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Deep-lying terms in two- and three-valency electron system spectra. R. A. Sawyer (J. Opt. Soc. Amer., 1926, 13, 431—442).—An analysis from the point of view of atomic structure of the following relations: (1) for elements in the first two horizontal rows of the periodic table (*a*) the lowest PP' multiplet in the spectra of trebly-ionised atoms is near in frequency to the first line in the principal singlet series of the spectrum of the atom after loss of one more electron, (*b*) the lowest PP' multiplet in two-valency electron system spectra is near to the first line of the principal series, both of singlets in that system and of doublets in the once more ionised system; (2) the lowest PP' multiplet in the arc spectra of calcium, barium, and strontium is near to the frequency difference of the lowest S and D terms, both of singlets in the arc spectrum and of doublets in the once-ionised spectrum. It is concluded that the energy difference between the two lowest states in the above spectra is little affected either by the absence of a second electron or by its presence in the normal or the metastable lowest state. Several new combinations have been located. R. A. Morton.

Specific frequencies associated with continuous spectra. A. Winter (Ann. Physik, 1926, [iv], 81, 577—586).—A mathematical paper on the theory of continuous spectra. R. W. Lunt.

Structure in the secondary hydrogen spectrum. V. O. W. Richardson (Proc. Roy. Soc., 1926, **A**, **113**, 368—419).—The bands which were previously shown to be associated with Fulcher's bands (A., 1926, 873) are now shown to form, with other related bands, a set of band systems the null lines of which are connected by a Rydberg–Ritz formula, having the normal value of the Rydberg constant. It is thus possible to apportion the effects observed as between electron jumps and vibration jumps. All the lines in Fulcher's red bands arise as a result of transitions in which the total quantum number (electron jumps) changes from 3 to 2 and the vibrational quantum is unchanged. There is much evidence that the emitters of Fulcher's bands are neutral H_2, although some difficulties are presented. The claims of H_2^+, which should have a band spectrum analogous to the spark spectra, are disposed of in view of the presence of the normal value of the Rydberg constant in the Rydberg–Ritz formula.
E. S. Hedges.

Hydrogen bands in the ultra-violet Lyman region. S. Werner (Proc. Roy. Soc., 1926, **A**, **113**, 107—117).—Twelve bands in the spectrum of hydrogen between 1000 and 1230 Å. have been examined. These show a marked temperature effect, indicating that each of the bands originates in the rotation of the hydrogen molecule. The origin of the different bands is the vibration of the molecule. An approximate relation between the bands is of the type to be expected from rotation-vibration bands, but the fact that this relation is not exactly fulfilled indicates that the motion of the particles in the molecule is of a complex character. No complete theoretical description of the structure is yet possible. The probable value of the moment of inertia of the initial states is about 7×10^{-41}, and for the end states, including the normal state, $2-3\times10^{-41}$ g. cm.^{2} The corresponding fundamental frequencies are 6400 cm.$^{-1}$ and 5000 cm.$^{-1}$, respectively, with an error of 10—20%. W. Hume-Rothery.

Wave-lengths of new lines in secondary spectrum of hydrogen. D. B. Deodhar (Proc. Roy. Soc., 1926, **A**, **113**, 420—432).—In addition to the lines tabulated by Merton and Barratt (A., 1922, ii, 461) and Tanaka (*ibid.*, 1925, ii, 909), 450 new lines, not previously recorded, have been found and the measurements are tabulated. The lines 4928·62, 4886·40, 4391·88, 4106·22, 4031·60, 4020·63, and 3858·74, recorded by Merton and Barratt and by Tanaka as single lines, are doublets, but their components have not been measured. E. S. Hedges.

Low-voltage vacuum arc. Carbon line 4267 Å. K. L. Wolf (Z. Physik, 1926, 39, 883—885).—An arc is described which permits the separation of the 4267 line into its components 4267·261±0·010 and 4267·031±0·010 (weaker). R. A. Morton.

Structure of second order spectrum [O II] of oxygen. C. Mihul (Compt. rend., 1926, 183, 876—877).—Five groups of combinations are given. For the majority of the lines the Zeeman effect has been studied. R. A. Morton.

Spectrum of fluorine. H. Dingle (Proc. Roy. Soc., 1926, **A**, **113**, 323—334).—The spectrum of fluorine was obtained by means of discharges through silicon tetrafluoride. Evidence of at least three successive spectra was obtained with gradual intensification of the exciting agency, and measurements were made of the lines in the red and infra-red region of the spectrum, which form under the gentlest stimulus. Analysis of the spectrum showed it to contain doublet and quadruplet systems of terms. The suggested arrangement is consistent with Carragan's observations of the Zeeman effect for fluorine. An ionisation potential of about 17 volts is indicated. It is suggested that lines of fluorine should appear with maximum intensity at or near type *AO* in the Harvard sequence. E. S. Hedges.

Large displacements of the spectral lines of chlorine. K. Asagoe (Mem. Coll. Sci. Kyōtō, 1926, **10**, 15—23).—The spectrum of chlorine in the region 5457—2577 Å. has been investigated under two sets of conditions: (*a*) with a Geissler discharge tube containing chlorine, (*b*) with a spark between carbon electrodes mounted in a fused quartz tube containing chlorine at a pressure of 1 atm. Many lines in (*b*) are shifted towards the red as compared with the corresponding lines under conditions (*a*). According to the manner in which they are broadened, the displaced lines are classified into three groups, one of which shows a shift of about 2 Å. towards the red. The broadening may be explained as the Stark effect due to the field of ions in the large current flowing through the gas when the pressure is increased. R. A. Morton.

Spectrum of the Pickering type in argon. M. Kahanowicz (Atti R. Accad. Lincei, 1926, [vi], **4**, 285—291).—Under suitable pressure and when strongly excited, argon gives rise to an enhanced spectrum of the Pickering type, represented by the series, $x=R[1/2^2-18^2/(2m+1/2)^2]$, with m equal to 35, 39, 40, 49, and 56. The emissive atom exhibits hydrogenoid behaviour. T. H. Pope.

Flash arc spectrum of potassium. F. H. Newman (Phil. Mag., 1926, [vii], **2**, 1042—1046).—Previous work (*ibid.*, 1926, **1**, 721) on the excitation of enhanced lines in an interrupted arc passed between sodium-potassium alloy electrodes has led to the view that in a flash arc at low pressures the actual *P.D.* between the electrodes at each flash or for some period of the duration of the flash will be the full applied voltage; if the vapour pressure is maintained sufficiently low, conditions are favourable for an appreciable fraction of the electrons to attain energy equivalent to that required for the production of the enhanced lines of the vapour. The theory has been tested by examining the spectrum appearing from a flash arc produced by applying an intermittent *E.M.F.* of 120 volts between two potassium electrodes in a tube in which the pressure was maintained below 10^{-3} mm. In this manner, 108 lines of a spectrum comprising almost entirely enhanced lines of potassium were obtained between 6307 and 2986 Å. No lines of wave-length less than 2986 Å. were obtained. Most of the lines measured occur in the spark discharge obtained by passing a heavy electrodeless discharge through a low-density vapour. The spectrum obtained is analogous to the argon red spectrum. A. E. Mitchell.

