $[\alpha]_D^{20}$ +103·09° in benzene, of which is hydrolysed by aqueous oxalic acid, forming menthone. Magnesium ethyl bromide converts I into a mixture of 3-*methyl*-6-iso*propyl*cyclo*hexylethylcarbinol*, b. p. 125°/12 mm., and α-3-*methyl*-6-iso*propyl*cyclo*hexylidene*-Δ^β-*butene*, $C_{10}H_{18}\colon CH\cdot CH\colon CHMe$, b. p. 99°/12 mm. Oxidation of I with alkaline potassium permanganate yields β-methyladipic and δ-*iso*butyryl-β-methyl-*n*-valeric acids (*semicarbazone*, m. p. 152°), whilst reduction with hydrogen and a nickel catalyst gives 3-*methyl*-6-iso*propyl*cyclo*hexylacetaldehyde*, b. p. 106—107°/12 mm., d_4^{20} 0·9032, n_D^{20} 1·46111, $[\alpha]_D^{20}$ −51·28°, purified through its *semicarbazone*, decomp. 222° (*oxime*, m. p. 102°, $[\alpha]_D^{20}$ +34·11°), together with the corresponding alcohol. H. BURTON.

Arylidene 2 : 4-diphenylsemicarbazones from aldehydephenylhydrazones and phenylcarbimide. G. MINUNNI and S. D'URSO [with S. GUGLIELMINO, P. SALANITRO, D. TORRISI, and M. VASTA] (Gazzetta, 1928, 58, 808—820).—The interaction of benzaldehydephenylhydrazone and phenylcarbimide to give benzaldehyde-2 : 4-diphenylsemicarbazone, $CHPh\colon N\cdot NPh\cdot CO\cdot NHPh$ (cf. Busch and Walter, A., 1903, i, 522), proceeds readily in benzene solution. In hot solution, the semicarbazone (new m. p. 174—175°) and some *s*-diphenylcarbamide are obtained; in the cold the former is produced more slowly, but in better yield, together with two yellow secondary *products*, one, a mixture, having m. p.

175—188°, and the other m. p. 194—196°. The semicarbazone is readily reduced to *s*-diphenylcarbamide, with a *substance*, m. p. 116—118°; when treated with phenylhydrazine it yields benzaldehydephenylhydrazone and other products.

o- and *m*-Nitrobenzaldehydephenylhydrazones do not react satisfactorily in benzene; with phenylcarbimide alone the corresponding *semicarbazones* are formed, m. p. 190—192° (decomp.) and 206—208° (decomp.), respectively, identified by reduction to the carbamides. The *p*-isomeride reacts very slowly in benzene, and more rapidly without solvent, giving the corresponding *semicarbazone*, m. p. 199—201°; piperonalphenylhydrazone gives, in cold benzene, *piperonal*-2 : 4-*diphenylsemicarbazone*, m. p. 169—169·5° (decomp.).
E. W. Wignall.

Action of bromine on some hydrazones. II. R. Ciusa and P. Mega (Gazzetta, 1928, 58, 831—840).—The compound described by Ciusa and Vecchiotti (A., 1916, i, 437) as *p*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone is found to be ω-*bromobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, since its aliphatic bromine atom will react with aniline, or can be determined by titration after boiling with sodium acetate in alcohol; the formation of *p*-bromobenzoic acid during oxidation must be attributed to bromination during the oxidation process, since benzoic acid is also formed. Similarly, anisaldehyde gives rise to ω-*bromoanisaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 135°, and benzaldehyde-*p*-nitrophenylhydrazone to *benzaldehyde*-2-*bromo*-4-*nitrophenylhydrazone*, m. p. 171°; in each of these compounds the bromine may be determined as above, the second giving, with sodium acetate and acetic acid, the O-*acetyl* derivative of N-*benzoyl*-N′-2-*bromo*-4-*nitrophenylhydrazine*. The benzoyl group of the last compound may be removed by boiling with hydrochloric acid and alcohol, giving rise to 2-*bromo*-4-*nitrophenylhydrazine*, m. p. 143° (*benzaldehyde*-2-*bromo*-4-*nitrophenylhydrazone*, m. p. 166°). *m*-Nitrobenzaldehyde-*p*′-nitrophenylhydrazone is brominated to ω-*bromo*-m-*nitrobenzaldehyde*-2-*bromo*-4-*nitrophenylhydrazone*, m. p. 212—213°, from which the above hydrazine may again be prepared. Finally, the same hydrazine is synthesised by brominating the benzoyl derivative of *p*-nitroaniline, hydrolysing the product, and diazotising and reducing the 2-bromo-4-nitroaniline thus obtained.
E. W. Wignall.

Trichloro- and tetrabromo-nitrobenzaldehydes, hexachloro- and octabromo-indigotins. C. van de Bunt (Rec. trav. chim., 1929, 48, 121—146).—3 : 4 : 5-*Tribromocinnamic acid*, m. p. 215—216°, and its 2-*nitro*-derivative, m. p. 264—265° (decomp.), are obtained from the corresponding benzaldehydes by the Perkin reaction. Treatment of both these acids with warm absolute nitric acid yields 3 : 4 : 5-*tribromo*-2-ω-*dinitrostyrene*, m. p. 228—230° (decomp.), which could not be reduced successfully to tribromoindole (cf. van der Lee, A., 1926, 179). When 3 : 4 : 5-tribromobenzaldehyde is treated with a mixture of absolute nitric and concentrated sulphuric acids at 100°, 3 : 4 : 5-*tribromo*-2 : 6-*dinitrobenzoic acid*, m. p. 245—248° (decomp.), is obtained. When crystallised from boiling alcohol this acid eliminates carbon dioxide, yielding 4 : 5 : 6-tribromo-1 : 3-dinitrobenzene. Chlorination of *p*-aminobenzaldehyde hydrochloride in 75% acetic acid solution gives 3 : 5-*dichloro*-4-*aminobenzaldehyde*, m. p. 144° [*phenylhydrazone*, m. p. 156—157°; p-*nitrophenylhydrazone*, m. p. 288—289° (decomp.); *semicarbazone*, m. p. 248—250° (decomp.); *semioxamazone*, m. p. 269—270°; *azine*, m. p. 285—286°], chlorinated further to 2 : 4 : 6-trichloroaniline, and converted by the Sandmeyer reaction into 3 : 4 : 5-*trichlorobenzaldehyde*, m. p. 90—91° [*phenylhydrazone*, m. p. 147°; p-*nitrophenylhydrazone*, m. p. 342° (decomp.); *semicarbazone*, m. p. 252—254°, resolidifying with m. p. 284°; *semioxamazone*, m. p. 297—298° (decomp.); *azine*, m. p. 289—289·5°]. Nitration of this with cold absolute nitric acid yields 3 : 4 : 5-*trichloro*-2-*nitrobenzaldehyde* (I), m. p. 118·5—119° [*phenylhydrazone*, yellow and red, m. p. 229° (decomp.), modifications; p-*nitrophenylhydrazone*, m. p. 293—294° (decomp.); *semicarbazone*, m. p. 278—279° (decomp.); *semioxamazone*, m. p. 303—304° (decomp.); *azine*, m. p. 287—288° (decomp.)], oxidised by alkaline potassium permanganate to 3 : 4 : 5-*trichloro*-2-*nitrobenzoic acid*, m. p. 181—181·5°, and converted by absolute nitric and concentrated sulphuric acids into 3 : 4 : 5-*trichloro*-2 : 6-*dinitrobenzoic acid*, m. p. 219—221·5°. This acid also eliminates carbon dioxide in boiling alcoholic solution, forming 4 : 5 : 6-trichloro-1 : 3-dinitrobenzene. 3 : 4 : 5-Trichlorobenzoic acid has m. p. 210—210·5° (lit. 203°).

Nitration of 2 : 3 : 4 : 5-tetrabromobenzaldehyde with a mixture of absolute nitric and concentrated sulphuric acids at 50—60° affords 3 : 4 : 5 : 6-*tetrabromo*-2-*nitrobenzaldehyde* (II), m. p. 225—227° (decomp.) after previous darkening and sintering, whilst oxidation with potassium permanganate gives 2 : 3 : 4 : 5-*tetrabromobenzoic acid*, m. p. 234° (slight decomp.). This last compound is nitrated to 3 : 4 : 5 : 6-*tetrabromo*-2-*nitrobenzoic acid*, m. p. 238—240° (decomp.), which does not lose carbon dioxide when its alcoholic solution is boiled. 2 : 4-*Dichloro*-3 : 5-*dibromobenzaldehyde*, m. p. 110—111°, prepared by the Sandmeyer reaction from the 2-chloro-4-amino-compound, is nitrated to 4 : 6-*dichloro*-3 : 5-*dibromo*-2-*nitrobenzaldehyde* (III), m. p. 198—199°.

Conversion of the halogeno-2-nitrobenzaldehydes into the polyhalogenated indigotins is effected by warming with acetone and sodium hydroxide solution. Thus, 5 : 5′ : 6 : 6′ : 7 : 7′-*hexachloro*-, 4 : 4′ : 5 : 5′ : 6 : 6′ : 7 : 7′-octabromo-, and 4 : 4′ : 6 : 6′-*tetrachloro*-5 : 5′ : 7 : 7′-*tetrabromo-indigotins* are obtained from I, II, and III, respectively.
H. Burton.

Products with an odour of musk and carbon rings containing a large number of linkings. L. Ruzicka (Bull. Soc. chim., 1928, [iv], 43, 1145—1173).—A lecture surveying recent work on the constitution of muscone and civetone, and the synthesis and behaviour of carbon ring systems containing a large number of linkings (cf. A., 1926, 614, 615, 726, 727, 1142; 1927, 1189; 1928, 642, 887). In further elucidation of the constitution of muscone, it is shown that neither the *d*-β-methyltridecane-αν-dicarboxylic acid, m. p. 69°, obtained by condensation with benzaldehyde and treatment of the benzylidenemuscone with ozone and chromic acid nor its methyl ether can be racemised, and the inactivity of the mixture of two acids, $C_{16}H_{30}O_4$, obtained by oxidation of muscone is consequently due to mutual compensation of the two acids. Muscone is thus regarded as *l*-2-methyl*cyclo*pentadecanone (cf. A., 1926, 1143). dl-2-*Methyltridecane-αν-dicarboxylic acid* obtained by synthesis has m. p. 76° (*anilide*, m. p. 133°), but shows no depression of m. p. when mixed with the degradation product of muscone. The molten acid on solidifying has m. p. 10° lower. Oxidation of exaltone with persulphuric acid affords the *lactone* of *o*-hydroxypentadecoic acid (exaltolide).

R. BRIGHTMAN.

3 : 5-Diphenyl*cyclo*hexenone. A. D. PETROV (J. Russ. Phys. Chem. Soc., 1928, **60** 1441—1445).—The reactions of 3 : 5-diphenyl*cyclo*hexenone with hydrogenating and dehydrogenating agents have been investigated. By hydrogenating the ketone at 240°/50 atm. in presence of nickel oxide as catalyst, 1 : 3-di*cyclo*hexyl*cyclo*hexane was obtained in two isomeric forms, m. p. 66° and b. p. 202°/14 mm., respectively. By heating the ketone at 300° in presence of platinised charcoal, 3 : 5-diphenylphenol, m. p. 88—92°, was obtained, whilst reduction with absolute alcohol and metallic sodium gave a 50% yield of 3 : 5-diphenyl*cyclo*hexanol, m. p. 127°, easily oxidised to 3 : 5-diphenyl*cyclo*hexanone, m. p. 139—140°.

M. ZVEGINTZOV.

Use of zirconium tetrachloride in organic synthesis. P. KRISHNAMURTI (J. Madras Univ., 1928, [Reprint], 5 pages).—Zirconium tetrachloride may be used in place of aluminium chloride in condensations involving (*a*) elimination of hydrogen chloride (preparation of acetophenone, benzophenone, anisaldehyde, and diphenylmethane), (*b*) elimination of water (phenolphthalein), (*c*) elimination of alkyl halide (demethylation of anisole), and (*d*) condensations of phenylcarbimide with benzene and its derivatives. It is more easy to handle and more readily preserved than the older reagent.

J. W. BAKER.

Reduction of phenyl naphthyl ketones by the binary system, magnesium–magnesium iodide. W. E. BACHMANN and R. V. SHANKLAND (J. Amer. Chem. Soc., 1929, **51**, 306—309).—Phenyl α-naphthyl ketone is reduced by the above system to an equilibrium mixture (I) of the green *ketyl* $-CPh(C_{10}H_7)\cdot OMgI$, and its *dimeride*, which is converted by water into *αβ-diphenyl-αβ-di-α-naphthylethylene glycol* (II), m. p. 220° (decomp.). When heated with acetyl chloride this is almost quantitatively converted into *benzoylphenyldi-α-naphthylmethane*, m. p. 216—217°, the naphthyl group wandering in preference to the phenyl. The second αβ-diphenyl-αβ-di-α-naphthylethylene glycol, m. p. 158° (Cohen, A., 1919, i, 124, 210), may be transformed into II by treatment with a Grignard reagent, when the radical formed by dissociation of the resulting iodomagnesium glycoloxide changes into I and is then decomposed by water. The second isomeride is converted by acetyl chloride into a *substance*, $C_{34}H_{24}O$, m. p. 232°, which is also formed from phenyl α-naphthyl ketone, zinc, and acetyl chloride and, unlike most pinacolins, is only slightly attacked by boiling alcoholic potassium hydroxide. Phenyl β-naphthyl ketone is reduced by the binary system, or by zinc and acetic acid to *αβ-diphenyl-αβ-di-β-naphthylethylene glycol*, m. p. 175°, which undergoes naphthyl wandering in presence of acetyl chloride, giving *benzoylphenyldi-β-naphthylmethane*, m. p. 181—182°.

H. E. F. NOTTON.

Organic compounds of sulphur. XI. Comparison of the tendency of polymeric thioketones towards dissociation with that of the corresponding compounds of the ethane series. A. SCHÖNBERG (Ber., 1929, 62, [*B*], 195—199; cf. A., 1928, 896, 1375).—Replacement of the phenyl groups of hexaphenylethane by hydrogen or methyl causes a stabilisation of the ethane linking; the same effect is observed when the phenyl groups of the hypothetical hexaphenyltrithian are substituted by hydrogen or methyl. In both series the effect of hydrogen is more marked than that of methyl. If two phenyl groups of triphenylmethyl are replaced by the substituted methylene residue, radicals are obtained which cannot exist "free"; this is also the case with thioketones. Complete or partial replacement of the phenyl groups of hexaphenylethane by the radicals, *p*-$OMe\cdot C_6H_4-$, $Ph\cdot C_6H_4-$, $C_6H_4{<}\overset{O}{}{>}C_6H_4$, *o*-$OMe\cdot C_6H_4-$, $NMe_2\cdot C_6H_4-$, $C_6H_4{<}\overset{S}{\underset{O}{}}{>}C_6H_4$, leads to compounds with a tendency towards dissociation similar to or greater than that of hexaphenylethane itself. As expected, replacement of the phenyl groups of thiobenzophenone by these radicals leads to compounds which, like thiobenzophenone, do not tend to polymerise. In the ethane series, the substituted vinyl group behaves similarly to the phenyl group; this is also the case with thioketones. If one or two phenyl groups of thiobenzophenone are replaced by substituted vinyl groups, thioketones are produced which do not tend to polymerise. On the other hand, attempts to convert *cyclo*hexanone into the corresponding thioketone give trithio*cyclo*hexanone, which does not become depolymerised when heated. The close analogy can be explained only by the hypothesis that the dissociation of ethanes and polymeric thioketones is produced and regulated by the same causes.

H. WREN.

Benzoinanilanilide and benzoin-*p*-tolil-*p*-toluidide as ammono-benzoin acetals. H. H. STRAIN (J. Amer. Chem. Soc., 1929, **51**, 269—273).—The formulation of these compounds as ammono-acetals of benzoin (cf. A., 1928, 1134) is in accordance with the following reactions. Benzoinanilanilide is hydrolysed by boiling alcoholic hydrochloric acid to benzoinanilide and aniline, and benzoin-*p*-tolil-*p*-toluidide to benzoin-*p*-toluidide and *p*-toluidine. They are nitrised by iodine in liquid ammonia, or in benzene by a current of air, to the ammono-benzils, benzildianil and benzildi-*p*-tolil. Ammonolysis by liquid ammonia at 130° for 10 hrs. affords a small yield of tetraphenylpyrazine, m. p. 252°. The mechanism proposed by Bischler (A., 1893, i, 519) for the formation of 2 : 3-diphenylindole from benzoin and aniline is confirmed by the almost quantitative conversion of benzoinanilanilide into this compound in benzene in presence of hydrogen chloride at 180—200°.

Benzoin-*p*-tolil-*p*-toluidide similarly yields 2 : 3-diphenyl-5-methylindole. H. E. F. NOTTON.

Persistence of optical activity during elimination of water from optically active glycols. II. Production of optically active ketones by semipinacolinic transformation. R. ROGER and A. MCKENZIE (Ber., 1929, 62, [*B*], 272—284).—Ethyl *l*-mandelate is converted by magnesium benzyl chloride into d-2-*hydroxy*-2-*phenyl*-1 : 1-*dibenzylethanol*, m. p. 136—137°, $[\alpha]_D^{14}$ +80·3° in ethyl alcohol, $[\alpha]_D^{16}$ +62·3° in chloroform, $[\alpha]_D^{20}$ +96·8° in acetone. The glycol is converted by concentrated sulphuric acid into *r*-*αγ*-diphenyl-*γ*-benzylacetone, m. p. 74·5—75·5°; this product is also obtained when the action is effected by boiling, dilute sulphuric acid, but is then accompanied by d-*αγ-diphenyl-γ-benzylacetone*, m. p. 77—78°, $[\alpha]_{5463}^{20}$ +208° in benzene, $[\alpha]_{5463}^{16}$ +202° in chloroform (among other values), and 1-phenyl-2-benzylindene, m. p. 100—102°, which appears to become isomerised to a product, m. p. 95—96°, when crystallised repeatedly from ethyl alcohol. The optically active ketone is racemised by concentrated sulphuric acid or by alcoholic potassium hydroxide; the latter change appears to be unimolecular. *d*-Methyldeoxybenzoin is likewise racemised by concentrated sulphuric acid. The first phase of the elimination of water from the *d*-glycol appears to consist of a semipinacolinic transformation yielding the *d*-ketone which, after transitory production of the sulphuric ester of the corresponding substituted vinyl alcohol, passes into the optically inactive ketone. The observation that triphenylacetaldehyde is converted by acids into phenyldeoxybenzoin suggests the possibility that aldehydes are intermediate products in the transformation of glycols to ketones in acid media (cf. Danilov and Venus-Danilova, A., 1927, 460; Tiffeneau and Orékhov, A., 1926, 171, 172). In the present instance and that recorded by McKenzie and Dennler (A., 1927, 243), the intermediate formation of the corresponding aldehyde is impossible, since the compound would be optically inactive owing to the absence of an asymmetric carbon atom and thus could not give rise to an optically active ketone. The preservation of optical activity during the formation of the *d*-ketone has its parallel in the elimination of the amino-group from optically active amino-alcohols (cf. McKenzie, Roger, and Wills, A., 1926, 610). It is suggested that in this transformation an electric charge plays the part of a group, so that the dissymmetry of the molecule remains undisturbed.

l-Benzoin is transformed by magnesium benzyl chloride into l-*benzylhydrobenzoin* (l-β-*hydroxy*-αβ-*diphenyl*-α-*benzylethanol*), m. p. 183—184·5°, $[\alpha]_{5463}^{20}$ −61° in chloroform, $[\alpha]_{5463}^{20}$ −22° in acetone (among other values), which is converted by protracted action of boiling acetyl chloride into 2 : 3-diphenylindene, m. p. 176—177°, isomerised by alcoholic potassium hydroxide to 1 : 2-diphenylindene, m. p. 107—108°; the last-mentioned compound is not affected by the protracted action of boiling acetyl chloride.

H. WREN.

Elimination of the amino-group from tertiary amino-alcohols. V. Semipinacolinic de-amination and Walden inversion. A. MCKENZIE and A. K. MILLS (Ber., 1929, 62, [*B*], 284—288; cf. A., 1927, 457).—Ethyl *l*-phenylaminoacetate hydrochloride is converted by magnesium benzyl chloride into d-β-*amino*-β-*phenyl*-αα-*dibenzylethanol*, $(CH_2Ph)_2C(OH)\cdot CHPh\cdot NH_2$, m. p. 144—145°, $[\alpha]_D^{17}$ +59·2° in chloroform, which is transformed by sodium nitrite in dilute acetic acid solution into a mixture of *d*-*αγ*-diphenyl-*γ*-benzylacetone, m. p. 77·5—78°, $[\alpha]_D^{16}$ +283° in benzene, and *d*-β-hydroxy-β-diphenyl-αα-dibenzylethanol, m. p. 136—137°, $[\alpha]_D^{16}$ +81° in ethyl alcohol, identical with the product obtained by Roger and McKenzie (preceding abstract). A further instance in favour of the semipinacolinic transformation and against the intermediate production of an aldehyde is afforded, since phenyldibenzylacetaldehyde could not yield an optically active ketone. H. WREN.

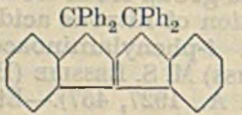
Elimination of the amino-group from tertiary amino-alcohols. VI. Action of nitrous acid on the amino-alcohols from *l*-phenylaminoacetic acid. A. MCKENZIE and (MISS) M. S. LESSLIE (Ber., 1929, 62, [*B*], 288—295; cf. A., 1927, 457).—Ethyl *l*-mandelate is converted by a slight excess of magnesium ethyl bromide into l-β-*hydroxy*-β-*phenyl*-αα-*diethylethanol*, m. p. 48—48·5°, $[\alpha]_D$ −26° in ethyl alcohol, $[\alpha]_D$ −32° in acetone. From ethyl *l*-phenylaminoacetate hydrochloride and magnesium ethyl bromide, l-β-*amino*-β-*phenyl*-αα-*diethylethanol hydrochloride*, m. p. 225—226°, $[\alpha]_D^{17}$ −28·7° in water, $[\alpha]_D^{16}$ −17° in ethyl alcohol, is derived. The amino-alcohol is converted by nitrous acid into a mixture of *r*-β-hydroxy-β-phenyl-αα-diethylethanol, m. p. 88—89°, and a substance which is dextrorotatory in ethyl alcohol; the optical activity cannot be ascribed to the ketone, Et·CO·CHPhEt, formed by semipinacolinic deamination, since it persists unchanged after addition of alcoholic potassium hydroxide.

Ethyl *r*-phenylaminoacetate hydrochloride is transformed by magnesium methyl iodide into r-β-*amino*-β-*phenyl*-αα-*dimethylethanol*, m. p. 82·5—83·5° (*hydrochloride*, m. p. 173—175°), from which methyl α-phenylethyl ketone is obtained by means of nitrous acid. The dissimilar course of the change in the cases of the dimethyl and diethyl derivatives is attributed to the superior saturating capacity of the methyl group, which causes a less firm union of hydroxyl to carbon in the methyl compound. Somewhat unexpectedly, r-β-*amino*-β-*phenyl*-αα-*di*-n-*propylethanol hydrochloride*, m. p. 210—212° (from ethyl *r*-phenylaminoacetate hydrochloride and magnesium *n*-propyl bromide), is converted by nitrous acid into *r*-β-hydroxy-β-phenyl-αα-di-*n*-propylethanol, m. p. 100—102°. Ethyl *d*-mandelate and magnesium *n*-propyl bromide afford d-β-*hydroxy*-β-*phenyl*-αα-*di*-n-*propylethanol*, m. p. 67—68°, $[\alpha]_D^{20}$ +26·4° in ethyl alcohol. l-β-*Amino*-β-*phenyl*-αα-*di*-n-*propylethanol*, m. p. 120—121°, $[\alpha]_D^{18}$ −93·4° in ethyl alcohol (from ethyl *l*-phenylaminoacetate hydrochloride and magnesium *n*-propyl bromide), is transformed by nitrous acid into a mixture of *r*- and *d*-β-hydroxy-β-phenyl-αα-*di*-*n*-propylethanol; the presence of the corresponding optically active ketone is excluded, since the activity of the product remains unchanged after treatment with alcoholic potassium hydroxide. H. WREN.

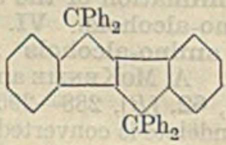
Phenylindene series. I. 3 : 3-Diphenylhydrindone. C. Moureu, C. Dufraisse, and P. M. Dean (Bull. Soc. chim., 1928, [iv], 43, 1367—1371).—βββ-Triphenylpropionic acid, m. p. 179—180°, obtained in 76% yield by condensing triphenylcarbinol with malonic acid in presence of acetic anhydride at 170—180° (cf. Fosse, A., 1907, i, 764), is converted into 3 : 3-*diphenylhydrindone*, m. p. 129—130° (*oxime*, m. p. 155—156°), when warmed with sulphuric acid below 70°.
R. Brightman.

Phenylindene series. II. Conversion of 3 : 3-diphenylhydrindone into 2 : 3-diphenylindone. C. Moureu, C. Dufraisse, and F. Baylocq (Bull. Soc. chim., 1928, [iv], 43, 1371—1380).—To obtain confirmation of the structure advanced for rubrene (A., 1928, 53, 594, 628, 996, 1127) the synthesis of the isomeric hydrocarbons I and II from 3 : 3-diphenylhydrindone has been attempted. The action of phosphorus pentabromide on 3 : 3-diphenylhydrindone or on its *monobromo*-derivative, m. p. 154—155°, gives a *dibromo*-derivative, m. p. 205°, $C_6H_4\cdot CPh_2\cdot CBr_2CO$, in which the methylene hydrogen atoms are substituted, and accordingly the acetylene, $C_6H_4\cdot CPh_2\cdot C⋮C$, cannot be obtained by the usual methods. Phosphorus tribromide converts the dibromo-ketone into a *substance*, m. p. 143—144°, neither the tetrabromide $-CBr_2\cdot CBr_2-$, nor the dibromide, $-CBr⋮CBr-$, being obtained. When heated at 200°, 3 : 3-diphenylhydrindone, and its mono- and dibromo-derivatives are converted into 2 : 3-diphenylindone (yield 75% with the monobromo-ketone), the yield being improved in presence of sulphur with unsubstituted and of iron with the dibromo-ketone, a transformation which throws doubt on the structure of 3 : 3-diphenylhydrindone. Amyl nitrite and sodium ethoxide in alcohol convert the latter into an *oximino*-derivative, m. p. 220°, which with acetic acid and nitrosyl sulphate (cf. Bouveault and Locquin, A., 1904, i, 847) affords a *substance* (N 7·98%), m. p. 164—165° (decomp.), and not the expected diketone. βββ-*Triphenylpropionyl chloride*, m. p. 120°, in presence of aluminium chloride in carbon disulphide at 50° is converted into 3 : 3-diphenylhydrindene. The yields of 2 : 3-diphenylindene claimed by Orékhov (A., 1920, i, 235) on heating the dibromide (m. p. 154—155°; cf. Stobbe and Niedenzu, A., 1902, i, 103) of benzylidenedeoxybenzoin were not obtained.
R. Brightman.

(I.)



(II.)

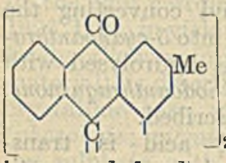


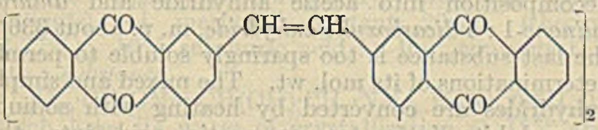
Phenylindene series. III. Derivatives of 2 : 3-diphenylindone. C. Moureu, C. Dufraisse, and M. Badoche (Bull. Soc. chim., 1928, [iv], 43, 1381—1388).—With phosphorus pentachloride at 165—170° 2 : 3-diphenylindone gives (yield 61%) a *dichloro*-derivative, $C_{21}H_{14}OCl_2$, m. p. 132—133°, from which with copper in benzene or magnesium in ether 2 : 3-diphenylindone is regenerated. Alcoholic potassium hydroxide removes only half of the chlorine, yielding a *substance*, m. p. 148—160°. Sodium in ether yields a *substance*, $C_{21}H_{16}O_2$, m. p. 127—128°, identical with that obtained, together with a *substance*, $C_{21}H_{16}O$, m. p. 87—88° (cf. Schlenk and Bergmann, A., 1928, 1031), by the action of sodium on 2 : 3-diphenylindone. The former, $C_{21}H_{16}O_2$, with phosphorus pentoxide or zinc chloride loses 1 mol. of water and is re-converted into 2 : 3-diphenylindone, but its structure is undetermined. The second compound is also obtained by the action of iron and acetic acid on 2 : 3-diphenylindone or its dichloro-derivative, and is possibly stereoisomeric with Schlenk and Bergmann's compound. When heated with lead oxide it is converted into 2 : 3-diphenylindone.
R. Brightman.

Diphthalimidobenzoquinones. M. Covello [with S. Palma] (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 149—151).—2 : 3-, 2 : 5-, and 2 : 6-*Diphthalimidoquinols*, m. p. 250—300° (decomp.), obtained by condensation of the corresponding diaminoquinols with phthalic anhydride, yield, when oxidised with nitric acid (*d* 1·4): 2 : 3-, m. p. 320°; 2 : 5-, m. p. 305°, and 2 : 6-*diphthalimidobenzoquinone*, m. p. 277°.
T. H. Pope.

Dehydration of *o*-benzoylbenzoic acid. A. H. Gleason and G. Dougherty (J. Amer. Chem. Soc., 1929, 51, 310—315).—Many substances, all of which are inferior to sulphuric acid, have been tried as catalysts in the condensation of benzoylbenzoic acid to anthraquinone. In presence of 96% sulphuric acid (6—10 parts) the reaction is unimolecular at 65—85° and k_{t+10}/k_t is greater than 3. Using 86—96% sulphuric acid, the reaction velocity is proportional to the initial concentration of the acid. Methyl, ethyl, and *iso*propyl *o*-benzoylbenzoates are converted into anthraquinone by sulphuric acid with approximately equal ease, the yield being slightly lower than from the free acid. Esters of the higher alcohols give poor yields. The acetate of enolic benzoylbenzoic acid condenses as readily as does the free acid itself. These results are explained by assuming that all the above compounds are rapidly transformed by sulphuric acid into the hydrogen sulphate of enolic benzoylbenzoic acid, which then passes with measurable velocity into a sulphuric acid additive product of anthraquinone. The smaller reaction velocity observed with the esters is due to the action of the alcohols on part of the sulphuric acid.
H. E. F. Notton.

Anthracene derivatives. III. Derivatives of 2-methylanthraquinone and anthraflavone. P. Ruggli and E. Merz (Helv. Chim. Acta, 1929, 12, 71—99).—Bromination of 1-iodo-2-methylanthraquinone in nitrobenzene solution at 160—170° gives 1-*iodo-2-dibromomethylanthraquinone*, m. p. 210°. The crude bromination product can be freed from the monobromomethyl derivative by warming with pyridine, when some 1-*iodo-2-anthraquinonylmethylpyridinium bromide* is formed. Similarly, the crude bromination product of 1-nitro-2-methylanthraquinone affords 1-*nitro-2-anthraquinonylmethylpyridinium bromide*, m. p. 262—269° (decomp.), together with the unaffected 2-dibromomethyl derivative. When 5 : 6 : 7 : 8-tetrachloro-2-dibromomethylanthraquinone is treated with copper powder (Naturkupfer C) in boiling nitrobenzene solution, s-*di*-(5 : 6 : 7 : 8-*tetrachloro-2-anthraquinonyl)ethylene*, m. p. above 300°, is obtained; no 1 : 1′-dianthraquinonyl derivative is formed by elimination of chlorine. 4-Bromo-1-amino-2-methylanthraquinone is converted by the usual method into 1-*bromo*-3-*methylanthraquinone* (I), m. p. 199—200°, which when treated with *p*-toluenesulphonamide in presence of amyl alcohol, anhydrous sodium acetate, and a trace of copper acetate yields 1-p-*toluenesulphonamido*-3-*methylanthraquinone*, m. p. 232—233°. This is hydrolysed by warm concentrated sulphuric acid to 1-*amino*-3-*methylanthraquinone*, m. p. 193°. Treatment of I with *p*-toluidine and anhydrous potassium acetate affords 1-p-*toluidino*-3-*methylanthraquinone*, m. p. 174—175°, whilst interaction with sodium sulphide in 80% alcoholic solution and atmospheric oxidation of the resulting violet solution yields 3 : 3′-*dimethyl*-1 : 1′-*dianthraquinonyl disulphide*. This is oxidised by concentrated nitric acid, giving 3-*methylanthraquinone*-1-*sulphonic acid* $+2H_2O$ (*potassium* salt), which when treated with hydrochloric acid and sodium chlorate affords 1-*chloro*-3-*methylanthraquinone* (II), m. p. 186—188°. When I is treated with copper powder in boiling nitrobenzene solution, 3 : 3′-*dimethyl*-1 : 1′-*dianthraquinonyl*, m. p. 354—355°, is produced. When a solution of this last compound in concentrated sulphuric acid is treated with copper powder at 55°, 3 : 3′-*dimethylhelianthrone* (3 : 3′-*dimethylmesobenzdianthrone*) (annexed formula), not melted at 300°, is obtained. Bromination of I in nitrobenzene solution at 150—160° gives 1-*bromo*-3-*dibromomethylanthraquinone*, m. p. 214—215°, which when treated with copper powder furnishes 4 : 4′-*dianthraflavone*, m. p. above 300°. Similar bromination of II yields 1-*chloro*-3-*dibromomethylanthraquinone*, m. p. 223—224°, which with copper powder yields s-*di*-(4-*chloro*-2-*anthraquinonyl)ethylene*, m. p. above 300°.





Treatment of 4-bromo-2-methylanthraquinone-1-diazonium sulphate with potassium thiocyanate gives 1 : 4-*dithiocyano-2-methylanthraquinone* (III), m. p. 250—251°, which is converted by hot aqueous-alcoholic potassium hydroxide solution into 1 : 4-dithiol-2-methylanthraquinone, isolated as the *diethyl ether*, m. p. 195—205° (*dibenzyl ether*). Oxidation of III with boiling concentrated nitric acid affords 2-*methylanthraquinone*-1 : 4-*disulphonic acid*, $+3H_2O$ (*potassium* salt), converted by treatment with hydrochloric acid and sodium chlorate into 1 : 4-*dichloro-2-methylanthraquinone*, m. p. 185—186°. This on bromination yields 1 : 4-*dichloro-2-dibromomethylanthraquinone*, m. p. 180—181°, whilst treatment with *p*-toluenesulphonamide in presence of amyl alcohol, anhydrous sodium acetate, and a trace of copper acetate gives 1 : 4-*di*-p-*toluenesulphonamido-2-methylanthraquinone*, m. p. 206—207°. Hydrolysis of this with hot concentrated sulphuric acid affords 1 : 4-diamino-2-methylanthraquinone, m. p. 246—248°.

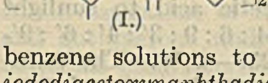
H. Burton.

Inductive method for study of natural products. I. Naturally occurring anthraquinone derivatives. P. C. Mitter and H. Biswas (J. Indian Chem. Soc., 1928, 5, 769—778).—Examination of the naturally occurring substituted anthraquinones shows empirically that not more than four groups are present in the benzene rings. Not more than three of these groups are hydroxyl and only one is methyl, hydroxymethyl, or carboxyl. Two of the substituents occupy α-positions and two (including methyl, hydroxymethyl, or carboxyl) occupy β-positions. If both β-substituents are in one ring then the other groups are in the same nucleus, but if they are in different rings the α-substituents are arranged symmetrically. Four fundamental types of anthraquinone derivatives are postulated, viz., 1 : 2 : 3-trihydroxy- (chayroot), 1 : 2 : 4-trihydroxy-3-methyl- (madder), 1 : 3 : 8-trihydroxy-6-methyl- (emodin), and 1 : 2 : 5-trihydroxy-6-methyl- (morindone). The products actually isolated from different plants conform, except in one or two doubtful cases, to the above types. The alizarin grouping occurs in three of the types.

1 : 5-*Dimethoxy*-6-*methylanthraquinone*, m. p. 176—177°, is demethylated by heating with a saturated solution of hydrogen chloride in acetic acid at 190—200°, to 1 : 5-*dihydroxy*-6-*methylanthraquinone*, m. p. 190° (*diacetyl* derivative, m. p. 230°), which resembles morindadiol (Oesterle and Tisza, A., 1908, ii, 527) in its colour reactions. Condensation of hemipinic anhydride with toluene in presence of aluminium chloride and treatment of the resulting 2-*p*-toluoylbenzoic acid derivative with boric and fuming sulphuric acids on the water-bath yields 1-*hydroxy*-2-*methoxy*-6-*methylanthraquinone*, m. p. 200° (*acetyl* derivative, m. p. 170°). This is demethylated by heating with aluminium chloride at 220° to 6-*methylalizarin*, m. p. 220° (*acetyl* derivative, m. p. 190°).

H. Burton.

Reduction products of hydroxyanthraquinones. X. R. W. Hardacre and A. G. Perkin (J.C.S., 1929, 180—193).—The dihydroxyhelianthrone (I) obtained from 3-hydroxyanthranol by gentle oxidation gives, after acetylation followed by halogenation in pyridine solution, 3 : 3′-*di-iodo*-2 : 2′-*diacetoxyhelianthrone*, m. p. 268—270° (decomp.), or 3 : 3′-dibromo-2 : 2′-diacetoxyhelianthrone. Monoiododihydroxyhelianthrone (Haller and Perkin, A., 1924, i, 301; Perkin and Yoda, A., 1925, i, 1160) cannot have an 8′-iodine atom (as previously supposed) because exposure of 3-iodo-2 : 2′-diacetoxyhelianthrone in benzene solutions to sunlight caused formation of *iododiacetoxynaphthadianthrone*, m. p. above 340°, without elimination of iodine.


(I.)

Treatment of 2-hydroxyanthraquinone with bromine and sodium hydroxide solution gives 1-*bromo*-2-*acetoxyanthraquinone*, m. p. 182—183°, and 1-*bromo*-2-*hydroxyanthraquinone*, m. p. 185—187° (*methyl ether*, m. p. 247°); the *benzoyl* derivative of the last compound, m. p. 229—230°, yields, when heated in naphthalene solution with copper powder, 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl (similar treatment of 1-*chloro-2-benzoyloxyanthraquinone*, m. p. 228—230°, gave smaller yields), identical with the chromic acid oxidation product from dihydroxyhelianthrone (I), which is therefore the 2 : 2′-compound.

The action of excess of sodium hypobromite on 2-hydroxyanthraquinone gives 1 : 3-*dibromo-2-hydroxyanthraquinone*, m. p. 216—217° (*acetyl* derivative, m. p. 195°; *methyl ether*, m. p. 226—227°), mild fusion of which with 40% sodium hydroxide in an autoclave gives 3-bromoalizarin.