Arc spectrum of copper. Complex spectra of copper. C. G. Bedreag (Bull. Sci. Acad. Roumaine, 1926, **10**, 95—98, 98—102).—See A., 1926, 651, 766.

Arc spectrum of copper. P. K. Kichlu (Z. Physik, 1926, **39**, 572—587).—The spectra were obtained by using (*a*) weak current, (*b*) strong current, (*c*) under-water spark. Considerable differences were noticeable between spectra (*a*) and (*b*); in the latter many lines were reversed, many new lines were found, some being due to forbidden jumps, others were higher members of known series. Tables are given of the sharp and of the diffuse series. E. B. Ludlam.

Excitation of enhanced lines of tin in arcs. Zeeman effect of enhanced lines of tin. M. Miyanishi (Mem. Coll. Sci. Kyōtō, 1926, **10**, 9—13).—The classification of the enhanced lines of tin (Kimura and Nakamura, A., 1925, ii, 166) has been confirmed. The spark lines 6453, 5800, 5589, 5563, 5333 Å. are emitted from a 440-volt a.-c. arc and from a Poulsen water-cooled arc charged with tin. At the instant of break of a heavy d.-c. arc (440 volts, no self-induction, capacity of 0·25 microfarad shunted between arc terminals, 7 amp.) the spark character of the light was intensified, and the super-spark (Sn^{++}) lines 5370, 5344, 5289, 5225, 5101, 5021, 4934, 4858, 4615, 4586 are recorded. The results show that the excitation energy of the super-spark lines is greater than that of the spark lines.

The Zeeman effects of the 5800, 5590, 5563, and 5333 lines were analysed only when the self-induction and capacity in the discharge circuit were adjusted and the field was 15,900 gauss. Their separations were only one third of the normal triplet separations. R. A. Morton.

Self-reversal of lines in the explosion spectrum of tin. B. Arakatsu and M. Shoda (Mem. Coll. Sci. Kyōtō, 1926, **10**, 31—34; cf. A., 1926, 875).—In the explosion spectrum of tin, almost all arc lines of wave-length shorter than 3200 Å. are self-reversed. The order of appearance of such lines can be determined by varying the pressure of the air surrounding the exploded tin wire. When explosion occurs in a vacuum, all the lines are sharp; with increasing pressure, however, they broaden, and later show self-reversal. The lines can therefore be classified into four groups according to the stage at which reversal occurs. The results are compared with those of McLennan, Young, and McLay (A., 1925, ii, 454). R. A. Morton.

Continuous spectrum of mercury. H. Volkringer (Compt. rend., 1926, **183**, 780—782).—The continuous spectrum of mercury is best excited at 240° and 35 mm. pressure by an oscillatory discharge and a circuit of small capacity. Under these conditions, an intense continuous background is obtained in a spectrum showing the arc lines feebly. The curve of spectral energy distribution has been determined using black body radiation (platinum) at 1520° as a standard for comparison. The curve is symmetrically disposed about a maximum at 512 μμ. It is noted that this wave-length is almost twice that of the resonance line 253·6 μμ. R. A. Morton.

Bands at 2536 and 2540 Å. of mercury. G. Nakamura (Mem. Coll. Sci. Kyōtō, 1926, **10**, 1—8).—In addition to the 2536 band, an absorption band at 2540 Å. has been found near the mercury cathode of a vertical arc, using a coreless carbon rod as anode. Non-luminous mercury vapour shows a strong absorption band at 2536 extending towards the red, and a very much weaker band at 2540 shading off in the opposite direction. When, however, the luminous vapour which can be isolated from the negative arc with a small horse-shoe magnet is examined, it is seen that its emission consists of the 2536 line shading off slowly on the red side, whereas its absorption is characterised by marked development of both the 2536 and 2540 bands. When the luminous vapour of the positive column of a vacuum tube is used, the 2540 emission predominates. The 2536 band is regarded as of the arc type of excitation and is connected with the neutral molecule Hg_2, whilst the 2540 band is regarded as of the spark type and is associated with the ionised molecule Hg_2^+.

R. A. Morton.

Scattered *X*-rays. *J*-Phenomenon. V. C. G. Barkla and (Miss) G. I. Mackenzie (Phil. Mag., 1926, [vii], 2, 1116—1121).—Previous work (A., 1926, 217, 987) has described two alternative ways in which beams of *X*-rays scattered in directions making angles of 60° and 120° with the direction of the primary radiation differed from one another. In one case, the beam at 120° was absorbed at the same rate as that at 60°, whilst the intensity of the former showed discontinuities when the heterogeneous beam was made to reach certain critical penetrating powers. In the other case, the beam at 120° appeared continuously more absorbable than that at 60°, giving an apparent Compton difference of wave-length with the angle of scattering. When the frequency of interruption of the *X*-ray tube and the thickness of the absorption medium are varied, the two cases can be made to show the same phenomenon, the beam at 120° behaving similarly to that at 60° above an interruption frequency of 97 per sec. Thus both cases are widely separated forms of the same phenomenon, and what appeared initially to support Compton's theory of scattering is merely the *J*-phenomenon in the scattered radiation. It is concluded that the factor deciding the degree of activity due to a complex beam acting as a whole is to be found in the details of the method of excitation of the *X*-rays.

A. E. Mitchell.

Control of the *J*-phenomenon. VI. C. G. Barkla and W. H. Watson (Phil. Mag., 1926, [vii], 2, 1122—1127).—The radiations scattered, from a paraffin cylinder, in the direction making an angle of 90° with that of the primary beam, have been compared with the primary beam itself. The ratio of the ionisation produced by the scattered radiation to that produced by the primary radiation is a constant for various thicknesses of aluminium showing equal absorptions of the scattered and primary beams between the *J*-discontinuities. The discontinuities show the sudden changes in the ionisation when this is reduced by filtration to certain critical absorbabilities. By careful control of the filament current in the Coolidge tube consistent results were obtained throughout the whole series of experiments, the *J*-discontinuities appearing in every case. In addition to the J_1-, J_2-, and J_3-discontinuities described previously, further discontinuities between J_1 and J_2 and between J_2 and J_3 have been found. The critical absorbabilities have been found to vary systematically with the current through the Coolidge tube. No difference has been observed between the absorptions of the primary and scattered radiations except by the occurrence of absorption lines (*J*-discontinuities) in the progressive absorption of the scattered radiation.

A. E. Mitchell.

Measurements in the *K*-series of *X*-ray spectra. A. Leide (Z. Physik, 1926, 39, 686—710).—Measurements have been made on the lines α_1 and α_2 of most of the elements from copper to tungsten, and on the lines β_1 and β_2 for those from copper to iodine. The line β_3 has been measured for molybdenum, palladium, silver, copper, and tin, and a β_4 line has been observed for molybdenum and palladium. The limit-frequencies of the *K*-series have been measured for elements copper to neodymium, with some exceptions, and also for holmium, and the scheme of energy levels is examined. From the values obtained for the *K* limit-frequencies for elements below tin, the other limit-frequencies are calculated. By plotting the difference in wave-length of β_1 and β_2 against atomic number, a connexion is shown with the sub-grouping of electrons. The measurements were made by the Seemann method.