2 : 2′-Dihydroxy-1 : 1′-dianthraquinonyl by reduction with boiling aqueous ammonia and zinc dust gives, after acetylation, 3 : 9-*diacetoxyanthracene*, m. p. 157—158°, and *tetra-acetyl*-2 : 2′-*dihydroxy*-1 : 1′-*dianthranolyl*, m. p. 267—268°, which by chromic acid–acetic acid oxidation gives 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl. 2 : 2′-*Dihydroxy*-1 : 1′-*dianthranonyl* has m. p. about 290° (blackening at 270°). Reduction of 1-chloro-2-hydroxyanthraquinone by sulphuric acid and aluminium powder gives *chlorodiacetoxyanthracene*, m. p. 167—168°, and *chlorohydroxyanthranol*, m. p. 230°. Similarly 3-*iodo-2-hydroxyanthraquinone*, m. p. 278—279° (*acetyl* derivative, m. p. 224—225°; *methyl ether*, m. p. 228—229°) (prepared by direct iodination in pyridine solution), gives only 2-*iodo-3-hydroxyanthranol*, m. p. 239—240° (*diacetyl* derivative, m. p. 196°), which with ammonia and a trace of copper under pressure yields 3-*amino-2-hydroxyanthraquinone* (?), decomp. above 300°. 3-*Iodo-2-benzoyloxyanthraquinone*, m. p. 185°, when boiled in naphthalene solution with copper powder, gives 3 : 3′-*diacetoxy*-2 : 2′-*dianthraquinonyl*, m. p. 315°.

Oxidation of the diacetyl derivative of 2-iodo-3-hydroxyanthranol by ferric chloride in acetic acid solution gives 2 : 2′-*di-iodo*-3 : 3′-*dihydroxydianthrone*, m. p. 267—268° [previous darkening at 255°; *diacetyl* derivative, m. p. 227—228°, darkening at 215°; *tetra-acetyl* derivative, m. p. 293—295° (the following compounds with solvents were isolated: acetone, $C_{36}H_{24}O_8I_2,2C_3H_6O$, m. p. 200—220°; alcohol, $C_{36}H_{24}O_8I_2,C_2H_6O$)]. Oxidation of 2 : 2′-di-iodo-3 : 3′-dihydroxydianthrone by alkaline potassium ferricyanide gives, after acetylation, 2 : 2′-di-iodo-3 : 3′-diacetoxydianthraquinone, whilst similar treatment using alkaline potassium persulphate gives 3 : 3′-*di-iodo*-2 : 2′-*diacetoxyhelianthrone*, m. p. 268—270°. Acetylanthrapurpurinanthranol is oxidised by ferric chloride in acetic acid solution to 3 : 4 : 6 : 3′ : 4′ : 6′-*hexa-acetoxydianthrone*, m. p. 250—251°, accompanied by a blue *compound* containing combined iron. Exposure of solutions of 3 : 4 : 6 : 9-tetra-acetoxyanthracene in acetic acid to sunlight results in slow formation of 3 : 4 : 6 : 9 : 3′ : 4′ : 6′ : 9′-*octa-acetoxydianthranol*, m. p. 239—240°. The tetra-acetyl derivative of 3 : 3′-dihydroxydianthranol crystallises with benzene and chloroform of crystallisation: $C_{36}H_{26}O_8,C_6H_6$, m. p. 175—177°; $C_{36}H_{26}O_8,CHCl_3$, m. p. 161°. R. J. W. Le Fèvre.

Anthraquinone-1 : 5-dicarboxylic acid and certain simple and mixed anthraquinonecarboxylic anhydrides. R. Scholl, S. Hass, and K. H. Meyer [with W. Winkler, C. Seer, O. Dischendorfer, S. Brissimdji, and W. Messe] (Ber., 1929, 62, [*B*], 107—115).—1 : 5-Dichloroanthraquinone is converted by treatment with *p*-toluenesulphonamide, potassium carbonate, and copper acetate in nitrobenzene into 1 : 5-*di*-p-*toluenesulphonamidoanthraquinone*, m. p. 310—311°, transformed by concentrated sulphuric acid at 50—60° into 1 : 5-diaminoanthraquinone, m. p. 318—319° (corr.). The diamine, which must be homogeneous, is diazotised in concentrated sulphuric acid and the crystalline bisdiazonium sulphate is transformed in the usual manner into 1 : 5-*dicyanoanthraquinone*, m. p. about 390° (decomp.) after darkening at 370°. Hydrolysis of the dinitrile with sulphuric acid or, preferably, with sodium hydroxide affords *anthraquinone*-1 : 5-*dicarboxylic acid*, which gradually becomes red above 300° but does not melt below 390°. Purification of the crude acid is most simply effected by boiling with nitric acid (*d* 1·35), which attacks and dissolves only the impurities. The *potassium*, *calcium*, and *pyridinium* salts are described. The acid is transformed by phosphorus pentachloride and phosphoryl chloride into *anthraquinone*-1 : 5-*dicarboxyl chloride*, m. p. 260—263° (decomp.), from which *methyl anthraquinone*-1 : 5-*dicarboxylate*, m. p. 236°, is derived. An alternative method for the preparation of anthraquinone-1 : 5-dicarboxylic acid consists in diazotising 5-aminoanthraquinone-1-carboxylic acid in sulphuric acid and converting the greenish-yellow *diazonium sulphate* into 5-*cyanoanthraquinone*-1-*carboxylic acid*, which is hydrolysed with 20% sodium hydroxide. 1 : 5-*Di-iodoanthraquinone*, m. p. 308—309°, is incidentally described.

Anthraquinone-1 : 5-dicarboxylic acid is transformed by boiling acetic anhydride into *acetic anthraquinone*-1 : 5-*dicarboxylic anhydride*, $C_{14}H_6O_2(CO{\cdot}OAc)_2$, m. p. about 202°, with incipient decomposition into acetic anhydride and *anthraquinone*-1 : 5-*dicarboxylic anhydride*, m. p. about 336°; the last substance is too sparingly soluble to permit determinations of its mol. wt. The mixed and simple anhydrides are converted by heating with sodium hyposulphite in water or acetic acid into the red anthraquinol-1 : 5-dicarboxylic dilactone (to be described later). Similarly, anthraquinone-1-carboxylic acid and acetic anhydride afford *acetic anthraquinone*-1-*carboxylic anhydride*, m. p. 188—190°, which decomposes at about 220° into acetic anhydride and *anthraquinone*-1-*carboxylic anhydride*, m. p. 285—287°. *Acetic* 2-*methylanthraquinone*-1-*carboxylic anhydride*, m. p. 173°, and 2-*methylanthraquinone*-1-*carboxylic anhydride*, m. p. 268·5° (decomp.), are described. The simple and mixed anhydrides give olive-green solutions when treated with sodium amalgam in absolute alcohol. The simple structure is assumed for the mixed anhydrides, but the ultimate decision between this and a hydroxylactone constitution can be made only on spectroscopic evidence. H. Wren.

Oxidation of anthracene by nitrogen oxides. M. A. Ilinski, B. V. Maksorov, and N. V. Elagin.—See B., 1929, 88.

Anthraquinone solutions in sulphuric acid. P. I. Sokolov and V. P. Dreving.—See B., 1929, 88.

Manufacture of monobenzoyldiaminoanthraquinones. I. G. FARBENIND. A.-G.—See B., 1929, 123.

Manufacture of vat [benzanthrone] dyes. I. G. FARBENIND. A.-G.—See B., 1929, 124.

Cerebronic acid. VI. P. A. LEVENE and F. A. TAYLOR (J. Biol. Chem., 1928, **80**, 227—230).—Repetition of the authors' previous work (A., 1922, i, 714) confirms the fact that the main product of oxidation of cerebronic acid with permanganate in acetone is lignoceric acid; the conclusions of Klenk (A., 1928, 868) are therefore not accepted.

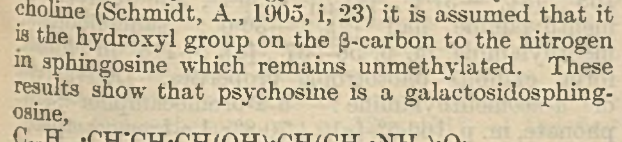
C. R. HARINGTON.

Cerebronic acid. E. KLENK (Z. physiol. Chem., 1928, **179**, 312—319; cf. A., 1928, 868).—Treatment of cerebronic acid with hydriodic acid dissolved in acetic acid gave lignoceric acid, thus confirming the constitution of cerebronic acid as α-hydroxylignoceric acid. The probable derivation of the lipins from the sugars is discussed. J. H. BIRKINSHAW.

Cerebrosides. VIII. Galactosido-sphingosine, the partial fission product of the cerebroside. E. KLENK and R. HÄRLE (Z. physiol. Chem., 1928, **178**, 221—238).—The preparation of psychosine sulphate, $[\alpha]_D^{18}$ −16·6° (A., 1926, 749), from (*a*) the first acetone-extracted cerebroside fractions (A., 1927, 691) and (*b*) the light petroleum-extracted nervone fraction (A., 1926, 1124) in yields of 77—85% and 65—73%, respectively (allowing for the recovery of unchanged starting material), is described, and hence is obtained the free crystalline base, m. p. indefinite 215°, decomp. 233° (*phosphate*; *picrate*). Catalytic reduction of psychosine sulphate with hydrogen and palladium gives a 94% yield of *dihydropsychosine*, m. p. 215°, decomp. 240°, which by exhaustive methylation gives the *substance*, $C_{26}H_{50}O_3N(OMe)_5$ (oily *picrate* and *chloroplatinate*), of methoxyl content 20·7% (theory, 26·77%); 16% sulphuric acid at 100° converts this into a *substance*,

$C_{14}H_{29}\cdot CH(OMe)\cdot CH(OH)\cdot CH_2\cdot NMe_3,H_2SO_4,0\cdot 5H_2O$,

which loses its water of crystallisation at 135° and then has m. p. 284° (*chloroplatinate*, decomp. 215°). The same substance is obtained by similar methylation of dihydrosphingosine (Levene and Jacobs, A., 1912, i, 575, the method being modified), the resulting *quaternary iodide*, m. p. 255° (decomp.), being converted into the same chloroplatinate (the carbon content of the specimen obtained from either source is 1% high, for which, at present, no explanation can be given). By analogy with the methylation of choline (Schmidt, A., 1905, i, 23) it is assumed that it is the hydroxyl group on the β-carbon to the nitrogen in sphingosine which remains unmethylated. These results show that psychosine is a galactosidosphingosine,



$$C_{12}H_{25}\cdot CH{:}CH\cdot CH(OH)\cdot CH(CH_2\cdot NH_2)\cdot O\cdot \underbrace{CH\cdot[CH\cdot OH]_3\cdot CH}_{O}\cdot CH_2\cdot OH,$$

(cf. Rosenheim's formula for kerasine, A., 1916, i, 493) and exclude the alternative structures suggested by Thierfelder (A., 1914, i, 339). J. W. BAKER.

Isoprene and caoutchouc. XIII. Constitution of caoutchouc. H. STAUDINGER, M. ASANO, H. F. BONDY, and R. SIGNER (Ber., 1928, **61**, [*B*], 2575—2595).—The rival views of Pummerer and Staudinger on the constitution of caoutchouc are discussed in detail. Pummerer's evidence for his conception is deemed inadequate and caoutchouc is regarded as composed of macro-molecules of polymeric-homologous polyprenes. The following criticisms are made. Crystallisation of a compound is not evidence that it is homogeneous and of low mol. wt., since the mixture of polymeric-homologous polymethylenes crystallises by parallel arrangement of chains in the same manner as the uniform polyoxymethylene diacetates of low mol. wt. The existence of a hydrocaoutchouc, $(C_5H_{10})_8$, distillable without decomposition is called into question; distillation of hydrocaoutchouc, mean mol. wt. 3000—5000, causes cracking with production of a mixture of unsaturated hydrocarbons. Re-examination of the determination of the mol. wt. of caoutchouc in menthol shows the process to be very difficult. Determinations can be effected only when crystallisation after addition of the substance occurs at approximately the same rate as in the pure solvent and the external temperature is maintained constant. Addition of caoutchouc, however, retards crystallisation in an unusual degree. Very varying depressions are observed and widely different values for the mol. wt. of caoutchouc are found according to the experimental conditions. Similar observations are recorded in determining the mol. wt. of a *cyclo*-caoutchouc for which the datum mol. wt.=8500 in benzene is in accordance with other properties; in menthol the value 150 is found.

Rast's method is found suitable for determining the mol. wt. of complex, stable hydrocarbons and their mixtures. Its application to caoutchouc gives results similar to those recorded by Pummerer. At the high temperature involved, slight decompositions occur, probably due to impurities containing oxygen. *cyclo*Caoutchoucs give considerably lower values in camphor than in benzene. Pummerer's view that menthol and camphor are particularly suitable solvents for caoutchouc does not meet acceptance.

The product derived by the action of nitrosobenzene on caoutchouc is not uniform but a mixture of polymeric-homologous substances.

Röntgenographic investigation cannot establish the existence of a small parent molecule. The small elementary cell does not permit conclusions with regard to the size of the molecule of highly-polymerised compounds. The molecule may be much greater than the elementary cell. H. WREN.

Isoprene and caoutchouc. XIV. H. STAUDINGER and H. F. BONDY (Annalen, 1929, **468**, 1—57).—An investigation of the degradation of caoutchouc and guttapercha under the influence of heat. The materials used were (*a*) crude caoutchouc containing about 5% of protein, (*b*) pure caoutchouc, obtained by Pummerer's method (A., 1927, 1193), and (*c*) guttapercha, obtained from a leaf guttapercha, the solution of which in carbon tetrachloride was centrifuged free from impurities, filtered, and precipitated with methyl alcohol. The viscosity of a benzene or toluene solution of guttapercha was not affected by boiling, but xylene or tetrahydronaphthalene solutions of this substance, as well as all four solutions of crude and pure caoutchouc, underwent appreciable change of viscosity, this change being the greater the higher is the b. p. of the solution. It follows that the caoutchouc undergoes degradation at fairly low temperatures, whereas guttapercha withstands higher temperatures. Degradation of caoutchouc in boiling xylene produces gummy products, mol. wt. about 4200, whilst guttapercha gives powdery products (mol. wt. about 2500). Both products are regarded as being lower members of the two different series of which caoutchouc and guttapercha respectively are complex members (evidence: both products contain one ethylenic linking per isoprene unit). At the higher temperature of boiling tetrahydronaphthalene, further degradation does not occur, although cyclisation of the open-chain residues takes place to some extent. It is only at temperatures above 300° that caoutchouc and guttapercha decompose to give identical products. The degradation of crude caoutchouc appears to be inhibited to some extent by the presence of the protein at temperatures up to 142°, but at higher temperatures it follows a course similar to that observed with pure caoutchouc. The interpretation of the results is, however, doubtful, owing to the uncertain function of the protein.

[With E. GEIGER.]—The pyrogenic decomposition of guttapercha begins at 285—290° at 11 mm., becomes vigorous at 300—315°, and then slackens (cf. the analogous decomposition of caoutchouc, A., 1926, 841). The product of such heating is a *poly*cyclo*guttapercha*, $(C_5H_8)_x$, mol. wt. (benzene at f. p.) 1950, reduced by hydrogen in presence of nickel at 275—285°/95 atm. to a *hydropoly*cyclo*guttapercha*, $(C_{25}H_{42})_x$, mol. wt. 1930, n_D^{10} 1·5238.

The cyclisation of caoutchouc and guttapercha by hydrogen chloride in the above solvents was studied. Crude caoutchouc in boiling tetrahydronaphthalene gave a cyclo*caoutchouc* (mol. wt. 2500), liquefying at about 123°, whilst guttapercha gave a cyclo*guttapercha* indistinguishable from the caoutchouc product. At lower temperatures, however, caoutchouc and guttapercha gave different cyclisation products. The cyclo*caoutchoucs* obtained in boiling xylene and toluene have mol. wt. 4000—12,900 and 14,000, respectively. The cyclo*guttaperchas* obtained in boiling xylene, toluene, and benzene have mol. wt. 2600—8100, 10,000, and about 8500, respectively. Cyclisation of caoutchouc and guttapercha in toluene solution at 20° gave different *products* with very high mol. wts.

The heat-degradation products of caoutchouc and guttapercha are hemicolloids, mixtures of polyprenes with an average mol. wt. of 10,000, which are relatively stable. This explains (1) the considerable solubility of the products, (2) the fact that the mol. wt. does not vary with concentration (as it would if the products had associated molecules merely), and (3) the fact that the viscosity of solutions of the products is roughly proportional to the concentration. Caoutchouc, on the other hand, is a eucolloid, consisting of a mixture of polyprenes having an average mol. wt. of 100,000. Even slight temperature elevation causes degradation. The macro-molecule is the colloid particle.

The conclusions of Pummerer (*loc. cit.*, and B., 1928, 793) are criticised on the grounds that at the m. p. of camphor caoutchouc undergoes considerable degradation. Further, had caoutchouc the formula $(C_5H_8)_8$, the heat-degradation products could be explained only as being due to polymerisation or condensation. The present authors agree with Meyer and Mark (A., 1928, 1252) as regards the suggestion that the isoprene molecules in caoutchouc are united with co-valencies, but differ from them in the conception of the colloid characters of caoutchouc, which is not regarded as a micelle. The structures of caoutchouc and guttapercha are discussed. The former contains about 1000 isoprene residues co-valently united and may be a *trans*-compound. The molecule of guttapercha is smaller (about 300—500 isoprene residues), is more symmetrical, and is possibly a *cis*-compound. E. E. TURNER.

Menthone series. VI. Crystallisation of menthylamines with optically active bases. J. READ, C. C. STEELE, and P. G. CARTER (J.C.S., 1929, 23—32; cf. A., 1927, 772, 1080).—*dl*-Menthylamine and *dl-neo*menthylamine are resolved by fractionally crystallising the hydrogen *d*-tartrates, the less soluble diastereoisomerides yielding *d*-menthylamine and *l-neo*menthylamine, respectively. No resolution was obtained when *dl-iso*menthylamine was similarly treated. *d*-Menthol is conveniently prepared by treating *d*-menthylamine with nitrous acid. The resolution of the three bases was also attempted with the *d*(or *l*)-α-bromocamphor-π-sulphonates, the *d*(or *l*)-camphor-10-sulphonates, and the normal *d*-tartrates, but complete resolution was not achieved. The observed molecular rotatory powers in dilute aqueous solution of the optically pure salts are in agreement with the calculated values except for the α-bromocamphor-π-sulphonates, the discrepancy being attributed to dynamic isomerism of the acid. When the salts of the three bases with *d*-α-bromocamphor-π-sulphonic acid or with *d*-camphor-10-sulphonic acid are fractionally crystallised, the rotatory powers of successive fractions oscillate irregularly, thus preventing complete resolution of the base. The following are described (rotations in water unless otherwise stated): Derivatives of *l*-menthylamine: *l*-α-bromocamphor-π-sulphonate, m. p. 183—184°, $[\alpha]_D$ −74·7°; *d*-α-bromocamphor-π-sulphonate, m. p. 225°, $[\alpha]_D$ +44·4°; l-*camphor*-10-*sulphonate*, $[\alpha]_D$ −28·9°; *d*-tartrate, $[\alpha]_D$ −24·6°, and hydrogen *d*-tartrate, $[\alpha]_D$ −8·0°; d-*menthylamine hydrogen* d-*tartrate*, m. p. 168°, $[\alpha]_D$ +37·1°, $[\alpha]_{5461}$ +39·1°, the derived *d*-menthylamine had $[\alpha]_D$ +36·6°; salicylidene-*d*-menthylamine, m. p. 56—57°, $[\alpha]_D$ +118° in chloroform, exhibits phototropic properties. Derivatives of *d-neo*menthylamine: *d*-α-bromocamphor-π-sulphonate, m. p. 166·5°, $[\alpha]_D$ +70·8°; l-*α-bromocamphor-π-sulphonate*, m. p. 171°, $[\alpha]_D$ −49·3°; *l*-camphor-10-sulphonate, m. p. 152°, $[\alpha]_D$ ±0°; *d*-camphor-10-sulphonate, m. p. 180°, $[\alpha]_D$ +24·0°; *d*-tartrate, m. p. 180°, $[\alpha]_D$ +25·0°, and hydrogen *d*-tartrate, m. p. 179°, $[\alpha]_D$ +27·4°; *l-neo*menthylamine hydrogen *d*-tartrate, m. p. 188°, $[\alpha]_D$ ±0°, resultant *l-neo*menthylamine hydrochloride, $[\alpha]_D$ −20·2°; salicylidene-*l-neo*menthylamine, m. p. 99°, $[\alpha]_D$ −31·3° in chloroform.

Derivatives of *d-iso*menthylamine: d-*α-bromocamphor-π-sulphonate*, $[M]_D$ +396° to +295°; *l*-α-bromocamphor-π-sulphonate, m. p. 206° (decomp.), $[M]_D$ −201° to −249°; *d*-camphor-10-sulphonate, m. p. 180°, $[\alpha]_D$ +24·6°; *l*-camphor-10-sulphonate, m. p. 188°, $[\alpha]_D$ ±0°; *d*-tartrate, m. p. 204°, $[\alpha]_D$ +32·9°, and hydrogen *d*-tartrate, m. p. 190°, $[M]_D$ +98°. Evaporation of aqueous solutions of *l*-menthylamine hydrochloride, salts of *d*-camphor-10-sulphonic acid with *d-neo-* and *dl-neo*-menthylamines, the normal *d*-tartrate of *d-neo*menthylamine and the normal and hydrogen *d*-tartrates of *dl-neo*menthylamine was accompanied by no change in rotatory power, whilst for the salts of *d*-α-bromocamphorsulphonic acid with *d-neo-* and *dl-neo*-menthylamine a decrease in molecular rotation was observed. A. I. Vogel.

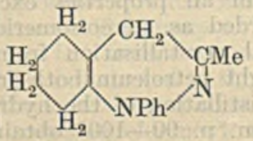
[Products of the addition of chlorine and bromine to pinene and their de-chlorination.] I. L. Kondakov (Ber., 1929, 62, [*B*], 151—152; cf. A., 1928, 526).—A reply to Aschan (A., 1928, 296, 893). H. Wren.

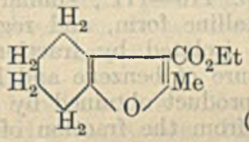
Ozonisation of nopinene and sabinene. H. Schmidt (Z. angew. Chem., 1929, 42, 126—127).—By the ozonisation of nopinene and subsequent decomposition with steam, nopinone was obtained as the chief product, which after purification by means of the semicarbazone had b. p. 209°, d^{20} 0·977, $[\alpha]$ +18·20°. In addition, smaller quantities of pinonic acid and pinonaldehyde were formed; the latter, which has $[\alpha]$ −13·8°, is probably isomeric with the compound, $[\alpha]$ +15°, obtained by Harries from pinene. Sabinene by similar treatment yields sabinaketone, b. p. 217—219°, d^{20} 0·957, $[\alpha]$ −23°. F. R. Ennos.

Transformation of pinocarveol and sabinol. H. Schmidt (Ber., 1929, 62, [*B*], 103—107).—When pinocarveol, b. p. 206—208°/756 mm., d^{20} 0·973, α_D −52°, is heated with aluminium *iso*propoxide, a vigorous reaction occurs at about 170°, whereby pinocamphone, b. p. 207°/756 mm., d^{20} 0·9572, α_D +14·20°, is produced. The semicarbazone, m. p. 223°, α_D +5·20° in alcohol, non-crystalline *oxime*, α_D +38°, and the *dibromide*, $C_{10}H_{14}OBr_2$, m. p. 65—96°, are described. Increase in the duration of heating and the action of the catalyst diminishes the proportion of alcoholic components in the crude product, but increases the amount of resin. Sodium and pinocarveol react vigorously at 170°, giving a product, b. p. 207—211°/756 mm., d^{20} 0·955, α_D +3·8°, which affords a semicarbazone, m. p. 215°. Sabinol and aluminium *iso*propoxide at about 160° yield a product which, after treatment with boric acid to remove alcohols, yields two fractions: (i) b. p. 198—204°, d^{20} 0·912, α_D +32°, (ii) b. p. 204—208°, d^{20} 0·920, α_D +2. The latter affords a semicarbazone, m. p. 206°, regarded as derived from *iso*thujone. The crude semicarbazone, m. p. 128—131°, of the first fraction is hydrolysed to tanacetone, b. p. 199—202°, d^{20} 0·914, α_D +36·4°. Similar products are derived from sabinol and sodium at 160°. Tanacetone, when heated, is readily acted on by sodium, giving *iso*thujone and is therefore probably the primary product of the action of sodium or aluminium *iso*propoxide on sabinol. The ring-unsaturated terpene alcohols verbenol and carveol, which also contain the hydroxyl group in proximity to the double linking, are not isomerised to saturated ketones under the influence of aluminium alkoxide. The hemicyclic unsaturated pinocarveol and sabinol appear to be particularly unstable compounds. H. Wren.

[Essential oil and alcohol from] ***Camphorosma Monspeliacum*** **from S. Cesarea (Lecce).** F. P. Mazza and G. Spagnolo (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 51—54).—The observation by Cassan (Thesis, Montpellier, 1901), that treatment of this plant with steam furnishes a yellow essential oil smelling of bitter almonds and containing nitrogen (the only essential oil stated to contain this element), is not confirmed. The steam distillate obtained by the authors is colourless, contains only traces of essential oil, and has not the above odour. By extraction with boiling benzene the plant gives a brown product; this when distilled in steam furnishes a volatile yellow oil, decomp. on heating, which contains no trace of nitrogen. Hydrolysis of the distillation residue by potassium hydroxide furnishes an alcohol, *camphorosmol*, $C_{14}H_{26}O_2$, m. p. 74—75°, which may be identical with an alcohol of the same formula, viz., glutanol, m. p. 76°, obtained by Euler (A., 1908, i, 40); it yields a *diacetyl* derivative, m. p. 80°. No other products were characterised. E. W. Wignall.

Derivatives of ***Bz*****-tetrahydrocoumarone.** F. Ebel, F. Huber, and A. Brunner (Helv. Chim. Acta, 1929, 12, 16—19).—2-Chloro*cyclo*hexanone condensed with ethyl sodioacetoacetate yields *ethyl* cyclo*hexanonylacetoacetate*, b. p. 110—113°/1·5 mm., which on keeping for some time passes mainly into the enol form, b. p. 119—122°/1·5 mm. Hydrolysis of this ester with an excess of 2·5% alcoholic potassium hydroxide solution gives 3% of 2-*acetonyl*cyclo*hexanone*, b. p. 112°/vac., which condenses with phenylhydrazine to form the *diazine* (I), m. p. 87°. When hydrolysis is effected with 15% hydrochloric acid *ethyl* 1-*methyl*-3 : 4 : 5 : 6-*tetrahydrocoumarone*-2-*carboxylate* (II), b. p. 134°/vac. (free *acid*, m. p. 156°, decomp. 159°), is obtained, whilst with 15% sulphuric acid there are formed, in addition to II, small amounts of acetonyl*cyclo*hexanone and a substance, m. p. 93° (probably II with CO_2Et=H). H. Burton.

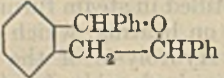

(I.)

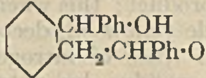

(II.)

So-called "*o*-ββ-dimethylacroylphenol" of S. Skraup. K. von Auwers and W. Mauss (Ber., 1928, 61, [*B*], 2545—2549).—Examination of the compound, m. p. 88°, obtained by Skraup and Beng (A., 1927, 560) by heating phenyl ββ-dimethylacrylate and regarded by them as *o*-ββ-dimethylacroylphenol, shows it to be 2 : 2-*dimethyl*-4-*chromanone*. Direct comparison shows that its properties differ entirely from those of *o*-ββ-dimethylacroyl-*p*-cresol. Skraup's compound is converted by bromine in carbon disulphide into 3 : 3-*dibromo*-2 : 2-*dimethyl*-4-*chromanone*, m. p. 95—96°; with *p*-nitrophenylhydrazine it affords 2 : 2-*dimethylchromanone*-p-*nitrophenylhydrazone*, m. p. 193—194°. Skraup's observation that his compound is converted by alcoholic potassium hydroxide into *o*-hydroxyacetophenone does not establish its phenolic nature, since 2 : 2 : 6-trimethylchromanone affords *o*-aceto-*p*-cresol under these conditions. Attempts to synthesise the compound, m. p. 88°, were unsuccessful owing to the instability of the required β-bromo*iso*valeric acid and its derivatives; *ethyl* β-*bromo*isovalerate, b. p. 78—80°/16 mm., is incidentally described. H. WREN.

Organometallic derivatives. IV. Diphenyl*iso*chromans. A. GARCÍA BANÚS [with L. MEDRANO and M. DÍAZ ROLDÁN] (Anal. Fís. Quím., 1928, 26, 372—398).—A further study has been made of the reaction which occurs when magnesium benzyl chloride is added to benzaldehyde, and of the mechanism by which diphenyl*iso*chroman (I) is formed (cf. A., 1913, i, 50; 1922, i, 734; 1924, i, 180).

(I.)





(II.)

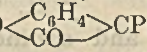
Diphenyl*iso*chroman was unaffected by potassium–sodium alloy. Whilst vigorous treatment with acetic anhydride and a little sulphuric acid yielded diphenylindene, gentle treatment yielded a *diacetate*, m. p. 117—118°, which gave on hydrolysis "*diphenyl*iso*chroman hydrate*," m. p. 114—115°, to which the constitution II is assigned. The new compounds developed the same green colour as diphenyl*iso*chroman with sulphuric acid. Oxidation of the hydrate by permanganate in acetone solution yielded benzoic and *o*-benzoylbenzoic acids and 2-benzoylbenzil. The hydrate has been previously assumed to be the parent substance of diphenyl*iso*chroman, and this is supported by its conversion into the latter when distilled with a small quantity of magnesium chloride and acetate. When heated with 50% sulphuric acid it yielded two *substances* (? phenyl-2-stilbenylcarbinols), m. p. 108—110°. Two forms of diphenyl*iso*chroman, m. p. 110—111°, similar in all properties except crystalline form, and regarded as stereoisomerides, were isolated by fractional crystallisation from a mixture of benzene and light petroleum both from the product obtained by distillation of the hydrate and from the fraction of m. p. 90—100° obtained from the product of reaction of magnesium benzyl chloride and benzaldehyde. The new β-*form* also yielded an unstable crystalline modification, the γ-*form*, m. p. 136—137°.

Attempts were made to demonstrate the presence of "diphenyl*iso*chroman hydrate" in the reaction mixture obtained from magnesium benzyl chloride and benzaldehyde. No crystalline compound could be obtained by treatment of the hydrolysed reaction mixture with acetic anhydride. Acylation of the reaction mixture before hydrolysis was also tried. In this way treatment with acetic anhydride or benzoyl chloride yielded αβ-diphenylethyl acetate, b. p. 202—205°/10 mm., and αβ-*diphenylethyl benzoate*, m. p. 70°, respectively, but no derivative of "diphenyl*iso*chroman hydrate" could be isolated. Similar treatment of the reaction product from magnesium benzyl chloride and anisaldehyde yielded β-*phenyl*-α-p-*anisylethyl acetate*, m. p. 81—82°, which gave *p*-methoxystilbene when hydrolysed by sulphuric acid, and β-*phenyl*-α-p-*anisylethyl alcohol*, m. p. 60—61°, when hydrolysed by dilute sodium hydroxide. αβ-Diphenylethyl alcohol yielded the *urethane*, m. p. 94—95°, with phenylcarbimide, but β-phenyl-α-*p*-anisylethyl alcohol was decomposed with the formation of an *isomeride* of *p*-methoxystilbene, m. p. 135—136°.

R. K. CALLOW.

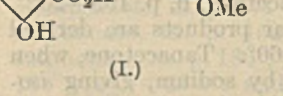
Action of calcium hydride on diphenylene oxide. W. FUCHS (Ber., 1928, 61, [*B*], 2599—2600).—Diphenylene oxide is converted into diphenyl by passage over calcium hydride at 450° in an atmosphere of hydrogen. H. WREN.

Constitution of hydrangenol and phyllodulcin. Y. ASAHINA and J. ASANO (Ber., 1929, 62, [*B*], 171—177; cf. Asahina and others, J. Pharm. Soc. Japan, 1909, No. 330; 1916, No. 406; Maniwa, A., 1924, i, 1090).—2-Methoxybenzil is converted by hydrobromic and glacial acetic acids into 2-*hydroxybenzil*, m. p. 74°, which is isomerised by alkali hydroxide to the amorphous 2-*hydroxybenzilic acid*, yielding with acetic anhydride the crystalline *acetoxybenzilolactone*,

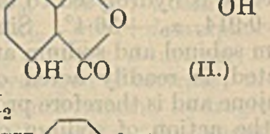


$O<\overset{C_6H_4}{\underset{CO}{}}>CPh\cdot OAc$, m. p. 115° (more readily prepared by the action of bromine and potassium acetate on 2-hydroxydiphenylacetolactone). 2-Hydroxybenzilic acid and the acetylated lactone give a dark violet coloration with concentrated sulphuric acid, whereas the supposedly corresponding natural products give colourless solutions. Similarly, 2 : 4′-dimethoxybenzil is converted successively into 2 : 4′-*dihydroxybenzil*, m. p. 164°, 2 : 4′-*dihydroxybenzilic acid*, and the corresponding *acetylated lactone*, $C_{18}H_{14}O_6$, m. p. 215°, which give the characteristic benzilic acid colour with sulphuric acid. Also, *iso*phyllodulcin is readily monomethylated, whereas the second hydroxyl group is more resistant; the *monomethyl ether*, $C_{15}H_{10}O_3(OMe)_2$, m. p. 115° (oxidised by permanganate in alkaline solution to veratric acid; *monoacetate*, m. p. 141°), gives a reddish-violet colour with ferric chloride, indicating the presence of a hydroxyl group in the *ortho*-position to the carbonyl. The constitutions assigned previously to hydrangenol and phyllodulcin are incompatible with these observations.

Treatment of *iso*phyllodulcin in aqueous alcohol with sodium amalgam in the presence of hydrochloric acid affords deoxyphyllodulcic acid, m. p. 158°, converted by methyl sulphate and alkali hydroxide into the corresponding *monomethyl ether*, m. p. 133°, obtained also by reduction of *iso*phyllodulcin monomethyl ether. This, when oxidised by permanganate, affords β- 2 : 3-dimethoxyphenylpropionic acid, m. p. 96—97°, in good yield. The constitutions I, II, and III are therefore assigned respectively to deoxyphyllodulcic acid monomethyl ether, phyllodulcin, and *iso*phyllodulcin :

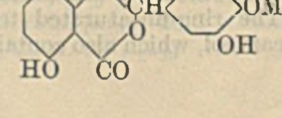


(I.)



(II.)

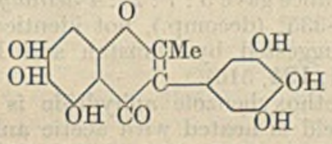
(III.)



Benzylphthalide and 3-phenylhydro*iso*coumarin are reduced by sodium amalgam in faintly acid, aqueous alcohol to αβ-diphenylethane-*o*-carboxylic acid and when heated with alkali are transformed through stilbene-*o*-carboxylic acid to *o*-toluic and benzoic acids. The production of these acids from *iso*phyllodulcin and molten potassium hydroxide is therefore readily understood. It is highly probable that the hydrangenols are demethoxyphyllodulcins. H. Wren.

Synthesis of naringenin and phloretin. K. W. Rosenmund and M. Rosenmund (Ber., 1928, 61, [*B*], 2608—2612; cf. this vol., 188).—Addition of benzoyl chloride to a solution of phloroglucinol and aluminium chloride in nitrobenzene gives benzoylphloroglucinol, m. p. 165°. The applicability of the method is established by the preparation of *phenylacetylphloroglucinol*, m. p. 164—166°, *anisylphloroglucinol*, m. p. 177—178°, β-*phenylpropionylphloroglucinol*, m. p. 137—138°, and p-*ethylcarbonatobenzoylphloroglucinol*, m. p. 172°. The additive compound of phloroglucinol and aluminium chloride in nitrobenzene is transformed by cinnamyl chloride at a temperature not exceeding 20° into much resinous matter, a *compound*, $C_{15}H_{12}O_4$, m. p. 202°, giving the reactions of a flavanone, and a substance, m. p. 210°. Under similar conditions, methylcarbonatocoumaryl chloride affords 2 : 4 : 6-*trihydroxyphenyl 4′-methylcarbonatostyryl ketone*, m. p. 166°, and 5 : 7-*dihydroxy-4′-methylcarbonatoflavanone* (*methylcarbonatonaringenin*), m. p. 183—184°. Treatment of the last-named substance with ammonia yields naringenin, m. p. 247° (cf. Asahina and Inubuse, A., 1928, 1020), further characterised by transformation into its dimethyl ether, m. p. 115—116°. Contrary to Asahina (*loc. cit.*), naringenin is reduced by hydrogen in presence of palladium to phloretin (β-*p*-hydroxyphenylpropionylphloroglucinol). H. Wren.

***iso*Flavone group. IV. Synthesis of 2-methylirigenol.** W. Baker and R. Robinson (J.C.S., 1929, 152—161).—4 : 6-Dinitroguaiacol, m. p. 119—121·5°, prepared by the action of nitrous fumes on guaiacol in ethereal solution, was converted by methyl sulphate and potassium carbonate in xylene solution at 120° into 3 : 5(4 : 6)-dinitroveratrole, m. p. 99—100°. The latter was successively converted into 3 : 5(4 : 6)-*diaminoveratrole*, m. p. 106°, and 4 : 5-dimethoxyresorcinol (I) (monohydrate, m. p. 74°; anhydrous, m. p. 115°) by the method of Chapman and others (A., 1928, 183). Reduction of 3 : 4 : 5-trimethoxybenzoyl chloride in boiling xylene solution in the presence of palladised barium sulphate gave 3 : 4 : 5-trimethoxybenzaldehyde, m. p. 74—75°, converted by hippuric acid in presence of anhydrous sodium sulphate and acetic anhydride at 100° into the azlactone. Alkaline hydrolysis of the latter gave 3 : 4 : 5-trimethoxyphenylpyruvic acid (II) (quinoxaline derivative, m. p. 196—197°); acetic anhydride at 100° converted the oxime of II into 3 : 4 : 5-*trimethoxyphenylacetonitrile*, m. p. 77° (III) (corresponding *amide*, m. p. 121°). Saturation with hydrogen chloride of a cold ethereal solution of III and 4 : 5-dimethoxyresorcinol in the presence of anhydrous zinc chloride, followed by decomposition of the resulting ketimine with dilute hydrochloric acid, furnished 2 : 6-*dihydroxy*-3 : 4-*dimethoxyphenyl* 3 : 4 : 5-*trimethoxybenzyl ketone*, m. p. 162° (IV). The constitution of this ketone follows from its conversion by anhydrous sodium acetate and acetic anhydride at 180° into the *acetyl* derivative, m. p. 232—233°, of 5-*hydroxy*-6 : 7 : 3′ : 4′ : 5′-*pentamethoxy-2-methyl*iso*flavone* (2-*methylirigenin* 7 : 3′-*dimethyl ether*) (V), m. p. 179—180°, a chromone which has the properties of a 5- and not of a 7-hydroxy-derivative. Excess of methyl sulphate and methyl-alcoholic potassium hydroxide converted (V) into 5 : 6 : 7 : 3′ : 4′ : 5′-*hexamethoxy-2-methyl*iso*flavone* (2-*methylirigenin trimethyl ether*), m. p. 166°; decomposition of the latter with concentrated alkali at 180° yielded antiarol (3 : 4 : 5-trimethoxyphenol), m. p. 147°, and 3 : 4 : 5-trimethoxyphenylacetic acid, m. p. 120°, thus establishing the direction of ring closure. Demethylation of V with excess of hydriodic acid at 130° afforded 5 : 6 : 7 : 3′ : 4′ : 5′-*hexahydroxy*-2-*methyl*iso*flavone* (2-*methylirigenol*) (VI), m. p. 325° (decomp.), which closely resembles irigenol (A., 1928, 646) in chemical and dyeing properties. When VI is methylated with methyl sulphate in an atmosphere of hydrogen its hexamethyl ether, m. p. 166°, identical with the methyl ether of 5-hydroxy-6 : 7 : 3′ : 4′ : 5′-pentamethoxy-2-methyl*iso*flavone, is obtained.



(VI.)

When IV is heated with cinnamic anhydride and sodium cinnamate and the product is hydrolysed with alcoholic potassium hydroxide, 5-*hydroxy*-6 : 7 : 3′ : 4′ : 5′-*pentamethoxy*-2-*styryl*iso*flavone*, m. p. 270°, is produced; its *methyl ether*, m. p. 214—215°, obtained in acetone solution with methyl sulphate and aqueous potassium hydroxide, did not yield a substituted *iso*flavone-2-carboxylic acid when oxidised in pyridine solution with potassium permanganate. *Iridamide* (3-*hydroxy*-4 : 5-*dimethoxyphenylacetamide*), m. p. 113°, from ammonia and methyl iridate, could not be dehydrated to the nitrile.

The reactivity of some phenolic ethers is discussed with especial reference to the Hoesch reaction. Phenylacetonitrile condenses with resorcinol monomethyl ether under the conditions of the Hoesch synthesis to give a mixture of 2-hydroxy-4-methoxyphenyl benzyl ketone, m. p. 90°, and 4-*hydroxy*-2-*methoxyphenyl benzyl ketone*, m. p. 68°, respectively insoluble and soluble in 1% sodium hydroxide; the orientation of the first follows from its conversion into 7-methoxy-2-methyl*iso*flavone, m. p. 135·5°, by acetic anhydride and sodium acetate at 180°. Phenylacetonitrile condenses similarly with orcinol monomethyl ether to produce 4-*hydroxy*-2-*methoxy*-6-*methylphenyl benzyl ketone*, m. p. 88°, together with some 2-*hydroxy*-4-*methoxy*-6-*methylphenyl benzyl ketone*, m. p. 110° (needles); the conversion of the latter into 7-*methoxy*-2 : 5-*dimethyl*iso*flavone*, m. p. 165°, by sodium acetate and acetic anhydride establishes its constitution. A. I. Vogel.

Anthoxanthins. VIII. Synthesis of morin and of 5 : 7 : 2′ : 4′-tetrahydroxyflavone. R. Robinson and K. Venkataraman (J.C.S., 1929, 61—67).—When ω-methoxyphloracetophenone, 2 : 4-

dimethoxybenzoic anhydride, and sodium 2 : 4-dimethoxybenzoate are heated together at 180—185° and the product is hydrolysed with alcoholic potassium hydroxide, *morin* 3 : 2′ : 4′-*trimethyl ether* (I), m. p. 132°, is formed. Methyl sulphate (4 mols.) and aqueous potassium hydroxide convert the latter into the pentamethyl ether, m. p. 155—157°, identical with morin pentamethyl ether. Demethylation of I gave a pale yellow compound, $C_{15}H_{10}O_7,H_2O$, m. p. 286—288°, identical with the compound, m. p. 290° (decomp.), synthesised by Kostanecki and others (A., 1906, i, 301) which exhibited all the reactions of natural morin [cf. Bablich and Perkin, J.C.S., 1896, **69**, 792; m. p. of natural morin about 300° (decomp.)]. Condensation of phloracetophenone, 2 : 4-dimethoxybenzoic anhydride, and sodium 2 : 4-dimethoxybenzoate at 180—185° followed by hydrolysis of the product gave 5 : 7-*dihydroxy*-2′ : 4′-*dimethoxyflavone*, $C_{17}H_{14}O_6,0{\cdot}5H_2O$, m. p. 258—259°. Demethylation of this substance gave 5 : 7 : 2′ : 4′-*tetrahydroxyflavone*, m. p. 332—335° (decomp.), not identical with lotoflavin as suggested by Dunstan and Henry (Phil. Trans., 1901, **194**, 515).

2 : 4-Dimethoxybenzoic anhydride is not formed when the acid is heated with acetic anhydride, but is obtained by treating the acid with thionyl chloride in ethereal pyridine. A. I. Vogel.

Anthoxanthins. IX. Syringetin. T. Heap and R. Robinson (J.C.S., 1929, 67—73).—When ω-benzoyloxyphloracetophenone (1 mol.) is heated at 180—185° with sodium *O*-trimethylgallate (1·5 mols.) and 3 : 4 : 5-trimethoxybenzoic anhydride (7 mols.; prepared by treatment of *O*-trimethylgallic acid with thionyl chloride at 0° in the presence of dry ether and pyridine) and the product is hydrolysed with alcoholic potassium hydroxide, *myricetin* 3′ : 4′ : 5′-*trimethyl ether*, m. p. 290—293°, is obtained; this forms an O-*triacetyl* derivative with acetic anhydride and pyridine and a *monomethylmyricetinsulphonic acid* (not melted at 330°) with fuming sulphuric acid. Benzoylation of syringic acid afforded O-*benzoylsyringic acid*, m. p. 229—232° (*chloride*, m. p. 116·5—118°), the *anhydride*, m. p. 200—228° (impure), of which did not give satisfactory results in an attempted synthesis of galangin. However, by heating a mixture of O-*benzylsyringic anhydride*, m. p. 112—113° (7 mols.; prepared by treating the acid in dry ether–pyridine suspension with thionyl chloride at 0°), sodium benzylsyringate (1·5 mols.), and ω-benzoyloxyphloracetophenone, (1 mol.) at 180—185° and hydrolysing the product with alcoholic potassium hydroxide *syringetin* 4′-*benzyl ether*, m. p. 240—241° (*triacetyl* derivative, m. p. 191—194°), was obtained. This was converted by boiling hydrochloric acid and alcohol into *syringetin* (5 : 7 : 4′-*trihydroxy*-3′ : 5′-*dimethoxyflavonol*) (II), m. p. 288—289° (*tetra-acetyl* derivative, m. p. 224—226°), which with methyl sulphate and potassium hydroxide furnished myricetin hexamethyl ether, m. p. 159—160° (lit. 154—156°). A. I. Vogel.

Anthoxanthins. X. Synthesis of gossypetin and of quercetagetin. W. Baker, R. Nodzu, and R. Robinson (J.C.S., 1929, 74—84).—1 : 2 : 3-*Tribenzyloxybenzene*, m. p. 70°, prepared by the benzylation of pyrogallol in the presence of anhydrous potassium carbonate and acetone in an atmosphere of hydrogen, was converted by nitric acid (*d* 1·19) first into 5-*nitro*-1 : 2 : 3-*tribenzyloxybenzene*, m. p. 139°, and then into 2 : 6-*dibenzyloxy*-p-*benzoquinone*, m. p. 201—202°; the latter was reduced by zinc dust and alcoholic sulphuric acid to 2 : 6-*dibenzyloxyquinol*, m. p. 116—117°, methylation of which with methyl sulphate, sodium hydroxide, and alcohol in an atmosphere of hydrogen gave 2 : 6-*dibenzyloxy*-1 : 4-*dimethoxybenzene*, m. p. 82—83°. Hydrolysis of this ether with hydrochloric and acetic acids at 65—70° afforded 2 : 5-*dimethoxyresorcinol* (*hydrated* form, $C_8H_{10}O_4,2H_2O$, m. p. 61—62°, *anhydrous* form, m. p. 86—88°), together with a small quantity of a *substance*, m. p. 180°. Saturation of a solution of anhydrous 2 : 5-dimethoxyresorcinol and of methoxyacetonitrile in dry ether with hydrogen chloride, followed by decomposition of the resulting ketimine hydrochloride with water, gave 2 : 4-*dihydroxy*-ω : 3 : 6-*trimethoxyacetophenone*, m. p. 150—151°. This was heated with potassium veratrate and veratric anhydride at 175—180° and the resulting product was hydrolysed with alcoholic potassium hydroxide, when there was obtained 7-*hydroxy*-3 : 5 : 8 : 3′ : 4′-*pentamethoxyflavone* (O-*pentamethylgossypetin*), m. p. 253—254°; demethylation of the latter with hydriodic acid followed by treatment with sulphurous acid gave 3 : 5 : 7 : 8 : 3′ : 4′-*hexahydroxyflavone* (I), m. p. 310—314°, the identity of which with natural gossypetin, m. p. 311—313°, was established by the m. p., by conversion (acetic anhydride and pyridine) into the *O*-hexa-acetyl derivative, m. p. 229—230°, and into 3 : 5 : 7 : 8 : 3′ : 4′-hexamethoxyflavone (*O*-hexamethylgossypetin), by certain characteristic reactions, and by the dyeing properties. These results are irreconcilable with those of Nierenstein (A., 1917, i, 149), who describes the synthesis of I and states that it is identical with hydroxyquercetin derived from quercetone and is different from gossypetin and from quercetagetin. For the synthesis of quercetagetin, 2 : 6-dihydroxy-ω : 3 : 4-trimethoxyacetophenone (Chapman and others, A., 1928, 183) was heated with veratric anhydride and sodium veratrate at 180—190° and the resulting resin was treated with warm dilute sodium carbonate solution followed by hydrolysis with alcoholic potassium hydroxide, when 5-*hydroxy*-3 : 6 : 7 : 3′ : 4′-*pentamethoxyflavone* (O-*pentamethylquercetagetin*), m. p. 159—160°, was obtained. Demethylation of the latter with hydriodic acid afforded 3 : 5 : 6 : 7 : 3′ : 4′-*hexahydroxyflavone*, m. p. about 316° (decomp.) (*hydrate*, $C_{15}H_{10}O_8,2H_2O$, from 50% acetic acid), the identity of which with natural quercetagetin was established by conversion into the *hexa-acetyl* derivative, m. p. 210°, by certain colour reactions, and by the dyeing properties. Confirmation of the view that gossypetin and quercetagetin are derivatives of the same 1 : 3 : 4 : 5-tetrahydroxybenzene is provided by the fact that both 2 : 5-dimethoxy- and 4 : 5-dimethoxy-resorcinol yield the same 1 : 2 : 3 : 5-tetramethoxybenzene, m. p. 45—46°, when treated with methyl sulphate and sodium hydroxide in aqueous acetone solution.

A. I. Vogel.

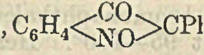
Thiochromondiols. F. Arndt and B. Eistert (Ber., 1929, 62, [*B*], 36—44; cf. Arndt, A., 1926, 177).—2 : 2-Dichloro-6-methylthiochromonol, $C_6H_3Me<\begin{matrix}CO\cdot CO\\ S-CCl_2\end{matrix}$, m. p. 138—139° (decomp.) (cf. A., 1925, i, 1312), is prepared by the action of sulphuryl chloride on 6-methylthiochromonol at the ordinary temperature and finally at 100°; 2 : 2-*dichlorothiochromonol*, m. p. 91—92° (decomp.), is prepared similarly under milder conditions. Decomposition of the methyl compound with boiling water yields 5-methylthionaphthenquinone and 6-methylthiochromondiol, $C_6H_3Me<\begin{matrix}CO\cdot C\cdot OH\\ \|\\ S-C\cdot OH\end{matrix}$, m. p. 224° (decomp.) after softening at 205° when rapidly heated (*diacetate*, m. p. 176°), whereas the simpler compound affords *thiochromondiol*, m. p. 210° (decomp.) after softening at 190° (*diacetate*, m. p. 174°), and thionaphthenquinone, m. p. 120—121°. The diol is transformed by ethereal diazomethane into 2-*methoxy*-6-*methylthiochromonol*, $C_6H_3Me<\begin{matrix}CO\cdot C\cdot OH\\ \|\\ S-C\cdot OMe\end{matrix}$, m. p. 157°, soluble in warm 2*N*-sodium hydroxide with production of a yellow *sodium* salt and smaller amounts of 2 : 3-*dimethoxy*-6-*methylthiochromone*, m. p. 120° (more readily prepared from the 2-methoxy-compound and an excess of ethereal diazomethane). Treatment of the dimethyl ether with boiling hydrochloric acid or of the diol with methyl sulphate and alkali hydroxide affords 2-*hydroxy*-3-*methoxy*-6-*methylthiochromone*, m. p. 125—126° (*monohydrate*, m. p. 106—107°), readily soluble in ammonia or sodium carbonate to colourless solutions. The compound is readily converted by diazomethane into a mixture of 2 : 3-dimethoxy-6-methylthiochromone, m. p. 120°, and a *substance*, $C_{12}H_{12}O_3S$, m. p. 52—53°, which does not react with ketonic reagents or bromine, is slowly soluble in boiling 2*N*-alkali hydroxide, and appears to yield an exceedingly unstable *hydrochloride*. The substance, together with 2 : 3-dimethoxy-6-methylthiochromone, is also derived by the action of an excess of ethereal diazomethane on the free diol.

The following method is adopted for the preparation of chromonols (cf. Arndt and Källner, A., 1924, i, 411). Chromanone dissolved in amyl alcohol is treated successively with a solution of potassium in the same alcohol and amyl nitrite, whereby *oximinochromanone*, m. p. 155° (decomp.) (*potassium* salt), is produced, which is converted by boiling 2*N*-hydrochloric acid into chromonol (3-hydroxy-1 : 4-benzopyrone), m. p. 181°. 6-Methylchromanone similarly yields *oximino*-6-*methylchromanone*, m. p. 162° (decomp.) (*potassium* salt), and 6-*methylchromonol*, m. p. 175°. Treatment of the chromonols with sulphuryl chloride affords 2-*chlorochromonol*, m. p. 208°, and 2-*chloro*-6-*methylchromonol*, m. p. 192°. H. Wren.

Synthesis of *iso*naphthathioxin. A. Cohen and S. Smiles (J.C.S., 1929, 209—213).—1-*Bromonaphthalene*-2-*sulphinic acid*, m. p. 146°, was prepared in 60% yield either by the interaction of alkaline sodium sulphite and 1-*bromonaphthalene*-2-*sulphonyl chloride*, m. p. 93—94° (prepared from β-naphthylamine-2-sulphonic acid through the diazo reaction and treating the resulting bromosulphonic acid with phosphorus pentachloride), or from 1-bromo-β-naphthylamine by diazotisation and subsequent treatment with copper and sulphur dioxide, and yielded *di*-1-*bromonaphthyl* 2-*disulphide*, m. p. 161°, with sulphur dioxide and hydriodic acid in alcoholic solution. 1-*Bromo*-2-*hydroxydinaphthyl* 2 : 1′-*sulphide* (I), m. p. 154° or 135—136° (*acetyl* derivative, m. p. 116—117°), was obtained by brominating 2′-hydroxydinaphthyl 2 : 1′-sulphide in acetic acid solution or by heating 1-bromonaphthalene-2-sulphinic acid and β-naphthol at 95—100°. Heating of the sodium derivative of I with copper acetate at 160—170°/1 mm. gave a 50% yield of αββ′α′-naphthathioxin, m. p. 154°, identical with the substance obtained by dehydrating β-naphthol 1-sulphide (Mauthner, A., 1906, i, 447) or *iso*-β-naphthol (J.C.S., 1913, **103**, 347, 909) or by treating dehydro-β-naphthol sulphide with acetyl iodide (J.C.S., 1914, **105**, 1741). A. I. Vogel.

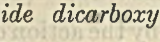
Action of ammonia and amines on diphenylbenzylpyronone. J. Schettle (J. Russ. Phys. Chem. Soc., 1928, **60**, 1521—1533).—The compounds formed by the action of ammonia, methyl-, ethyl-, triethyl-, and propyl-amine, and of aniline on 3 : 5-diphenyl-2-benzylpyron-2-one were investigated. The compounds are somewhat unstable, ammonia or the corresponding amine being evolved on heating. Since the pyronone has distinctly acidic properties, the compounds are concluded to belong to the type of ammonium salts. With ammonia, diphenylbenzylpyronone gave a *compound*, m. p. 190—191°, which decomposed on prolonged heating below the m. p., giving ammonia and the original pyronone. If heated rapidly a partial conversion into the corresponding pyridonone took place. With methylamine, a *compound*, m. p. 180—182°, decomposed by heat was obtained. Ethylamine, triethylamine, propylamine, and aniline gave *compounds* of m. p. 180—183°, 122—123°, 186—190°, and 100—120°, respectively. The last two products are highly unstable, decomposing below the m. p. None of these compounds gave the corresponding pyridonone derivative. M. Zvegintzov.

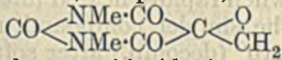
By-products of the hydrogenation of quinoline under pressure in presence of osmium and cerium oxides as catalysts. V. S. Sadikov and A. K. Michailov (J. Russ. Phys. Chem. Soc., 1928, **60**, 1557—1566).—When quinoline is hydrogenated by Ipatiev's method in presence of varying amounts of osmium and cerium dioxides, the properties of the resulting liquid mixtures depend both on the amounts and on the proportions in which the two catalysts are present. With cerium oxide, tetrahydroquinoline is formed almost exclusively. With osmium oxide, higher reduction products, up to decahydroquinoline, together with condensation products of hexahydroquinoline and alkylated derivatives due to the partial decomposition of the ring compounds, are obtained. If both osmium and cerium oxides are present, both condensation of hydrogenated quinoline derivatives and fission of the rings with formation of piperidine compounds, and secondary reactions, resulting in alkylamine derivatives, occur. Complex secondary reactions are especially prominent if the hydrogenation is carried on intermittently. Since the primary products of hydrogenation are very reactive, they must be removed as soon as formed. M. Zvegintzov.

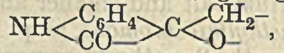
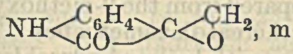
Phenylisatogen. M. Bakunin and T. Vitale (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 270—278).—The red compound, m. p. 186—187°, obtained together with phenyl-*o*-nitrocinnamic acid when *o*-nitrobenzaldehyde is treated with sodium phenylacetate and acetic anhydride (Bakunin and Parlati, A., 1906, i, 664) is now found to be phenylisatogen (2-phenylindolone-1-oxide),  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\ \mathrm{NO}\end{matrix}>\mathrm{CPh}$, and appears to be identical with the compound obtained by oxidising 3-*iso*nitroso-2-phenylindole with acetic acid and chromic anhydride (Angeli and Angelico, A., 1904, i, 526). Treatment of phenylisatogen with hydroxylamine hydrochloride yields almost exclusively *C*- and *N*-oximes, but in presence of alcoholic sodium hydroxide the reaction gives 3-nitroso-2-phenylindole, m. p. 258° (cf. Möhlau, A., 1883, 342; Fischer and Schmidt, A., 1888, 698). The action of alcoholic sodium hydroxide solution on phenylisatogen, partly dissolved and partly suspended in alcohol, yields a compound, m. p. 209—210°, which is probably identical with the compound obtained by Pinner (A., 1894, i, 385) by boiling diphenyltetrazide with alcoholic potassium hydroxide and subsequently treating with dilute hydrochloric acid and with Bamberger and Szolayski's benzylidenebenzhydrazide (A., 1901, i, 84). The action of concentrated nitric acid on a chloroform solution of phenylisatogen in presence of a trace of sulphuric acid or ferric chloride or phosphoric anhydride yields 1-(or 3- or 3′- or 4′-)*nitrophenylisatogen*, m. p. 220°.

T. H. Pope.

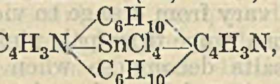
Syntheses with diazomethane. VI. Reaction of ketones and aldehydes with diazomethane. F. Arndt, B. Eistert, and W. Ender (Ber., 1929, **62**, [*B*], 44—56; cf. A., 1928, 739).—*p*-Nitrobenzaldehyde is converted by ethereal diazomethane into a mixture of *p*-nitroacetophenone, m. p. 80°, *p*-nitrophenylacetone, m. p. 62°, and *p*-nitrophenylethylene oxide, m. p. 84—85°, which adds hydrogen chloride, benzoyl chloride, and acetic anhydride without giving crystalline compounds. Addition of methyl alcohol to the reactants increases the yield of nitrophenylacetone without affecting that of the other products. Since nitrophenylacetones are obtained by the prolonged action of ethereal diazomethane on *o*- or *p*-nitroacetophenone, the authors adopt Meerwein's interpretation of the change (A., 1928, 1217) and accept the possibility of radical migration. The results, considered in connexion with those of Mosettig (A., 1928, 887), show that the reaction between the aldehydic group and diazomethane may be accelerated by catalysts but is not altered in its qualitative results. Aldehydes of the type of chloral with "negative carbonyl" afford ethylene oxides and thereby the reaction is concluded, whereas those like benzaldehyde yield methyl ketones. The influence of catalysts is felt in its effect only on the further interaction of the methyl ketone with diazomethane. Thus piperonal without catalyst yields mainly acetylpiperone, whereas in the presence of much methyl alcohol it affords piperonylacetone and other products.

Ethyl ketomalonate adds ethereal diazomethane in exothermic action without evolution of nitrogen, which occurs only when the solvent is evaporated; its hydrate immediately evolves nitrogen briskly. In both cases, the main product of the change is *ethyl asethylene oxide dicarboxylate*,  $\begin{matrix}\mathrm{CH_2}\\ \mathrm{O}\!-\!-\end{matrix}>\mathrm{C(CO_2Et)_2}$, b. p. 127—128°/16 mm., characterised by conversion into the corresponding *chlorohydrin*, $\mathrm{C_8H_{13}O_5Cl}$, b. p. 132—133°/15 mm., and *glycoldiacetate*, b. p. 152—156°/11 mm.

Repetition of the work of Biltz and Paetzold (A., 1923, i, 1233) has led to a different interpretation of the action of diazomethane on alloxan. Instead of 5 : 6-methylenedioxy-1 : 3-dimethyluracil, the primary product, m. p. 176°, is regarded as the *ethylene oxide*,  $\mathrm{CO}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{NMe{\cdot}CO}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{O}\\ \mathrm{CH_2}\end{matrix}$, which is transformed by hydrogen chloride into 5-*hydroxy*-5-*chloromethyl*-1 : 3-*dimethylbarbituric acid* (*benzyl* derivative, m. p. 173—174°) and by acetic anhydride in the presence of ferric chloride into 5-*acetoxy*-5-*acetoxymethyl*-1 : 3-*dimethylbarbituric acid*, m. p. 97°.

As expected, the ketonic group in position 3 in isatin reacts with diazomethane, giving the intermediate product,  $\mathrm{NH}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CO}\!-\!-\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}-\\ \mathrm{O}-\end{matrix}$, which gives rise to the *ethylene oxide*,  $\mathrm{NH}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CO}\!-\!-\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\ \mathrm{O}\end{matrix}$, m. p. 175°, or passes through 2 : 3-diketo-1 : 2 : 3 : 4-tetrahydroquinoline into 2 : 3-dihydroxyquinoline (cf. Heller and others, A., 1919, i, 283; 1926, 620); in addition, further methylation of dihydroxyquinoline occurs to a greater or smaller extent. The ethylene oxide is transformed by hydrochloric acid into 2 : 3-*dihydroxy*-3-*chloromethylindoline*, m. p. 182—183° (decomp.), which does not yield an immediate precipitate of silver chloride when treated with silver nitrate in aqueous-alcoholic solution. 3-Hydroxycarbostyril, m. p. 257—258°, is converted by short treatment with 1 mol. of benzoyl chloride in boiling pyridine into 3-*benzoyloxycarbostyril*, m. p. 286—287°, readily hydrolysed by alkali hydroxide. With excess of benzoyl chloride the *dibenzoyl* derivative, m. p. 45—46°, is produced, hydrolysed by 2*N*-alkali hydroxide to the 2-monobenzoyl compound, but by concentrated hydrochloric acid to the 3-benzoyl derivative; 3-acetoxycarbostyril has m. p. 211°. 3-*Methoxycarbostyril*, m. p. (anhydrous) 194°, is obtained by the action of diazomethane on isatin or on hydroxycarbostyril; the *sodium* salt and the *benzoyl* derivative, m. p. 130—131°, are described. In absence of water, 3-hydroxycarbostyril is converted by diazomethane solely into the 3-monomethyl ether, which is not further attacked. In presence of water, the latter substance is slowly transformed into non-crystalline 2 : 3-*dimethoxyquinoline* (*compound* with mercuric chloride and hydrochloric acid). When preserved, the dimethoxy-compound becomes isomerised to 3-*methoxy*-1-*methylcarbostyril*, m. p. 70—71°.

H. Wren.

Subsidiary valency forces of pyrrole nitrogen. O. Schmitz-Dumont (Ber., 1929, **62**, [*B*], 226—234).—The co-ordinative valency of pyrrole compounds, with the exception of tripyrrole, is equal to the number of nitrogen atoms which they contain. The additive capacity of pyrrole nitrogen is greatly influenced by substituents and constitution. The additive compounds of pyrroles and tin tetrahalides are prepared by mixing the components in an indifferent solvent and either removing the latter and excess of tin tetrachloride by evacuation or by filtering the product in absence of moisture. Pyrrole and tin tetrachloride give the pale yellow *compound*, $SnCl_4,2C_4H_5N$, from which pyrrole cannot be regenerated; it is therefore regarded as derived from dipyrrole. Attempts to isolate the latter compound failed, but it appears relatively strongly basic, since it is not displaced from its additive compound by pyridine, a process which takes place quantitatively with all the other compounds investigated, giving the dipyridine compound of the tin tetrahalide. The basic properties of pyrrole are strengthened by its polymerisation, since tripyrrole yields the *compounds* $SnCl_4,(C_4H_5N)_3$ and $SnBr_4,2(C_4H_5N)_3$. Introduction of methyl groups so increases the additive capacity of pyrrole that 2 : 4-dimethylpyrrole without polymerisation yields the crystalline *substance*, $SnCl_4,2C_4H_3Me_2N$, from which the pyrrole component can be quantitatively regenerated. Replacement of the 1-hydrogen atom by methyl has little effect, since 1-methylpyrrole and tin tetrachloride do not give a compound from which the pyrrole can be obtained. αβ-Di-*NN'*-2 : 5-dimethylpyrrylethane gives a *compound*, $2SnCl_4,C_{14}H_{20}N_2$, for which a structure is suggested which avoids the unusual co-ordination number 5 for tin. 2-Acetylpyrrole affords the *compounds* $SnCl_4,2C_4H_4AcN$ and $SnBr_4,2C_4H_4AcN$, and, since 2 : 5-diacetylpyrrole yields the *substances* $SnCl_4,C_4H_3Ac_2N$ and $SnBr_4,2C_4H_3Ac_2N$, it is assumed that the subsidiary valency linking is essentially localised at the nitrogen atom. Di-3-carbethoxy-2 : 4-dimethylpyrrylmethene yields a *compound*, $SnCl_4,C_4HMe_2N(CO_2Et)\cdot CH\!:\!C_4Me_2N\cdot CO_2Et$, in which the nitrogen atoms appear precisely equivalent, thus suggesting that the imino-hydrogen atom is not definitely attached to either nitrogen atom. The compound obtained by Tschelincev (A., 1917, i, 91, 93) does not add tin tetrachloride, whereas that obtained from *cyclo*hexanone (A., 1917, i, 412) gives the *compound*  $C_4H_3N{<}\overset{C_6H_{10}}{\underset{C_6H_{10}}{—SnCl_4—}}{>}C_4H_3N$, whilst the *substance* obtained with tin tetrabromide has the unusual composition $C_{20}H_{26}N_2[SnBr_5H,C_{20}H_{26}N_2]_2$. H. Wren.

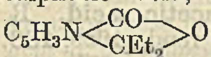
Formation of 2-aminopyridine. G. Koller and H. Ruppersberg (Monatsh., 1928, **50**, 436—438).—When 2-chloropyridine is heated at 200° with pyridine an appreciable amount of 2-aminopyridine (*chloroaurate*, m. p. 231—232°) is formed, probably through the intermediate *N*-2-pyridylpyridinium chloride. A small quantity of the aminopyridine is produced also from 2-chloro- and 3-methyl-pyridine at 200°. H. Burton.

Manufacture of 2-hydroxypyridine-5-carboxylic acid. C. Räth.—See B., 1929, 149.

5- and 8-Aminoquinolines. R. P. Dikshoorn (Rec. trav. chim., 1929, **48**, 147—154).—When 5-nitroquinoline is reduced with a mixture of stannous chloride and hydrochloric acid the impure 5-amino-derivative is obtained, but 8-nitroquinoline affords 8-aminoquinoline, 5-chloro-8-aminoquinoline, and a small quantity of 3(?)-*chloro-8-aminoquinoline*, m. p. 85°. These halogenated derivatives are formed presumably through the intermediate hydroxylamine (cf. Blanksma, A., 1906, i, 345). An excess of a powerful reducing agent causes hydrogenation of the pyridine nucleus, and optimum yields (75%) of the 5- and 8-amino-compounds are best obtained with iron powder and 50% acetic acid. H. Burton.

Manufacture of 8-hydroxyquinoline and derivatives thereof. I. G. Farbenind. A.-G.—See B., 1929, 149.

Manufacture of ethers of 6 : 8-dihydroxyquinoline. I. G. Farbenind. A.-G.—See B., 1929, 149.

Action of magnesium [alkyl] compounds on anhydrides of asymmetric polycarboxylic acids : action of magnesium ethyl iodide on cinchomeronic anhydride. F. P. Mazza [with O. Fici] (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], **34**, 59—65).—The action of magnesium ethyl iodide on cinchomeronic anhydride in ether, followed by treatment with sulphuric acid, gives two *diethylcinchomeronides*,  $C_5H_3N{<}\genfrac{}{}{0pt}{}{CO—}{CEt_2}{>}O$, viz., 2-*α-hydroxy-α-ethylpropylpyridine-3-carboxylic acid lactone*, b. p. 132—133°/60 mm., hydrolysed to diethyl ketone and *iso*nicotinic acid, and 3-*α-hydroxy-α-ethylpropylpyridine-2-carboxylic acid lactone*, b. p. 165—166°/60 mm., hydrolysed to diethyl ketone and nicotinic acid. E. W. Wignall.

Preparation of quinaldinyl chloride and ethyl quinaldinylacetoacetate. D. L. Hammick and W. P. Dickinson (J.C.S., 1929, 214—215).—Contrary to the statement of Besthorn and Ibele (A., 1905, i, 612) and in agreement with that of Meyer (A., 1905, i, 155, 666; cf. Besthorn, A., 1908, i, 681), it is found that only quinaldinyl chloride of m. p. 175—176° is obtained by the action of thionyl chloride (redistilled over quinaldinic acid) on the acid. The acid chloride, m. p. 97°, is, however, obtained by the action of phosphorus pentachloride on the acid or on ethyl quinaldinate, m. p. 36°, in light petroleum solution (b. p. 100—120°). Only hydrochloric and quinaldinic acids are obtained when the acid chlorides of high and low m. p. are treated with water. *Ethyl 2-methylquinolinylacetoacetate*, m. p. 61° [*copper* derivative, m. p. 178° (decomp.)], is formed from quinaldinyl chloride and ethyl sodioacetoacetate in benzene. Dry ammonia in ether or a mixture of ammonia and ammonium chloride at 50° and ethyl quinaldinylacetoacetate yield only quinaldinamide and no ethyl quinaldinylacetate. A. I. Vogel.

Derivatives of quinoneacridone. B. B. Scharvin and D. I. Galperin (J. Russ. Phys. Chem. Soc., 1928, **60**, 1423—1499).—The formation of the derivatives of quinoneacridone was investigated with the view of preparing vat dyes of the type $R'(NHR)_2$, where R is an anthraquinone and R' a quinoneacridone derivative. Crystalline quinoneacridone can readily be obtained by hydrolysing the sulphate. The monochloro- and monobromo-derivatives can be obtained only with great difficulty, by the direct halogenation of quinoneacridone dissolved in phosphoryl chloride. Tetrabromoquinoneacridone . was synthesised from *p*-benzoquinone and dibromoanthranilic acid by way of *tetrabromoquinoneanthranilic* *acid*, m. p. 269°, which, when heated at 200° for 3 hrs. in sulphuric acid, gave dark red *tetrabromoquinoneacridone*. Sodium hydrogen sulphite reduces it to the *di-* and *tetra-hydro*-derivatives. By reducing dinitroquinoneacridone, the deep violet *diamino*-compound can be obtained; it gives coloured reduction and sulphonation products, and when diazotised and coupled with β-naphthol yields a violet *dye*. If the diamino-compound is benzoylated in nitrobenzene solution, a brown *dibenzoyl* derivative is obtained, whilst hydrolysis of the diazonium compound yielded a dark red *dihydroxyquinoneacridone*. All these derivatives can be reduced with sodium hydrogen sulphite, but since the reduction products are all insoluble, they cannot be used as vat dyes. If, however, the di- and tetra-bromo-derivatives are heated for 20 hrs. with β-aminoanthraquinone in nitrobenzene solution in the presence of alkali, *dianthraquinonyl-* and *tetra-anthraquinonyl-diaminoquinoneacridone* are obtained, which are dark brown vat dyes suitable for cotton. M. Zvegintzov.

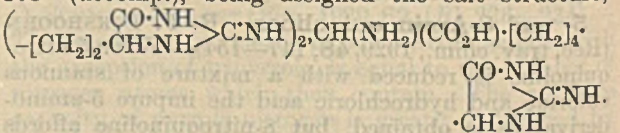
Derivatives of hydantoin-3-acetic acid. R. Locquin and V. Cherchez (Compt. rend., 1929, **188**, 177—179; cf. A., 1928, 744).—Treatment of ethyl aminomalonate, either in the form of the sodium derivative or in the presence of pyridine, with carbonyl chloride yields *ethyl carbonyldiaminomalonate*, m. p. 167°, which gives *carbonyldiacetic acid*, m. p. 208° (efferv.), when heated at 100° with 4% sodium hydroxide and hydantoin-3-acetic acid, m. p. 195—196°, when refluxed with 10% hydrochloric acid. The 3-acetic acid, when heated with thionyl chloride, affords a *chloride*, which in turn yields *amides* with aniline, ethyl aminomalonate, ethyl aminoacetate, and 3-methyl-5-*iso*propylpyrazoline, m. p. 215°, 172—173°, 168°, and 185°, respectively. The interaction of aqueous ammonia and ethyl hydantoin-3-acetate yields *carbonyldiacetamide*, decomp. about 240°, and *hydantoin-3-acetamide*, m. p. 225—226° (cf. Gränacher and Landolt, A., 1928, 74; Fischer, A., 1901, i, 192; 1902, i, 350). G. A. C. Gough.

Hydantoins. XLVII. Polypeptidehydantoins from 2-thiohydantoin-3-acetic acid. A. G. Renfrew and T. B. Johnson (J. Amer. Chem. Soc., 1929, **51**, 254—259).—2-Thiohydantoin-3-acetic acid (A., 1925, i, 583) and *p*-anisaldehyde in glacial acetic acid in presence of sodium acetate yield 2-*thio*-5-p-*anisylidenehydantoin*-3-*acetic acid*, m. p. 280—282°. This is desulphurised by chloroacetic acid to 5-*p*-anisylidenehydantoin-3-acetic acid (cf. Gränacher, A., 1928, 74), which may also be obtained from hydantoin-3-acetic acid and *p*-anisaldehyde. 2-*Thio*-5-*salicylidenehydantoin*-3-*acetic acid*, m. p. 253—254° (decomp.), prepared similarly, is desulphurised to 5-*salicylidenehydantoin*-3-*acetic acid*, m. p. 273—274° (decomp.) (*ethyl* ester, m. p. 164°), which is reduced by hydriodic acid to 5-o-*hydroxybenzylhydantoin*-3-*acetic acid*, m. p. 189—190°. 2-*Thio*-5-*piperonylidenehydantoin*-3-*acetic acid*, m. p. 291° (decomp.), is desulphurised to 5-*piperonylidenehydantoin*-3-*acetic acid*, m. p. 275—276°, the constitution of which is established by the formation of its *ethyl* ester, m. p. 159—160°, from ethyl chloroacetate and the sodio-derivative of piperonylidenehydantoin. H. E. F. Notton.

Direct substitution on the nitrogen of 5 : 5-dialkylbarbituric acids. A. W. Dox and E. G. Jones (J. Amer. Chem. Soc., 1929, **51**, 316—318).—When 5 : 5-dialkylbarbituric acids (1 mol.) are refluxed with *N*-sodium hydroxide (1 mol.) and benzyl chloride or allyl bromide (1 mol.) the product contains mainly the trialkyl derivative with some unchanged material and tetra-alkyl derivative, and occasionally a little acetyldialkylcarbamide. In this way the following *barbituric acids* have been prepared: 1-*benzyl*-5 : 5-*diethyl*-, m. p. 127°; 1-*benzyl*-5 : 5-*diallyl*-, m. p. 116°; 1-*benzyl*-5-*ethyl*-5-iso*amyl*-, m. p. 90°; 5-*phenyl*-1-*benzyl*-5-*ethyl*-, m. p. 113°; 1-*benzyl*-5-sec.-*butyl*-5-*allyl*-, m. p. 90—91°; 5 : 5-*diethyl*-1-*allyl*-, m. p. 75°; 1 : 5 : 5-*triallyl*-, m. p. 68—69°; 5 : 5-*dipropyl*-1-*allyl*-, m. p. 73°; and 5 : 5-*dipropyl*-1 : 3-*diallyl*-, m. p. 62—63°. H. E. F. Notton.

Colour on basis of molecular strain. V. Absorption spectra and dissociation constants of organic salts of violuric acid. N. Ghatak and S. Dutt (J. Indian Chem. Soc., 1928, **5**, 665—672).—Although solid violuric acid is almost colourless, its aqueous solution is pink (Donnan and Schneider, J.C.S., 1909, **95**, 956; Morton and Tipping, *ibid.*, 1925, **127**, 2514). This is ascribed to the change $\cdot CO\cdot\dot{C}:N\cdot OH$(solid) $\rightleftharpoons$ $\cdot C(OH):C\cdot\dot{N}:O$ (solution); the highly strained nitroso-group is thus responsible for colour formation. The coloured alkali salts are also regarded as nitroso-compounds; the intensity of colour is greater with increasing basic strength of alkali (cf. Hantzsch, A., 1909, i, 331). This relationship is also true for the organic salts of violuric acid which have been examined. The absorption maxima and dissociation constants of *N*/128 aqueous solutions of the following salts are recorded: ammonium, *methylamine*, dimethylamine, *trimethylamine*, *ethylamine*, *diethylamine*, n-*propylamine*, *n*-butylamine, *aniline*, o-, m-, and p-*toluidine*, p- and o-*phenylenediamine*, α- and β-*naphthylamine*, *pyridine*, piperidine, quinoline, α-*picoline*, *nicotine*, morphine, brucine, *strychnine*, *cinchonine*, quinine, and *cocaine*. The colours of the salts vary from orange to violet, whilst the aqueous solutions range from pale pink to violet-red. The above salts decompose when heated to about 85°, or when exposed to air for a long time. H. Burton.