E. B. Ludlam.

Secondary and tertiary cathode rays produced by external and internal absorption of homogeneous *X*-rays. H. R. Robinson and A. M. Cassie (Proc. Roy. Soc., 1926, **A**, **113**, 282—301).—A continuation of previous work (cf. A., 1923, ii, 818; 1925, ii, 728) on the line spectra of the secondary and tertiary cathode radiation produced by targets of uranium oxide, thorium nitrate, bismuth oxide, gold, tungsten oxide, cerium oxide, barium carbonate, silver, molybdenum, zirconium oxide, ammonium bromide, arsenic oxide, copper, and calcium sulphate. The primary *X*-radiation was an unfiltered beam of molybdenum *K*-rays.

E. S. Hedges.

Structure of spectra of the third order. C. Mihul (Compt. rend., 1926, **183**, 1035—1036; cf. this vol., 1).—From the study of the Zeeman effect of some of the rays of the oxygen spectrum of the third order, 5 multiplets have been recognised which result from the combination between 5 terms of multiplicities $r=3$. Data are given for the multiplets represented by the combinations $a^3P-{}^3S$, ${}^3S-b^3P$, ${}^3D-b^3P$, ${}^3P'-b^3P$, and ${}^3P'-a^3P$.

J. Grant.

Scattering of cathode rays. B. F. J. Schonland (Proc. Roy. Soc., 1926, **A**, **113**, 87—106).—The laws governing the encounter of a fast electron with an atomic nucleus have been investigated by measurements of the scattering of fast cathode rays by thin foils of aluminium, copper, silver, and gold. This method avoids the difficulties due to γ-radiation when radioactive β-rays are used. The velocity of the rays was 0·497 of that of light, and their energy 77,300 volts. The ratio of the scattered portion to the rest of the beam was directly determined by a balance method. The variation of scattering with thickness, at first approximately linear, becomes more rapid as the thickness is increased, owing to the incidence of plural scattering, but with aluminium single scattering could be obtained over a range of thicknesses. The variation of scattering with the thickness and atomic number of the material, and with the energy of the rays, confirms Rutherford's theory of single scattering with the relativity correction postulated by Crowther and Schonland (*ibid.*, 1922, **A**, **100**, 526). The inverse square law of force holds for encounters between a moving electron and the nucleus of an aluminium atom at distances of approach ranging from 1·8 to $3{\cdot}4\times10^{-11}$ cm., which are the critical distances within which cathode rays of energy 77·3 and 39·0 kilovolts must come to be deflected through 90° by an aluminium nucleus. The atomic numbers of aluminium, copper, and silver calculated from the scattering results are in good agreement with theory, but with gold the calculated value is 86·5 (instead of 79) owing to abnormal secondary emission.

W. HUME-ROTHERY.

Scattering of positive rays by gases. II. G. P. THOMSON (Phil. Mag., 1926, [vii], 2, 1076—1084).—Previous work on the scattering of positive rays by hydrogen (A., 1926, 656) has been extended to helium, argon, and oxygen. Argon and helium show a maximum scattering for protons of velocity $0{\cdot}75\times10^8$ and $1{\cdot}4\times10^8$ cm./sec., respectively. These results are analogous to those of Ramsauer and others with electrons of about the same velocity. With both argon and helium the experiments indicate a collision relation of the form $A0^{-1\cdot35}$, the index being independent of the velocity. A few results for oxygen show a large scattering, but no maximum has been observed. A. E. MITCHELL.

Effective area of hydrogen and nitrogen molecules towards electrons of slow velocity. E. BRÜCHE (Ann. Physik, 1926, [iv], **81**, 537—571).—From measurements of the weakening of an electron stream in the gases at pressures of the order of 0·001 mm. it has been found that there is a maximum effective area of the hydrogen molecule for electrons of velocity $1{\cdot}2-1{\cdot}5\sqrt{\text{volts}}$; and that there are two maxima for nitrogen, one in the same region and a second smaller one at $4{\cdot}2\sqrt{\text{volts}}$. The experimental procedure is based on that of Lenard and Mayer. Determinations on argon gave values in good agreement with those of Ramsauer. The data obtained are compared with those of other workers in the same field. R. W. LUNT.

Detection of unimolecular ions in air and the forces between ions and gas molecules. W. BUSSE (Ann. Physik, 1926, [iv], **81**, 587—602).—The velocity of ions in air at the ordinary temperature and pressure has been examined with respect to the age of the ions and to the partial pressure of water vapour. Ions were generated from a thorium preparation and their velocity was determined by streaming the ionised gas through a cylindrical condenser. The results are construed to indicate the existence of unimolecular ions of short life having velocities, in air dried by phosphorus pentoxide or by liquid air, of the order of 15 cm./sec. per volt/cm., and that Langevin's theory of an inverse fifth power law of force between ions and gas molecules is invalid.

R. W. LUNT.

Ionisation by the slow oxidation of phosphorus. W. BUSSE (Physikal. Z., 1926, 27, 738—741).—A preliminary account of experiments on the ionisation produced in air streaming over white phosphorus. It is shown that the temperature falls and the ionisation increases with increasing distance of a point in the stream from the phosphorus. From the sizes and charges of the ion clusters, it is held that these are to be identified with the formation of acids corresponding with the oxides formed. R. W. LUNT.

Long-range particles emitted by the active deposit of actinium-*B*+*C*. P. MERCIER (Compt. rend., 1926, **186**, 962—964).—For investigations on long-range particles from active deposits, an apparatus has been employed which eliminates the use of metallic screens by means of a compressed gas placed between the source and screen. The stopping-power of the gas and the distance from the source to the screen being known, the thickness of air equivalent to the gas-screen may be measured for each pressure. The ratio of the number of long-range α-particles to ordinary α-particles emitted from actinium-*C* is 2·8 per 1000. The number of the former falls off slowly to within 2 mm. of the end of their range, when it decreases rapidly, and extrapolation from the curve obtained indicates a maximum range of 6·47 mm. If any particles other than those due to substances such as thorium-*C* of range longer than 6·5 mm. are emitted from this deposit, their number is less than 30 per 10^6 ordinary particles. J. GRANT.

Determination of the mass of particles arising from the disintegration of atoms. G. STETTER (Physikal. Z., 1926, 27, 735—738; cf. A., 1925, ii, 1021).—The method of Aston's mass spectrograph is applied to analyse the particles emitted when α-rays are allowed to impinge on a substance. They are shown to consist of singly-charged helium atoms, reflected α-particles, and positively-charged hydrogen atoms, in confirmation of Rutherford's experiments. The method is discussed at length with reference to the scintillation method. R. W. LUNT.