Reaction between guanidine and esters of amino-acids. III. E. Abderhalden and H. Sickel (Z. physiol. Chem., 1929, **180**, 75—89; cf. A., 1928, 511, 623).—αα′-Diaminosuberic acid is converted (contrary to the statement of Neuberg and Neimann, A., 1905, i, 687) by 10 parts of methyl alcohol and anhydrous hydrogen chloride into the *methyl ester dihydrochloride*, decomp. 270° (the difficulty in esterification being the insolubility of the acid dihydrochloride in alcohol), which reacts with guanidine at 0° in the expected manner, the isolated *compound*, m. p. 305° (decomp.), being assigned the salt structure,



$$\left(\begin{matrix}CO\cdot NH\\ -[CH_2]_2\cdot CH\cdot NH\end{matrix}\!>\!C:NH\right)_2,CH(NH_2)(CO_2H)\cdot[CH_2]_4\cdot\begin{matrix}CO\cdot NH\\ |\\ \cdot CH\cdot NH\end{matrix}\!>\!C:NH.$$

Guanidine similarly condenses with methyl *dl*-α-amino-δ-benzamidovalerate [*hydrochloride*, m. p. 128—130° (corr.)] to yield the corresponding *cyanidine* derivative [2-*amino*-5-*keto*-4-γ-*benzamidopropyl*-4 : 5-*dihydroglyoxaline*], m. p. 198° (corr.) [*picrate*, decomp. 220° (corr.)], which by debenzoylation with hydrochloric acid yields 2-*imino*-4-γ-*aminopropyl*-5-*glyoxalidone* [isolated as its *dipicrate*, m. p. 230° (decomp.) (corr.)]; this is hydrolysed by *N*-sodium hydroxide at the ordinary temperature to yield δ-*amino*-α-*guanidinovaleric acid* (*iso*arginine) (*picrate*), which is not attacked by arginase. *as*-Dimethyl-, *N*-methyl-, and *N*-*iso*amyl-guanidine react only to a very small extent with glycine ester, no condensation product being isolated, whilst *N*-α-naphthyl- and *N*-acetylguanidine do not react. Guanidine condenses with ethyl hippurate at the ordinary temperature to yield *hippurylguanidine* (*picrate*, decomp. above 320°) and with acetylglycine to yield the *guanidonium* salt, m. p. 217—218°. J. W. Baker.

N-Substituted derivatives of piperazine and ethylenediamine. I. Preparation of N-monosubstituted derivatives. T. S. Moore, M. Boyle, and V. M. Thorn (J.C.S., 1929, 39—51).—Interaction of piperazine with substances capable of attacking the imino-groups usually gives the *N*-disubstituted derivatives. If the interaction takes place in two stages, the velocity of the reaction in the second stage would therefore appear to be much greater than that in the first stage. Theoretical considerations, based on the relative values of the primary and secondary dissociation constants of a diacid base and the ionic product of water, lead to the conclusion that the possibility of survival of a monosubstituted derivative is greatest in weakly acid solution, a result confirmed by experiment. Thus piperazine (3 mols.) reacts with ethyl chloroformate (2 mols.) at p_H 2·8—4·6 (constant) to give *ethyl piperazine*-1-*carboxylate* (I), b. p. 116—117°/12 mm. and 237°/760 mm., and ethyl piperazine-1 : 4-dicarboxylate in yields of 70% and 12%, respectively. Under similar conditions, benzoyl chloride gives a 22% yield of 1-*benzoylpiperazine*, m. p. 64°, whilst no monotoluenesulphonyl compound could be isolated with *p*-toluenesulphonyl chloride owing to the slowness of the reaction. Carbon dioxide and I form an additive *compound*, whilst carbon disulphide and I give the additive *compound*, $2C_4H_9N_2{\cdot}CO_2Et,CS_2$, m. p. 148° (decomp.). Benzoylation of I in the cold affords *ethyl* 4-*benzoylpiperazine*-1-*carboxylate*, m. p. 82° (shaking of the latter with cold 0·1*N*-sodium hydroxide gave chiefly sodium benzoate and a poor yield of *N*-benzoylpiperazine), whilst treatment with *p*-toluenesulphonyl chloride in weakly alkaline solution afforded *ethyl* 4-p-*toluenesulphonylpiperazine*-1-*carboxylate*, m. p. 121°, which yielded N-p-*toluenesulphonylpiperazine*, m. p. 110° [additive *compound* with carbon dioxide, $2C_{11}H_{16}O_2N_2S,CO_2$, m. p. 107° (decomp.); additive *product* with carbon disulphide, $2C_{11}H_{16}O_2N_2S,CS_2$, m. p. 171°]. Interaction of I with ethyl iodide in alcoholic solution gave an inseparable mixture of a quaternary iodide and ethylpiperazine-1-carboxylate, whilst interaction of I with excess of ethyl *p*-toluenesulphonate in dry alcohol at 100° in presence of sodium carbonate gave a 70—75% yield of *ethyl* 4-*ethylpiperazine*-1-*carboxylate*, b. p. 136°/28 mm. The latter was converted by boiling concentrated hydrochloric acid into 1-*ethylpiperazine dihydrochloride*, which when heated with dry slaked lime gave 1-*ethylpiperazine*, b. p. 155—158° (*chloroplatinate*; *chloroaurate*; additive *compound* with carbon disulphide, $C_6H_{14}N_2,CS_2$). When I is heated with ethylene chlorohydrin and anhydrous sodium carbonate at 110°, *ethyl* 4-β-*hydroxyethylpiperazine*-1-*carboxylate*, b. p. 184°/17 mm., is formed; this is hydrolysed by concentrated hydrochloric acid, giving 1-β-*hydroxyethylpiperazine dihydrochloride* (*chloroplatinate*; *chloroaurate*). Ethyl chloroacetate and anhydrous sodium carbonate convert I into *ethyl* 4-*carbethoxypiperazinoacetate*, b. p. 183°/18 mm., hydrolysed by alkali or (better) hydrochloric acid, to *piperazinoacetic acid dihydrochloride*. Treatment of the latter with silver carbonate gave *piperazinoacetic acid* $(+H_2O)$, m. p. 279° (decomp.). *Ethyl* 4-*carbethoxypiperazino*-β-*propionate*, b. p. 198°/22 mm., and *ethyl* 4-*carbethoxypiperazino*-γ-*butyrate*, m. p. 207°/21 mm., were similarly prepared from ethyl β-iodopropionate and ethyl γ-chlorobutyrate, respectively. Further treatment of these two esters gave *piperazino*-β-*propionic acid dihydrochloride*, *piperazino*-β-*propionic acid*, m. p. 215° (decomp.), the *chloroplatinate* of piperazinobutyric acid dihydrochloride, and piperazino-γ-butyric acid, m. p. 235° (decomp.).

Ethylenediamine and ethyl chloroacetate (p_H controlled by bromocresol-green) react to give *carbethoxyethylenediamine*, b. p. 135°/20 mm., which yields ethylenecarbamide when heated or when treated during several days with dilute aqueous "soda" and gives an additive *compound* with carbon dioxide, m. p. 102—103°, which is best prepared by passing carbon dioxide into an ethereal solution. The following are described: N-*benzoyl*-N′-*carbethoxyethylenediamine*, m. p. 130°; N-p-*toluenesulphonyl*-N′-*carbethoxyethylenediamine*, m. p. 66°; N-p-*toluenesulphonylethylenediamine*, m. p. 121°; *ethyl* N′-*carbethoxyethylenediamino*-N-*acetate* (decomposes on distillation and affords the *hydrochloride* of β-aminoethylglycine on hydrolysis); β-*aminoethylglycine*, m. p. 144°. A. I. Vogel.

Quinoxalines from camphorquinone and aromatic o-diamines. A. Heckendorn (Helv. Chim. Acta, 1929, **12**, 50—60).—*Camphanoquinoxalines* have been prepared from camphorquinone (1 mol.) and the following 1 : 2-diamines (1 mol.): *o*-phenylenediamine, m. p. 74° (cf. Singh and Mazumder, J.C.S., 1919, **115**, 574); o-*tolylenediamine*, m. p. 50°; 4-*chloro*-o-*phenylenediamine*, m. p. 98° after previous softening; 4-*nitro*-o-*phenylenediamine*, m. p. 149° [the quinoxaline derivative is reduced by stannous chloride and hydrochloric acid to the corresponding *amino*-derivative, m. p. 135° (*picrate*, m. p. 216°; *acetyl* derivative, m. p. 118°)]; 3 : 4 : 5-*triaminobenzoic acid*, m. p. 128—130° (decomp.) [*picrate*, m. p. 203° (decomp.); *acetyl* derivative, m. p. 279° (decomp.)]; 1 : 2-*naphthylenediamine*, m. p. 85—86°; 2 : 3-*diaminoanthraquinone*, m. p. 211°. 1 : 2 : 3 : 4-Tetraaminobenzene condenses with camphorquinone yielding a mixture of *diaminocamphanoquinoxaline*, m. p. 153—154° (*picrate*, m. p. 175°), and *dicamphanoquinoxaline*, m. p. 245°. From 1 : 2 : 4 : 5-tetra-aminobenzene and 1 mol. of the quinone a *diaminocamphano-*

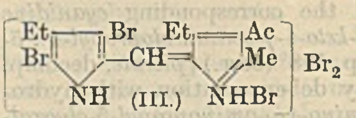
quinoxaline, m. p. 165° after softening at 130—140° (*picrate*, m. p. 176° after softening), is obtained. This furnishes three types of salts with sulphuric acid, namely, mono- (orange), di- (permanganate-red), and tri- (colourless). With 2 mols. of camphorquinone a *dicamphanoquinoxaline*, m. p. 333—335°, results.

H. Burton.

Syntheses of heterocyclic nitrogen nuclei. III. Triaryl derivatives of 1 : 2 : 4-triazole from arylidene [aromatic aldehyde] 2 : 4-diphenylsemicarbazones. G. Minunni and S. D'Urso [with S. Guglielmino, P. Salanitro, D. Torrisi, and M. Vasta] (Gazzetta, 1928, **58**, 820—831; cf. this vol., 196).—1 : 3 : 4-Triphenyl-1 : 2 : 4 : 5-triazolone (new m. p. 221·5—222°) is readily obtained by oxidising benzaldehyde-2 : 4-diphenylsemicarbazone with amyl nitrite in benzene solution (cf. Busch and Walter, A., 1903, i, 522; Minunni, A., 1927, 1073). *o*-Nitrobenzaldehydediphenylsemicarbazone reacts less readily, but with excess of amyl nitrite, in absence of solvent, 1 : 4-*diphenyl*-3-o-*nitrophenyl*-1 : 2 : 4 : 5-*triazolone*, m. p. 135—137° (decomp.), is formed. Under similar conditions the *m*- and *p*-compounds are oxidised to the 3-m- and 3-p-*nitrophenyltriazolones*, m. p. 199—200° (decomp.) and 193—194°, respectively. The *o*-nitrophenyltriazolone is reduced by zinc and acetic acid to 1 : 4-*diphenyl*-3-o-*aminophenyl*-1 : 2 : 4 : 5-*triazolone*, m. p. 192·5—193·5° (decomp.), with a secondary product, m. p. 244—247°; similar treatment of the *p*-compound gives a *substance*, m. p. 235—238°, which is not the *p*-aminophenyl derivative, since it contains 14·16—14·28% N. The piperonal semicarbazone gives rise to 1 : 4-*diphenyl*-3-*piperonyl*-1 : 2 : 4 : 5-*triazolone*, m. p. 169—170°.

E. W. Wignall.

Synthesis of octaethylporphin. H. Fischer and R. Bäumler (Annalen, 1929, **468**, 58—98).—Reductive condensation (using zinc dust and acetic acid) of the *iso*nitroso-derivative of ethyl propionoacetate with acetylacetone produces *ethyl* 3-*acetyl*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 115°, converted by the Wolff–Kishner method into 2-*methyl*-3 : 4-*diethylpyrrole* (I), b. p. 104—105°/13 mm. or 202—203°/760 mm., d^{17} 0·90996, n_D^{17} 1·49879 (*picrate*, m. p. 101°). Hydrolysis of the above ester affords the *acid*, m. p. 208°, and this when heated passes into 3-*acetyl*-2-*methyl*-4-*ethylpyrrole* (II), m. p. 129°, b. p. 280—290°. Since ethyl propionoacetate is not readily obtainable by Willstätter's method (A., 1914, i, 286) I was synthesised by the Wolff–Kishner method from II, obtained by the Friedel–Crafts reaction from 2-methyl-4-ethylpyrrole, the latter being obtained from ethyl 5-propionyl-2-methyl-4-ethylpyrrole-3-carboxylate by means of sulphuric acid. Both methods of synthesis were abandoned in favour of the following: Reductive condensation of the *iso*nitroso-derivative of dipropionylmethane with acetylacetone gives 3-*acetyl*-5-*propionyl*-2-*methyl*-4-*ethylpyrrole*, m. p. 137°, converted by diluted sulphuric acid at above 70° into 2-methyl-4-ethylpyrrole, but by the same reagent at 65—70° into II. The latter (II) affords 5-*bromo*-3-*acetyl*-2-*methyl*-4-*ethylpyrrole*, m. p. 149°, when treated in glacial acetic acid with 1 mol. of bromine; in hot acetic acid, the requisite bromine gives rise to 3 : 5-*dibromo*-2-*methyl*-4-*ethylpyrrole*, m. p. 161°, which withstands further attempts at bromination; 4 mols. of bromine convert II into the *perbromide* (III), not melting at 260°. This substance does not brominate acetone, so that the bromine is unusually non-reactive, and cannot be converted into the parent base, or into a porphyrin, or into a copper salt. Proof that in the formation of III an acetyl group is eliminated is given by the fact that oxidation of III with chromic anhydride in warm glacial acetic acid affords bromoethylmaleimide, m. p. 128°.



(III.)

Excess of bromine converts 2 : 4-dimethylpyrrole-5-aldehyde into the methene obtained by brominating 2 : 4-dimethylpyrrole (Fischer and Scheyer, A., 1924, i, 80), but ethyl 2 : 4-dimethylpyrrole-5-aldehyde-3-carboxylate under similar conditions merely gives the hydrobromide of the methene derived from ethyl 2 : 4-dimethylpyrrole-3-carboxylate. Ethyl 2 : 4-dimethylpyrrole-3-carboxylate shows a marked tendency to pass into methenes. Thus it condenses with ethyl 3-methyl-4-ethylpyrrole-5-aldehyde-2-carboxylate, the aldehyde group of the latter being eliminated in the process.

Boiling aqueous formaldehyde, in absence of hydrochloric acid, converts II into *bis*-(3-*acetyl*-2-*methyl*-4-*ethyl*-5-*pyrryl*)*methane*, m. p. 259°, a fact which demonstrates the great reactivity of II as compared with that of lower homologues. Bromination of the methane gives (3-bromo-2-methyl-4-ethyl-5-pyrryl)-(3'-bromo-4'-ethyl-2'-bromomethyl-5'-pyrrolenyl)-methene hydrobromide, convertible with difficulty into a porphyrin.

Stepwise bromination of ethyl 3-acetyl-2-methyl-4-ethylpyrrole-5-carboxylate gives, first, *ethyl* 3-*acetyl*-4-*ethyl*-2-*bromomethylpyrrole*-5-*carboxylate* (impure, m. p. 120°, converted by warm dilute alcohol into *ethyl* 3-*acetyl*-4-*ethyl*-2-*hydroxymethylpyrrole*-5-*carboxylate*, m. p. 101°) and, secondly, into *ethyl* 3-*bromo*-4-*ethyl*-2-*bromomethylpyrrole*-5-*carboxylate*, m. p. 170°. The latter is the product of excess bromination of the above ester and also results by the excess bromination of ethyl 2-methyl-4-ethylpyrrole-5-carboxylate. The stepwise bromination of the latter produces, intermediately, *ethyl* 3-*bromo*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 124°. The fact that the acetyl radical resists replacement by bromine appears to explain why in the conversion of II into III only one acetyl group is lost. This conversion appears to involve: (1) 5-bromination, (2) bromination in the 2-methyl group, and (3) displacement of the 3-acetyl group by a bromine atom (giving possibly a perbromide). The resulting substance is exceedingly reactive, and condenses with unchanged 5-bromo-derivative to give III. This explanation accords with the facts regarding the bromination of ethyl 2 : 4-dimethylpyrrole-3-carboxylate. In this case, bromine in ether produces *ethyl* 5-*bromo*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m. p. 96° (decomp.), whilst further bromination (in acetic acid) gives (5-*bromo*-3-*carbethoxy*-4-*methyl*-5-*pyrryl*)(3'-*carbethoxy*-2' : 4'-*dimethylpyrrolenyl*)*methene hydrobromide*, not melting at 260° (free *methene* has m. p. 153°).

The above ethyl 3-acetyl-4-ethyl-2-bromomethylpyrrole-5-carboxylate reacts with boiling methyl alcohol to give the corresponding 2-methoxymethyl compound, and not *bis-(2-carbethoxy-4-acetyl-3-ethyl-5-pyrryl)methane*, m. p. 115°, which results when the bromomethyl compound is heated with aqueous formaldehyde. 2-Methyl-3 : 4-diethylpyrrole (I), the physiological action of which (on rats and mice) has been studied (it is a weak poison), is convertible (1) into a well-defined *picrate*, (2) into well-defined, although unstable, *azo-dyes*, and (3), by Gattermann's hydrogen cyanide method, into *2-methyl-3 : 4-diethylpyrrole-5-aldehyde*, m. p. 74° (*copper acetate* additive compound of the intermediately formed aldimine hydrochloride is described). This aldehyde is transformed by sodium nitrite and diluted sulphuric acid into the monoxime of diethylmaleimide, m. p. 194°, and by nitric acid into diethylmaleimide, which is not an oil as stated by Küster (A., 1908, i, 303), but melts at 68° (crystallographic data by STEINMETZ). Repetition of Küster's synthesis of the imide gave an identical solid product.

2-Methyl-3 : 4-diethylpyrrole is readily brominated in acetic acid, giving the well-defined *perbromide hydrobromide*, m. p. 132°, converted by benzene–light petroleum crystallisation into the *hydrobromide*, m. p. 194°, of *(5-bromo-3 : 4-diethyl-2-pyrryl)(2′-methyl-3′ : 4′-diethyl-5′-pyrrolenyl)methene*, m. p. 97°, obtained by treating the perbromide hydrobromide with alcoholic ammonia. The methene, or either of the salts, is converted into *octaethylporphin*, m. p. 318° (*hydrochloride*, m. p. 318°), either by fusion, or by concentrated sulphuric acid, or by boiling formic or acetic acid, or best, either by the action of hydrogen bromide in glacial acetic acid under pressure, or by succinic acid fusion (35% yield in the last case). Treatment of the last-named perbromide hydrobromide or of the hydrobromide with zinc dust and glacial acetic acid produces *octaethylporphyrinogen*, m. p. 184°, passing slowly if pure, but rapidly if impure, into octaethylporphin (m. p. 322° ?) by aërial oxidation. The mechanism of the synthesis of the porphyrinogen is regarded as involving first of all the formation of 5-bromo-2′-methyl-3 : 4 : 3′ : 4′-tetraethyl-2 : 5′-dipyrrylmethane, since the picrate of I was isolated from the product containing the porphyrinogen.

Octaethylporphin is spectroscopically identical with ætioporphyrin (data tabulated). In hydrochloric acid the porphin shows the same spectrum as ætioporphyrin; after some time another spectrum is observed and a hydrochloride separates.

Iron is readily introduced into octaethylporphin in good yield. All three *hæmins* of the formula $C_{36}H_{44}NFeX$, where X=Cl, Br, or I, are obtainable in well-defined forms. They are spectroscopically different in pyridine solution, in which additive compound formation probably takes place. The *copper* salt, $C_{36}H_{44}N_4Cu$, in described (spectroscopic data given). The *phyllin* is well defined (m. p. not below 400°) and forms a *copper* salt.

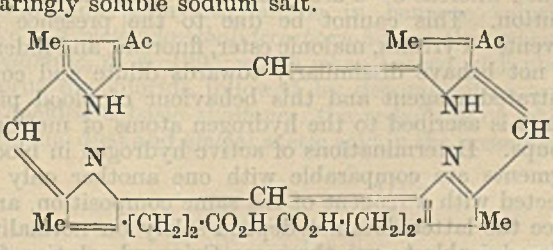
Octaethylporphin is oxidised by oxygen to diethylmaleimide, forms a *tetrabromo*-compound, and is oxidised by lead dioxide in chloroform and glacial acetic acid to the yellow *octaethylxanthoporphinogen*. The latter contains xH_2O, difficult to remove, and decomposes at 274°.

Octaethylporphin was also synthesised as follows: Magnesium ethyl bromide, followed by ethyl chloroformate, converts I into ethyl 2-methyl-3 : 4-diethylpyrrole-5-carboxylate. The latter, with bromine in absolute ether, passes into a bromo-compound which, when boiled with methyl alcohol and then submitted to hydrolysis, affords *3 : 4 : 3′ : 4′-tetraethyl-2 : 2′-dipyrrylmethane-5 : 5′-dicarboxylic acid*, m. p. 186°. When air is passed through a formic acid solution of this substance at 40°, octaethylporphin, m. p. 326°, is produced. Bromination of the same acid in glacial acetic acid affords *(5-bromo-3 : 4-diethyl-2-pyrryl)-(5′-bromo-3′ : 4′-diethyl-2′-pyrrolenyl)methene hydrobromide*, decomp. 206°.

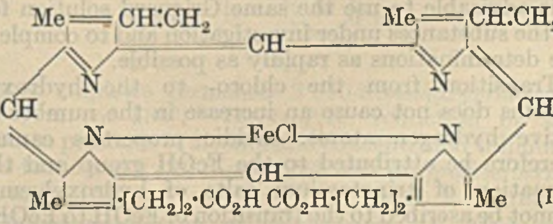
Condensation of I with formic acid in presence of hydrochloric, hydrobromic, or perchloric acid gives either the *hydrochloride*, or the *hydrobromide*, m. p. 202°, or the *perchlorate*, m. p. 173°, of the expected *methene*, m. p. 92° (*copper* salt, $C_{38}H_{54}N_4Cu$, m. p. 176°). Bromination of the methene at 100° in glacial acetic acid gives (3 : 4-diethyl-5-bromomethyl-2-pyrryl)(3′ : 4′-diethyl-5′-bromomethyl-2′-pyrrolenyl)-methene, which when submitted to succinic acid fusion with the above methene, m. p. 92°, gives octaethylporphin.

Ethyl 2 : 4-dimethylpyrrole-5-carboxylate reacts with *iso*valeryl chloride in presence of aluminium chloride to give *ethyl 3-isovaleryl-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 99°.
E. E. TURNER.

Synthesis of hæmatoporphyrin, protoporphyrin, and hæmin. H. FISCHER and K. ZEILE (Annalen, 1929, **468**, 98—116).—Although deuteroporphyrin cannot be condensed with acetic anhydride in presence of aluminium or stannic chloride, deuterohæmin is converted into the *CC*-diacetyl derivative when it is treated with acetic anhydride and stannic chloride at the ordinary temperature (cf. Stadnikov and Rakovski, A., 1928, 427). A poor yield of the diacetyl derivative is obtained when aluminium chloride is used, but in both cases removal of iron from the product (using hydrogen bromide and glacial acetic acid at 40°), followed by esterification, gives the *methyl* ester, m. p. 234°, of *diacetyldeuteroporphyrin* (I). The latter forms a soluble ammonium salt, a sparingly soluble potassium salt, and a still more sparingly soluble sodium salt.



(I.)



(II.)

The methyl ester is converted by a solution of iron in glacial acetic acid, in presence of sodium chloride and hydrochloric acid, into the complex *iron* salt, $C_{36}H_{36}O_6N_4FeCl$, m. p. 229°, and by copper acetate in presence of pyridine and acetic acid into the complex *copper* salt, $C_{36}H_{36}O_6N_4Cu$, m. p. 230°.

When an absolute alcoholic potassium hydroxide solution of diacetyldeuteroporphyrin is boiled, hæmatoporphyrin is formed. Its hydrochloride is crystallographically (STEINMETZ) and spectroscopically identical with natural hæmatoporphyrin hydrochloride. At 105° in a high vacuum, the free hæmatoporphyrin passes almost quantitatively into protoporphyrin, the methyl ester of which melts at 228°. Both substances are identical with the products derived from blood.

The synthetic hæmatoporphyrin hydrochloride is converted by hydrogen iodide in glacial acetic acid (Fischer and Kögl, A., 1924, i, 1130) into mesoporphyrin, the sparingly soluble sodium salt of which reacts with methyl-alcoholic hydrogen chloride to give mesoporphyrin dimethyl ester, m. p. 210°, identical with an authentic specimen. From the synthetic protoporphyrin, hæmin, $C_{34}H_{32}O_4N_4FeCl$, has been prepared (cf. Fischer and Pützer, A., 1926, 854). The product is crystallographically and spectroscopically identical with natural hæmin. At the moment the authors regard II as the most satisfactory formula for hæmin. E. E. TURNER.

Porphyrins and their metallic salts. F. HAUROWITZ and K. ZIRM (Ber., 1929, 62, [*B*], 163—170).—The lack of constancy in the results of determination of active hydrogen in blood pigment derivatives (cf. Fischer, A., 1926, 630; 1927, 1099; 1928, 903) by Zerevitinov's method is attributed to change in concentration of the Grignard reagent which rapidly loses strength if exposed to oxygen. This is usually unimportant, since the majority of organic compounds evolve methane quantitatively provided that the reagent is at least 0·8*N*. Compounds containing water of crystallisation require a 1·5*N*-reagent if both hydrogen atoms are to react quantitatively. The porphyrins appear to behave similarly to hydrated compounds, containing hydrogen atoms which react only with the concentrated reagent. With a dilute solution chlorohæmin indicates 2—3 active hydrogen atoms, whereas 3—6 are found with the concentrated solution. This cannot be due to the presence of solvent. Pyrroles, malonic ester, fluorene, and indene do not behave dissimilarly towards dilute and concentrated reagent and this behaviour of blood pigments is ascribed to the hydrogen atoms of methine groups. Determinations of active hydrogen in blood pigments are comparable with one another only if effected with a reagent of the same composition, and since the latter does not depend solely on normality it is advisable to use the same Grignard solution for all the substances under investigation and to complete the determinations as rapidly as possible.

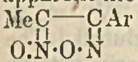
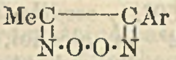
Transition from the chloro- to the hydroxyhæmins does not cause an increase in the number of active hydrogen atoms. Acidic properties cannot therefore be attributed to the FeOH group and the formation of tripotassium salts of hydroxyhæmin cannot be ascribed to the transition of FeOH to FeOK; the third acidic group is possibly the NH group of a pyrrole ring. The number of active hydrogen atoms of porphyrins is diminished at most by one equivalent by the formation of complex metallic compounds with Cu, Zn, or FeCl. (The experiments are made with the dimethyl ester of mesoporphyrin.) These complex derivatives are therefore not formed analogously to potassium pyrrole by simple salt production involving two pyrrole hydrogen atoms. The organic porphin skeleton suffers marked alteration by union with metals.

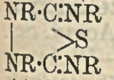
The FeCl compound of mesoporphyrin ester contains the same number of active hydrogen atoms as the zinc or copper salt, suggesting that the residue is bivalent and the iron atom tervalent. Porphyrins do not, however, in general form hæmins with ferric salts unless a reducing agent is present. The possibility that ferrous passes into ferric iron by reducing the solvent appears unlikely, since no evidence could be obtained of the reduction of water to hydrogen or of valeric acid to the aldehyde or alcohol. Elimination of iron from hæmins by acid occurs in the ferric form without production of ferrous iron. The apparent contradiction is not fully explained. H. WREN.

1 : 3 : 4-Oxdiazines. III. J. VAN ALPHEN (Rec. trav. chim. 1929, 48, 163—172).—α-Bromopropionyl bromide reacts with β-acetylphenylhydrazine in benzene solution forming β-*acetyl*-α-(α′-*bromopropionyl*)*phenylhydrazine*, which when treated with anhydrous potassium carbonate in acetone yields Δ^2-5-*keto*-4-*phenyl*-2 : 6-*dimethyl*-1 : 3 : 4-*oxdiazine*, b. p. 165—170°/15 mm., n_D^{15} 1·5583. The following substituted 5-keto-1 : 3 : 4-oxdiazines are obtained similarly from the appropriate α-halogenoacyl halide and β-acylphenylhydrazine: 4-*phenyl*-2-*methyl*-6-*ethyl*-, b. p. 146—148°/12 mm., n_D^{15} 1·5512; 4-*phenyl*-2 : 6 : 6-*trimethyl*-, b. p. 150—153°/15 mm., n_D^{15} 1·5423; 4 : 6 : 6-*triphenyl*-2-*methyl*-, m. p. 136°, isolated directly from β-acetylphenylhydrazine and diphenylchloroacetyl chloride; 2 : 4 : 6-*triphenyl*-, m. p. 141°; 2 : 4 : 6 : 6-*tetraphenyl*-, m. p. 151°, from β-benzoylphenylhydrazine and diphenylchloroacetyl chloride; 4-*phenyl*-2-β-*phenylethyl*-, m. p. 79°, hydrolysed by aqueous-alcoholic sulphuric acid to β-phenylpropionphenylhydrazide; 4-*phenyl*-2-*styryl*-, m. p. 128°, from cinnamphenylhydrazide and chloroacetyl chloride. The action of 10% aqueous-alcoholic sulphuric acid on the above and previously described oxdiazines (A., 1928, 780, 1386) shows that fission of the oxdiazine ring is partly inhibited with three methyl groups in the 2 and 6 positions, and completely stopped by one phenyl or styryl group in position 2.

Δ^2-5-Keto-2 : 4 : 6-triphenyl-1 : 3 : 4-oxdiazine is soluble in boiling aqueous-alcoholic sodium hydroxide, reacting in its enol form. This modification appears to be fairly stable, since the freshly-precipitated solid from an alkaline solution forms a chloroform-soluble copper salt, whereas the original compound does not. β-*Benzoyl*-α-*phenylchloroacetylphenylhydrazine* has m.p. 136°, not sharp. H. BURTON.

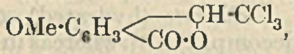
Dioximes. LI. G. PONZIO and M. MILONE (Gazzetta, 1928, 58, 844—853).—On the basis that the components of solid solutions resemble one another in molecular structure, the structure of dioxime peroxides is deduced from cryoscopic data, formation of

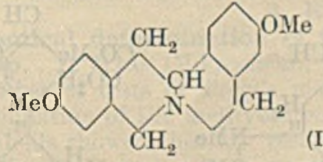
solid solutions being indicated by elevation of apparent mol. wt. The two structures in question are  $\begin{matrix}MeC-CAr\\ \|\quad\ \|\\ O{:}N\cdot O\cdot N\end{matrix}$ (I) and  $\begin{matrix}MeC-\!\!-\!\!-CAr\\ \|\qquad\quad \|\\ N\cdot O\cdot O\cdot N\end{matrix}$ (II) (cf. A., 1928, 888). Compounds of type I, oxadiazole *N*-oxides, would be expected to form solid solutions with the oxadiazoles themselves, and actually it is found that 3-phenyl-, 3-*p*-bromophenyl-, and 3-*p*-anisyl-4-methyl-1 : 2 : 5-oxadiazole-5-oxides show elevation of apparent mol. wt. in 3-*p*-anisyl-4-methyl-1 : 2 : 5-oxadiazole. The last is therefore used as a test substance, and it is found that bromo- and nitro-anisylmethyloxadiazole oxides, m. p. 109° and 88°, respectively, show increased mol. wt., and thus probably have similar structures, *i.e.*, are *N*-oxides, whilst the corresponding compounds of m. p. 115—116° and 112° have normal mol. wt., and are thus probably described correctly as bromo- and nitro-anisylglyoxime peroxides. Determinations of the apparent mol. wt. of the test substance in oxadiazole oxides, and of the compounds of m. p. 109° and 88° in bromo- and nitro-anisylmethyloxadiazoles, respectively, have also been made.
E. W. WIGNALL.

Oxidation. II. Action of ferric chloride and hydrogen peroxide on *s*- and *as*-disubstituted thiocarbamides and synthesis of thiodiazoles. T. CHAKRAVARTI and S. DE (J. Indian Chem. Soc., 1928, **5**, 661—664).—Oxidation of diarylthiocarbamides with hydrogen peroxide proceeds thus: $NHR\cdot C(NR)\cdot SH \longrightarrow [NHR\cdot C(NR)\cdot S\cdot]_2 \longrightarrow$  $\begin{matrix}NR\cdot C{:}NR\\ |\quad\ >S\\ NR\cdot C{:}NR\end{matrix}$ (I). The following substituted 1 : 3 : 4-thiodiazoles were obtained from the requisite *s*-diarylthiocarbamide: 2 : 5-*diphenylimino*-3 : 4-*diphenyl*- (I, R=Ph), m. p. 228—230°; 2 : 5-*di*-p-*tolylimino*-3 : 4-*di*-p-*tolyl*-, m. p. 261°; 2 : 5-*di*-o-*tolylimino*-3 : 4-*di*-o-*tolyl*-, m. p. 249°; 2 : 5-*di*-m-*xylylimino*-3 : 4-*di*-m-*xylyl*-, m. p. 247°; 2 : 5-*di*-α-*naphthylimino*-3 : 4-*di*-α-*naphthyl*-, m. p. 285°, and 2 : 5-*di*-β-*naphthylimino*-3 : 4-*di*-β-*naphthyl*-, m. p. 288° after sintering at 268°. From the necessary *as*-disubstituted thiocarbamides 2 : 5-*di*(*phenylmethylamino*)-, m. p. 94°, 2 : 5-*di*-(*phenylethylamino*)-, m. p. 107—109°, and 2 : 5-*di*-(*diphenylamino*)-1 : 3 : 4-*thiodiazoles*, m. p. 155°, were prepared.
H. BURTON.

3-Chlorotropan. The non-existence of the bellatropine of Hesse. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1928, **188**, 179—181).—Bellatropine, the hydrolytic product obtained by treating belladonine with hydrochloric acid at 140° and considered by Hesse to be an isomeride of tropine, is actually 3-*chlorotropan*, b. p. 163—165° (partial decomp.) (*hydrochloride*, m. p. 234°; *picrate*, m. p. 216—217°). The *methiodide*, m. p. 306°, affords tropan methiodide when treated with zinc dust and hydrochloric acid. 3-Chlorotropan yields a crystalline *amine oxide* (*hydrochloride*, m. p. 210°; *picrate*, m. p. 175°; *chloroplatinate*, m. p. 252°; *chloroaurate*, m. p. 168° after darkening and softening at 150°). The use of hydrobromic acid in the hydrolysis leads to the formation of 3-bromotropan. Belladonine yields partly polymerised atropic acid, tropine, and tropidine when hydrolysed with alcoholic potassium hydroxide or 2% sulphuric acid. [Throughout the paper the authors write the formulæ of 3-chlorotropan and its derivatives as containing an atom of oxygen.]
G. A. C. GOUGH.

Amine oxides of hydrastine and narcotine. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1929, **188**, 341—343).—Hydrastine is converted by an acetic acid solution of 30% hydrogen peroxide into *hydrastine oxide*, $[\alpha]_D$ +88° in 3% chloroform solution (*hydrochloride*, m. p. about 125°, $[\alpha]_D$ +160° in 12% aqueous solution; *picrate*, m. p. 128°). The oxide behaves like an amine oxide in most respects, although it slowly passes into a yellow *substance*, $C_{20}H_{18}O_7NMe$, m. p. 189° (*hydrochloride*, m. p. 196°), which behaves differently. Similarly, narcotine affords *narcotine oxide*, $[\alpha]_D$ +135° in chloroform (*hydrochloride*, m. p. 193°, $[\alpha]_D$ +100°; *picrate*, m. p. 130°; *chloroplatinate*, m. p. 175°), changing into a *substance*, m. p. 228—229°, identical with that obtained by Drummond and McMillan (A., 1926, 1263) except that it is optically inactive.
G. A. C. GOUGH.

Synthesis of 3 : 10-dimethoxytetrahydroprotoberberine. S. N. CHAKRAVARTI and W. H. PERKIN, jun. (J.C.S., 1929, 196—201; cf. A., 1927, 1096).—*m*-Methoxybenzoic acid, m. p. 109—110° (methyl ester, b. p. 121—124°/10 mm.), was obtained in 90% yield by oxidising *m*-methoxybenzaldehyde with potassium permanganate in aqueous acetone solution. It condenses with formaldehyde in the presence of hydrochloric acid or, better, of the latter together with glacial acetic acid to give 4-methoxyphthalide, m. p. 120°. This is converted by manganese dioxide and sulphuric acid or alkaline potassium permanganate into 4-methoxyphthalic acid, m. p. 168—170° (decomp.), and not into the expected 4-methoxyphthalaldehydic acid which was required for the synthesis of 4-methoxyphthalidecarboxylic acid. The latter was, however, prepared by condensing methyl 4-methoxybenzoate with chloral hydrate in presence of a large excess of sulphuric acid. The 4-methoxytrichloromethylphthalide,  $OMe\cdot C_6H_3{<}\begin{matrix}CH\cdot CCl_3\\ CO\cdot O\end{matrix}$, so obtained, m. p. 135°, was hydrolysed by aqueous sodium hydroxide to 4-methoxyphthalidecarboxylic acid, m. p. 170°. Condensation of the acid chloride of the latter with β-*m*-methoxyphenylethylamine in benzene solution gave 4-*methoxyphthalidecarboxy*-β-m-*methoxyphenylethylamide*, m. p. 129°, which when heated with phosphorus oxychloride followed by decomposition with ice yielded a basic *substance*, the reduction of which with zinc dust and glacial acetic acid in the presence of



(I.)

copper sulphate furnished 3 : 10-*dimethoxyprotoberberine*, m. p. 180°. Electrolytic reduction of the latter in presence of alcohol and concentrated sulphuric acid furnished 3 : 10-*dimethoxytetrahydroprotoberberine* (I), m. p. 139°.
A. I. VOGEL.

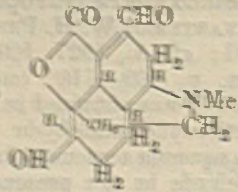
Dehydrogenation of yohimbine. F. MENDLIK and J. P. WIBAUT (Rec. trav. chim., 1929, **48**, 191—

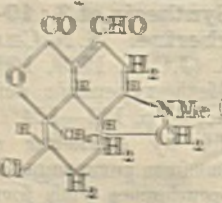
192).—Dehydrogenation of yohimbine with powdered selenium at 300—310° (cf. Diels, A., 1928, 51) gives a colourless *compound*, $C_{18}H_{16}N_2$, m. p. 212—213° (corr.), soluble in dilute acids with a blue fluorescence, and giving various alkaloidal precipitation reactions, together with a *substance*, m. p. 326°, yellow, not obtained pure, which dissolves in alcohol with a bluish-green fluorescence. H. Burton.

Fissions with ozone in the morphine series. E. Speyer (Ber., 1929, 62, [*B*], 209—218; cf. Wieland and Small, this vol., 81).—α-Thebaizone is converted by short treatment with 30% hydrogen peroxide into thebaizonedicarboxylic acid, decomp. 208—210° (lit. 189—190°); the presence of two carboxyl groups is established by potentiometric titrations. The *monohydrated hydrochloride*, m. p. 242° (decomp.), is described.

Ozodihydrocodeine hydrochloride (cf. Speyer and Popp, A., 1926, 532) is transformed by ozonisation in aqueous solution into methyl glyoxylate (phenylhydrazone, m. p. 138°) and dihydrocodinal (I)

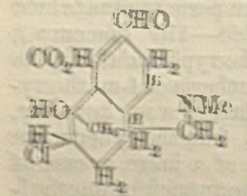
(I.)



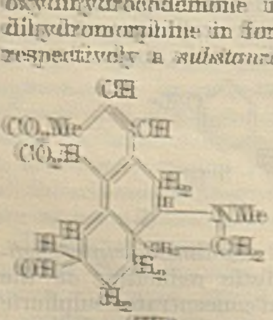


(II.)

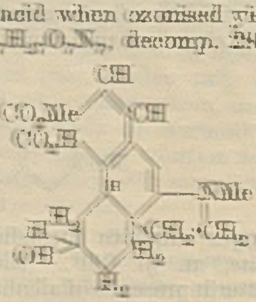
(amorphous *phenylhydrazone* and its *hydriodide*, decomp. 247°). Similarly, ozoethyldihydromorphine (*loc. cit.*) affords dihydrocodinal and ethyl glyoxylate; *dihydrocodinalsemicarbazone* decomposes at 278°. Chloro-ozodihydrocodeine dissolved in a mixture of ethyl alcohol, dilute acetic acid, and perchloric acid is transformed by ozonisation into *chlorodihydrocodinal* (II), m. p. 206—207° (decomp.) [*perchlorate* (hydrated) softening at 165° (anhydrous, decomp. 270°)], whereas in acetic acid solution it affords *chlorodihydrodicinal perchlorate* (cf. III), decomp. 266°, $[\alpha]_D$ −33·48° in water (also *monohydrate*). Chlorodihydrocodeide in alcohol containing perchloric acid is ozonised to chlorodihydrocodinal and methyl glyoxylate, whereas in formic acid solution it yields chlorodihydrodicinal. Hydroxydihydrocodeinone in acetic acid solution and dihydromorphine in formic acid when ozonised yield respectively a *substance*, [illegible], decomp. 285°, and dihydrocodinal. α-Ozodihydrocodeine hydrochloride is converted by alcoholic sodium ethoxide at a temperature not exceeding 15° into δ-*ozodihydrocodeine* (IV), m. p. 170·5°, $[\alpha]_D^{18}$ +24·4° in absolute alcohol, in 93% yield. If the reaction is allowed to proceed at 45—50°, γ-*ozodihydrocodeine* (V), m. p. 175°, $[\alpha]_D^{18}$ −8·2° in alcohol, is produced. The δ-compound is transformed into the γ-derivative by alcoholic sodium ethoxide at 50°. H. Wren.



(III.)



(IV.)



(V.)

Synthesis of aromatic arsenic compounds containing iodine. A. D. Macullum.—See B., 1929, 150.

Organo-antimony compounds. III. S. C. Niyogi (J. Indian Chem. Soc., 1928, 5, 753—757).—Carbamide and *p*-aminophenylstibinic acid react in boiling aqueous suspension to give "ureastibamine" (Brahmachari, Indian J. Med. Res., 1922, 10, 508; 1924, 12, 423), proved to be ammonium 4-carbamidophenylstibinate (*sodium* and *potassium* salts) by its preparation from cyanic and *p*-aminophenylstibinic acids and ammonia. H. Burton.

Attempt to prepare mercury compounds of triphenylmethane dyes. F. R. Greenbaum (Amer. J. Pharm., 1929, 101, 34—46).—Mercuration of brilliant-green, malachite-green, gentian-violet, night-blue, and basic fuchsin with mercuric chloride gave mixtures of mono- and di-mercury *compounds* which were almost insoluble in alcohol and water. Alkali-soluble dimercury *compounds* were obtained by mercuration of the condensation products of benzotrichloride and phenol and resorcinol.

E. H. Sharples.

Aromatic compounds containing tellurium. F. P. Mazza and E. Melchionna (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 54—59).—*Diphenyltelluride-oo′-dicarboxylic acid*, m. p. 215° (soluble *sodium* salt), is obtained from an alkali telluride and diazotised anthranilic acid. The method of Ernyei (A., 1901, ii, 94) for the preparation of potassium telluride not being satisfactory, sodium telluride was prepared by the reaction between sodium and tellurium in liquid ammonia in an autoclave. When the above acid was reduced by zinc and potassium hydroxide, and treated with sodium chloroacetate, *o-carboxyphenyltelluroglycollic acid*, m. p. 195°, was obtained. This decomposed when treated with fused potassium hydroxide, but when boiled with acetic anhydride it furnished *3-hydroxytelluronaphthen*, m. p. 200° (after decomp. at 160°) (*acetyl* derivative). By analogy with the corresponding selenium compound (Lesser and Weiss, A., 1912, i, 642) this was expected to yield telluroindigotin, but all attempts to carry out this oxidation were unsuccessful. E. W. Wignall.

Metal-protein compounds. VII. Changes in physico-chemical properties of egg-albumin treated with cobalt powder. G. B. Bonino and A. Garrino (Arch. Sci. biol., 1928, 11, 212—216; Chem. Zentr., 1928, ii, 1191—1192).—The electrical conductivity and p_H of dialysed egg-albumin solutions are increased by addition of cobalt powder.

A. A. Eldridge.

Action of carbon monoxide on hæmatin catalysis. H. A. Krebs (Biochem. J., 1928, 22, 480).—Dixon's suggestion (A., 1928, 1140) that stale solutions of hæmatin were used by the author is incorrect. That Dixon obtained no evidence of inhibition by carbon monoxide is due to his having used impure reagents. J. H. Birkinshaw.

Inhibition of ferrocysteine catalysis by carbon monoxide. W. Cremer (Biochem. Z., 1928, **201**, 490).—Dixon's failure (A., 1928, 1149) to obtain inhibition of ferrocysteine catalysis is due to his having used the ratio of carbon monoxide to oxygen (p_{CO}/p_{O_2}) applicable to hæmin. This is unsuitable for ferrocysteine. J. H. Birkinshaw.

Micro-Dumas apparatus. S. Okido (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 2).—Improvements in Dubsky's micro-method for nitrogen determination are described : (*a*) by passing carbon dioxide through the preheated combustion tube while still red hot, to avoid occlusion of air, and (*b*) by use of a three-way cock between the carbon dioxide generator and the bubble counter. B. W. Anderson.

Determination of iodine (halogen) in organic material. J. Schwaibold (Chem.-Ztg., 1929, **53**, 22—23).—For the determination of small amounts of iodine in organic material, a weighed amount (up to several grams) of the dried substance is burnt in a porcelain or nickel boat in a stream of oxygen in a wide combustion tube. The vapours pass over heated platinised asbestos and through wash-bottles containing very dilute potassium carbonate. The boat and tube are finally washed out, the extract is combined with the potassium carbonate, the whole evaporated, and iodine determined by an appropriate method. Examples are given of the determination of iodine in thyroid extract, milk, urine, and soil. R. K. Callow.

Micro-determination of iodine in organic matter. J. F. Reith (Chem. Weekblad, 1929, **26**, 26—27).—The author claims a method similar to that of Schwaibold (preceding abstract) but arrived at independently. The material is burned in oxygen and the gases are drawn through alkaline solutions, which are added to the ash. S. I. Levy.

Determination of sulphur in organic compounds. I. Marek (Bull. Soc. chim., 1928, [iv], **43**, 1405—1408).—The organic substance is burnt in a quartz, pyrex, or Jena glass combustion tube (50 cm. × 18—20 mm.), the forward end of which is bent over at right angles, constricted slightly, and drawn out. Moist oxygen is admitted through a sealed-in side tube at the opposite end and the combustion boat can be pushed forward into the heated zones by means of a nickel rod. The combustion products are swept into water containing 2% of dissolved oxygen, and the sulphuric acid is determined by titration or, in presence of halogen, phosphorus, nitrogen, or arsenic, by gravimetric methods. Halogen can be determined in the same way, using a 3% solution of equal parts of sodium carbonate and sodium sulphite as absorbent. R. Brightman.

Microchemical detection of glycerol, ethylene glycol, and *d*-mannitol. H. Alber (Mikrochem., 1929, **7**, 21—29).—The sensitivity of the following tests for the detection of glycerol, glycol, and mannitol has been determined and the conditions for carrying them out microchemically have been standardised : Fischer and Tafel's hypobromite method and its various modifications (A., 1888, 358), Gläser and Moravski's formic acid method (A., 1890, 20), and Rose's boric acid method (Diss., Erlangen, 1902). A. R. Powell.

Micro-determination of the acetyl value. F. Pregl and A. Soltys (Mikrochem., 1929, **7**, 1—9).—The substance (3—5 mg.), preferably compressed into a pastille, is introduced into a small pear-shaped flask, the bulb of which is then filled with dry glass beads. The flask is connected by means of a side tube at the top of the bulb to a purifying and drying apparatus for air, and by means of a side tube in the neck with a U-tube packed with glass beads moistened with a saturated solution of potassium dihydrogen phosphate to absorb any sulphur dioxide. The other limb of the U-tube is connected by a silver tube and condenser to the absorption flask containing standard sodium hydroxide. The flask is heated in a water-bath for 20—40 min. while 1 c.c. of a 25% solution of toluene-*p*-sulphonic acid is introduced by means of a dropping funnel. The flask is then cooled and a slow current of purified air is drawn through it by attaching the side tube of the absorption flask to a vacuum pump capable of exhausting the apparatus to 15 mm. pressure. After 10 min., 1 c.c. of water is allowed to drop into the decomposition flask and the air current continued for another 10 min. without interrupting the suction. The U-tube is then immersed in hot water and the suction continued for a further 10 min. to ensure that all the acetic acid distils into the absorption flask. The solution in the latter is finally titrated with hydrochloric acid, using a slight excess which is determined by titration with 0·01*N*-sodium hydroxide. A. R. Powell.

Microchemical determination of hydrocyanic acid by the Brunswik reaction. W. P. Malitzky and M. T. Koslovsky (Mikrochem., 1929, **7**, 94—99).—The sensitivity of the Brunswik reaction is increased by the use of a silver nitrate solution acidified with nitric acid. The material to be tested is placed in a small tube together with a few drops of a saturated solution of oxalic acid and 2—3 drops of potassium permanganate solution if sulphides are present; the tube is covered with a watch-glass to the bottom of which is attached a small drop of the silver nitrate solution coloured with methylene-blue. If cyanides are present a turbidity due to silver cyanide appears in a few minutes; under the microscope blue needles are seen. The sensitivity of the test is 6×10^{-8} g. of hydrogen cyanide. A. R. Powell.

Microchemical determination of the methylimino-group. P. Haas (Mikrochem., 1929, **7**, 69—87).—A number of tests of Pregl's method for the micro-determination of the methylimino-group using various alkaloids showed that low results are almost invariably obtained, especially when the substance contains more than one :NMe group. The errors seem to be due to the difficulty of removing the whole of the :NMe from the substance and to the incomplete absorption of the hydrogen iodide by the red phosphorus suspension even when two or three absorption vessels are used. A. R. Powell.

Biochemistry.

Hæmoglobin. III. Equilibrium between oxygen and hæmoglobin in relation to changing $p_{\rm H}$. R. M. Ferry and A. A. Green (J. Biol. Chem., 1929, **81**, 175—203).—Horse-blood corpuscles diluted with 1·5% sodium chloride at 2° were run through a Sharples centrifuge, the concentrated cell suspension was added to distilled water and the solution again centrifuged, the mother-liquor was stirred and adjusted to about $p_{\rm H}$ 6·6 by addition of phosphate or dilute hydrochloric acid, and the hæmoglobin was recrystallised by dissolving in dilute potassium hydroxide and readjustment to $p_{\rm H}$ 6·6. Oxygen dissociation curves for the hæmoglobin thus prepared were determined at varying $p_{\rm H}$ in solutions buffered with phosphate or borate. The affinity of hæmoglobin for oxygen passed through a minimum at $p_{\rm H}$ 6·55. The combination of hæmoglobin with oxygen does not follow the simple mass law unless hæmoglobin be regarded as acting as a mixture of substances. Mathematical consideration of the results leads to the development of an empirical equation expressing the equilibrium, and to a theoretical expression for the change of the dissociation curve with $p_{\rm H}$, based on the theory of intermediate compound formation (cf. Adair, A., 1925, i, 849). C. R. Harington.

Structure of the hæmoglobin molecule. I. Nitrogen distribution in the hæmoglobin molecule of horse's blood. II. Nitrogen distribution in the globin molecule of horse hæmoglobin. A. Poljakov (Biochem. Z., 1929, **204**, 88—96, 97—105).—I. After repeated crystallisations of horse hæmoglobin elementary analyses and determinations of nitrogen in the various fractions obtained after hydrolysis were made. The content of arginine is 6·25%, histidine 13·78%, cystine 1·2%, and lysine 5·76%.

II. Globin was prepared by adding an aqueous solution of pure hæmoglobin to alcohol containing hydrochloric acid, precipitation by ether, washing with alcohol, and precipitating the aqueous solution with alcohol and ether. A globin hydrochloride was obtained. Analysis showed arginine 6·1%, histidine 13·25%, cystine 1·2%, lysine 6·2%.
J. H. Birkinshaw.

Formation of hæmatin from carboxy- and oxy-hæmoglobin by dilute acids. W. Lintzel and T. Radeff (Biochem. Z., 1928, **203**, 212—217).—When oxy- and carboxy-hæmoglobin solutions of the same molar concentration are treated with dilute acids the amount of hæmatin formed is 5—10% less for oxy- than for carboxy-hæmoglobin, whilst iron in an ionised form appears in the solution from the former but not from the latter. Oxyhæmoglobin, therefore, appears to undergo partial decomposition by the acid treatment. P. W. Clutterbuck.

Synthesis of hæmatoporphyrin, protoporphyrin, and hæmin. H. Fischer and K. Zeile.—See this vol., 333.

Relation of proteins and lipins of blood-serum to osmotic pressure. E. H. Fishberg (J. Biol. Chem., 1929, **81**, 205—214).—The relationship between the protein concentration and the (colloid) osmotic pressure of blood-serum is expressed by $p=e^{av}$, p and v being the reciprocals of the osmotic pressure and of the protein concentration, and a a constant specific for an individual serum. In lipæmic blood the osmotic pressure per g. of protein is greater than in normal blood diluted to a similar content of protein; this indicates that the lipins exercise an osmotic pressure, and that the development of lipæmia in hæmorrhage and in nephrosis represents an attempt to compensate, as regards the osmotic pressure, for the loss of protein.
C. R. Harington.

Viscosity of blood-serum as a function of temperature. P. L. du Noüy (J. Gen. Physiol., 1929, **12**, 363—377).—The viscosity of serum at various temperatures was determined by the rotating-drum method. Heating decreases the viscosity until the critical temperature, 55°, is reached; above this the viscosity rises rapidly, and heating above 57° for short periods causes a permanent increase in viscosity. This effect is due to the change in hydration of the protein. E. Boyland.

$p_{\rm H}$ of arterial and venous blood. A. Lumière, (Mme.) R. H. Grange, and R. Malaval (Compt. rend., 1929, **188**, 364—367).—Determination of the $p_{\rm H}$ of arterial and venous blood-serum of the dog by means of the hydrogen electrode and with precautions against the displacement of part of the carbon dioxide by atmospheric oxygen, gives 7·78 and 7·43 as the respective average values. When the serum, the plasma, or the whole blood is placed in a vacuum, the $p_{\rm H}$ values rise towards 8 and consequent heating of these liquids at 56° causes a further rise to $p_{\rm H}$ 8·4.
G. A. C. Gough.

Physiological ontogeny. A. Chicken embryos. XIV. Hydrogen-ion concentration of the blood of chicken embryos as a function of time. A. E. Cohn and A. E. Mirsky (J. Gen. Physiol., 1929, **12**, 463—468).—The $p_{\rm H}$ of the blood of 8—20-day chicken embryos was determined with a glass electrode. At 8 days the $p_{\rm H}$ of the reduced blood was 6·92; at 20 days, 7·22, whilst the blood of normal adults is 7·30. There was a tendency for the $p_{\rm H}$ to remain at about 7·15 between the 10th and 14th days. The change in $p_{\rm H}$ seems to follow the same course as the oxygen consumption (cf. Murray, A., 1925, i, 1353), so that the change in $p_{\rm H}$ probably follows the change in metabolism. E. Boyland.

[**$p_{\rm H}$ of blood.**] J. Holló and E. Weiss (Bull. Soc. Chim. biol., 1928, **10**, 1372—1375).—A reply to criticisms by Bigwood (A., 1928, 564) of the author's method for the determination of the $p_{\rm H}$ of blood.
G. A. C. Gough.

[**$p_{\rm H}$ of blood.**] E. J. Bigwood (Bull. Soc. Chim. biol., 1928, **10**, 1376—1377).—Whilst no objection is made to the method of Holló and Weiss (preceding abstract), it is doubtful whether their method is more accurate than those of Cullen and Hastings.
G. A. C. Gough.

Behaviour of ethyl iodide in the body. I. STARR and C. J. GAMBLE (Amer. J. Physiol., 1928, **87**, 474—485).—Ethyl iodide is constantly present in the venous blood of men or dogs inhaling it and exerts pressure against gases in contact with it.

B. A. EAGLES.

Absorption of ethyl chloride by blood, serum, and water. M. NICLOUX and L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1928, **98**, 229—232; Chem. Zentr., 1928, ii, 682).—The solubility of ethyl chloride in pig or ox blood is greater than in the corresponding serum, and greater still than in water.

A. A. ELDRIDGE.

Rôle of the blood in transmineralisation. C. OEHME and P. TÖRÖK (Deut. Arch. klin. Med., 1928, **160**, 233—248; Chem. Zentr., 1928, ii, 1114).

Determination of calcium in blood. J. H. ROE and B. S. KAHN (J. Biol. Chem., 1929, **81**, 1—8).—A modification of the authors' method (A., 1926, 763) is described, calcium being precipitated as phosphate and the phosphorus in the precipitate determined by the method of Fiske and Subbarov (A., 1926, 443).

C. R. HARINGTON.

Micro-determination of free phosphate in blood. E. JORPES and H. MAGNUSSON (Acta Paed., 1927, 7, No. 1—2, 14 pp.; Chem. Zentr., 1928, ii, 925—926).—The phosphate in blood deproteinised by means of trichloroacetic acid is precipitated as phosphomolybdate and collected on a micro-filter. Organic non-lipoid phosphorus in adults amounted to 0·25—0·35 mg.% (4—9% of the total non-lecithin phosphorus), and the phosphorus as free phosphate to 3·44 mg.%.

A. A. ELDRIDGE.

Is there an iodine value of the blood dependent on the thyroid gland ? F. BLUM (Schweiz. med. Woch., 1927, **57**, No. 34, 14 pp.; Chem. Zentr., 1928, ii, 1111).—The thyroid gland does not pass iodine into the blood. Fellenberg's method for the determination of iodine is not suitable for blood.

A. A. ELDRIDGE.

Peptide-nitrogen of blood. R. MARTENS (Bull. Soc. Chim. biol., 1928, **10**, 1336—1371).—Peptide-nitrogen is determined as the difference between the amino-nitrogen content after hydrolysis and elimination of ammonia and the original amino-nitrogen content of the filtrate from deproteinisation with 20% trichloroacetic acid, the method of Folin being used (A., 1922, ii, 536, 540). The trichloroacetic acid solution does not effect complete precipitation of leucylglycine, glycine, or proteoses. Blood from pathological cases is examined. G. A. C. GOUGH.

Amide-nitrogen of blood. II. Determination. III. Muscular exercise; rôle of ammonia in neutralisation of lactic acid. S. BLISS (J. Biol. Chem., 1929, **81**, 129—135, 137—158).—II. The proteins of blood are precipitated with tungstic acid, the precipitate is hydrolysed by heating at 100° with 4*N*-sulphuric acid, and the ammonia liberated determined in the usual way. The amide-nitrogen of blood determined in this manner amounts normally to 134—144 mg. per 100 c.c.

III. A dog is able to tolerate an amount of ammonium carbonate administered intra-arterially which, if given intravenously, causes toxic symptoms; after the intra-arterial administration an increase in the amide-nitrogen of the venous blood is observed, which, in dogs with normal kidneys, is of short duration only. After muscular exercise the amide-nitrogen of the arterial blood is diminished and that of the venous blood increased; this is accounted for in part by the increased excretion of ammonia, and in part on the view that ammonia, derived from the amide-nitrogen of the blood, is utilised in the neutralisation of lactic acid formed during exercise. C. R. HARINGTON.

Hypobromite method for the determination of small quantities of ammonia, particularly of residual nitrogen in blood. W. ENGELHARDT and M. LJUBIMOVA-KREMLEVA (J. exp. Biol. Med. [Moscow], 1927, No. 16, 26 pp.; Chem. Zentr., 1928, ii, 1241).—The iodometric hypobromite method is combined with the micro-Kjeldahl method for the determination of residual nitrogen in blood.

A. A. ELDRIDGE.

Distribution of uric acid in blood, and cause of errors in the determination of blood-uric acid. R. VLADESCO (Compt. rend. Soc. Biol., 1928, **98**, 462—464; Chem. Zentr., 1928, ii, 682).—The determination of uric acid in whole blood is more exact than that in serum; it must be preceded by complete hæmolysis of the red cells. Tungstic acid is preferred as a clarifying agent to trichloroacetic acid.

A. A. ELDRIDGE.

Blood-sugar regulation in mammals. I. Action of cold and hunger on blood-sugar. B. KISCH, A. SIMONS, and P. WEYL (Biochem. Z., 1929, **204**, 179—191).—Temperatures around 0° caused no marked increase in the blood-sugar of dogs and rabbits in the open air. When the animals were placed in an ice-box for 5—11 hrs. dogs showed an initial increase in blood-sugar of 10—30% followed by a decrease to below normal. Fasting rabbits showed a small decrease; when freshly fed there was a transient hyperglycæmia as with dogs. At 23—26° the blood-sugar regained its normal value. Fasting caused only a slight fall in the blood-sugar.

J. H. BIRKINSHAW.

Blood-catalase. H. BISCHOFF (Arch. Kinderheilk., 1927, **82**, 189—198; Chem. Zentr., 1928, ii, 1113).—The catalase content of the blood of children does not differ greatly from that of adults, but varies according to the point of extraction of the sample. The value is unchanged in infection or irradiation.

A. A. ELDRIDGE.

Interfacial adsorption as a factor in the clotting of blood-plasma. J. M. JOHLIN (J. Biol. Chem., 1929, **81**, 99—113).—The blood-plasma of fishes, which can normally be kept indefinitely without clotting, can be induced to clot by emulsification with air, ether, or chloroform (but not with paraffin), or by treatment with barium sulphate, kaolin, or powdered glass; ether-extracted plasma will cause normal plasma to clot, whilst the ethereal extract contains a substance which antagonises the accelerating effect of kephalin on clotting. The phenomena are regarded as being due to the adsorption of an antiprothrombin at the interface of the plasma with the various substances mentioned.

C. R. HARINGTON.

Hæmolysis. K. C. Sen, A. C. Ray, and N. N. Mitra (Nature, 1929, **123**, 242).—Both acceleration and retardation of hæmolysis in presence of normal serum can readily be obtained in taurocholate and oleate hæmolysis by varying concentrations of the reacting substances. Similar curves are obtained when the serum is replaced by a dilute solution of sodium hydroxide. Acceleration with saponin has not been observed. A. A. Eldridge.

Hæmolysis. III. Photochemical transformation of lecithin in the presence of hæmatoporphyrin. R. Fabre and H. Simmonet (Bull. Soc. Chim. biol., 1928, **10**, 1306—1325).—Irradiation of an alcoholic solution of lecithin and hæmatoporphyrin by the light of a mercury-vapour lamp leads to the formation of a substance which, when dissolved in normal saline, exerts a powerful hæmolytic action on the red blood-corpuscles of the dog (cf. Fabre, A., 1926, 750). The hæmolytic agent is not altered by dialysis or by boiling in an isotonic solution for 1 hr.; it is insoluble in ether but partly soluble in acetone and in alcohol. It is unaffected by 0·1*N*-hydrochloric acid, but treatment with 0·1*N*-sodium hydroxide increases its activity nearly tenfold. G. A. C. Gough.

Time-dilution curves in hæmolytic systems. K. C. Sen and N. N. Mitra (J. Indian Chem. Soc., 1928, **5**, 683—695; cf. MacLean and Hutchinson, A., 1909, ii, 816; Ponder, A., 1922, i, 292; 1923, i, 975; 1926, 751; 1927, 585).—The time-dilution curves for the hæmolysis of sheep's erythrocytes by hydrochloric acid, sodium hydroxide, potassium oleate, and saponin are all normal, the time of hæmolysis decreasing with increasing concentration of added substance. With sodium taurocholate marked abnormality is observed over the range of concentrations studied (approx. 1 in 50—16,000), but at low concentrations (below 1 in 1400) using small amounts of erythrocytes the curve is normal. The differences in results obtained by various workers (*loc. cit.*) are probably due to the concentrations of the hæmolytic systems. Sodium hydroxide retards the hæmolytic action of saponin, and inhibits completely that of sodium taurocholate over the range of concentrations examined. With potassium oleate and sodium hydroxide an acceleration is found for low oleate concentration; at higher oleate concentration inhibition takes place. With the same concentration of oleate hæmolysis always takes place first in presence of alkali. H. Burton.

Immuno-chemical investigations on globin and globin derivatives. L. Hektoen and K. Schulhof (Biochem. Z., 1929, **204**, 125).—A reply to Ottensooser and Strauss (A., 1928, 540).

Relation of lipins to proteins and immunity. S. Belfanti (Z. Immunitäts., 1928, **56**, 449—463; Chem. Zentr., 1928, ii, 1116).—The hæmolytic action of animal poisons on addition of lecithin is due to lecithinase whereby lysocithin is produced. A corresponding lipin has been isolated from the pancreas. Egg-yolk contains two proteins, one coagulable and the other soluble; with these is associated a large part of the lecithin, together with lysocithin, which may be extracted with alcohol. The soluble portion of egg-vitellin detoxicates lysocithin. Wasp- and hornet-poisons decompose lysocithin. A. A. Eldridge.

Rôle of lipins in immunisation. V. Brazil and J. Vellard (Z. Immunitäts., 1928, **56**, 191—208; Chem. Zentr., 1928, ii, 1116).—Animals could be immunised against animal and bacterial poisons with lipins prepared from serum and liver. A. A. Eldridge.

Concentration of sera containing anti-bodies by physico-chemical methods. (Electrodialysis and adsorption.) M. Eisler and M. Spiegel-Adolf (Biochem. Z., 1929, **204**, 28—45).—The use of electrodialysis in the concentration of serum agglutinating typhoid bacilli had no special advantages over half saturation with ammonium sulphate. A method depending on repeated precipitation of the active component by means of aluminium hydroxide and subsequent elution by 0·01*N*-sodium hydroxide is described. It was applied to typhoid-agglutinating serum of the horse, to hæmantitoxic sera of the horse, rabbit, and goat, and to diphtheria-antitoxic serum of the horse. By this method the protein content of the agglutinating serum was reduced to one sixth of its original volume without serious loss of agglutinin. In the case of antitoxic sera, only a single treatment could be applied and the protein content of the product corresponded with the original albumin content. J. H. Birkinshaw.

Proteins in egg-white and their relationship to the blood-proteins of the hen as determined by the precipitin reaction. L. Hektoen and A. G. Cole (J. Infect. Dis., 1928, **42**, 1—24).—Ovalbumin, ovomucin, and ovomucoid may be completely separated from ovoglobulin and conalbumin. Antisera against ovalbumin, ovoglobulin, ovomucin, and ovomucoid gave no reactions when tested with solutions of fibrinogen, euglobulin, or albumin prepared from the blood-plasma. An antiserum against the whole egg-white reacts with the blood-albumin only; the reaction is due to conalbumin, which is, probably, chemically identical with blood-albumin. Chemical Abstracts.

Agglutination and colloidal reactions. F. W. Mulsow (Proc. Iowa Acad. Sci., 1927, **34**, 85).—The agglutination reaction appears to be dependent on changes in surface tension and other colloidal properties. Alkalis have a stronger inhibiting action than acids. The effect of sodium or potassium hydroxide is much greater than that of ammonia, whilst strong and weak acids have an equal inhibiting action. Certain colloidal solutions, saponin, bile, and bile salts also have an inhibiting effect. Chemical Abstracts.

Hæm and tissue-iron. M. L. Anson and A. E. Mirsky (J. Gen. Physiol., 1929, **12**, 401—405).—The hæm of muscle and of yeast is estimated as pyridine-hæmochromogen, by spectroscopical examination of the band, corrected for the absorption by other pigments. Both yeast and muscle appear to contain about 40% of their total iron combined as hæm. E. Boyland.

Occurrence of lead in hen's eggs. W. B. S. Bishop (Med. J. Austral., 1928, **1**, 480—488).—The wet material (100 g.) contained the following amounts of lead : shell 0·1—1·6 mg., yolk 0·2—1·0 mg., white 0·12—0·48 mg. Chemical Abstracts.

Occurrence of molybdenum in hen's eggs. W. R. Mankin (Med. J. Austral., 1928, 2, 87).—Egg-white contains 0·01 mg. of molybdenum in 100 g. A modification of Koppel's method was employed. Chemical Abstracts.

Connexion of ropiness and structure in egg-white. J. Jochims (Biochem. Z., 1928, **203**, 142—146).—The ropiness of egg-albumin depends on the presence of substances which readily form filaments. When an albuminous rope is coagulated or when the albumin is dropped into boiling water a fibrillar coagulum is obtained, but when the albumin is whipped into a froth and allowed to reliquefy ropiness is lost and a fibrillar coagulum is no longer obtained. P. W. Clutterbuck.

Copper content of normal and pathological organs. I. Method. II. Copper content of normal and hæmochromatose liver, gallstones, and whole blood. R. Schönheimer and F. Oshima (Z. physiol. Chem., 1929, **180**, 249—258).—I. The solution obtained by heating 5—10 g. of the organ with concentrated nitric and sulphuric acids is treated with hydrogen sulphide, and subsequently with a few drops of bromine water, when the precipitated sulphur carries down the copper sulphide with it. This mixture is then washed free from iron, incinerated with a small amount of Neumann's reagent, and subsequently treated with ammonium thiocyanate and pyridine (cf. Fleming, A., 1924, ii, 502). The coloured complex is dissolved in chloroform and determined microcolorimetrically. The method is sensitive within the following limits of error : for 0·01 mg. 5%, for 0·008 mg. 8%.

II. The copper content of normal liver is 1·09—3·92 mg. per kg. (extreme values for 17 varying specimens), whilst hæmochromatose liver contains 98·6—63·29 mg. (extreme values for 16 cases). There is also a large increase in the amount of iron. Pigmented gallstones contain varying amounts (0·0159—0·206%), and blood has a content of 1·13—1·44 mg. per kg. in the three cases examined. H. Burton.

Cerebronic acid. P. A. Levene and F. A. Taylor. Also E. Klenk.—See this vol., 321.

Succinic acid as a product of decomposition of organs. L. van Itallie and A. J. Steenhauer (Pharm. Weekblad, 1929, **66**, 14—15).—The acid has been identified in the ethereal extracts of acid aqueous solutions obtained by treatment of partly decomposed organs, and is regarded as a normal decomposition product. S. I. Levy.

Determination of the carbohydrates in animal organs and in blood by characteristic colour reactions. I. Colour reactions of the carbohydrates and their use in the microchemical determination of different sugars in dilute solution. Z. Dische (Mikrochem., 1929, **7**, 33—68).—The solution (1 vol.) is mixed with 0·1 vol. of 10% α-naphthol solution and 8 vols. of concentrated sulphuric acid without cooling—a brown colour indicates glycuronic acid and a red colour glycollaldehyde or a sugar. In the latter case a further portion of the solution (1 vol.) is heated with 9 vols. of a mixture of 8 vols. of concentrated sulphuric acid and 1 vol. of water for 3 min. in a water-bath, cooled, and treated with 0·2 c.c. of a 5% α-naphthol solution—a brown colour develops in 10 min. if glycollaldehyde or a triose is present and a red colour in other cases. If a red colour is obtained, a third portion of the original solution (2 vols.) is heated for 30 min. in a water-bath with 4 vols. of a mixture of 100 vols. of concentrated hydrochloric acid, 80 vols. of glacial acetic acid, and 20 vols. of a 10% alcoholic solution of diphenylamine; pentoses give a brown, hexoses a blue, and carbohydrates or thymonucleic acid a violet-red colour. To distinguish between glycollaldehyde and trioses the solution (1 vol.) is mixed with 0·1 vol. of a 10% α-naphthol solution and 4 vols. of concentrated sulphuric acid without cooling; glycollaldehyde gives a greenish-blue and the trioses a red colour. The presence of the latter may be confirmed by mixing 1 vol. of the sugar solution with 4 vols. of sulphuric acid, cooling, and adding 0·1 vol. of a 10% α-naphthol solution; a green colour indicates trioses. If the hexose test is positive 1 vol. of the original solution is mixed with 0·1 c.c. of a 2% alcoholic solution of α-naphthol and 9 vols. of 75 vol.-% sulphuric acid; a blue colour indicates lævulose or hexosediphosphoric acid and a red colour aldoses. On dilution with water the red solution becomes colourless and a red precipitate is formed, but the blue solution is stable. The aldoses are differentiated by repeating the diphenylamine test previously mentioned but heating only for 1·5 min.; galactose produces a violet, mannose a brown, and dextrose a blue solution. To distinguish lævulose from hexosediphosphoric acid the diphenylamine test is repeated with only a 3 min. heating; the acid gives a violet and lævulose a brown colour. All the above tests serve to detect the respective compounds when they are present alone in a solution, but it is possible to use the tests for the approximate determination of lævulose, mannose, and galactose in the presence of dextrose by indirect analysis. A. R. Powell.

Micro-determination of glycogen in the liver. H. Bierry and B. Gouzon (Compt. rend. Soc. Biol., 1928, **99**, 186—188; Chem. Zentr., 1928, ii, 1132).—The liver is treated in an autoclave at 120° for 30 min. with 35% potassium carbonate solution; an excess of hydrochloric acid is then added and the heating at 120° for 30 min. repeated. After neutralisation and removal of protein with mercuric nitrate the dextrose is determined by a micro-method. A. A. Eldridge.

Plasmalogen. I. Properties of plasmalogen and preparation and nature of plasmal. R. Feulgen, K. Imhäuser, and M. Behrens (Z. physiol. Chem., 1929, **180**, 161—179).—Ox brain contains about ten times as much phosphatide as horse flesh, and this can be precipitated from ethereal solutions by acetone, or from alcoholic solution by alcoholic cadmium chloride solution. This precipitate contains the plasmalogen (cf. Feulgen and Voit, Pflüger's Archiv, 1924, **206**, 404). Treatment of plasmalogen emulsion (*loc. cit.*) with dilute acids or mercuric chloride and precipitation with acetone gives plasmal. When the emulsion is made alkaline with sodium hydroxide solution and then extracted with ether both plasmalogen and phosphatides go into solution, but after alkaline hydrolysis plasmalogen is not extracted. Acidification of the soap produced and subsequent extraction gives plasmal and fatty acids. Whereas plasmal is a powerful reducing agent plasmalogen does not contain a free aldehyde group. So far plasmalogen has only been obtained associated with phosphatides. Distillation of the emulsion from 10 kg. of horse flesh after treatment with mercuric chloride, with steam in an atmosphere of carbon dioxide gives crude plasmal, which when treated with thiosemicarbazide yields 1—2 g. of plasmalthiosemicarbazone, sinters at 105°, melts at 106°, and becomes clear at 107—107·5°. This m. p. is unaltered by repeated crystallisation from alcohol. Analysis indicates that it is essentially a mixture of stearaldehydethiosemicarbazone (10%) and palmitaldehydethiosemicarbazone (90%). The m. p. of such a mixture does not depress the m. p. of plasmalthiosemicarbazone, nor do the colour reactions (A., 1927, 369) of the two differ. H. BURTON.

Occurrence of methylguanidine in animal organism. I. Detection of methylguanidine in dog's muscle. I. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, **180**, 192—197).—Methylguanidine picrate has been isolated from the aqueous muscle extract either by direct precipitation with picric acid solution, or by precipitation of the extract with mercuric chloride and sodium acetate, and after removing mercury from this precipitate treatment of the residue with methyl and ethyl alcohols, platinum chloride, and finally picric acid. The yield of methylguanidine by this last method is 0·0134%. H. BURTON.

Relation between cystine yield and total sulphur in wool. C. RIMINGTON (Biochem. J., 1929, **23**, 41—46).—The whole of the sulphur of wool is liberated as cystine when the protein is hydrolysed by acid. The cystine determinations were carried out by the Sullivan and by the Folin and Looney methods in each case. S. S. ZILVA.

Enzymes in the fluid of ovarian cysts. I. Amylase. T. TACHIBANA (J. Kinki Gynæcol. Soc., 1927, **10**, 1—14; Chem. Zentr., 1928, ii, 1221).

Analysis of the liquid from a splenic cyst. S. GRILLON (Bull. Soc. Chim. biol., 1928, **10**, 1382).—The liquid, *d* 1·124, contained 24·27% of solid matter, which, when incinerated, gave 52·41% of an ash containing 0·431% Cl, 5·9% P_2O_5, and 6·59% $CaCO_3$. The cholesterol, protein, carbamide, and fat contents were 0·1, 8·25, 0·043, and 2·28%, respectively. G. A. C. GOUGH.

Membrane studies with the human amnion. H. RUNGE and H. SCHMIDT (Biochem. Z., 1928, **203**, 394—399).—When sacks made of the amnion of a freshly-born placenta and containing methylene-blue–Tyrode solution are placed in Tyrode solution at 37°, in some cases the epithelial and in others the connective-tissue side being in contact with the outer fluid, it is found by colorimetric examination of the outer fluid at intervals that diffusion is always greater when the dye is in contact with the epithelial side. Similar results are obtained with patent-blue, the direction of diffusion being unaffected by the presence of cyanide or mercuric chloride. Similar results are also obtained with Congo-red and cyanol at 37° and 2°. P. W. CLUTTERBUCK.

Histochemistry of the insect skeleton. W. KÜHNELT (Zool. Anzeiger, 1928, **75**, 111—113; Chem. Zentr., 1928, ii, 1109—1110).

Staining of elastic tissue. R. W. FRENCH (Stain Tech., 1929, **4**, 11—12).—The addition of dextrin to crystal-violet and basic fuchsin is advantageous in staining elastic tissue by Weigert's method. H. W. DUDLEY.

Staining of glial cells. R. ALTSCHUL (Atti R. Accad. Lincei, 1928, [vi], **8**, 594—595).—By mordanting nervous tissue with a solution containing 2 c.c. of hydrobromic acid and 2 g. of ammonium bromide to 100 c.c. of water, staining with either methyl-violet or Victoria-blue, and differentiating with xylene–aniline oil, the glial cells are revealed more certainly and more simply than by Weigert's process. T. H. POPE.

Differentiation of safranine in cytology. R. HAYNES (Stain Tech., 1929, **4**, 27—28).—An acid dye, such as "light green SF yellowish," is preferable to hydrochloric acid for the differentiation of safranine. H. W. DUDLEY.

Colloid chemistry of cerebrospinal fluid. J. KISS (Deut. Z. Nervenheilkunde, 1927, **98**, 227—272; Chem. Zentr., 1928, ii, 1229—1230).—Cerebrospinal fluid is best studied by means of gold sol. A. A. ELDRIDGE.

Digestive enzymes in stomach juices of snails. E. GRAETZ (Z. physiol. Chem., 1929, **180**, 305—307).—The stomach juices from *Helix pomatia*, *Limax maximus*, *L. flavus*, *Agriolimax agrestis*, and *Arion empericorum* all cause fission of Witte's peptone at p_H 7—8 and 37°. Caseinogen and fibroin are also digested by *H. pomatia*. The action of the juices on fats is also manifested, more particularly with the lower neutral fats. Sucrose, maltose, raffinose, and arbutin are also hydrolysed. H. BURTON.

Protease content of pylorus secretion. O. KESTNER, R. WILLSTÄTTER, and E. BAMANN (Z. physiol. Chem., 1929, **180**, 187—191).—The secretion gives a slight reaction for pepsin and trypsin, and a somewhat greater one for erepsin. After removal of leucocytes by centrifuging the secretion has no proteolytic action. H. BURTON.