Slow β-particles from mesothorium-2. D. K. YOVANOVITCH and A. PROCA (Compt. rend., 1926, **183**, 878—880).—By the classical method of deviation in a magnetic field and registration on a photographic plate, the energy of the β-particles of mesothorium-2 has been investigated down to energies of 2900 volts. The variation of the intensity of the lines on the plate with the energy of the particles is as follows: constant intensity from 2880 to 4500 volts, then diminution almost to zero; from 18,000 to 32,000 a slow increase, until at 38,000 volts great intensity is reached. A further increase occurs at 41,600 and then a decrease to the original intensity. The measurements of intensity are only qualitative, but they support the theoretical conclusions of Curie (A., 1926, 655).

S. J. GREGG.

Calorific effect of the β- and γ-rays of radiothorium. D. K. YOVANOVITCH and (MLLE.) A. DORABIALSKA (Compt. rend., 1926, **183**, 1037—1038).—The authors' calorimetric method for the determination of the absorption of β- and γ-rays (A., 1926, 772) has been used in the case of radiothorium prepared from mesothorium-1. The curves obtained for aluminium, copper, and lead show an increase in the calorific effect as a function of the mass per cm.² In terms of the notation previously used, $\mu/\rho=38{\cdot}3$ for β-rays and aluminium and $Q/I=1{\cdot}60$ for the γ-rays. The γ-radiation of radiothorium is equivalent to that of 28·95 mg. of radium, as measured through 1 cm. of lead. J. GRANT.

Transmutation of mercury into gold by means of a high-pressure mercury arc of great current density. F. Bernhardt (Physikal. Z., 1926, 27, 713—715).—A description is given of the construction and manipulation of a mercury arc working at 600 kg./cm.^{2} carrying 400 amp. at 6 volts. Gold is determined in mercury by applying the borax bead method of Donau to a residual drop obtained by dissolving nearly all of 150 g. of redistilled mercury in pure nitric acid; $0{\cdot}025\times10^{-9}$ g. of gold can be detected in this way. In two experiments working with mercury found to be free from gold by the above method, and operating the arc under the conditions mentioned above with a current consumption of 2092 and 2125 amp.-hrs., the quantities of gold found were, respectively, 81×10^{-7} g. and $3{\cdot}0\times10^{-7}$ g.

R. W. Lunt.

Structure of boron. H. Collins (Chem. News, 1926, **133**, 321—323).—Speculative.

Existence of the sub-electron. M. Reiss (Z. Physik, 1926, **39**, 631—635).—Polemical.

E. B. Ludlam.

Spectra of atomic systems with two electrons. W. Heisenberg (Z. Physik, 1926, **39**, 499—518).—Formulæ are deduced for the motions of the two electrons and applied to helium and Li^+. The agreement with experimental values is not very good.

E. B. Ludlam.

Ionised hydrogen molecule and [Schrödinger's] wave mechanics. W. Alexandrov (Ann. Physik, 1926, [iv], **81**, 603—614).—Mathematical. On the basis of Schrödinger's theory, the relationship between the ionisation potential and the fine-line spectrum is analysed. R. W. Lunt.

System of orbital planes in the inner region of an atom. *O*-Triplets in *X*-ray spectra belonging to the *L*-series. H. Hirata (Mem. Coll. Sci. Kyōtō, 1926, **10**, 35—55).—Theoretical. Sommerfeld's theory of elliptic orbits is modified by the use of three quantum numbers corresponding with three co-ordinates in space. A selection principle is proposed for electron transitions in the inner region of an atom, and the formation of *O*-triplets in *X*-ray spectra is discussed. R. A. Morton.

Excitation by the absorption of light in crystals. Z. Gyulai (Z. Physik, 1926, **39**, 636—643).—The maximum excitation is found to be independent of the intensity of the exciting light for the yellow-coloured sodium chloride; the lower the temperature the greater the excitation. Crystal phosphorescence is regarded as a special case of the more general excitation produced by light.

E. B. Ludlam.

Band spectra of helium and hydrogen at low temperatures. J. C. McLennan, H. G. Smith, and C. A. Lea (Proc. Roy. Soc., 1926, **A**, **113**, 183—195).—Bands in the spectrum of helium have been studied at the temperatures given by surrounding the discharge tube with water, liquid air, or liquid hydrogen at approximately 300°, 85°, and 21° Abs., respectively. For certain series the change in the quantum number *m* corresponding with the maximum intensity is very clearly shown, whilst for other series the first line is the most intense at all temperatures; the lowering of the temperature has only the effect of reducing the relative intensity of the higher members of the series. Where a maximum of intensity is found, it is in all cases shifted to a lower value of *m* with lower temperatures. The bands studied were at 6400, 5730, 5130, 4650, 4546, 4450, 4000, 3680, and 3630 Å., respectively. Under similar conditions, the relative intensities of the strong lines of the hydrogen spectrum from 6900 to 3850 Å. have been studied at the ordinary temperature and at that of liquid air. W. Hume-Rothery.

Absorption spectrum of nickel. K. Majumdar (Z. Physik, 1926, **39**, 562—571).—The absorption spectra were obtained from an under-water spark and from the vapour in a carbon tube furnace. The absorption lines are tabulated and grouped and a diagram of energy levels is given. E. B. Ludlam.

Infra-red absorption spectra of carbonates. C. Schaefer, C. Bormuth, and F. Matossi (Z. Physik, 1926, **39**, 648—659).—The spectrum falls into two groups, a short-wave portion common to all the carbonates, due to the internal vibrations of the carbonate ion, and a long-wave portion ($\lambda>9\,\mu$) different for different crystals except for the fundamental frequency at 14 μ. The carbonates examined were: magnesite, calcite, dolomite, spathic iron, witherite, and cerussite. Tables are given and a diagram representing the combinations of frequencies found; both difference and summation frequencies are recognised. Some combinations which might be expected do not appear and others are found for which there is no obvious explanation.

E. B. Ludlam.

Absorption spectrum of strontianite in the short-wave infra-red. F. I. G. Rawlins, A. M. Taylor, and E. K. Rideal (Z. Physik, 1926, **39**, 660—662; cf. preceding abstract).—The absorption spectrum was obtained by means of a spectrometer and thermopile; the results are shown on a curve and the minimum transparency is about 3·4 μ.

E. B. Ludlam.

Term representation of the aluminium hydride bands. H. Ludloff (Z. Physik, 1926, **39**, 519—527; cf. following abstract).—A term system is developed as fully as the data allow for four of the aluminium hydride bands, which are shaded towards the red and indicate a labile molecule.

E. B. Ludlam.

Molecular binding and band spectra. H. Ludloff (Z. Physik, 1926, **39**, 528—546).—The effect on a diatomic molecule of the absorption of light is studied by means of the analysis of the band spectra, particularly the effect of increasing rotation and vibration on the stability of the molecule. The criterion for stability when applied to the spectra of the hydrides of mercury, aluminium, calcium, zinc, and cadmium, and the band spectrum of iodine at 3460 is in good agreement with other evidence. In such compounds as the hydrides of zinc, cadmium, and mercury, in the band spectra of which the shading is on the red side, increase of electronic energy reduces the separation between the nuclei; the molecule is stable in the excited state, but not in the unexcited state; the attraction between the two atomic cores is greater when the opposing influence of the valency electrons is reduced, as is the case when they are further from the nucleus.