Studies in milk secretion based on the variations and yields of butter fat and milk produced at morning and evening milkings. S. BARTLETT (J. Agric. Sci., 1929, **19**, 36—47).—Numerous milking records are presented and examined. Lower yields of milk and fat in morning milkings were general, but most notable in heifers and in heavy-milking, small-uddered cows. The possibility of the reabsorption of milk in these cases is discussed. The summer stimulus to milk secretion, usual in May and June, is more effective in the evening milk than in the morning. A. G. POLLARD.

Clarification and decolorisation of urine. FISCHER and HORKEIMER (Pharm. Ztg., 1929, **74**, 45—46).—Adsorption of sugar may be avoided by using only a small proportion of animal charcoal (0·7 g. for 25 c.c.) or by shaking with freshly-ignited kieselguhr. S. I. LEVY.

Graph for urine analysis. J. DÉCADE (Bull. Soc. Chim. biol., 1928, **10**, 1383—1384).—In the graph described the acidity and normal total nitrogen, carbamide, uric acid, phosphorus pentoxide, and sodium chloride contents are multiplied by a suitable factor so that each possesses an equal numerical value. Thus, when analyses of pathological and normal urine are compared graphically, the deviations from the normal may be easily read. G. A. C. GOUGH.

Ammonia coefficient of urine and its dependence on various sources of nitrogen. M. POLONOVSKI and P. BOULANGER (Compt. rend. Soc. Biol., 1928, **99**, 233—235; Chem. Zentr., 1928, ii, 1117).—The urinary ammonia is independent of the p_H and of the nitrogen excretion. The alkali reserve and the acid content of the food, particularly the sulphur and phosphorus content of the proteins, are, however, concerned. A. A. ELDRIDGE.

Analysis of the acid–base equilibrium in the urine. F. MAINZER and A. JOFFE (Biochem. Z., 1928, **203**, 50—87).—The quotients "alkali-sparing tendency" measured by the ratio $100[NH_3+$titratable acid$-$hydrogen carbonate$]$/total nitrogen and the "alkali-sparing effect," measured by the ratio $100[NH_3+$titratable acid$-$hydrogen carbonate$]$/total base, are introduced and their theoretical importance is explained. The "base-sparing effect" permits the quantitative comparison of urines of the same titratable acidity but of different p_H. The practical importance of the quotients for an analysis of acid–base equilibrium is illustrated in a series of experiments on the effect of administration of ammonium chloride and hydrogen carbonate. The determination of titratable acidity is critically examined. The simultaneous variation of the excretion of ammonia and carbon dioxide—fixed as hydrogen carbonate—makes possible the regulation of acid–base equilibrium by the kidney irrespective of the material excretion requirement and it is therefore unjustifiable to regard increased ammonia and acid excretion as indicating acidosis; it is rather the symbol of the alkali-sparing tendency of the organism. A method for determination of the fixed carbon dioxide of urine is laid down and the influence of the concentration of the urine on the solubility of carbon dioxide and its apparent dissociation constant discussed. Preliminary balance experiments indicate that a considerable amount of unknown organic bases is present in urine.

P. W. CLUTTERBUCK.

Bile pigments in urine. C. KUHN (J. Pharm. Chim., 1928, [viii], **8**, 546—549).—The following method for the detection of bilirubin is described. 2 C.c. of a phosphoric acid (*d* 1·71) diluted with 20 c.c. of water are added to a mixture of 20 c.c. of the urine, 2 c.c. of a mixture of 2 vols. of 5% aqueous copper sulphate (crystals) solution, and 1 vol. of ammonia solution (*d* 0·924), and, immediately after mixing, 6 drops of toluene are added and the mixture is vigorously shaken. After a time biliverdin, formed by the action of the alkaline copper solution on bilirubin and liberated in the free state on acidification, rises to the surface; 3·4 c.c. of 95% alcohol are then carefully added. If the bile pigments are present in appreciable quantity a green zone is rapidly formed at the boundary of the two liquids, and the alcohol is quickly coloured green, most of the biliverdin dissolving. If bile pigments are absent the alcohol remains colourless or assumes a faint rose or greyish-blue colour. The presence of protein, dextrose, indoxyl, uric acid, or urobilin does not interfere. E. H. SHARPLES.

Detection of bile pigment in urine. L. VAN ITALLIE (Pharm. Weekblad, 1929, **66**, 13—14).—The pigment is adsorbed on filter-paper or talc, and, after washing with water, removed again in acid alcohol solution; treatment of the solution with an oxidising agent gives the characteristic green coloration. S. I. LEVY.

Uric acid elimination and diuresis. R. GOIFFON (Compt. rend. Soc. Biol., 1928, **98**, 941—943; Chem. Zentr., 1928, ii, 1229).—The uric acid concentration of the urine of an individual is constant.

A. A. ELDRIDGE.

Uric acid in organic fluids. R. MENASCI (Folia clin. chim. micros., 1927, **2**, No. 5, 12 pp.; Chem. Zentr., 1928, ii, 1229).

Concentration of acid and base in blood-serum in normal pregnancy. H. C. OARD and J. P. PETERS (J. Biol. Chem., 1929, **81**, 9—27).—During pregnancy there is a reduction of about 5% in the total base concentration in the blood-serum which is accounted for by disappearance of sodium; at the same time, there is equivalent reduction in the total anions, due principally to diminution in the hydrogen carbonate and organic acid, and, to a smaller extent, in the protein. There is thus no true acidosis in normal pregnancy. C. R. HARINGTON.

Physical chemistry of cerebrospinal fluid and serum diagnosis. Lange's gold sol reaction. G. ETTISCH and O. EINSTEIN (Biochem. Z., 1928, **203**, 389—393).—Many of the reactions obtained by Lange (Z. Chemother., 1913, **1**, 44) with cerebrospinal fluid and gold sol, claimed to be characteristic of pathological conditions, may be obtained merely by alteration of the p_H of the gold sol added. Thus the reaction with normal fluid may be made to approximate to that of fluid in progressive paralysis by acidifying the sol, and the reaction of a fluid in paralysis may be converted into normal by making the sol alkaline. P. W. CLUTTERBUCK.

Metabolism of under-nourished children. III. Urinary nitrogen; creatinine. C. C. WANG, M. FRANK, R. KERN, and B. B. HAYS (Amer. J. Dis. Children, 1926, **32**, 360—366).—Creatinine-nitrogen increased with increasing weight and age; creatine was always present; ammonia and total nitrogen were fairly constant. The creatinine coefficient was 5·5—9·5; creatinine excretion was constant in individuals. CHEMICAL ABSTRACTS.

Deposition of sulphur in the skin after extirpation of the adrenals. M. LOEPER, J. DECOURT, and A. LESURE (Compt. rend. Soc. Biol., 1928, **98**, 1098—1099; Chem. Zentr., 1928, ii, 1231).

Saponin hæmolysis in anæmic blood. H. D. Kesten and T. F. Zucker (Amer. J. Physiol., 1928, **87**, 274—279).—Red blood-cells from persons with severe secondary anæmia are hæmolysed more slowly by saponin than are those from normal individuals.
B. A. Eagles.

Saponin hæmolysis of reticulocyte-containing blood. T. F. Zucker and H. D. Kesten (Amer. J. Physiol., 1928, **87**, 280—287).—The curve of saponin hæmolysis of a reticulocyte-containing blood shows a rate of hæmolysis which at first is faster and later slower than that of normal blood. B. A. Eagles.

Splenic substance in Gaucher's disease. H. Beumer (Klin. Woch., 1928, **7**, 758; Chem. Zentr., 1928, ii, 679).—After death from Gaucher's disease investigation of the spleen showed that a mixture of cerebron and kerasin was concerned.
A. A. Eldridge.

Splenic substance in Gaucher's disease. E. Epstein and H. Lieb (Klin. Woch., 1928, **7**, 1085; Chem. Zentr., 1928, ii, 679).—Examination of the spleen in Gaucher's disease has never revealed the presence of cerebron (phrenosin) as well as kerasin (cf. preceding abstract). A. A. Eldridge.

Reaction for diagnosis of cancer. A. H. Roffo (Z. Krebsforsch., 1926, **23**, 89—98; Chem. Zentr., 1928, ii, 1018).—The serum (2 c.c.) is coloured red on addition of a neutral-red solution (0·1%, 5 drops).
A. A. Eldridge.

Activation of proteolysis in animal organs and its significance in the metabolism of malignant tumours. E. Waldschmidt-Leitz, I. J. Bek, and J. Kahn (Naturwiss., 1929, **17**, 85).—Proteolytic enzymes such as lienokathepsin are accompanied by an activator which extends the specificity of the enzyme. The activator of the protease of the spleen may be replaced by hydrocyanic acid or by hydrogen sulphide. As these latter substances check cell respiration there appears to be a connexion between arrest of cell respiration and increased proteolysis. This connexion may be extended to tumours. W. E. Downey.

Protein metabolism of normal and malignant tissues in vitro. F. Demuth and I. von Riesen (Biochem. Z., 1928, **203**, 22—49).—Hen sarcoma cultures readily liquefy the clot of hen plasma, the coagulum being converted from the gel into the sol condition and the fibrin network being dissolved. The amount of the smaller decomposition products, not precipitable by tungstate, does not increase. The liquefaction is an enzymic process. The action of the enzymic system in a medium of plasma and embryonic extract proceeds so slowly (if at all) that it cannot be detected, but substances present in small amount in normal tissues, and in very much greater amount in sarcoma, are able to activate the enzyme. This activator is heat-stable and to some extent ultra-filterable. Activation is favoured by the hydrogen, acetate, and lactate ions, but is inhibited by calcium. This fibrinolysis is not specific for the sarcoma cell.
P. W. Clutterbuck.

Protein metabolism in cystinuria. W. Robson (Biochem. J., 1929, **23**, 138—145).—The cystinuric patient oxidised cystine to inorganic sulphate normally. The amount of the cystine in the urine appeared to bear a relation to the protein consumed. The administration of sodium hydrogen carbonate but not of disodium hydrogen phosphate was accompanied by a marked disturbance of the sulphur fractions of the urine. The excretion of cystine was not affected to any extent by either of these compounds. Tyrosine, leucine, putrescine, and cadaverine were not found in the urine. S. S. Zilva.

Connexion between sodium chloride elimination and insulin administration in diabetes. M. Tinker and A. Saidenberg (Russ. Klin., 1927, 8, 223—235; Chem. Zentr., 1928, ii, 1229).—In diabetes there is sodium chloride insufficiency, but retention of sodium chloride in the tissues is prevented by polyuria; excess of administered salt is retained, but the smaller the concentration of sugar in the urine, the greater is then the sodium chloride concentration. On administration of insulin the diminished urinary excretion of sugar is paralleled by an increase in the sodium chloride concentration, but the water retention leads to sodium chloride retention in the tissues. The sodium chloride concentration in the blood is increased. A. A. Eldridge.

Protein and energy economy in pancreatic diabetes of dogs. E. Enderlen, H. Glatzel, and Pü (Arch. exp. Path. Pharm., 1929, **139**, 20—31).—The protein metabolism of depancreatised dogs is raised 28—66% and the basal metabolism is 3—28% above normal. B. A. Eagles.

Amino-acid content of the blood in leucæmia. E. Wiechmann (Münch. med. Woch., 1928, **75**, 1115—1116; Chem. Zentr., 1928, ii, 907).—The amino-acid content of the plasma and erythrocytes is normal, whilst that of the leucocytes and whole blood is high, if the leucæmia is accompanied by a high leucocyte count. A. A. Eldridge.

Metabolism of salts in nephritis. I. G. L. Boyd, A. M. Courtney, and I. F. MacLachlan. II. G. L. Boyd and A. M. Courtney. III. G. L. Boyd, A. M. Courtney, and I. F. Maclachan (Amer. J. Dis. Children, 1926, **32**, 29—39, 192—199; 1927, **34**, 218—233).—The blood-phosphate (of children) was usually increased, and blood-calcium decreased, the calcium balance being independent of the blood-calcium. The relation between calcium and phosphate is discussed. Plasma-potassium was normal, but plasma-magnesium was low, and there was usually retention of sulphate. Sodium and chlorides were determined in the food, fæces, urine, and plasma; high values are usually obtained in the plasma except in chronic azotæmic nephritis.
Chemical Abstracts.

Albuminuria in the mechanism of detoxification. E. Andrews, W. A. Thomas, and W. F. Welker (Arch. Int. Med., 1929, **43**, 139—143).—The urine of nephritic patients contains, besides the normal blood-proteins, a relatively non-toxic peptone combined with or adsorbed by serum-proteins and also a highly toxic blood-protein so highly dispersed in solution as to pass readily through a collodion membrane. B. A. Eagles.

Proteases and antiproteases of pleural exudates. C. Weiss (J. Infect. Dis., 1927, 41, 467—471).—The activity of proteases and antiproteases of pleural exudates over a range of p_H values was studied. Chemical Abstracts.

Tetany of fasting in experimental rickets. T. S. Wilder (J. Biol. Chem., 1929, 81, 65—72).—Rachitic rats, when starved for 24—36 hrs., show tetanic convulsions, whilst normal animals similarly treated show no such symptoms; there is no marked hypoglycæmia, but a slight decrease in the calcium of the blood, and a marked rise in the inorganic phosphate, the latter being apparently derived from endogenous tissue breakdown (cf. Cavins, A., 1924, i, 680). C. R. Harington.

Inorganic blood-phosphate. E. M. Koch and M. H. Cahan (Amer. J. Dis. Children, 1927, 34, 187—197).—In rats on a rachitic diet the inorganic blood-phosphate is lowered; for mature, but not young, animals the value is raised by irradiation, whilst addition of cod-liver oil raises the value in both cases. Non-irradiated cholesterol produces normal values, but does not prevent rickets. Chemical Abstracts.

Creatine-phosphoric acid content of white and red muscle in experimental scurvy and polyneuritis. A. Palladin and S. Epelbaum (Biochem. Z., 1929, 204, 140—149).—The creatine-phosphoric acid in guinea-pigs suffering from scurvy was below normal, especially in red muscle, and the lactacidogen was above normal. In the heart-muscle creatine-phosphoric acid was absent and lactacidogen was diminished. In chronic polyneuritis of pigeons similar effects were observed to those for scurvy, but in acute polyneuritis creatine-phosphoric acid was increased and lactacidogen was diminished. J. H. Birkinshaw.

Variations of the potassium : calcium quotient in the lymph in experimental sepsis. W. F. Petersen, G. Milles, and E. F. Müller (Z. ges. exp. Med., 1928, 60, 336—354; Chem. Zentr., 1928, ii, 790).

Experimental uræmia and chloride content of the cortex. F. Leövey and E. Kerpel-Fronius (Arch. exp. Path. Pharm., 1929, 138, 373—378).—Rabbits suffering from sodium chloride starvation show a smaller decrease of chloride in the grey substance of the brain than in the white or in the other organs. Conversely, if excess of sodium chloride is administered to a rabbit after ligation of the ureters, the largest increase of chloride is found in the grey substance. W. O. Kermack.

Parenteral absorption of colloids. I. M. Jacoby (Biochem. Z., 1928, 203, 278—279).—Introductory to work not yet published. P. W. Clutterbuck.

Carbon dioxide from the unsevered vagus of the snake. G. H. Parker (J. Gen. Physiol., 1929, 12, 419—425).—The nerve produced 0·0017—0·0032 mg. of carbon dioxide per g. per min. Separation of the nerve from the brain and heart produced no appreciable change in the carbon dioxide output. E. Boyland.

Metabolism of two breeds of pigs. T. Deighton (J. Agric. Sci., 1929, 19, 140—184).—Calorimetric investigations of the metabolic changes in Middle White and Berkshire pigs are recorded. Internal and external thermal changes during fasting catabolism are examined. The bearing of the experimental results on the energy relationships of an animal during experiment and on the computation of maintenance rations is discussed. A. G. Pollard.

Spleen and calcium metabolism. F. P. Underhill and E. G. Cross (J. Biol. Chem., 1929, 81, 163—165).—In rabbits no alteration in the calcium metabolism was produced by splenectomy or by injection of nucleoprotein prepared from the spleen. C. R. Harington.

Factors influencing calcium balance. I. Influence of potential alkalinity on the utilisation of supplementary calcium lactate in the mature rat. V. V. Cole, J. H. Speer, and F. W. Heyl (J. Amer. Pharm. Assoc., 1929, 18, 36—42).—To maintain calcium balance, adult rats fed on an acidotic, calcium-deficient diet required a daily addition of 4—5 mg. of calcium lactate, and with calcium carbonate the rat came into calcium balance at about the same level. Calcium carbonate was probably entirely dissolved at this level and it gave a much better utilisation of the phosphorus than was secured with calcium lactate. Small additions of alkaline citrate to calcium lactate increased the percentage utilisation of both calcium and phosphorus; larger additions caused a greater, although not proportional, increase. Alkalinity probably had a favourable influence on the magnesium balances. E. H. Sharples.

Factors influencing the excretion of calcium. B. Hamilton and M. Moriarty (Amer. J. Dis. Children, 1928, 36, 450—462).—The amount of calcium excreted by breast-fed infants depends only on the amount of calcium, magnesium, sodium, and potassium in the milk. Increase in p_H of the (naturally buffered) intestinal contents may favour the formation of calcium soaps and phosphate. Addition of alkali or acid to the milk respectively increases or decreases the proportion of calcium excreted. Chemical Abstracts.

Creatine and creatinine excretion in women. P. Hodgson and H. B. Lewis (Amer. J. Physiol., 1928, 87, 288—292).—In women with physical development greater than that of the ordinary woman, creatinine coefficients of the same order of magnitude as those of men were observed. Creatine was present in 93% of the urines analysed, indicating that creatinuria in women is probably not related to the difference in muscular development between men and women. B. A. Eagles.

Influence of hunger on the creatine content of muscle and on the creatine and creatinine excretion of cats. A. Palladin and S. Epelbaum (Biochem. Z., 1929, 204, 150—164).—Fasting cats show creatine present in the urine at the fourth to sixth day and continually increasing; creatinine gradually falls so that the two curves cross. The sum of creatine- and creatinine-nitrogen increases throughout. The creatine content of the muscles increases during fasting up to the third fasting period and then diminishes. J. H. Birkinshaw.

Have histidine and arginine any influence on purine synthesis in the growing human organism? P. György and S. J. Thannhauser (Z. physiol. Chem., 1929, **180**, 286—304).—Addition of histidine and arginine to the ordinary milk diet of babies of 4—8 months had no effect on uric acid or creatinine excretion. Addition of histidine to a synthetic diet consisting of caseinogen hydrolysate freed from histidine and arginine had no noticeable effect on the purine or other constituents of the urine. There is no evidence of any direct relation between histidine administered and the purine metabolism. J. H. Birkinshaw.

Cholesterol metabolism. H. Beumer and F. Hepner (Klin. Woch., 1928, **7**, 1470; Chem. Zentr., 1928, ii, 1121).—After injection of cholesterol (1—2 g.) no marked increase of the bile cholesterol or bile acid was observed in dogs with biliary fistula, but after intravenous injection of cholesterol into normal dogs the fæcal cholesterol was increased.

A. A. Eldridge.

Animal calorimetry. XXXVIII. Specific dynamic action of meat in hypophysectomised dogs. O. H. Gaebler (J. Biol. Chem., 1929, **81**, 41—47).—The specific dynamic effect of protein in dogs was not altered by removal of the pituitary gland; the magnitude of the specific dynamic effect does not run parallel with changes in the amino-acid nitrogen of the blood. C. R. Harington.

Physiology of the liver. XVI. Respiratory quotient and basal metabolic rate following removal of the liver and injection of dextrose. F. C. Mann and W. M. Boothby (Amer. J. Physiol., 1928, **87**, 486—496).—The total amount of heat produced in dogs is not directly affected by the total loss of hepatic tissue. The respiratory quotient increases immediately after removal of the liver. Dextrose has a greater specific dynamic action in the dehepatised animal than in the normal one.

B. A. Eagles.

Physiology of the liver. XVII. Specific dynamic action after removal of liver. C. M. Wilhelmj, J. L. Bollman, and F. C. Mann (Amer. J. Physiol., 1928, **87**, 497—509).—Intravenous injection of alanine or glycine into hepatectomised animals fails to raise the level of the consumption of oxygen but elevates the respiratory quotient. It is suggested that the specific dynamic action of amino-acids is not the result of direct stimulation brought about by the presence of unchanged amino-acids in the tissues.

B. A. Eagles.

Significance of adenylic acid for muscle function. II. Deamination of adenylic acid by minced muscle and ammonia formation on muscle contraction. G. Embden, C. Riebeling, and G. E. Selter. **III. Ammonia formation in muscular work under various conditions.** G. Embden and H. Wassermeyer. **IV. Fission and resynthesis of the ammonia-producing substance in muscle activity.** G. Embden, M. Carstensen, and H. Schumacher. **V. Source of the ammonia formed on contraction.** G. Embden and H. Wassermeyer (Z. physiol. Chem., 1928, **179**, 149—160, 161—185, 186—225, 226—237).—II. The formation of ammonia by fresh minced muscle on keeping is considerably increased in presence of adenylic acid, but not of urea. More than 80% of the amino-group of the adenylic acid added may appear as ammonia. Electrical stimulation of frog's muscle even for 1 sec. leads to an increase in the ammonia content. After prolonged stimulation the ammonia figure may be nine times its original value.

III. *Rana esculenta* has in May a higher content of ammonia-forming substance in the muscle than in winter or summer. Prolonged jumping causes a considerable increase in the ammonia content of the gastrocnemius. A similar effect is produced by electrical stimulation. After resting, especially in the dark, the ammonia decreases. In the autumn *R. temporaria* maintained at 26—27° showed effects similar to those observed in *R. esculenta* in May. Phosphorus poisoning likewise caused an increase in the ammonia content of the muscle. The ratio of lactic acid to ammonia showed wide variations.

IV. The formation of free ammonia on the contraction of isolated frog's muscle (gastrocnemius) is a reversible change. The recombination of the ammonia eliminated is most easily demonstrated in spring and summer frogs. In winter the reversibility is greater, so that it is difficult to show the initial increase in the ammonia under electrical stimulation except when this is so prolonged as to damage the muscle-tissue, thus interfering with the resynthesis. If the number of stimuli per sec. is doubled or quadrupled, however, the resynthesis can be demonstrated; the ammonia shows a definite increase, the intervals being now too short for complete re-amination.

V. Extracts from the hind-limb muscle of the frog and from the biceps femoris of the rabbit were investigated. The nitrogen in the copper–lime precipitate together with that of the ammonia originally present in the extract was found to be equal to five times the nitrogen of the ammonia obtained after complete deamination by 2% sodium hydrogen carbonate solution. It is concluded that adenosinephosphoric acid and probably adenosine are the sole sources of the ammonia formed by muscle activity.

J. H. Birkinshaw.

Enzymic deamination in muscle. G. Schmidt (Z. physiol. Chem., 1928, **179**, 243—282).—Adenylic acid from muscle and adenosine are easily deaminated by muscle juice from the rabbit, but adenine, guanine, guanosine, and guanosinephosphoric acid are unaffected. The ammonia production is due to two different deaminases, one specific for adenylic acid, the other for adenosine. A highly active muscle extract of adenylic acid deaminase was prepared by adsorption on aluminium hydroxide, from which it could be eluted by sodium phosphate solution. The adenosine deaminase remains in solution during the adsorption process. The optimum p_H for the adenylic acid enzyme is 5·9.

Adenylic acid from muscle differs chemically from that of yeast, since the latter is unattacked by the muscle enzyme. The inosinic acid obtained by enzymic deamination of muscle-adenylic acid was isolated. J. H. Birkinshaw.

Action of ions on the ageing of muscle press-juice, and the influence of hydrogen-ion concentration. H. Wassermeyer (Z. physiol. Chem., 1928, **179**, 283—311).—Muscle juice in comparison with minced muscle shows a much smaller " ageing " effect as measured by loss of power to synthesise complex phosphoric acids. The artificial production of " ageing " by the addition of various substances to rabbits' muscle juice was examined. Sodium hydrogen carbonate, sodium hydroxide, and ammonia increase the rate of ageing. All these substances increase the p_H of muscle juice which is normally low, but carbon dioxide has a similar ageing effect although lowering the p_H value. J. H. Birkinshaw.

Lactacidogen in denervated muscle. L. de Caro (Boll. Soc. Ital. Biol. sper., 1927, **2**, 642—646; Chem. Zentr., 1928, ii, 784).—Denervated muscle contains less lactacidogen and free calcium ions than normal muscle. The results accord with the known smaller content of lactic acid and greater content of glycogen. A. A. Eldridge.

Presence and exchange of pyrophosphate in cells. II. Amount of readily hydrolysable phosphorus compounds in animal and plant cells. III. Physiological behaviour of pyrophosphate. K. Lohmann (Biochem. Z., 1928, **203**, 164—171, 172—207).—II. Yeasts and striated muscle of vertebrates and invertebrates have the highest pyrophosphate content, muscles containing 0·4—0·9 mg., and yeast 1·6—1·8 mg. P_2O_5 per g. moist wt. In frogs and rabbits, the pyrophosphate content of the heart and smooth muscle, liver, kidney, spleen, testicles, brain, and red blood-cells is smaller, corresponding with the smaller acid-soluble P_2O_5 content, and amounts to 0·1—0·4 mg. P_2O_5 per g. moist wt. With the roots of pea seedlings, 9% of the total acid-soluble phosphate is present as pyrophosphate. Three kinds of bacteria gave similar figures and it appears therefore that all cells which can utilise carbohydrate possess readily hydrolysable phosphorus compounds.

III. The pyrophosphate content of the intact frog's muscle remains unchanged while resting for 20 hrs. in oxygen and also during moderate stimulation, but when the stimulation is prolonged, hydrolysis of pyrophosphate and formation of orthophosphate occur. In heat and chloroform rigor, almost all the pyrophosphate is hydrolysed. Pyrophosphate does not diffuse out of muscle into Ringer's solution, but is probably present in the cell and in the extract as a (protein) adsorption complex. The pyrophosphate of frog's muscle-pulp or of the hydrogen carbonate–potassium chloride extract is completely hydrolysed during autolysis at 40°, about 75% of the orthophosphate arising during such autolysis being thus formed from pyrophosphate. The remaining 25% (*i.e.*, 0·2—0·3 mg. P_2O_5 per g. moist wt. of frog's muscle) arises only in part from Embden's lactacidogen. Enzymic hydrolysis of pyrophosphate is inhibited by orthophosphate. Respiration and the degradation of carbohydrates by the cell are independent of the pyrophosphate fraction. The hydrolysis of pyrophosphate existing in fresh muscle pulp is accelerated by 0·5*M*- and by 0·01—0·003*M*-potassium fluoride, but is inhibited by intermediate concentrations (0·1*M*), whereas hydrolysis of added pyrophosphate is always inhibited by fluoride. Pyrophosphate administered by the mouth is excreted in the urine as orthophosphate. P. W. Clutterbuck.

Extraction of pyrophosphate containing iron from muscle. O. Meyerhof and K. Lohmann (Biochem. Z., 1928, **203**, 208—211).—Some of the iron contained in muscle is but loosely combined and may be removed along with pyrophosphate by treatment with a solution of mercuric chloride in hydrochloric acid. It could not be decided, however, whether the iron was combined with the pyrophosphate in the cell. P. W. Clutterbuck.

Muscle-lactic acid in decapsulated rats. P. Mazzocco (Compt. rend. Soc. Biol., 1928, **99**, 174—176; Chem. Zentr., 1928, ii, 1121).—After tetanisation the muscle-lactic acid is somewhat greater in decapsulated than in normal rats. A. A. Eldridge.

Metabolism of carbohydrates in normal conditions and in starvation. G. Mouriquand and A. Leulier (Compt. rend. Soc. Biol., 1928, **98**, 1110—1113; Chem. Zentr., 1928, ii, 1230—1231).—With normal rabbits the liver-glycogen varies from 0·14 to 12·86%; values for muscle are 0·07—1·52%. Starvation values are 0·16—1·34 and 0·10—0·48, respectively. The blood-sugar of normal guinea-pigs is 0·93—1·50, and is reduced in starvation to 0·85—1·38. A. A. Eldridge.

Metabolism of lævulose; determination in blood and urine. R. C. Corley (J. Biol. Chem., 1929, **81**, 81—98).—Lævulose may be determined in aqueous solution, diluted urine, and protein-free blood-filtrates by heating with hydrochloric acid and diphenylamine, followed by treatment of the solution with phenol and alcohol; the resulting blue colour is compared with that obtained by similar treatment of a standard solution of lævulose. The error of the method is ±5%. After oral administration to rabbits of 6—7 g. per kg. of lævulose, small amounts of the latter appear in the blood; after intravenous injection of 2 g. per kg. the excess lævulose disappears from the blood within 90 min. Hepatic poisons had little effect on the metabolism of lævulose; the latter exercises a protective effect against overdosage with insulin, although its rate of disappearance from the blood is not affected by the presence of excess of insulin. C. R. Harington.

Physico-chemical theory of the cause of sweet and bitter taste. N. W. Taylor (Protoplasma, 1928, **4**, 1—17; Chem. Zentr., 1928, ii, 901).—A discussion. A. A. Eldridge.

Distribution in the organism of oil injected in the arterial system. L. Binet and R. Fabre (J. Pharm. Chim., 1929, [viii], **9**, 16—19).—Distribution of the oil was followed by examination of solvent extracts of the organs with Wood's light (λ=3650 Å.) after injection of olive oil containing 0·01% of diphenylanthracene. Extracts of the lungs, heart, skeletal muscle, liver, kidney, and spleen of a rabbit were examined. Visual examination with Wood's light showed that the lung extract contained most of the diphenylanthracene. Photographic examination was necessary to compare the remaining extracts and, after the lungs, the muscle, followed by the liver and kidneys, showed the strongest deposition. Injection of aqueous suspensions of diphenylanthracene gave extracts from the organs which were only very faintly fluorescent. E. H. Sharples.

Explanation of oligodynamic action. H. Freundlich and K. Söllner (Biochem. Z., 1928, **203**, 3—13).—When 40 sq. cm. of pure silver foil are kept in 100 c.c. of tap-water or distilled water for 3 days, 2×10^{-5} g. of silver per litre is dissolved and can be determined by Haber's method (A., 1926, 699). Algæ brought into such solutions adsorb most of the dissolved silver, the algæ suffering oligodynamic injury. The silver adsorbed in 1 g. of dry algæ amounts to 5×10^{-5} g. The silver is present in these solutions as silver ions, and the poisonous action on algæ may be imitated by a solution of silver nitrate containing the same concentration of silver ions. The fact that a glass surface which has been brought into contact with a silver solution retains its oligodynamic activity after washing is confirmed and depends on the adsorption of the silver by the glass, the silver penetrating deeply into its structure. When dilute solutions of silver nitrate are evaporated in glass vessels, the silver is almost completely adsorbed by the glass and may be recovered therefrom after careful washing away of all traces of the solution. P. W. Clutterbuck.

Neutralisation of the oligodynamic power of copper by solutions of electrolytes. Application to mineral waters. P. L. Violle and A. Giberton (Compt. rend., 1929, **188**, 409—411).—The property of distilled water of becoming toxic (*e.g.*, to fish) when placed in contact with a copper surface for a few hours at the ordinary temperature is due to copper in the colloidal state, and the antitoxic effect of certain mineral waters is due to its precipitation by the ions of the dissolved salts. The antitoxic properties of anions increase with the valency, whilst cations are usually toxic and only calcium has a protecting effect. J. Grant.

Chemical nature of allergic substances. L. F. Loeb (Biochem. Z., 1928, **203**, 226—236).—Guinea-pigs are sensitised specifically against an aqueous extract of goose-feathers. The extract contains 0·4 mg./c.c. of total nitrogen, about half of which is colloidally dispersed and precipitable by colloidal ferric hydroxide and gives reducing, sulphosalicylic acid, ninhydrin, and Molisch reactions. The colloidally dispersed nitrogenous substance may be precipitated by alcohol and then contains only a trace of reducing substance and gives a positive sulphosalicylic acid reaction, a negative ninhydrin, and a doubtful Molisch reaction. Specific sensitisation is similarly obtained with this alcohol precipitate, but not with the filtrate, which contains only molecular dispersed nitrogen and considerable amounts of reducing substance and gives positive ninhydrin and Molisch reactions. Guinea-pigs are similarly sensitised against aqueous extracts of pollen of the ordinary pine (*Pinus sylvestris*) and against the alcoholic precipitate thereof, the latter containing only the colloidally dispersed nitrogen and no reducing substance. P. W. Clutterbuck.

Value of dextrose in maintaining acid-base equilibrium of the blood in pregnant animals. II. Effect of period of chloroform anæsthesia in pregnant animals: lack of protection conferred by dextrose. W. de B. MacNider (J. Pharm. Exp. Ther., 1929, **35**, 31—48).—The degree of protection afforded by the administration of a solution of dextrose to pregnant dogs against the toxic effects which follow periods of ether anæsthesia was greatest in young dogs in the early stages of pregnancy. No protection is afforded when chloroform is substituted for ether as the anæsthetic. The toxic action of the chloroform is revealed in a decrease in the reserve alkali of the blood, in the elimination of phenolsulphonephthalein, and in urine formation; albumin, casts, and acetoacetic acid also appear in the urine. F. C. Happold.

Fixation of colloids caused by chloroform. G. Spagnol (Atti R. Accad. Lincei, 1928, [vi], 8, 515).—If colloidal mercuric sulphide (0·15 g.) is injected into the ear vein of a rabbit and at the same time chloroform is applied to the side of the animal by means of a pad of cotton-wool, the subcutaneous tissue beneath the chloroformed spot shows a distinct black deposit of the sulphide when the rabbit is killed (after 2 hrs. or 8 days). A similar result is observed when trypan-blue (0·001 g.) is injected into the jugular vein of a guinea-pig. T. H. Pope.

Ethyl*iso*amylbarbituric acid (amytal) as anæsthetic for cats. M. G. Mulinos (J. Pharm. Exp. Ther., 1928, **34**, 425—435).—Subcutaneous doses of 0·1 g. of amytal per kg. body-weight give a safe anæsthesia with quiet induction. This anæsthetic does not affect the blood-sugar or interfere with the effect of insulin. E. Boyland.

Binding power of serum for alkaloids, and the inhibition of this effect by homologous alcohols. Theory of narcosis. R. Beutner and E. Hyden (J. Pharm. Exp. Ther., 1929, **35**, 25—30).—The relative amounts of the alcohols of the series propyl to octyl alcohol which will set free a trace of the bound pilocarpine in mixtures of cattle-serum with pilocarpine have been determined. It is suggested that the action is one of adsorptive replacement. The activity of hexyl alcohol represents a maximum in this series. Since the narcotic power of these alcohols increases continuously with the length of the carbon chain, it is suggested that these results support a theory of narcosis based on lipoid solubility rather than Traube's theory of surface action. F. C. Happold.

Occurrence of caffeine in human milk after ingestion of coffee. E. Schilf and R. Wohinz (Klin. Woch., 1928, 7, 1186; Chem. Zentr., 1928, ii, 684).—Of the ingested caffeine, 1% was found in the milk. A. A. Eldridge.

Influence of choline on blood-sugar. F. P. Underhill and J. Petrelli (J. Biol. Chem., 1929, **81**, 159—162).—Subcutaneous injection of sub-lethal doses of choline causes in rabbits (but not in dogs) marked hyperglycæmia but no glycosuria.

C. R. Harington.

Changes in blood-dextrose in rabbits after intravenous injections of histamine. M. L. Menten and H. M. Krugh (J. Infect. Dis., 1928, **43**, 117—120).—Experiments with normal and immunised rabbits are described. Chemical Abstracts.

Influence of ergotamine on blood-sugar concentration. L. Rigó and L. Veszelszky (Arch. exp. Path. Pharm., 1929, **139**, 10—13).—Small doses of ergotamine (0·5—1·5 mg. per kg.) in rabbits produce a hypoglycæmia; larger amounts (2·0—2·5 mg. per kg.) cause a hyperglycæmia. B. A. Eagles.

Influence of ergotamine on the blood-sugar of animals and man. M. Bufano and A. Masini (Riforma Med., 1927, **43**, No. 38, 21 pp.; Chem. Zentr., 1928, ii, 908).—Administration of ergotamine causes a fall in the blood-sugar which is ascribed to diminished glycogenolysis in the liver.

A. A. Eldridge.

Reduction processes in muscle under the action of guanidine. L. Califano and M. d'Alise (Riv. Pat. sper., 1927, **2**, 288—293; Chem. Zentr., 1928, ii, 1121).—The muscular oxidation processes of *Bufo* are increased by guanidine.

A. A. Eldridge.

Effect of hydrazine, hydroxylamine, and aminoguanidine on the excretion of uric acid. N. Nielsen and G. E. Widmark (Upsala Läkareför. förh., 1927, [ii], **33**, 327—333; Chem. Zentr., 1928, ii, 1229).—The uric acid excreted by normal rats was 7—8 mg. per kg. per day; the administration of hydrazine, hydroxylamine, or aminoguanidine did not cause increased elimination of uric acid.

A. A. Eldridge.

Effects of drugs on secretion of uric acid in the fowl. O. S. Gibbs (J. Pharm. Exp. Ther., 1929, **35**, 49—62).—The immediate response of the blood-uric acid content and the uric acid output to procedures which change the renal activity renders the fowl especially suitable for studies of renal function. Clamping of the ureters leads to a rise in the blood-uric acid concentration; there does not, however, appear to be any storage of uric acid by the kidneys. The effects of atropine, pilocarpine, physostigmine, adrenaline, pituitrin, atophan, hexamine, and uric acid were studied, but no changes suggestive of nervous control other than vascular effects were observed. Uric acid stimulated its own excretion, pituitrin caused a decrease in the urinary water secreted, and atophan of the uric acid.

F. C. Happold.

Action of certain heterocyclic compounds on the autonomic nervous system. R. Hunt and R. R. Renshaw (J. Pharm. Exp. Ther., 1929, **35**, 75—98).—The muscarine- and nicotine-like actions of certain compounds on the circulation have been studied. 1-Carboxymethylpyridinium bromide gave a weak muscarine effect, the action was more marked with methyl nicotinate and 1-acetoxyethyl-1-methylpiperidinium iodide and it became intense with 1-carbethoxymethylpyridinium bromide and 3-carbomethoxy-1-methylpyridinium iodide. In all cases there was an absence of nicotine-like action. 1-Acetoxymethylpyridinium chloride had a weak nicotine-like stimulating action, and methyl 1-methyltetrahydronicotinate and 3-carbomethoxy-1-methyl-1-ethyl piperidinium bromide gave an even more definite action in addition to an active muscarine effect. 1-Carbethoxymethyl-2-methylpyridinium bromide had a brief, weak, paralysing, nicotine-like action. 1-Carbethoxymethylpiperidinium bromide, 1-methyl-2-pyridone, 1-ethyl-2-pyridone hydrobromide, and 1-diethylpyrrolidinium bromide were devoid of muscarine or nicotine actions. The muscarine-like actions of 1-carbethoxymethyl-1-methylpiperidinium iodide and 1-carbethoxymethyl-1-ethylpiperidinium bromide were not very pronounced but were more marked after the administration of large doses of nicotine, although neither salt had a marked nicotine-like stimulating action. *N*-Dimethylhexamethyleneammonium bromide had no muscarine-like action. Other effects are noted and the relationship between chemical constitution and pharmacological action is discussed.

F. C. Happold.

Comparative studies of ephedrine, *r*-ephedrine, and ψ-ephedrine. II. Comparative toxicity. C. Pak and B. E. Read. **III. Effects on the nasal mucous membranes.** T. King and C. Pak (Chinese J. Physiol., 1929, **3**, 81—92, 95—108).—II. In rabbits, frogs, rats, and dogs ephedrine is definitely more toxic than *r*-ephedrine (ephetonine) and the latter is more toxic than ψ-ephedrine.

III. Ephedrine, *r*-ephedrine, and ψ-ephedrine cause shrinkage of the nasal mucous membrane, the activity being greatest with the first compound and smallest with the last. W. O. Kermack.

Biochemical properties of pyridine and quinoline derivatives. A. Binz and C. Räth (Biochem. Z., 1928, **203**, 218—222).—The chemotherapeutic action of a number of derivatives of pyridine and quinoline containing arsenic and iodine (A., 1927, 580, 890) is investigated with the view of establishing a relationship between chemical constitution and biological activity. The dose of 2-hydroxypyridine-5-arsinic acid just tolerated by a mouse is 30 times as great as that of atoxyl and 2·66 times that of tryparsamide. Rabbits tolerate 1 g./kg. body-weight, the arsenic content of which is 75 times the normal toxic dose of arsenic. The curative dose of this acid for mice which had been infected with trypanosomes was 1·2 mg./g. body-weight. 5-Iodo-2-hydroxypyridine has no action on animals infected with trypanosomes, but a decidedly beneficial action in staphylococcal and streptococcal infections. 2-Aminopyridine-5-arsinic acid behaves similarly to the corresponding hydroxy-derivative. Pyridine-3-arsinic acid causes only a transient decrease of the number of trypanosomes. 2-Halogenopyridine-5-arsinic acids are more toxic and have less action on trypanosomes, but when the halogen is in the *ortho*-position to a hydroxy-group, *e.g.*, in 3-chloro-2-hydroxypyridine-5-arsinic acid, the action on trypanosomes is retained and increases with increasing weight of the halogen. Chemotherapeutic action appears therefore to depend on the presence adjacent to nitrogen of a group which permits tautomerism. Similarly, whereas unsubstituted quinolinearsinic acids have no chemotherapeutic action, the corresponding 2-hydroxy- (carbostyryl) derivatives are strongly parasitotropic.

P. W. Clutterbuck.

Tobacco smoking. II. A. Winterstein and E. Arosnon (Z. Hyg. Infekt.-Krankh., 1928, **108**, 530—553; Chem. Zentr., 1928, ii, 689—690).—The main current from a cigarette carries about 25% of the nicotine into the mouth, at least 50% passing into the air; from a cigar 60% reaches the mouth. The main current from cigarettes of light tobaccos contains markedly less nicotine than that from dark tobaccos. A. A. Eldridge.

Pharmacology of pyridylpyrroles and derivatives of 2-aminopyridine. E. Dingemanse and J. P. Wibaut (Arch. exp. Path. Pharm., 1929, **138**, 379; cf. A., 1928, 919).—A question of priority.

W. O. Kermack.

Chemical changes in muscle produced by drugs. H. N. Ets (Amer. J. Physiol., 1928, **87**, 399—405).—Pilocarpine produces a decrease and atropine an increase in the sodium, potassium, calcium, and magnesium content of trichloroacetic acid extracts of the small intestine. Adrenaline produces an increase in the sodium and calcium and a decrease in the potassium and magnesium. B. A. Eagles.

Relationship between chemical constitution and physiological action. II. Miotic activity of urethanes derived from the isomeric hydroxybenzyldimethylamines. E. Stedman (Biochem. J., 1929, **23**, 17—24).—The following urethanes were prepared: *methylurethane* of m-*hydroxybenzyldimethylamine*, m. p. 86° (*hydrochloride*, m. p. 175°; *methiodide*, m. p. 162°); *ethylurethane* of m-*hydroxybenzyldimethylamine*, an oil (*hydrochloride*, m. p. 156°; *methiodide*, m. p. 155—156°); *phenylurethane* of m-*hydroxybenzyldimethylamine*, m. p. 93° (*hydrochloride*, m. p. 175°); *methylurethane* of p-*hydroxybenzyldimethylamine*, m. p. 72° [*hydrochloride*, m. p. 180°; *methiodide*, m. p. 188° (decomp.); *methochloride*, m. p. about 110°]; *ethylurethane* of p-*hydroxybenzyldimethylamine* (*hydrochloride*, m. p. 165°; *methiodide*, m. p. 186°); *phenylurethane* of p-*hydroxybenzyldimethylamine*, m. p. 126° (*hydrochloride*, m. p. 182°); *methylurethane* of o-*hydroxybenzyldimethylamine*, m. p. 76° (hygroscopic *hydrochloride*; *methiodide*, m. p. 175°); *ethylurethane* of o-*hydroxybenzyldimethylamine* (*methiodide*, m. p. 149°); *phenylurethane* of o-*hydroxybenzyldimethylamine*, m. p. 90° (*methiodide*, m. p. 171°); *methylurethane* of *choline iodide*, m. p. 174°; *methylurethane* of *tropine*, m. p. 126° (*hydrochloride*, m. p. 263°).

Miotic activity was confined to the methylurethanes of the isomeric hydroxybenzyldimethylamines, the urethanes of choline iodide and tropine being inactive in 2% solutions. The activities of the methylurethanes of the isomeric hydroxybenzyldimethylamines are in the order $o > p > m$. Conversion of the tertiary basic group into the quaternary ammonium group increased the activity of the *o*-, diminished that of the *m*-, and abolished that of the *p*-compound.

S. S. Zilva.

Bio-assay of aconite and its preparations. I. Lethal dose of aconitine to rats. J. C. Munch and G. S. Gittinger (J. Amer. Pharm. Assoc., 1929, **18**, 17—24).—The fatal dose of aconitine (killing 2 out of 3 animals), when injected subcutaneously into white rats by the U.S.P. method, is 0·175 mg./kg. Wild rats are equally or somewhat less susceptible. Injected intraperitoneally the fatal dose is 0·10 mg./kg. Variations in susceptibility of individual rats are large and a number of test animals must be used.

E. H. Sharples.

Adsorption of poisons by "adsorbin," kieselguhr, and kaolin. Y. Takahashi (Okayama Ig. Zasshi, 1927, **39**, 1123—1132; Chem. Zentr., 1928, ii, 970).—The poisonous action on excised rabbit's intestine of strychnine, cocaine (strongly absorbed), adrenaline, strophanthin, or pilocarpine (absorbed with difficulty) is inhibited by adsorption from the nutrient solution or from the tissue by the above substances, in order of decreasing effect. Animal charcoal is more effective. A. A. Eldridge.

Adsorptive effect of barium sulphate on intestinal toxins. I. Spadolini (Boll. Soc. Ital. Biol. Sper., 1927, **2**, 597—601; Chem. Zentr., 1928, ii, 1002).

Action of magnesium salts on blood-sugar. S. Láng and L. Rigó (Arch. exp. Path. Pharm., 1929, **139**, 1—9).—Subcutaneous injection of small quantities of magnesium salts (0·0025—0·1 g. of magnesium chloride and 0·0025—0·005 g. of the sulphate per kg.) in rabbits produces a decrease in the blood-sugar concentration; larger doses result in an increase. Ergotamine increases the blood-sugar-raising action of magnesium salts. B. A. Eagles.

Action of chlorates, in particular potassium chlorate, on blood in animals. J. L. Ulrich and V. A. Shternov (J. Pharm. Exp. Ther., 1928, **34**, 391—406).—Toxic doses of chlorates were given orally and intraperitoneally. Potassium chlorate, which converts hæmoglobin into methæmoglobin *in vitro*, does not always do so *in vivo*. Magnesium and calcium chlorates are both toxic and produce no methæmoglobin *in vivo*. Definite doses of sodium chlorate (6—8 g. per kg. body-weight) invariably produced methæmoglobin. Such doses were toxic in 45 min. E. Boyland.

Comparative [toxic] action of hypertonic solutions of chlorates and chlorides of potassium, sodium, calcium, and magnesium. J. L. Ulrich and V. A. Shternov (J. Pharm. Exp. Ther., 1929, **35**, 1—15).—Hypertonic solutions of the above salts were administered either intraperitoneally or orally to rabbits, guinea-pigs, cats, and albino rats. Approximately isotonic solutions were also occasionally injected intravenously. The average lethal doses of these salts for rats were determined for the two methods of administration. The chlorides were gram for gram more toxic than the chlorates, but if the average lethal doses were expressed on a molecular basis and administered intraperitoneally the chlorates of sodium and calcium were more toxic than the chlorides, *i.e.*, a greater number of chloride molecules were required to produce death. This was also true with orally administered magnesium salts. The toxicity of the chlorates decreased in the order calcium, magnesium, potassium, and sodium, irrespective of the method of administration; when injected intraperitoneally the chlorides decreased in toxicity in the order magnesium, calcium, potassium, and sodium, but administered orally the decrease followed the order potassium, magnesium, calcium, and sodium. The effect of these salts on the heart and respiration has been studied and the general symptoms are described and discussed. The salts were toxic only in large doses; their toxicity is ascribed to the cations rather than to the common chloride and chlorate anions. F. C. HAPPOLD.

Influence of calcium on the fauna of peaty waters. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1928, **10**, 1298—1305).—Water from *Carex* swamps (average p_H 7·728, average calcium content per litre, 46·83 mg.) contains large numbers of the larvæ of *Anopheles*, whilst water from sphagnum swamps (average p_H 5·04, average calcium content per litre, 10·61 mg.) is invariably devoid of these larvæ. Examination of other peaty waters shows that low calcium contents generally accompany low p_H and small number of larvæ.

G. A. C. GOUGH.

Pharmacology of bismuth salts. V. Distribution of bismuth in tissues. C. S. LEONARD. **VI. Permeability of the placenta to bismuth.** C. S. LEONARD and R. B. LOVE. **VII. Concentration of bismuth in the blood of dogs after intramuscular injection of bismuth antiluetics.** C. S. LEONARD and A. F. SEIBERT (J. Pharm. Exp. Ther., 1928, **34**, 333—346, 347—354, 355—364).—V. Lethal and sub-lethal doses of soluble bismuth salts were injected intramuscularly into rabbits and the bismuth present in different organs was determined by the method previously described (A., 1926, 975). The average order of fixation was: kidney (highest), spleen, adrenals, liver, lung, brain, and heart. Twenty-four hrs. after injection of the bismuth compound blood contained 0·0035 mg. bismuth per c.c., whilst bile contained 0·03 mg. per c.c. The significance of this in the bismuth treatment of neuro-syphilis is discussed.

VI. Intramuscular injection of dipotassium bismuth tartrate and sodium bismuth tartrate in rabbits and cats produced no trace of bismuth in fœtal organs, unless the lethal dose were exceeded, when appreciable amounts were found in the fœtal kidneys. The placenta, however, always contained bismuth.

VII. The bismuth content of blood and urine of dogs was determined after injection of 40—50 mg. Bi (as dipotassium bismuth tartrate) per kg. body-weight. The urine always had a higher concentration of bismuth than the blood. With massage of the injection site, bismuth was found in the blood 2 hrs. after injection; without massage this took 24 hrs. The maximum concentration in the blood of 0·001—0·003 mg. per c.c. is maintained for 48 hrs. after the injection, after which it declines, although bismuth is detectable in the blood for some weeks.

E. BOYLAND.

Liposoluble bismuth compounds. C. LEVADITI (Ann. Inst. Pasteur, 1928, **42**, 1489—1535)—The tolerated dose of basic bismuth α-carbethoxy-β-methylnonoate in the rabbit after intramuscular injection is 0·033 g. of bismuth per kg. body-weight. Its therapeutic efficiency in rabbits infected with *Spirochæta cuniculi* depends on its rapid resorption, the creation of a local bismuth depot, and its gradual assimilation. B. A. EAGLES.

Adsorption of dyes by the serum in lead poisoning. A. SEITZ (Klin. Woch., 1928, **7**, 1234—1235; Chem. Zentr., 1928, ii, 1115—1116).—Inhibition by serum of the diffusion of dyes is less marked in lead poisoning. A. A. ELDRIDGE.

Marked action of organic compounds of lead on experimental carcinoma in mice. E. KRAUSE (Ber., 1929, **62**, [*B*], 135—137).—The following compounds have been used: lead tri-*n*-propyl fluoride, tri*iso*butyl bromide, tri*iso*amyl bromide, lead tri*cyclo*hexyl and its iodide, lead triphenyl*cyclo*hexyl, lead tetraphenyl, triphenyl, triphenyl bromide, triphenyl fluoride, diphenyl dibromide, tin tetraphenyl, triphenyl, triphenyl bromide, and triphenyl *n*-propyl. The toxicity of organo-metallic compounds depends to a greater extent on constitutive influences than on solubility in water, which is possessed to a sensible degree only by lead tri-*n*-propyl fluoride. The latter compound is particularly effective against carcinoma. Lead tri*iso*butyl bromide and lead tetraphenyl are very useful and lead tri*cyclo*hexyl is relatively active. The other compounds are less useful and the tin derivatives are unsuitable. H. WREN.

Influence of heavy metals on the basal metabolism of guinea-pigs. G. SOSTBERG and M. STEUBER (Biochem. Z., 1928, **203**, 385—388).—Injection of Ringer's solution and of "electroferrol" had no effect on basal metabolism but of "collargol" caused a 12% and of "solganol" (a gold preparation) a 20% increase. P. W. CLUTTERBUCK.

Behaviour of the blood-sugar values after oral administration of yeast. A. BICKEL and G. NIGMANN (Biochem. Z., 1928, **203**, 421—428).—Oral administration of 5 g. of dried yeast in 100 c.c. of water to normal dogs which had been starved for 24 hrs. caused a considerable decrease of blood-sugar 4—6 hrs. after administration. P. W. CLUTTERBUCK.

Effect of oral administration of yeast on carbon- and oxidation-quotients of urine. P. HOFFMANN (Biochem. Z., 1929, **204**, 208—214).—Dried yeast orally administered to rabbits decreases the carbon and oxidation quotients of the urine when these have been artificially raised by feeding dextrose. The action is very similar to that of insulin.

J. H. BIRKINSHAW.

Concentration of the [respiratory] enzyme-iron in the cell. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1928, **203**, 95—98).—1 g. of baker's yeast (dry substance) contains less than 4×10^{-7} g. of iron combined as the respiratory enzyme. Since 1 g. of baker's yeast (dry weight) contains about 10^{-4} g. of iron, less than 1/250 of the iron is present as iron of the respiratory enzyme. P. W. CLUTTERBUCK.

Bioluminescence. VI. Mechanism of luminescence in *Cypridina*: luciferin and luciferase. S. KANDA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1929, **9**, 265—269).—When equal volumes of an aqueous solution of luciferase and a methyl-alcoholic solution of luciferin are mixed in the dark no luminescence is observed, but if distilled water is then added slowly luminescence becomes just perceptible in presence of about 60% of water and 40% of methyl alcohol. When further water is added the intensity of luminescence reaches a maximum and then gradually decreases. A theory is suggested to explain these phenomena. W. O. KERMACK.

Separation of the enzymes of barley malt. III. Amylase and maltase. H. PRINGSHEIM and E. THILO (Biochem. Z., 1928, **203**, 99—102).—When malt is kept for 3 days at the ordinary temperature with 87% glycerol, the extract freed from glycerol by dialysis contains a highly active amylase, but is free from maltase. The residue containing maltase is not, however, completely freed from amylase by such extraction. Extraction with glycol effects a similar separation, but the maltase activity is considerably decreased (cf. A., 1926, 202, 976). P. W. CLUTTERBUCK.

Complement of the amylases. VII. J. BONDI (Biochem. Z., 1928, **203**, 88—94).—Egg-albumin digested with pepsin has only a slight, but digested with trypsin a greater, complement action, whilst albumin digested first with pepsin and then with trypsin has a still greater action. It is suggested that the activator contained in yeast complement is formed from the yeast-protein by the proteolytic enzymes of the yeast (cf. A., 1928, 1280). P. W. CLUTTERBUCK.

Enzymes and light. XIII. L. PINCUSSEN. Action of light on takadiastase in presence of sensitisers. Y. KAMBAYASHI (Biochem. Z., 1928, **203**, 334—342).—The variation of the extent of inactivation of takadiastase on irradiation with ultraviolet light with changes of p_H and of purity and dilution of enzyme is investigated in presence and absence of the sensitisers eosin, sodium anthraquinonedisulphonate, and sodium dichloroanthracenedisulphonate. With a concentration of 0·01% of sensitiser, the action of light is no greater than in its absence. The degree of inactivation decreases with increasing concentration of sensitiser but to different extents with the three substances. The action of light on takadiastase purified by adsorption on aluminium hydroxide and eluted with phosphate is considerably greater than on the untreated enzyme, 16—22% of the untreated and 36—48% of the purified enzyme being destroyed. Dilute enzyme solutions are more strongly inactivated than concentrated. Injury of the purified enzyme by light is never greater and often less in presence than in absence of sensitisers (cf. A., 1926, 432, 757; 1928, 795). P. W. CLUTTERBUCK.

Specificity of enzymic fission of maltose. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 788—795).—Leibowitz has assumed the existence of two types of maltase, viz., glucosido-maltase present in yeast, and gluco-maltase present in barley and in takadiastase, the latter type being incapable of hydrolysing α-methylglucoside or maltosazone (cf. A., 1925, 184; 1926, 322). This view is not shared by the author, who found that α-methylglucoside is readily hydrolysed by barley maltase if sufficiently concentrated enzyme solutions are used. The fact that maltase in different materials may exert its maximum activity at different p_H values does not disprove the identity of the enzyme in the different materials, since the effect of activating and inhibiting substances has to be considered. J. H. LANE.

Enzymic fission of sucrose. II. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 781—787; see also A., 1928, 1157, 1281).—Of the two sucrose-splitting enzymes in yeast, viz., α-glucosidase and β-*h*-fructosidase, the former is present in much smaller amount than the latter and is inactive at p_H 4·7, the optimum reaction for fructosidase. Their behaviour towards raffinose affords a means of distinguishing them, since α-glucosidase has no action, whilst the fructosidase produces melibiose and lævulose. Melezitose, a glucosidofructosidoglucose in which the fructosidoglucose portion of the molecule is supposed to have the constitution of sucrose, is not attacked by fructosidase, but is completely hydrolysed to hexoses by α-glucosidase; hence it appears to be α-glucosido-β-*h*-fructosido-α-glucoside. J. H. LANE.

Liberation of invertase from yeast. R. WILLSTÄTTER and W. GRASSMANN (Biochem. Z., 1928, **203**, 308—312).—Yeast is treated with ethyl acetate and digested with pepsin or trypsin and the invertase finally liberated into aqueous solution from the residue by treatment with malt diastase or papain. Activation of papain by hydrogen cyanide accelerates the liberation of invertase (cf. A., 1921, i, 823). P. W. CLUTTERBUCK.

Formation of acetaldehyde from pyruvic acid in the autolysis of red and white muscle. A. UTEVSKI (Biochem. Z., 1929, **204**, 81—87).—In the autolysis of white muscle of the rabbit, cock, and hen, smaller amounts of acetaldehyde are formed than in the red muscle and in the breast muscle of the pigeon. Only red muscle and the breast muscle of the pigeon can convert sodium pyruvate into acetaldehyde. J. H. BIRKINSHAW.

Titration method for lipase. L. GÓZONY, J. GSELL, and F. HOFFENREICH (Biochem. Z., 1929, **204**, 126—139).—Mono- or tri-butyrin is added to serum in a number of known dilutions, and caseinogen dissolved in sodium hydroxide and brought to p_H 5·6 is then added; the free acid liberated by the serum-lipase precipitates the caseinogen. The dilution at which turbidity just ceases is observed. A comparative series of lipase determinations in various animal sera is given and the effect of various substances on lipase action is studied. J. H. BIRKINSHAW.

Stereochemical specificity of liver- and pancreas-lipase. H. H. WEBER and R. AMMON (Biochem. Z., 1929, **204**, 197—207).—The dissociation constant of the compound of liver-lipase with methyl *d*-mandelate is $10^{-3\cdot75}$ and with the *l*-mandelate $10^{-2\cdot9}$. The ratio of the hydrolysis constants is 1 : 1·75. The dissociation constants of the corresponding compounds of pancreas-lipase are equal and have the value $10^{-1\cdot8}$. The ratio of the hydrolysis constants is 1 : 1·7 in favour of the *l*-ester. The optical decomposition specificities peculiar to the two lipases agree quantitatively in spite of the opposite nature of their optical total specificity. J. H. BIRKINSHAW.

Hydrolysis of ethyl lactate by liver-esterase. P. Rona and R. Itelsohn-Schechter (Biochem. Z., 1928, **203**, 293—297).—Of the ethyl esters of *d*-, *l*-, and *dl*-lactic acid, the esterase of pig's liver hydrolyses the *d*-ester most readily. P. W. Clutterbuck.

Activation of *Ricinus* lipase by acids. S. Mukai (J. Soc. Chem. Ind. Japan, 1928, **31**, 759—765).—There is a magnesium compound in castor seeds which inhibits the activity of lipase, and acids used for the activation of lipase dissolve and remove this compound. The activated lipase, which had been previously treated with 0·05N-sulphuric acid, showed nearly the same activity from $p_{\rm H}$ 3·5 to 6·8. Y. Tomoda.

An enzyme [effecting hydrolysis of allantoin]. R. Fosse and A. Brunel (Compt. rend., 1929, **188**, 426—428).—A new enzyme, *allantoinase*, which hydrolyses allantoin to allantoic acid, is found in the seeds of many leguminous plants. G. A. C. Gough.

Enzymic proteolysis. IV. E. Mislowitzer (Biochem. Z., 1928, **203**, 323—333).—The amino-groups liberated during hydrolysis of the CO·NH groups of protein belong to the lower degradation products and the carboxyl groups to the colloidal residue. In the initial hydrolysis of caseinogen (cf. A., 1928, 923, 1401) the amino-groups present in the colloidal fraction show scarcely any change, whilst the carboxyl groups increase considerably. P. W. Clutterbuck.

Specific action of proteolytic enzymes and its significance in determining the structure of proteins. E. Waldschmidt-Leitz (Collegium, 1928, 543—554).—Clupeine, salmine, and scombrine are strongly hydrolysed by trypsin-kinase, and moderately by trypsin and papain–hydrocyanic acid, but not by erepsin, pepsin, and papain. Histone, caseinogen, fibrin, gelatin, gliadin, and albumin are not hydrolysed by erepsin or trypsin, but are moderately hydrolysed by trypsin-kinase, pepsin, or papain, and, except albumin, are strongly hydrolysed by papain–hydrocyanic acid. Globulin is hydrolysed by trypsin-kinase and pepsin. Silk fibroin and keratin are not hydrolysed by any of these enzymes. Synthetic dipeptides, derived from amino-acids occurring in proteins, *e.g.*, glycyl- and leucyl-glycine, glycyltyrosine, and histidylglycine, are hydrolysable by erepsin only, except in certain instances, *e.g.*, phenylalanylarginine and glutamyltyrosine, which are hydrolysable by trypsin and trypsin-kinase also. Mere lengthening of the peptide chain does not induce hydrolysis. The introduction of a tyrosine molecule renders tri-, tetra-, and pentapeptides capable of hydrolysis by trypsin and trypsin-kinase, respectively. Leucyltriglycyltyrosine is not split by erepsin, which shows that the modes of action of erepsin and trypsin are different. The trypsin eliminates tyrosine from the carboxyl group, whereas erepsin eliminates the amino-acids carrying free amino-groups and then proceeds to the complete hydrolysis of the peptide. These observations explain the effects of fractional hydrolysis. Leucylglycyltyrosine would give a hydrolytic ratio 1 : 1 with trypsin followed by erepsin, whereas leucyltriglycyltyrosine would show 1 : 3. The action of yeast polypeptidase and yeast erepsin depends on the length of the peptide chain, independent of its composition. Dipeptides are attacked by yeast erepsin only, and tri- and higher peptides by polypeptidase only. Yeast erepsin requires the close proximity of both a free amino-group and a free carboxyl group; the polypeptidase requires a free amino-group without the close proximity of the carboxyl group. A certain electronegative property is required in trypsin substrates. Dipeptides, which are specific erepsin substrates, can be converted into specific pancreatic trypsin substrates by introducing acyl groups. D. Woodroffe.

Specific action of erepsin, trypsin, and trypsin-kinase. Effect of the addition of α- and β-amino-acids, amines, etc. to the substrate–enzyme mixture. E. Abderhalden, E. Rindtorff, and A. Schmitz (Fermentforsch., 1928, **10**, 233—250; cf. Abderhalden and Gigon, A., 1907, ii, 892).—That the action of erepsin, trypsin, and trypsin-kinase on various polypeptides is not affected in the same manner by the addition of various amino-acids or amines is shown by a study of the hydrolysis of *dl*-leucylglycine, glycyl-*dl*-leucine and its phenylurethane, *dl*-α-aminobutyrylglycine, and benzoyl-*dl*-leucylglycine by these enzymes at various concentrations, with or without the addition of a large number of amino-acids. The hydrolysis of *dl*-leucylglycine by erepsin ($p_{\rm H}$ 7·8) for 20 hrs. at 37° is slightly increased by the addition of β-aminobutyric acid, whilst *l*-leucine, glycine, *l*-valine, *l*-alanine, β-alanine, *d*-alanine, sarcosine, *l*-phenylalanine, and hippuric acid have a retarding effect which increases in the order given. A small retarding action is also observed by addition of α- and β-naphthylamine, *p*-toluidine, and colamine, which again increases in the order given. On the other hand, with trypsin-kinase ($p_{\rm H}$ 8·3) at 37° for 20 hrs. the retarding action on the hydrolysis of benzoyl-*dl*-leucylglycine increases in the order, *d*-alanine, hippuric acid, sarcosine, *l*-phenylalanine, *l*-leucine, glycine, *l*-alanine, and β-aminobutyric acid; and in the second series, in the order, colamine, α- and β-naphthylamine, and *p*-toluidine. Similarly for the hydrolysis of glycyl-*dl*-leucine by erepsin for 30 hrs. the retarding effect increases in the order glycine, β-aminobutyric acid, *l*-leucine, *d*- and *l*-valine, sarcosine, benzoyl-*dl*-alanine, *d*-alanine, *l*-alanine, β-alanine, hippuric acid, and *l*-phenylalanine; and in the second series, in the order colamine, β-naphthylamine, carbamide, *p*-toluidine, and α-naphthylamine. The corresponding order for the hydrolysis of the phenylurethane of glycyl-*dl*-leucine with trypsin-kinase for 30 hrs. is sarcosine, *l*-valine, *l*-leucine, β-aminobutyric acid, β-alanine, *l*-alanine, benzoyl-*dl*-alanine, phenylalanine, glycine, and hippuric acid; and in the second series, α- and β-naphthylamine, *p*-toluidine, carbamide, and colamine. The hydrolysis of *dl*-α-aminobutyrylglycine by erepsin is similarly retarded in the order *l*-leucine, glycine, *d*-alanine, *l*-alanine, sarcosine, *l*-phenylalanine, hippuric acid, the last two having a very large effect. The interaction of the enzyme-complex with the original substrate (polypeptide) and its fission products (amino-acids) is discussed, and on the basis of the above results it is concluded that neither the free amino-group nor the carboxyl group of itself is responsible for the specific action of the enzyme, but that this depends in a complicated manner on the whole structure of the substrate and its fission products. J. W. Baker.

Proteases of gastric mucosa. R. Willstätter and E. Bamann (Z. physiol. Chem., 1928, **180**, 127—143).—A glycerol extract of the gastric mucosa of the pig or dog contains kathepsin, a protease having its optimum activity at p_H 4. Erepsin is also present. B. A. Eagles.

Enzymic synthesis of protein. P. Rona and H. A. Oelkers (Biochem. Z., 1928, **203**, 298—307).—The formation of sparingly soluble products by the action of pepsin and trypsin on the concentrated aqueous solution of protein decomposition products at a suitable p_H as reported by Wasteneys and Borsook (A., 1925, i, 97, 102, 472, 865) is confirmed and the conclusion of the latter that this represents synthesis of protein, previously contested (Rona and Chrometzka, A., 1927, 1220), is now regarded as proved correct in the case of peptic digestion, since the process is accompanied by a decrease of amino-nitrogen and carbonyl groups, but the authors' view that these products are the result of further hydrolysis is maintained in the case of tryptic digestion, there being a further increase in amino-nitrogen and carbonyl groups during the formation of the products. The less soluble products obtained during the action of pepsin, on digestion again with pepsin under optimal conditions again break down with the formation of free carbonyl groups and an increase in amino-nitrogen. P. W. Clutterbuck.

First phases of the chemistry of the dissimilation of the hexoses. II. A. J. Kluyver and A. P. Struyk (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 882—893; cf. A., 1928, 398).—When dextrose is fermented by maceration juice from yeast under certain conditions the amount of hexosemonophosphoric acid formed may exceed that of the hexosediphosphoric acid. The smaller the concentration of maceration juice used to ferment a mixture of dextrose and disodium hydrogen phosphate the larger is the ratio of hexosemonophosphoric acid to hexosediphosphoric acid. The ratio between the number of molecules of carbon dioxide and of hexosediphosphoric acid formed is frequently greater than 2. Various theories of alcoholic fermentation are discussed. W. O. Kermack.

Biochemical conversion of dihydroxyacetone into hexose by fermentation and the velocity of fermentation of dihydroxyacetone in relation to its heat of combustion. I. C. Neuberg and M. Kobel (Biochem. Z., 1928, **203**, 452—462).—The velocity of fermentation of dihydroxyacetone by fresh *Saccharomyces Ludwigii* is never greater than the velocity with dextrose. From the energy content (heat of combustion) of dihydroxyacetone, which is higher than that of dextrose, it follows that dihydroxyacetone is fermented, not as such, but after condensation to hexose. This is confirmed by the isolation as products of fermentation of hexosemono- and hexosedi-phosphoric acid. Using dried *S. Ludwigii* to which co-enzyme of bottom yeast had been added, the chief product is optically active hexosemonophosphate [α_D of the barium salt in two preparations $+17{\cdot}7°$ ($c=2{\cdot}63$), $+13{\cdot}8°$ ($c=1{\cdot}7$)] consisting of a little of Neuberg's and a large amount of Robison's ester together with decreasing amounts of hexosediphosphate. P. W. Clutterbuck.

Mechanism of the fermentation of dihydroxyacetone. K. Iwasaki (Biochem. Z., 1928, **203**, 237—266).—Fermentation of dihydroxyacetone by *Saccharomyces Ludwigii*, using either the living yeast or the maceration extract, leads to the conclusion that fermentation depends on the condensation of dihydroxyacetone to hexose, direct fermentation of the triose not taking place. With living yeast, the maximal rate of fermentation of 0·10% dextrose solution is not increased by adding dihydroxyacetone, but with lower concentrations of sugar the rate becomes maximal, but never exceeds it on adding dihydroxyacetone. The oxidation quotient for the fermentation of dihydroxyacetone is at first low, but eventually increases to the same value as for the fermentation of sugar. The calorimetrically determined heat of fermentation of dihydroxyacetone is 70—80 g.-cal. per g. higher than for dextrose. The activity of maceration juice from freshly-prepared dry yeast in fermenting dihydroxyacetone corresponds with that of the living yeast from which the dry yeast is prepared. When by storage its activity decreases, the original activity is restored by mixing with dried yeast before macerating. The velocity of fermentation of dihydroxyacetone by extract is 30—40% of that of sugar in the phosphate period. Inorganic phosphate becomes esterified and the esters examined after 80 min. consisted of 80% of hexosediphosphate and 20% of Robison's hexosemonophosphate. The rate of fermentation of dihydroxyacetone is limited by the rate of condensation of triose to hexose. P. W. Clutterbuck.

Desmolytic formation of methylglyoxal by the enzymes of yeast. C. Neuberg and M. Kobel (Biochem. Z., 1928, **203**, 463—468).—By keeping magnesium hexosediphosphate for 3 days with an enzyme solution (prepared by suspending for 2 days at 37° dried yeast in distilled water, adding toluene, shaking occasionally, and centrifuging) and removing the protein with trichloroacetic acid, a clear solution was obtained containing considerable amounts of methylglyoxal, characterised as the 2 : 4-dinitrophenylosazone. P. W. Clutterbuck.

Bacteriological conductivity culture cell and some of its applications. L. B. Parsons, E. T. Drake, and W. S. Sturges (J. Amer. Chem. Soc., 1929, **51**, 166—171).—A conductivity cell which can also be used as a growth vessel is described. The cell is used to investigate the effect of environment factors (*e.g.*, p_H, temperature, oxygen pressure) on the biochemical activity or growth of ammonia-producing anaërobes, the conductivity change being used to measure the ammonia production. Other possible applications are suggested. S. K. Tweedy.

Biological reactions on the concentration of gels. S. Prát (Kolloid-Z., 1929, **47**, 36—38).—When micro-organisms are grown in agar, the forms developed vary with the concentration of the gel. E. S. Hedges.

Microbiology of aqueous solutions. K. C. Berthelsen (Pharm. Zentr., 1929, **70**, 37—44).—A study of the types of growth colonies found in simple aqueous solutions of a large number of inorganic salts and of the commoner alkaloids. B. A. Eagles.

Relation of the growth of certain micro-organisms to the composition of the medium. IV. Addition of mannitol. V. Reader (Biochem. J., 1929, **23**, 61—67).—The anomalous results obtained by Orr-Ewing and Reader (A., 1928, 556) with *Streptothrix corallinus* when crude aqueous extracts of yeast were added to the medium can be artificially reproduced by adding mannitol to the purer extracts. The increased weight of bacteria grown in the presence of mannitol is not due to increased fat production. The amount of growth is independent of the concentration of the mannitol. Dulcitol, sorbitol, glycerol, or inositol could not replace mannitol in this respect. S. S. Zilva.

Metabolism of the *Bacillus abortus–melitensis* group. II. Nitrogen. III. Dextrose utilisation. J. G. McAlpine and C. A. Slanetz (J. Infect. Dis., 1928, **42**, 66—71, 73—78).—Differences in sugar and nitrogen metabolism are employed for the differentiation of human and porcine from bovine *B. abortus* and from *B. melitensis*.
Chemical Abstracts.

Gas production by bacterial symbiosis with special reference to the influence of nitrogenous substances. M. Ishikawa (J. Infect. Dis., 1927, **41**, 238—256).—Non-proteolytic bacteria cannot produce gas from carbohydrates and formates in media containing only complex nitrogenous substances unless proteolytic bacteria or simple nitrogenous substances are present. Probably the simple nitrogenous compounds increase the activity or production of formiase, which is considered to be responsible for the production of gas. Chemical Abstracts.

Influence of anions and cations on the viability of *Bacillus coli*. C. H. Boissevain and E. Webb (J. Lab. Clin. Med., 1928, **13**, 1027—1035).
Chemical Abstracts.

Reduction potential, energy exchange, and cell growth. Experiments with *B. coli*. J. H. Quastel and W. R. Wooldridge (Biochem. J., 1929, **23**, 113—137).—Succinate inhibits anaërobic growth of *B. coli* in a lactate–formate medium. Cysteine (or thiol compounds) also inhibits growth. Formate at relatively low concentrations increases the rate of proliferation of the organism. Rate of growth of *B. coli* is not dependent on the oxidation or reduction intensity of its environment (cf. Quastel and Stephenson, A., 1926, 1177). S. S. Zilva.

Resting bacteria. J. H. Quastel (Bull. Soc. Chim. biol., 1928, **10**, 1282—1292).—A discussion of work already published (A., 1926, 434, 868; 1927, 280, 1113; 1928, 797). G. A. C. Gough.

Lactic acid fermentation. A. I. Virtanen (Förh. III nord. Kemistmötet, 1928, 217—226).—A *résumé* of recent work on the lactic acid fermentation of sugar. H. F. Harwood.

Precipitation of organic iron compounds by bacteria. I. M. Lewis (Zentr. Bakt. Par., II, 1928, **75**, 45—52; Chem. Zentr., 1928, ii, 677).—When grown on a medium containing certain iron salts and tap, spring, or river water, various bacteria caused precipitation of iron, the effect depending to some extent on the amount of phosphorus present.
A. A. Eldridge.

Nitrogen-fixing bacteria of the genus *Rhizobium*. R. H. Walter (Iowa Agric. Exp. Sta. Res. Bull., 1928, **113**, 371—406).—Legume bacteria attack monosaccharides with a greater production of acid than in the case of di- or tri-saccharides, dulcitol, inositol, or dextrin. Agglutination and gelatin liquefaction were studied. Chemical Abstracts.

Bacteria. XXIV. Timothy-grass bacillus. R. D. Coghill and O. D. Bird (J. Biol. Chem., 1929, **81**, 115—122).—Dried Timothy-grass bacilli (*Mycobacterium phlei*) when extracted with ether and chloroform yielded 2·72% of fat; after hydrolysis of the residue with hydrochloric acid a further 14·9% of fat could be extracted. The dried organisms, after defatting with ether, were extracted successively with water and 0·5% sodium hydroxide; the water removed 12—15% of the total nitrogen, and yielded a protein and a carbohydrate fraction, the latter containing reducing sugars. The alkaline extract contained about 16% of the total nitrogen, of which about 6% was represented by a second protein; the insoluble residue contained about 60% of the nitrogen, the remainder having been lost as ammonia. This organism therefore, although biologically similar to the tubercle bacillus, differs markedly from the latter in chemical composition (A., 1926, 1277).
C. R. Harington.

Pneumococcal hæmolysin. L. Cotoni and N. Chambrin (Ann. Inst. Pasteur, 1928, **42**, 1536—1572).—Media containing dextrose are favourable to the production of pneumococcal hæmolysins. Cultures grown on media containing animal sera are entirely lacking in hæmolytic activity. B. A. Eagles.

Oxidations by *Bacterium xylinum*. II. Formation of gluconic and 5-ketogluconic acids [from dextrose]. K. Bernhauer and K. Schön (Z. physiol. Chem., 1929, **180**, 232—240).—A bacterium resembling *B. xylinum* (cf. A., 1928, 1285) can convert dextrose, in acid solution, into gluconic acid. The change proceeds best in presence of $0\cdot02N$-butyric acid when 79% of the acid is obtained after 23 days. Formic and acetic acids are not so suitable. The conversion takes place also in presence of calcium carbonate. When the reaction mixture is slightly alkaline (p_H 8) 5-ketogluconic acid is obtained, but the yield diminishes from 64 to about 40%, when 36% of the experiments were infected with *Aspergillus niger*. This mould contamination is prevented by addition of $0\cdot006N$-butyric acid. H. Burton.

Formation of acid by species of *Penicillium* (Link). T. Chrzaszcz and D. Tinkov (Biochem. Z., 1929, **204**, 106—124).—The titratable acidity, citric and oxalic acids, and acids having soluble calcium salts were determined for 42 species of *Penicillium*. All species produced acid. Citric acid is a normal product of metabolism and is produced in considerable amount by some species; oxalic acid is formed only by a few species and is not regarded

as a stage in the normal oxidation process. The acid (or acids) with soluble calcium salt appears regularly. Some species form fatty substances, possibly esters.
J. H. BIRKINSHAW.

Resins of *Aspergillus niger*. C. PONTILLON (Compt. rend., 1929, **188**, 413—415).—The alcoholic extract of the mycelium of *A. niger* yields resins when freed from fats by dilution with water to a concentration of 70% followed by filtration. The resins may also be isolated by virtue of their solubility in sodium carbonate or by the difference between the solubility of the magnesium resinates and the magnesium soaps arising from the hydrolysis of the fats. The resin is soluble in ether, light petroleum, and concentrated solutions of chloral hydrate.
G. A. C. GOUGH.