E. B. Ludlam.

Ultra-violet spectrum of potassium nitrate, and its variations as a function of p_H. (Mme.) E. Siegler-Soru (Compt. rend., 1926, **183**, 1038—1040).—In the measurement of the absorption spectra of solutions containing 0·1% of potassium nitrate of various p_H values by the method of Vlès and Gex (A., 1925, ii, 472), curves have been obtained similar to those previously found. When the p_H is plotted against the ratio $\varphi_1=(\lambda 300)/(\lambda 310)$ or $\varphi_2=(\lambda 300)/(\lambda 289)$, the curves obtained may be divided into 3 parts, included between the p_H ranges 0·2—2·5, 2·5—5·5, and 5·5—13, respectively. It is assumed that these divisions correspond with dissociation equilibria dependent on the law of mass action, and represented respectively by the bivalent systems in which p_K=0·3—1·8, and 3·9—4·3, and by the univalent system for which p_K=7·0. The equilibria involved appear to be due to successive stages of hydration of the anion, rather than to its acidic nature.

J. Grant.

Reversing action of red and infra-red rays on sensitised and fogged photographic plates and the absorption of the sensitising dyes. M. Miyanishi (Mem. Coll. Sci. Kyōtō, 1926, **10**, 25—29).—When a photographic plate sensitised with iodo-green and fogged by candlelight is exposed in a spectrograph, reversed spectra of the red and infra-red rays up to 1·13 μ are obtained (Terenin, A., 1924, ii, 363). It is shown that of the dyes tested only those having absorption bands of which the maxima lie on the long-wave side of 5500 Å. are effective in obtaining the reversed impression up to 0·9 μ. Green light appears to be the most effective fogging agency for plates sensitised with iodo-green (absorption maximum near 5700 Å.).

R. A. Morton.

Technique of photographic spectrophotometry. G. Rössler (Ber., 1926, **59**, [*B*], 2606—2615).—Examination of potassium chromate solution by the rotating sector method, using an arc between iron or copper and iron electrodes, shows a mean error of ±2%, which can be reduced considerably by repeated measurement of the plate; if a spark discharge is used as source of light, the absorption curve becomes irregular when the sector is rapidly rotated, but agrees well with the normal curve at slow speeds. Winther's method, slightly modified, gives results agreeing well with those of the sector methods when a single arc light is used, thus establishing the trustworthiness of these methods, since the Winther process under these conditions is theoretically free from error; when a spark discharge is used, the mean error is 2%. The utility of Henri's method depends greatly on the constancy of the source of light, and is considerably influenced by the difficulty of accurate measurement of short intervals of time. Compensation for the absorption of the solvent is best effected by the use of a short layer of the solvent itself.

Ordinary photographic plates are conveniently sensitised to 186 mμ by rubbing them with white vaseline, the excess of which is removed with cotton wool; before development, the plates are bathed in acetone. Similarly, for regions to 800 mμ, the plates are treated for 4 min. at 18—20° with water (50 c.c.), alcohol (96%, 25 c.c.), ethyl-red solution (0·1%, 2·0 c.c.), pinacyanol (0·1%, 1·5 c.c.), and dicyanine (0·1%, 1·5 c.c.). For the region 800—950 mμ, lepidinedicyanine is used as sensitiser.

H. Wren.

Spectrographic investigation of amino-acids, polypeptides, and diketopiperazines. II. Absorptive power of mixtures of known compounds. E. Abderhalden and R. Haas (Z. physiol. Chem., 1926, **160**, 256—262).—Ultra-violet absorption curves are given for glycylglycine and glycine anhydride, alanylalanine and alanine anhydride, leucylglycine, glycyl-leucine, and leucylglycine anhydride, leucylglycylglycine, and leucylglycyl-leucine. Glycine anhydride absorbs much less than glycylglycine, whereas its diketopiperazine absorbs much more strongly than that of the dipeptide. Mixtures of amino-acids absorb more strongly than would be expected from the additive absorptions of the components. Such molecular mixture (abscissæ)-wave-length (ordinates) curves show maxima when the proportions are: for glycine and alanine, 1 : 1; for alanine and valine, 2 : 1; for glycine and glycine anhydride, 2 : 1; for alanine and leucylglycylglycine, 1 : 1; for glycine and calcium chloride, 2 : 1; and for lævulose and alanine, 1 : 2. The increased absorption of mixtures decreases as the mixture becomes either more acid or more alkaline (cf. A., 1926, 959).

P. W. Clutterbuck.

[Mutability of absorption spectra in solutions in relationship to the distribution of charge of the molecules and connexion between absorption and refraction.] G. Scheibe (Ber., 1926, **59**, [*B*], 2616; cf. A., 1926, 774).—The measurements of the absorption spectrum of 0·2939*M* aqueous potassium nitrate by von Halban and Ebert (A., 1924, ii, 824) are affected by a fundamental error; after correction, they agree with those of the author (*loc. cit.*).

H. Wren.

Mutability of absorption spectra in solutions and the distribution of charge of the molecules. IV. G. Scheibe [with F. Backenköhler and A. Rosenberg] (Ber., 1926, **59**, [*B*], 2617—2628; cf. A., 1926, 774).—The absorption of completely symmetrical molecules, carbon tetrachloride, carbon disulphide, benzene, and hexamethylbenzene, is only very slightly influenced by such solvents as methyl and ethyl alcohols or hexane. Chloroform and, particularly, carbon tetrachloride behave abnormally as solvents. Among unsymmetrically constituted molecules, there are found electrosymmetrical compounds such as the saturated hydrocarbons and unsaturated hydrocarbons like βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene. A chromophor made up of electrons which unite two carbon atoms joined only to C–C or C–H groups generally has no dipolar properties. When the chromophor is composed of different atoms, dipolar properties are generally present, as shown by the carbonyl group of acetone; if, however, the methyl groups of the latter are successively replaced by the $\cdot CMe_3$ group, the susceptibility to the influence of dipolar solvents is diminished; the chemical reactivity of the carbonyl group diminishes in the same sequence. Symmetrical chromophors can become asymmetric by the introduction of polar groups, as shown by mesityl oxide and phorone, and particularly by the series of compounds, benzene, hexamethylbenzene, benzophenone, nitrobenzene, ethyl benzoate, and benzonitrile. The groups, $\cdot NO_2$, $\cdot CO_2R$, $CO\cdot R$, and $\cdot CN$ cause the band I of benzene to be displaceable to the regions of longer wave-length, whereas the groups, $\cdot CH_2\cdot CO_2R$ and, probably, $\cdot NH_2$ render it displaceable in the opposite direction. The first group of substituents comprises those which direct halogenation or nitration mainly towards the *meta* position, whereas the directive effect of the second group is to the *ortho* and *para* positions. The extent to which the displaceability of the bands is in harmony with the substitution rules is further examined in the cases of anisole, phenol, benzonitrile, phenylacetonitrile, benzyl alcohol, β-phenylethyl alcohol, *p*-benzoquinone, and aniline. Direct comparison is generally very difficult, since the chemical reactions are commonly effected in solvents such as concentrated sulphuric and nitric acids, which frequently induce profound optical change. H. WREN.

Rate of decay of fluorescence of solutions of dyes. E. GAVIOLA (Ann. Physik, 1926, [iv], **81**, 681—710).—A more detailed account of work already published (A., 1926, 335).

Rare earths as activators of luminescence. E. L. NICHOLS and H. L. HOWES (J. Opt. Soc. Amer., 1926, **13**, 573—587; cf. Nichols and Slattery, A., 1926, 659).—Observations have been made of the photo- and cathodo-luminescence of solid solutions of traces of salts of samarium, europium, thulium, dysprosium, terbium, neodymium, praseodymium, yttrium, and erbium in calcium fluoride, calcium oxide, borax (bead), sodium phosphate (bead), sodium fluoride (bead), and alumina, and the luminescence spectra have been roughly mapped by means of a hand spectroscope. Solutions in calcium oxide are more brilliantly luminescent than those in any other solvent, and give spectra in which the bands are very bright and line-like. Many cases are noted of the tendency of certain activators to suppress the luminescence due to other elements present in the solvent. Thus, the samarium spectrum is invariably given by solutions of neodymium, assumed to contain infinitesimal quantities of samarium, in calcium oxide. The bands in the spectra of solutions containing traces of thulium, europium, terbium, and samarium may be arranged in sets having a common and constant frequency interval, found to be 18 for europium and 16 for thulium, terbium, and samarium. There are one or more sets of positions in the spectrum which are characteristic of a given activator, and whatever the solvent, all the luminescence bands of substances containing the activator in question are so located that their crests coincide with these positions. This relationship, first established for the spectra of solid solutions containing uranium, is designated as the "principle of essential identity." L. L. BIRCUMSHAW.

Luminescence of potassium vapour in the electrodeless discharge. G. BALASSE (Bull. Acad. Roy. Belg., 1926, [v], **12**, 193—201).—Wave-lengths below 4427·314 Å. emitted by potassium vapour under the influence of the electrodeless discharge are recorded. With rise in temperature, the luminescence changes in colour, and both limits of the spectrum move towards the infra-red, whilst at a certain temperature modifications appear in the spectral lines, indicating that two types of luminescence are occurring simultaneously. One of these gives the arc spectrum, the other one the spark spectrum. R. CUTHILL.

Spectra of phosphorescent flames of carbon disulphide and ether. H. J. EMELÉUS (J.C.S., 1926, 2948—2951).—The spectra of the cool phosphorescent flames of carbon disulphide and ether have been compared with those of their normal flames. For carbon disulphide, the difference is mainly one of distribution of intensity, although a group of closely-spaced bands between 3400 and 2900 Å. was not observed in the low-temperature flame. The phosphorescent ether flame gives a band spectrum totally different from the normal one. Examination of the corresponding wave-numbers shows the existence of nearly constant differences, indicating that this spectrum has a normal structure. M. S. BURR.

Photo-electric effect in natural blue rock-salt. R. HILSCH and R. OTTMER (Z. Physik, 1926, **39**, 644—647).—The photo-electric conductivity of the rock-salt was measured when the crystal was illuminated with light ranging from 186 to 2000 μμ; curves are given showing the absorption coefficient over this range and the induced conductivity. E. B. LUDLAM.

Dielectric constant of solutions of good conducting electrolytes. II. H. HELLMANN and H. ZAHN (Ann. Physik, 1926, [iv], **81**, 711—756; cf. A., 1926, 778; Physikal. Z., 1926, **27**, 636).—The electrolytes so far investigated are divided into two groups: (*a*) those exhibiting only a small decrease of dielectric constant at high concentrations, *e.g.*, hydrochloric acid, alkali chlorides, etc.; (*b*) those which show a minimum in the dielectric constant when the concentration reaches a critical value beyond which there is a rapid increase in dielectric constant with increasing concentration, *e.g.*, copper sulphate. The sulphates of other heavy metals behave similarly. R. A. MORTON.

Variation of dielectric constant of benzene with pressure. L. CAGNIARD (Compt. rend., 1926, **183**, 873—875).—The variation of the dielectric constant of benzene with pressure has been determined under isothermal conditions up to 22 atm., by a method previously described (*ibid.*, 1926, **182**, 1528). It has been found that the dielectric constant ε varies linearly with the pressure p, and that $d\varepsilon/dp$ increases with rise of temperature. The experimental values of $d\varepsilon/dp$ have been compared with those calculated from Debye's theory of dielectrics using the equation $(\varepsilon-1)/(\varepsilon+2)\,.\,d=f(T)$, where d is the density and T the temperature; considerable divergence is obtained, indicating that Debye's theory in its original form is insufficient. The variation in $d\varepsilon/dp$ per degree is of the same order as that calculated from the theory. S. J. Gregg.

Colour of the ruby [and the sapphire]. C. W. Stillwell (J. Physical Chem., 1926, 30, 1441—1466).—The conditions under which chromic oxide imparts colour to corundum and the state of the chromium have been studied. The red colour imparted to α-alumina by chromic oxide is not due to colloidal chromic oxide (cf. Hull, B., 1903, 28) or to the presence of a higher or lower oxide of chromium, or to a change in concentration of the chromium oxide. Correlation of colour and X-ray analysis affords strong evidence that it is due to a second modification of chromic oxide having the same crystal structure as the green modification and as α-alumina. The axial ratio of this second form of chromic oxide is nearer to that of α-alumina than to that of the green form, and hence the red modification tends to be produced when chromic oxide is added to α-alumina. This occurs up to a point beyond which α-alumina is unable to stabilise it. The occurrence of the red or green modification depends on the value of the axial ratio of the mixed crystal. Changes in the axial ratio can be effected by changing the chromic oxide content, and by varying the atmosphere in which fusion is accomplished for mixtures containing 30—45% of chromic oxide. The bluish-red colour of certain rubies is due to limited amount of reduction of the red chromic oxide to blue chromous oxide. The chromic oxide content of the natural ruby is approximately 2%, and the cause of colour of the natural ruby is identical with that of the artificial product. When no stabilisation of the red modification occurs, as in the case of the emerald, a green colour is obtained with very low concentrations of chromic oxide. The temporary colour change to green which occurs when rubies are heated is still unexplained.

The cause of the blue colour of the natural sapphire is discussed at length, but with no definite result. Chromium oxide (1%) can impart a typical sapphire-blue colour to a mixture of beryllium, aluminium, and silicon oxides heated in a reducing atmosphere. L. S. Theobald.

Systematic errors introduced into the measurement of the depolarisation of light diffused by gases by stray light. Study of some organic vapours. J. Cabannes (J. Phys. Radium, 1926, [vi], 7, 338—344; cf. A., 1926, 559).—The values obtained by different authors for the depolarisation factor of light diffused by various gases are not concordant; reasons for this divergence are considered. Further values are given for the depolarisation factor ρ and the depolarisation limit ρ_0 of some organic vapours. A. S. Corbet.