Disinfectants for preserving the amylase solution of *Aspergillus oryzæ*. K. OSHIMA (J. Soc. Chem. Ind. Japan, 1928, **31**, 750—753).—The following antiseptics were proved to be suitable for preserving the amylase solution: cresol (0·15—0·40%), lysol (0·5—2·0%), phenol (0·4—1·5%), thymol (0·05—0·20%), phenol+cresol (0·3%+0·1%—1·0%+0·2%).
Y. TOMODA.

Grouped organisms. Action of alkaloids on *Convoluta Roscoffensis*. J. A. THOMAS (Compt. rend., 1929, **188**, 195—197).—The time of survival of groups of these organisms in dilute solutions of various alkaloids is sometimes greater and sometimes smaller than that of the individual organisms. In many cases a particular concentration is observed at which the groups possess a greater time of survival. Increase in p_H generally increases the toxicity and the addition of quinol decreases the toxicity in some instances.
G. A. C. GOUGH.

[Bactericidal] action of sodium ricinoleate. A. KOZLOWSKI (J. Bact., 1928, **16**, 203—209).

Bactericidal properties of the acyl and alkyl derivatives of resorcinol. B. HAMPIL (J. Infect. Dis., 1928, **43**, 25—40).—The bactericidal properties of alkyl- and acyl-resorcinol depend on the composition of the medium; the inhibitory power of organic material increases from *n*-butyl- to *n*-cetyl-resorcinol, where disinfecting power has disappeared. The bactericidal power is greater at 37° than at 20°. At 45°, nonyl- and decyl-resorcinol are bactericidal in aqueous solution. By increasing the solubility, addition of sodium carbonate (1%) increases the bactericidal action of hexyl and higher derivatives. Acyl derivatives of resorcinol (*n*-butyryl- to *n*-hexoyl-) are more potent at 37° than at 20°; they are ineffective in a standard organic mixture at 37°. With hexyl-, heptyl-, and cetyl-resorcinol a specificity in disinfective action was observed.
CHEMICAL ABSTRACTS.

Thermodynamic activity and biological action. Disinfecting power and activity of the mercury ion. I. A. [illegible] and G. B. BONINO (Arch. Sci. Biol., 1928, **12**, [illegible]; Chem. Zentr., 1928, ii, [illegible]).—The activity of the mercuric ion and the disinfecting power diminish with increasing addition of sodium chloride to the solution. When log f_{Hg}·· is plotted against log *c*, where *c* is the number of colonies of *B. [illegible]* developed after 6 mins.' disinfection, a straight line is obtained except for very high sodium chloride concentrations.
A. A. ELDRIDGE.

Bactericidal action of nitroso-compounds. E. A. COOPER and R. B. HAINES (Biochem. J., 1929, **23**, 10—16).—The hydrochloride and methiodide of nitrosoanilines are weaker germicides than the bases from which they are derived. Nitrosophenol, nitrosoaniline, and nitrosodimethylaniline have little or no action on amino-acids and proteins, but react gradually with nucleic acid, forming a dark green, insoluble product. The nitroso-compounds are readily absorbed by lecithin. The nitroso-compounds, therefore, most probably owe their slow germicidal action and marked inhibitory power to their gradual chemical interaction with the nuclear constituents of the cell.
S. S. ZILVA.

Chemical action of quinones on proteins and amino-acids. II. E. A. COOPER and R. B. HAINES (Biochem. J., 1929, **23**, 4—9).—Saline constituents of Ringer's solution accelerate considerably the reaction between benzoquinone and glycine, but have only a slight effect with toluquinone. Benzoquinone loses much of its germicidal activity on forming an additive compound with anthranilic acid. The temperature coefficient of disinfection in the case of quinones is 6 or even higher; on the other hand, the coefficient for the chemical action on glycine is normal (2 for 10°). In the case of phenol the temperature coefficient for germicidal action is approximately 3 and agrees more closely with the coefficient for the process of protein-coagulation by phenol. The velocity of coagulation by *m*-cresol is only very slightly increased by rise in temperature, as is also that of its bactericidal action. It is suggested that the main factor in the germicidal action of the quinones is the interaction with the amino-acids, but another factor fundamental in the action of oxidising disinfectants is operating simultaneously.

The chemical reactivity ratio benzoquinone/toluquinone with the nitrogenous constituents of urines is highest in glycosuria (5·5), intermediate in value with leucæmia (2), and lowest in nephritis, jaundice, and hæmaturia (1·4).
S. S. ZILVA.

Production of monochromatic X-rays of long wave-length. Quantitative action on micro-organisms. F. HOLWECK (Compt. rend., 1929, **188**, 197—199).—X-Rays of 4 and 8 Å., emitted from the silver cathode of a Coolidge tube through a silver window 5 μ thick and a cellophane sheet 20 μ thick, possess a bactericidal action on *B. pyocyaneus*. In the quantitative experiments the technique of Lacassagne (following abstract) is used. Mathematical investigation shows that, when light of 4 Å. is used, one quantum is sufficient to kill one organism and the number of surviving organisms is an exponential function of the time of irradiation. With light of 8 Å. at least 4 quanta are required and the mathematical relationship is more complex.
G. A. C. GOUGH.

Action of X-rays of long wave-length on micro-organisms. Statistics of the mortality of the irradiated bacteria. A. LACASSAGNE (Compt. rend., 1929, **188**, 200—202).—An appropriate amount of a culture of *B. pyocyaneus*, suspended in water, is evenly distributed on the surface of gelatin in a Petri dish so that a field of 10 mm. diameter contains 100 bacteria. A number of fields are then irradiated by X-rays (preceding abstract) of known intensity, the dishes incubated, and the resultant colonies in the irradiated fields compared with those in control dishes. It is assumed that each bacterium possesses a sensitive zone, which, if it absorbs a certain minimum of quanta, is destroyed by irradiation; the mathematical development depends on this assumption.

G. A. C. Gough.

Probability curves describing the action of X-rays on bacteria. (Mme.) P. Curie (Compt. rend., 1929, 188, 202—204).—The equations of curves relating the time of irradiation to the probability of survival of bacteria irradiated by X-rays are given (see preceding abstracts).

G. A. C. Gough.

Staining methods for bacteria and yeasts. W. E. Maneval (Stain Tech., 1929, 4, 21—25).—In order successfully to stain the flagella of bacteria actively motile organisms 20—24 hrs. old must be used. They should be transferred to sterile water, and after 30 min. droplets should be evaporated on slides. These should then be treated for 2—4 min. with the following mordant: 50 c.c. of 10—20% tannic acid, 10—15 c.c. of 5% ferric chloride, 5 c.c. of carbolfuchsin (Ziehl-Nielsen), 6—8 c.c. of 3% hydrogen peroxide. The slides should be washed and then treated for 2—3 min. with a mixture of 10 c.c. of saturated alcoholic basic fuchsin, 5 c.c. of a solution of aniline (1 part) in 95% alcohol (3 parts), 30 c.c. of distilled water, 1 c.c. of 4% acetic acid, after which they should be washed with water. Gutstein's methods of staining bacteria and yeasts are satisfactory.

H. W. Dudley.

Loeffler's methylene-blue. H. J. Conn (Stain Tech., 1929, 4, 27).—Instead of using Loeffler's formula for making up methylene-blue for use as a stain it is recommended that an alcoholic solution of the dye diluted with water be used.

H. W. Dudley.

Simultaneous determination of the adrenaline liberation, sugar content, and coagulation time of the blood in non-fasted, non-anæsthetised dogs after hæmorrhage. S. Saito, B. Kamei, and H. Tachi (Tôhoku J. Exp. Med., 1928, 11, 205—217).

Chemical Abstracts.

Significance of the augmented adrenaline secretion after hæmorrhage in dogs in the simultaneous occurrence of hyperglycæmia. H. Tachi and S. Saito (Tôhoku J. Exp. Med., 1928, 11, 205—217).

Chemical Abstracts.

Influence of adrenaline and insulin on distribution of glycogen. N. R. Blatherwick and M. Sahyun (J. Biol. Chem., 1929, 81, 123—127).—The conclusion of Cori and Cori (A., 1928, 1286) that adrenaline causes increased deposition of glycogen in the liver is confirmed by experiments on rabbits.

C. R. Harington.

Action of insulin in normal young rabbits. M. W. Goldblatt (Biochem. J., 1929, 23, 83—98).—Young rabbits 6—10 weeks old of the same litter when starved for 24 hrs. show a very satisfactory uniformity in their liver-glycogen (average of twelve animals was 50 mg. per liver). On treating such starved animals with insulin a rise in liver-glycogen invariably occurs (average for twelve animals 237 mg. per liver). An increased liver- and a considerable muscle-glycogen content is observed even in animals dying in hypoglycæmic convulsions. Adrenaline, whilst relieving hypoglycæmia, does not interfere with the action of insulin in increasing liver-glycogen. On the other hand, in continuous deep anæsthesia insulin fails to bring about this increase. Light ether anæsthesia relieves hypoglycæmic convulsions. Hypoglycæmic animals are very susceptible to strychnine poisoning. Continuous strychnine convulsions can prevent the typical action of insulin in promoting an increased glycogen content of the liver. In fed animals insulin does not bring about an increase in liver-glycogen and the animal goes into hypoglycæmic convulsions with large quantities of glycogen in the liver. Muscle-glycogen is definitely lowered. It is suggested that the immediate effect of insulin is to inhibit the release of liver-glycogen.

S. S. Zilva.

Glycogen content of the liver and muscle of rabbits; comparison of insulin and decamethylenediguanidine (synthalin). P. Rubino, J. A. Collazo, and B. Varela-Fuentes (Compt. rend. Soc. Biol., 1928, 99, 178—180; Chem. Zentr., 1928, ii, 1113).—Insulin, but not synthalin, stimulates not only the utilisation of dextrose in the tissue, but also the synthetic process leading to the formation of dextrose.

A. A. Eldridge.

Insulin. III. Standardisation of insulin. K. Freudenberg and W. Dirscherl. **IV. Action of pepsin on insulin and its acetyl derivative.** W. Dirscherl (Z. physiol. Chem., 1929, 180, 212—216, 217—231).—III. The standard used by the authors is the amount of insulin necessary to reduce the blood-sugar of a 2-kg. rabbit from an initial value of 0·1% to 0·045%. This unit is equivalent to 1·8 standard units. Abel's crystalline insulin is found to contain 26 standard units/mg. (cf. du Vigneaud and others, A., 1928, 1160).

IV. The action of pepsin on insulin, "regenerated" insulin, and acetylinsulin (A., 1928, 675) at different p_H values and temperatures has been examined. The results show that the inactivation of insulin is comparable to the pepsin digest of a protein and optimum activity is at p_H 1·8 and 45°. A suspension of acetylinsulin was only slightly affected after 3 hrs. The acetylinsulin obtained by Jensen and Geiling (A., 1928, 1160) probably differs from the author's, since a different method of preparation was employed.

[With H. Eyer.]—Formol titration of the pepsin digest of insulin shows an increase in the amino-nitrogen. Acetylinsulin shows only a slight increase after 24 hrs.

H. Burton.

Insulin content of the pancreas following intoxication of rabbits with paratyphoid-*B* filtrate and dysentery bacilli. M. L. Menten and H. M. Krugh (J. Infect. Dis., 1928, 43, 121—125).

Insulin-like plant extracts. III. Phaseolin. E. Kaufmann (Z. ges. exp. Med., 1928, 60, 285—288;

Chem. Zentr., 1928, ii, 674).—The insulin-like effect of phaseolin on the blood-sugar is recorded; the active principles of such substances may be biogenic amines. A. A. Eldridge.

Denaturation of insulin protein by concentrated sulphuric acid. F. Bischoff and M. Sahyun (J. Biol. Chem., 1929, **81**, 167—173).—Various preparations of insulin were dissolved in ice-cold sulphuric acid, or in a mixture of the latter with acetic acid, and the solution was poured on to ice; the product was acid-insoluble and retained half the physiological activity of the original material. Addition of nitrite to the sulphuric acid reduced the activity to one third, and addition of formaldehyde abolished it entirely, whilst cyanide and methyl sulphate had no effect. The denaturation by sulphuric acid is irreversible. C. R. Harington.

Hyperglycæmia following injection of secretin. H. Herman (Rev. franç. Endocrinol., 1926, **4**, 381—415; Chem. Zentr., 1928, ii, 1115).—The hyperglycæmia following intravenous administration of Bayliss and Starling's secretin is due to the presence of impurities which depress the blood-pressure and cause the adrenals to produce adrenaline. A. A. Eldridge.

Sexual hormone in the urine of males. S. Loewe, H. E. Voss, F. Lange, and A. Wähner (Klin. Woch., 1928, **7**, 1376—1377; Chem. Zentr., 1928, ii, 1111—1112).—Testicular hormone is present in the urine of males, although it does not respond to the Allen–Doisy test. Testicular and ovarian hormones can be separated by fractionation. A. A. Eldridge.

Sexual hormone in blood. E. Fels (Arch. Gynäkol., 1927, **130**, 606—625; Chem. Zentr., 1928, ii, 1111).—From the sixth month of pregnancy the serum contains much ovarian hormone; the hormone of the anterior lobe of the pituitary is not then found. A. A. Eldridge.

Hormones and tissue respiration. I. Function of the thyroid gland. M. Maeda (Folia Endocrinol., 1928, **3**, No. 4, 2 pp.; Chem. Zentr., 1928, ii, 1111).—By feeding of thyroid to rabbits the oxygen consumption of thyroid tissue is reduced, whilst in the spleen, pancreas, sexual glands, and liver it is increased. The respiratory quotient in the liver is unchanged, but in the kidneys it is increased. After removal of the thyroid gland the oxygen consumption of the suprarenals is increased, but that in other organs is reduced. The respiratory quotient falls in the liver and remains unchanged (the oxygen and carbon dioxide both diminishing) in the kidneys. A. A. Eldridge.

Thyroid hormone regulating cerebral excitability. (Mlle.) G. Fuchs, J. Régnier, D. Santenoise, and P. Vare (Compt. rend., 1929, **188**, 419—421).—The thyroid gland, taken from a dog in which the vagus nerve has been excited by eserine, yields an extract which, when injected into the brain of a second dog, considerably lowers the chronaxia of the sigmoid convolution of the brain. It is suggested that the extract contains a hormone which regulates the excitability of this part of the brain. G. A. C. Gough.

Resolution of *dl*-thyroxine. C. R. Harington.—See this vol., 313.

Derivatives of thyroxine. J. N. Ashley and C. R. Harington.—See this vol., 313.

Vitamin content of honey. E. Hoyle (Biochem. J., 1929, **23**, 54—60).—A fresh English comb honey and a West Indian honey were found to contain no appreciable quantities of vitamins-*A*, -B_1, -B_2, -*C*, and -*D*. S. S. Zilva.

Vitamin-*A* action of lipochromes. B. von Euler, H. von Euler, and H. Hellström (Biochem. Z., 1928, **203**, 370—384).—The vitamin-*A* colour reaction (antimony chloride and chloroform) is given by pure carotin and lycopin. The spectra of the blue solutions so obtained and the displacement of the absorption maxima by fat are determined spectrophotometrically. Carotin in daily doses of less than 0·005 mg. causes an increase in the weight of young rats, the action being similar to the growth-promoting characteristic of vitamin-*A*. The antimony reaction of blood-serum and of butter runs parallel with their carotin content. P. W. Clutterbuck.

Vitamins. L. S. Foglieni (Arch. Fisiol., 1928, **26**, 83—153; Chem. Zentr., 1928, ii, 1118).—In absence of air, vitamins-*A*, -*B*, and -*C* withstand exposure to 120—134° without loss of activity. Vitamin-*B* consists of two components which separately have only a small and transient action; one gives Folin's reaction, is non-volatile, and has no effect on yeast growth, whilst the other gives Folin's reaction, is largely volatile between 120° and 134°, and stimulates the development of yeast. Similarly, vitamin-*C* appears to consist of two substances; one is non-volatile, gives Bezssonoff's test, and alone has a healing effect on acute, but not chronic, scurvy, whilst the other is volatile, fails to respond to Bezssonoff's test, and has no antiscorbutic action. In both cases the substances together exert a strong effect. When a solution containing vitamin-*C* is made slightly alkaline with sodium hydroxide, and heated, the vitamin is rapidly inactivated. A. A. Eldridge.

Homogeneity of vitamin-*B*. E. Schmitz and E. George (Biochem. Z., 1929, **204**, 165—178).—By feeding sunflower seeds along with polished rice to pigeons an attempt was made to induce the neuritic symptoms unaccompanied by secondary phenomena such as loss in weight. This was found to be impossible. When the ration of seeds was sufficiently reduced all the symptoms of *B*-avitaminosis appeared simultaneously. The work of di Mattei (Arch. Fisiol., 1927, **25**, 56) is therefore not confirmed. J. H. Birkinshaw.

Attempt to separate the antineuritic vitamin with fuller's earth. L. Randoin and R. Lecoq (Compt. rend. Soc. Biol., 1928, **99**, 148—150; Chem. Zentr., 1928, ii, 1119).—In aqueous medium fuller's earth extracts from yeast almost all the antineuritic vitamin, together with a certain quantity of vitamins essential for nutrition. Fuller's earth activated in alcoholic medium contains almost exclusively antineuritic vitamin. A. A. Eldridge.

Effect of desiccation on the antiscorbutic principle. P. Lavialle (Bull. Soc. Chim. biol., 1928, **10**, 1293—1297).—A diet of bread, meat, water, and salts, heated at 130° for 45 min., resulted in the development of scurvy in a dog in 9—10 months, whilst a similar animal fed on malted biscuit powder, milk, and sugar dried under reduced pressure resisted scurvy for at least 18 months. A freshly-weaned dog, fed on the last-named diet, resisted scurvy for 16 months. G. A. C. Gough.

Experimental rickets. XXVIII. Does vitamin-*D* pass into the milk? E. V. McCollum, N. Simmonds, J. E. Becker, and P. G. Shipley (Amer. J. Dis. Children, 1927, **33**, 230—243).—Experiments with rats suggest that vitamin-*D* passes into the milk when cod-liver oil is fed to the mother, but the amount is considerable only when the oil is administered during pregnancy as well as during lactation. Chemical Abstracts.

Vitamin content of olive oil irradiated with ultra-violet rays. G. Rigobello (Rev. sud-amer. endocrinol., 1928, **11**, 456—466).—The bone calcification of rats receiving irradiated olive oil was almost normal, and 25% greater than that of the controls; young rats exhibit increased, although abnormal, bone growth. Increase in weight and alleviation of severe avitaminosis were observed. The effect is not regarded as being truly antirachitic.

Chemical Abstracts.

Action of the cholesterol of cod-liver oil on the photographic plate. L. Hugounenq and E. Couture (Compt. rend., 1929, **188**, 349—350).—Cholesterol obtained from cod-liver oil, when allowed to rest directly on the sensitive coating of a photographic plate or placed above it on a quartz plate for 3—15 days, produces a latent image which gives rise to dark markings on development; these effects are not produced by cholesterol from ox brain or gallstones nor are they produced if a glass plate is interposed between the cholesterol and the sensitive film. G. A. C. Gough.

Antirachitic potency of ergosterol irradiated by ultra-violet light and by exposure to cathode rays. A. Knudson and C. N. Moore (J. Biol. Chem., 1929, **81**, 49—64).—The highest degree of antirachitic potency was induced in ergosterol by ultra-violet irradiation for 15 sec. to 3 min.; exposure to cathode rays rendered ergosterol antirachitic, although the highest activity was 1/25 of that obtainable with ultra-violet irradiation. The material exposed to cathode rays showed a similar ultra-violet absorption spectrum to that irradiated with ultra-violet light. C. R. Harington.

Spectrographic determination of the activation of ergosterol by ultra-violet light. G. Tixier (Compt. rend., 1929, **188**, 206—208).—The maximum absorption of light of wave-length 2537 Å. during the irradiation of ergosterol does not correspond with the maximum antirachitic activity. Under standardised conditions, however, this may be determined from the absorption by an empirical rule. G. A. C. Gough.

Comparative value of biological and physical determinations of the [antirachitic activity of] irradiated ergosterol. R. Fabre and H. Simonnet (Compt. rend., 1929, **188**, 424—426).—Ergosterol, irradiated in an inert atmosphere for 20 min., is sufficient to prevent avitaminosis in rats in doses of 0·001 mg. per 100 g. body-weight. The fraction of this preparation capable of precipitation by digitonin is almost as great as that of the original sterol. Longer irradiation gives a product which is not entirely crystalline, but, although the fractions show different absorption spectra, they possess approximately the same activity.

G. A. C. Gough.

Specific colour reaction for ergosterol. O. Rosenheim (Biochem. J., 1929, **23**, 47—53).—Both chloral hydrate and trichloroacetic acid give a characteristic blue colour reaction with ergosterol, whilst all the other naturally occurring sterols investigated when purified from ergosterol remain colourless under the same conditions. Anhydrous chloral is non-reactive. The production of an immediate red colour with either of these reagents is specific for the $\Delta^{1:2}$ (or $\Delta^{11:13}$) linking of the sterol ring. S. S. Zilva.

Toxic action of milk and other substances exposed to ultra-violet radiation. P. Reyher and E. Walkhoff (Münch. med. Woch., 1928, **75**, 1071—1073; Chem. Zentr., 1928, ii, 909—910).—Ultra-violet irradiation gives rise to no antirachitic vitamin, but to a toxic substance which causes calcium deposition in rachitic bones, and in organs (heart, kidneys), together with pathological symptoms. The toxic effect is more marked if the diet of the animal is poor in vitamins, and is greatest in pregnancy. The vitamin-*C* content of milk is reduced proportionally to the oxygen present, and to the duration and intensity of irradiation by ultra-violet light.

A. A. Eldridge.

Presence of an ozonide in the vitamin-rich fraction of cod-liver oil. J. A. de Loureiro (Compt. rend. Soc. Biol., 1928, **97**, 878—879; Chem. Zentr., 1928, ii, 685).—The unsaponifiable fraction of cod-liver oil gives with petroleum a precipitate. This insolubility is characteristic of ozonides.

A. A. Eldridge.

Diet and reproduction. III. G. Grijns, K. de Haan, and J. A. van der Loeff (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 721—732).—The addition of serum-albumin to a diet poor in reproductive vitamins results in a marked improvement in the milk secretion, which has previously (Sure, A., 1926, 981) been shown to be dependent on a factor associated with that necessary for fertility but more readily destroyed by heat. It is not clear whether the albumin itself or a small quantity of some associated compound is responsible for the improvement in lactation. Various experiments are described demonstrating the effect of diet on reproduction.

W. O. Kermack.

Changes in the chlorophyll of a green alga. A. Perrier (Compt. rend., 1929, **188**, 339—341).—Cultivation of a unicellular alga in media composed of gelatin, inorganic salts, and organic substances shows that chlorophyll is formed in the absence of light and that growth is rapid in the presence of ethyl or methyl alcohol, but slower in the presence of glycerol, mannitol, or arabinose. In the absence of nitrogenous organic matter, the chlorophyll is gradually replaced by an orange-red substance (greenish-white in the absence of light).

G. A. C. Gough.

Natural colour preserved in sectioned green plant tissue. E. A. Jirouch (Stain Tech., 1929, 4, 17—19).—The tissue is fixed in Keefe's solution (Science, 1926, 64, 331), frozen in a 20% gum arabic solution, sectioned, and finally mounted in glycerol jelly. H. W. Dudley.

Forcing [of plants] by warm baths. III. K. Boresch (Biochem. Z., 1928, 202, 180—201).—The fermentative processes of hazel catkins are followed in terms of the alcohol and acetaldehyde liberated and the oxygen utilised. By placing the buds in luke-warm water, the amount of oxygen they can obtain becomes insufficient for their needs and metabolic products of anaërobic respiration (alcohol and aldehyde) accumulate. The oxygen utilisation of the buds 19 hrs. after treatment is still only one half that of the controls, whilst 42 hrs. afterwards it has attained the control value and after a further 2 days it has become greater than the control. It seems probable that some causal relationship exists between the injury to respiration and the forcing of the buds. P. W. Clutterbuck.

Influence of radiations on the germination of seeds and the growth of plants. G. Mezzadroli and E. Vareton (Zymologica, 1928, 3, 172—173).—The presence of an oscillating circuit increases the percentage germination of seeds by 25—50%. This influence continues, usually to the third or fifth day after germination, the plants showing double the aërial development of those not treated in this way. The waves used (0·5—2 metres in length) appear to be without further effect on the plants, since by the twelfth or fifteenth day both the treated and the untreated plants show the same aërial growth.

T. H. Pope.

Dynamics of the waxy gene in maize. II. Nature of waxy starch. R. A. Brink (Biochem. J., 1928, 22, 1349—1361).—The waxy and non-waxy maize starches contain nearly equal proportions of α- and β-amylose (amylopectin and amylose) if determined by the Ling and Nanji method (J.C.S., 1923, 123, 2666). Both starches on hydrolysis with malt amylase yield mainly maltose together with traces of dextrose associated with dextrinous materials. The common maize starch is converted to maltose in this way more rapidly than is waxy starch. Intermediate products of a lower specific rotatory power appear during the conversion of waxy starch than during the hydrolysis of common maize starch. The pure starch of the latter origin contains more than twelve times as much organic phosphorus as does waxy starch. This difference in the organic phosphorus content is not due to a deficiency of this element in the endosperm tissue. The total phosphorus content of waxy and common endosperm meal is nearly the same. S. S. Zilva.

Relationship of tetra-araban to tetragalacturonic acid, the chief complex of pectin. F. Ehrlich and F. Schubert (Biochem. Z., 1928, 203, 343—350).—Further examination of the crude araban obtained from hydropectin of beet by treatment with alcohol (A., 1926, 441) shows that it can be precipitated from solution as a white amorphous powder, the elementary analysis and mol. wt. determinations of which indicate that it is tetra-araban or tetra-anhydrotetra-arabinose, $C_{20}H_{32}O_{16}$, $[\alpha]_D^{20}$ −123°, and yields *l*-arabinose on hydrolysis with mineral acids. The substance under aseptic conditions is very slowly but almost completely hydrolysed to *l*-arabinose by takadiastase. The fact that tetragalacturonic acid, $C_{24}H_{32}O_{24}$, must lose 4 mols. of carbon dioxide to give a compound of the same empirical formula as tetra-araban and the close spatial similarity of *d*-galacturonic acid and *l*-arabinose make it probable that the tetra-araban component of pectin is formed from tetragalacturonic acid by loss, as a result of enzymic processes, of the four free carbonyl groups.

P. W. Clutterbuck.

Iodine liberator from *Laminaria*. T. Dillon (Nature, 1929, 123, 161—162).—An aqueous extract of the fresh fronds of *Laminaria*, when acidified, liberates iodine from potassium iodide. Preliminary experiments suggest that the agent is a dialysable organic substance. A. A. Eldridge.

Favourable action of potassium iodide on the volatilisation of iodine [in sea-weeds]. P. Dangeard (Compt. rend., 1928, 187, 1156—1158).—Sea-water containing 0·1% of potassium iodide greatly increases the evolution of iodine from certain sea-weeds (*e.g.*, *Laminaria flexicaulis*), whilst it is without effect on other species (*e.g.*, *Fucus platycarpus*)

G. A. C. Gough.

High- and low-frequency measurements with *Laminaria*. L. R. Blinks (Science, 1928, 68, 235).—Osterhout's view that the observed change of resistance is actually a change in the permeability of protoplasm to ions is supported by the author's experiments. A. A. Eldridge.

Osmotic pressure of cell-sap of plants. H. Walter (Ber. deut. bot. Ges., 1928, 46, 539—549).—The osmotic pressure of the cell-sap from the leaves of certain plants has been determined and comparisons have been made of the living sap and the sap from plants killed in various ways.

E. A. Lunt.

Cell-sap of *Valonia* and *Halicystis*. W. C. Cooper, jun., and L. R. Blinks (Science, 1928, 68, 164—165).—Determinations of potassium are recorded.

Chemical Abstracts.

Penetration of strong electrolytes [into plant cells]. W. C. Cooper, jun., M. J. Dorcas, and W. J. V. Osterhout (J. Gen. Physiol., 1929, 12, 427—433).—The addition of ammonium chloride to sea-water causes *Valonia* cells to float, because the very permeable salt reduces the specific gravity of the sap. Cæsium chloride causes flotation because it raises the specific gravity of the water but does not penetrate the cell-wall. Strong electrolytes penetrate very slowly. Potassium is absorbed much more rapidly than sodium. Lithium, rubidium, bromides, bromates, iodides, iodates, and selenites are able to penetrate, but most of the complex anions and the heavy metals are unable to penetrate the cell-wall.

E. BOYLAND.

Spectrophotometric studies of penetration. V. Resemblances between the living cell and an artificial system in absorbing methylene-blue and trimethylthionine. M. IRWIN (J. Gen. Physiol. 1929, **12**, 407—418).—The partition coefficients of methylene-blue and azure-B between water, chloroform, and sap as determined by spectroscopic methods are compared with the penetration of these dyes in cells. The layer of protoplasm of *Valonia* at p_H 9·5 behaves like a layer of chloroform in absorption of these dyes, but the sap of *Nitella* dissolves more azure-B from chloroform than it does from protoplasm.

E. BOYLAND.

Permeability test with radioactive indicators. K. LARK-HOROVITZ (Nature, 1929, **123**, 277).—By the use of thorium-*B* as radioactive indicator, it is shown that lead ions do not enter the sap of living cells of *Valonia macrophysa* even if the cells are kept for several months in lead nitrate solution; lead ions, however, readily enter the sap of dead cells. Radium emanation quickly becomes evenly distributed between the sap of living cells and the surrounding sea-water. A. A. ELDRIDGE.

***E.M.F.* in plants arising on contact with potassium chloride solutions of different concentrations.** K. STERN and E. BÜNNING (Biochem. Z., 1928, **203**, 400—408).—The current of injury found with *Nitella* by Osterhout and Harris (J. Gen. Physiol., 1928, **11**, 673; **12**, 167) to be positive when the cell is in contact with concentrated solutions and negative with dilute solutions, is found with a variety of leaves always to be negative whether the solution is of higher or lower concentration than that of the cell sap. P. W. CLUTTERBUCK.

Permeability. Viscosity and interfacial surface tension. J. TRAUBE and S. H. WHANG (Biochem. Z., 1928, **203**, 363—369).—The velocity of flow through a capillary of aqueous solutions of surface-active materials increases inversely with the surface tension, and the permeability and therefore the absorption of a fluid are dependent on its surface activity. The velocity of flow of water in a glass tube provided with a membrane layer of cholesterol or lecithin is increased, but with a layer of gelatin, albumin, or peptone is scarcely altered in comparison with the velocity without these layers. In plants a decrease of surface activity causes therefore an increased movement of sap and so may result in accelerated growth. P. W. CLUTTERBUCK.

Formation of plant membranes. K. HESS (Biochem. Z., 1928, **203**, 409—420).

P. W. CLUTTERBUCK.

Preparation of lipins from organs containing chlorophyll. B. REWALD (Biochem. Z., 1928, **202**, 399—402).—By means of a process involving extraction with cold acetone, lipins, free from chlorophyll, can be obtained from vegetables.

W. MCCARTNEY.

Nature of the unsaponifiable fraction of the lipoid matter extracted from green leaves. E. CLENSHAW and I. SMEDLEY-MACLEAN (Biochem. J., 1929, **23**, 107—109).—Crystals containing about 5% of oxygen, m. p. 72—75°, separate from the hot alcoholic solution of the unsaponifiable matter from cabbage leaves after the removal of the sterols. Hentriacontane is also present in this fraction. Similar treatment of the unsaponifiable matter from spinach yielded only hentriacontane.

S. S. ZILVA.

Constancy of the essential oil of seedlings of aniseed fruit. N. V. IVANOV and V. F. GRIGOROJEVA (Biochem. Z., 1928, **202**, 284—293).—In seedlings of aniseed fruit during germination in the dark for 20 days the essential oil remains unchanged both in amount and in composition. No physiological explanation for the presence of the oil has so far been found. W. MCCARTNEY.

Composition of the root of *Geum urbanum*, L. J. CHEYMOL (Schweiz. Apoth.-Ztg., 1928, **66**, 283—284; Chem. Zentr., 1928, ii, 457).—The glucoside geoside, m. p. 146—147°, $[\alpha]_D$ −53·80° in water, on acid hydrolysis affords eugenol, dextrose, and *l*-arabinose; hydrolysis by gease affords eugenol and vicianose; by emulsin, eugenol, dextrose, and arabinose. Gease is present in the root as an insoluble compound, *e.g.*, with tannin. Dry gease is decomposed above 98°; in aqueous solution, above 75°. It is inactivated by sulphuric or acetic acid. The action of gease on geoside is not specific.

A. A. ELDRIDGE.

Glutamine and allantoin in beetroot. C. RAVENNA and R. NUCCORINI (Annali Chim. Appl., 1928, **18**, 509—512).—The aqueous extract of the roots is treated with a slight excess of basic lead acetate, to the filtrate is added a small excess of mercuric nitrate, and the precipitate, suspended in water, is decomposed with hydrogen sulphide. The filtrate, freed from hydrogen sulphide by distillation in a vacuum, is neutralised with ammonia and concentrated to a syrup under diminished pressure. Sufficient alcohol is then added to cause separation of a syrup, which is redissolved by addition of a few drops of water. On keeping, the liquid deposits crystalline glutamine.

As the growth of the beet proceeds, the percentage of glutamine present increases from 0·035 (June) to 0·112 (October). If the beets are stored during the winter and planted again at the beginning of spring, the glutamine gradually disappears, its place being taken by allantoin, which itself disappears later.

T. H. POPE.

Total alkaloids of *Datura fastuosa*, L., and *Datura alba*, Nees, from the Philippines. J. M. MARANON (Philippine J. Sci., 1928, **37**, 251—260).—The total alkaloid content of different parts of *Datura fastuosa* and *D. alba*, collected at Manila at different times of the year, has been determined. *D. fastuosa* contains more alkaloids in its leaves, seeds, fruits, and roots than does *D. alba*; the latter contains a higher percentage than the former in its flowers. As the fruit ripens there is a migration of alkaloids from the pericarp to the seeds. Apart from the seeds, the younger portions of different parts of the plants contain more alkaloid than the

more mature portions. The possible mode of formation of alkaloids in plants is discussed.
C. W. Gibby.

Hydrocyanic acid in *Lotus*. P. Guérin (Compt. rend., 1928, **187**, 1158—1160).—Mainly qualitative investigations show that a large number of the plants of this genus contain hydrocyanic acid. The leaves and the growing cotyledons contain most of this constituent. The hydrocyanic acid of *L. corniculatus* (0·02% in the fresh plant) is probably insufficient to injure cattle.
G. A. C. Gough.

Physiology of apples. X. Chemical changes in stored apples. F. Haynes and H. K. Archbold (Ann. Bot., 1928, 42, 965—1017).—Methods of determining the principal chemical constituents of the apple are described. The properties which favour keeping are found to be: low nitrogen and high sucrose contents and probably a large amount of cell-wall material. Exhaustion of sucrose and acid is coincident with the death of the apple, and it is therefore suggested that acid metabolism may be an essential part of the respiratory cycle of this fruit.
E. A. Lunt.

Composition of the juices of some American apples. J. S. Caldwell (Fruit Prod. J. Amer. Vinegar Ind., 1928, 8, 14—18).—Climatic conditions during development and maturity produce consistent and sustained effects on the composition of apples. Analytical data for various varieties are recorded.
Chemical Abstracts.

Boron compounds in fruits and vegetable products. A. S. Dodd (Analyst, 1929, **54**, 15—22).—The proportion of boric acid present in currants and raisins was small but over 100 parts per million; in miscellaneous dried fruits it varied from 40 parts per million in prunes to 300 in apricots and peaches, enough being present to make it necessary to allow for the presence of boron in jams, tarts, etc. In fresh fruits boron compounds were small, from 31 to 62 in 10^6, but calculated on the dried fruits boric acid varied from 240 to 1090 in 10^6. The prepared dried acid fruits lose boric acid as the drying process is carried out without the presence of an alkaline fixing agent.
D. G. Hewer.

Boric acid in oranges. J. T. Dunn and H. C. L. Bloxam (Analyst, 1929, **54**, 28—29).—Three Californian, three South African, and one West Indian samples of oranges were examined for the presence of boric acid in the rind and pulp. In every case it was present in quantities comparable with that found as a natural constituent of a large number of vegetable substances, and no evidence of addition was adduced.
D. G. Hewer.

Zinc content of vegetable foods. G. Bertrand and B. Benzon (Compt. rend., 1928, **187**, 1098—1101).—The zinc content of a wide variety of fruits and vegetables is of the order of 1—3 mg. per kg. of the fresh material. In general, the amount of zinc increases with the chlorophyll content. Garlic and onion bulbs, millet, maize, lentil, and similar grains contain 10—50 mg. per kg. Polished rice contains about 2 mg., whilst the husks give values as high as 30 mg. per kg.
G. A. C. Gough.

Biology of metals. I. Localisation of lead by growing roots. II. Retardative influence of lead on root growth. F. S. Hammett (Protoplasma, 1928, 4, 183—186, 187—191).—Lead absorbed by growing roots of *Allium cepa*, *Phaseolus vulgaris*, and *Zea mais* from solutions of the nitrate was deposited in the regions of growth by cell division as a compound. Lead (10^{-5} to 5×10^{-4}) retards the root growth of seedlings.
Chemical Abstracts.

Effect of hydrogen-ion concentration on the fixation image of various salts of chromium [in plants]. C. Zirkle (Protoplasma, 1928, 4, 201—227).—Experiments with root tips of *Zea mais* are described. It is assumed that the fixation consists of a double decomposition in which the cation of the fixative unites with certain elements of the cell and the anion with others, followed by reduction of part of the chromate to a chromium salt, the chromium then being combined with the tissue both as anion and as cation.
Chemical Abstracts.

Chlorosis of fruit trees. II. Composition of leaves, bark, and wood of shoots in cases of lime-induced chlorosis. III. Chlorosis of plums due to potassium deficiency. T. Wallace (J. Pomology, 1928, 7, 172—183, 184—198).—The leaves and bark of chlorotic shoots in the apple, pear, plum, and raspberry exhibit a high percentage of ash in the dry matter, and low calcium and high potassium contents in the ash itself. In the wood of chlorotic shoots the changes in the calcium and potassium contents do not obtain.

III. A chlorosis of plum trees due to deficiency of potassium is described in which the chlorotic leaves show a low ash content, and high iron, calcium, magnesium, and phosphorus, and low potassium contents in the ash. The conditions in which this disease is observed suggest water-logging as a possible cause.
E. A. Lunt.

Micro-determination of carbon. M. Nicloux.—See this vol., 204.

Determination of iodine. J. Schwaibold; also J. F. Reith.—See this vol., 337.

Dehydration apparatus. W. D. Courtney (Science, 1928, 67, 653—654).—An apparatus for biological use is described.
A. A. Eldridge.

Use of Hildebrand hydrogen electrode in biological solutions. R. E. Cornish (J. Amer. Chem. Soc., 1928, **50**, 3310—3311).—The Hildebrand hydrogen electrode (A., 1913, ii, 721) may be brought rapidly to equilibrium in those biological solutions in which it normally attains equilibrium only very slowly by repeated saturation with hydrogen, which is attained by squeezing a rubber bulb inserted in the hydrogen lead, so that the solution level is forced entirely below the platinum a few times.
S. K. Tweedy.