Dispersion and molecular refraction of the alkali halides. K. L. Wolf (Ann. Physik, 1926, [iv], 81, 637—648).—A theoretical paper which extends a previous theory of the dispersion of sodium and potassium chlorides (Herzfeld and Wolf, A., 1925, ii, 1119; 1926, 11) by associating with it the theory of deformation advanced by Fajans and Joos (Z. Physik, 1925, 23, 1), and from considerations of the relations between the structures of the ions concerned and those of the corresponding rare gases. From Cuthbertson's data for the refractivities of hydrogen chloride, bromide, and iodide, values are calculated for the refractivities of the anions in the halides of the alkali metals; and thence the values for the molecular refractivities of these salts. The values so obtained are held to be in satisfactory agreement with the experimental data of Spangenberg (Z. Krist., 1923, 57, 494). R. W. Lunt.

Anomalous optical rotation–dispersion and magnetic rotation–dispersion of substances of which the optical dispersion of rotation is anomalous. W. Pfleiderer (Z. Physik, 1926, 39, 663—685).—Determinations and comparisons are made of the optical and magnetic rotation–dispersion, the absorption, and ordinary dispersion of camphorquinone in toluene, diphenylmethylenecamphor in benzene, phenylmethylenecamphor in benzene, diphenylcamphormethane in benzene, copper tartrate and sodium hydroxide in water, and the copper and ferric compounds of hydroxymethylenecamphor in ethyl alcohol. The curves show a point of inflexion where the dispersion begins to be anomalous, and with increasing concentration this point is displaced towards longer wave-lengths. Measurements of the magnetic rotation of toluene at twenty-four places in the visible region show that it is proportional to $\lambda dn/d\lambda$ (Becquerel's relation, n is the refractive index for wave-length λ). E. B. Ludlam.

Molecular theory of rotatory power and the calculation of Verdet's constant. R. de Mallemann (J. Phys. Radium, 1926, [vi], 7, 295—315).—From an analysis of the general equation of motion of an electron when subjected to a magnetic field an expression is developed for Verdet's constant, for substances the permeability of which is approximately unity, involving three constants derived from those characterising the three restraining forces on an electron conceived in a three co-ordinate system. Similarly, the Kerr constant and the molecular refractivity, which is shown to be additive in form, are derived in terms of these three constants. By assigning a fixed number of optically effective electrons to each molecule, an expression is then obtained for Verdet's constant in terms of the Kerr constant, for media in which the molecules are assumed isotropic, whereby the three undeterminable constants are eliminated. The expression so deduced is therefore independent of any assumptions concerning the law of intramolecular forces, and is in a form readily compared with known data. A more complicated expression is then derived for media of anisotropic molecules by expressing the Kerr constant in terms of the Tyndall constant. It is shown that the correction for anisotropy in the case of nitrobenzene, which has a very large value for the Kerr constant, does not amount to more than 3%, and may therefore be neglected for most substances. By assuming that the number of optically effective electrons in *cyclo*hexane is equal to the total number of valency electrons, the value obtained for Verdet's constant agrees within 1% of that observed by Perkin. For a large number of aliphatic compounds a similar agreement is recorded by assigning the total number of valency electrons in the molecule less four as the number of optically effective electrons. Similarly, by assigning fifteen effective electrons to the benzene nucleus and normal values to substituent groups a similar concordance between observed and calculated values of Verdet's constant is obtained for a large number of benzene derivatives.

It is shown further that an approximate agreement, which is considered satisfactory in view of the difficulty of experimental determination, is obtained for hydrogen, where the number of electrons is known definitely. A further consequence of this derivation of Verdet's constant is that its variation with respect to temperature, pressure, and physical states is independent of assumptions relating to the equivalence of different electrons in the molecule. Data are given showing a satisfactory agreement between the observed and calculated values of the temperature variation for carbon disulphide.

It is shown that the ratio of the magnetic rotatory dispersion to electric double-refraction dispersion is equal to the ratio of the corresponding wave-lengths, which is in agreement with experiment for water, carbon disulphide, and camphor. By introducing the assumption that paramagnetic atoms exert a negative molecular field, the phenomena of negative magnetic rotation and of anomalous dispersion are correlated with the normal phenomena.

R. W. LUNT.

Theoretical and experimental foundations for a general stereochemistry. K. WEISSENBERG (Z. Elektrochem., 1926, **32**, 470—478).—The recent proof of a pyramidal structure for certain carbon compounds has important implications for stereochemistry. Isomerism is discussed from a very general point of view and experiments are suggested.

R. A. MORTON.

Scattering of light by the individual particles of smokes. H. S. PATTERSON and R. WHYTLAW-GRAY (Proc. Roy. Soc., 1926, **A**, **113**, 312—322).—The experiments involved the determination of the size of a particle and of the intensity of light scattered by a particle. The former was determined by the rate of fall, and the latter by comparison with a standard artificial particle. A special eye-piece is described, containing the artificial particle, which consisted of a minute sphere at the end of a glass thread. The measurements were carried out by comparing the intensity of the light scattered by a selected smoke particle with that scattered by the artificial particle, the latter being adjustable by means of a neutral wedge, calibrated so that the relative intensity at different positions could be read off from a curve. The clouds studied were of magnesium oxide, silver, mercuric chloride, and mercury. The results are not in agreement with Rayleigh's law, nor with Mie's theory. It is suggested that the scattering is modified by the close or loose packing of the units of which the larger aggregates are composed.

E. S. HEDGES.

Search for element 61. II. W. PRANDTL and A. GRIMM (Z. angew. Chem., 1926, **39**, 1333—1334; cf. *ibid.*, 892).—A criticism of the work of Harris, Yntema, and Hopkins (A., 1926, 780). The authors consider that the apparatus used for examining the *X*-ray spectrum of the rare-earth oxides was unsuitable; a vacuum tube is essential to obtain sufficient dispersion to differentiate the characteristic lines of element 61 from those of other elements, especially of bromine, platinum, and barium. Harris and his collaborators assumed the absence of these elements without conducting exhaustive tests, but the present authors state that, in their experience, traces are always present under the conditions of working described.

A. R. POWELL.

Element of atomic number 61. II. L. ROLLA and L. FERNANDES (Gazzetta, 1926, **56**, 688—694). Details are given of the principles and procedure of the fractionation methods employed in isolating the element of atomic number 61 (cf. A., 1926, 1083).

T. H. POPE.

Metallography of solid mercury and amalgams. W. ROSENHAIN and A. J. MURPHY (Proc. Roy. Soc., 1926, **A**, **113**, 1—6).—A description of experimental methods for the microscopical examination of solid mercury and of amalgams which are solid only at low temperatures. The low temperatures were maintained by means of carbon dioxide snow, usually made into a paste with acetone. A smooth surface was obtained either by casting on a glass slip or by polishing at the low temperature. The cast surfaces were satisfactorily etched by 25% hydrochloric acid (f. p. −86°), but the polished surface could not be etched, the surface behaving as though passivity were produced by the polishing. Attachments to the microscope to prevent the deposition of frost are described, and photographs of solid mercury and of amalgams of tin and thallium are included.

W. HUME-ROTHERY.

Interpretation of *X*-ray, single-crystal, rotation photographs. J. D. BERNAL (Proc. Roy. Soc., 1926, **A**, **113**, 117—160).—A discussion of the mathematical interpretation of the experimental results obtained by (*a*) the rotation method proper of *X*-ray crystal analysis, in which a small crystal is rotated at uniform speed in front of a narrow beam of homogeneous *X*-rays, and (*b*) the oscillation method, in which the revolving spindle is turned backwards and forwards at a constant speed, through a definite small angle. The determination of the size and shape of the unit cell of the fundamental lattice of the crystal, and of the indices of reflecting planes leading to the determination of the space-group are dealt with. The treatment involves the conception of the reciprocal lattice (Ewald, Z. Krist., 1921, **56**, 129). Tables and charts to save laborious calculations are included.

W. HUME-ROTHERY.

Lead suboxide. A. FERRARI (Gazzetta, 1926, **56**, 630—637).—The results of *X*-ray analysis demonstrate the existence of lead suboxide, which is highly unstable and exhibits monometric structure of the cuprite type. The dimensions of the basic cell containing 2 mols. of Pb_2O are $a=5{\cdot}38$ Å., vol.$=155{\cdot}72$ Å.^{3}, the corresponding density being 9·16. The value of the diameter for lead calculated from this lattice agrees with that of the non-ionised lead atom.

T. H. POPE.

Polymorphism of silicon dioxide and structure of tridymite. R. E. Gibbs (Proc. Roy. Soc., 1926, **A**, **113**, 351—367).—A review is given of the β-structures of quartz and cristobalite, and, on the assumption of the conservation of the tetrahedron of oxygen atoms around any silicon as the building unit, a structure is suggested for the intermediate form, tridymite. This is justified by *X*-ray analysis, showing that tridymite has a similar structure to ice, with 4 molecules per cell, $a=5\cdot03$, $c=8\cdot02$. The framework can be considered as a close-packed arrangement of oxygen atoms, whilst the silicon atoms occupy the spaces formed between four neighbouring oxygen atoms. The structures are probably ionic in nature. β–β transitions appear to be characterised by a change of partners between neighbouring ions, whilst the α–β transition of quartz is merely a small atomic rearrangement. The α-states are probably created by distortion of the β-forms, involving lower symmetry and possibly larger cells. α-Tridymite it orthorhombic, $a=9\cdot9$, $b=17\cdot1$, $c=16\cdot3$, in which the units must be polymerised groups $n\text{SiO}_2$. The existence of a third form, α′, of tridymite was confirmed.

E. S. Hedges.

***X*-Ray measurements on compounds of the system soda–lime–silica.** R. W. G. Wyckoff and G. W. Morey (Amer. J. Sci., 1926, [v], 12, 419—440; cf. A., 1925, ii, 1146, 1161).—*X*-Ray powder photographs show that the orthosilicate Na_2CaSiO_4 is cubic, with four molecules in the unit cell and $a=7\cdot497$ Å. The metasilicate $Na_4Ca(SiO_3)_3$, which is also crystallographically and optically cubic, is, however, pseudo-cubic according to the *X*-ray data, with $a=7\cdot547$ Å. and two molecules in the cell. The metasilicate $Na_2Ca_2(SiO_3)_3$, which shows weak birefringence and lamellar twinning like leucite, is also pseudo-cubic according to the *X*-ray data. These three compounds show very nearly the same *X*-ray patterns, and they present an anomalous case similar to that of mullite and fibrolite (A., 1926, 664).

L. J. Spencer.

Mineral component of bones. W. F. De Jong (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 870—872).—See A., 1926, 781.

Solidification temperatures of organic compounds. Fusion temperature and spectrograms in homologous series. J. Timmermans (Bull. Soc. chim. Belg., 1926, 35, 276—283).—A discussion of the relation between the spectrograms of members of homologous series and their fusion temperature. The straight-chain molecular structure of aliphatic hydrocarbons is considered in relation to this and to related crystalline phenomena.

P. V. McKie.

Crystal structure of quinol. I. W. A. Caspari (J.C.S., 1926, 2944—2948).—The crystal structure of quinol has been examined goniometrically, and also by *X*-ray rotation and oscillation photographs. The unit cell is hexagonal, and the lattice unit consists of a group of three molecules forming an asymmetric whole. This association appears to have no connexion with the molecular association in the liquid or gas phase. The results obtained are not in complete agreement with those of Becker and Jancke (A., 1922, ii, 128), who employed only the powder method.

M. S. Burr.

Production of large copper crystals. H. C. H. Carpenter and S. Tamura (Proc. Roy. Soc., 1926, **A**, **113**, 28—43).—Large copper crystals exceeding 4 in. in length have been prepared from polycrystalline copper strip of section 0·5×0·125 inch by the method of critical straining and heat treatment previously used for aluminium (A., 1922, ii, 69). The copper crystals, unlike those of aluminium, always contain twin crystals, which may be oriented in as many as three directions in any one crystal. There is no marked difference between the tensile strength of the large crystals and of the polycrystalline material, but the large crystals are much the less ductile, their elongation values being only about one third of those for the polycrystalline strip; this effect is due to the presence of the twin crystals, since single copper crystals prepared direct from the liquid, which are free from twins, are remarkably ductile.

W. Hume-Rothery.

Formation of twinned metallic crystals. H. C. H. Carpenter and S. Tamura (Proc. Roy. Soc., 1926, **A**, **113**, 161—182).—"Annealing twins" are produced in certain metals by straining, followed by heat treatment, during which recrystallisation and crystal growth occur, and are distinguished from "mechanical twins," produced by straining alone. The formation of annealing twins has been examined with special reference to copper and its alloys and indium. They develop by a process of boundary migration in which crystal growth and twin formation occur simultaneously, and any twin crystals existing in the old crystal grains are consumed. If proper care is taken that cast metals or alloys are free from strain, they do not develop twins on heating. Unlike mechanical twins, annealing twins are very stable thermally. Twinning planes are more stable chemically than crystal boundaries; thus at high temperatures hydrogen attacks the crystal boundaries of copper, but not the twinning planes. The principal cause of twinning is crystal growth, deformation being an indirect cause, because it results in growth on annealing. The mechanism of the atomic rearrangement is discussed, and the suggestion made that twin formation is possible only if the atomic arrangement permits twinning on the planes of densest atomic concentration. Metals crystallising in the face-centred cubic, tetrahedral cubic, or face-centred tetragonal lattices readily produce annealing twins (aluminium being an exception), but not those crystallising in the close-packed hexagonal lattice, and what are called twins in the last-named are probable examples of parallel growth. W. Hume-Rothery.

Properties of electrolytic iron. G. P. Fuller.—See B., 1926, 949.

Specific vibrations of tetrahedral molecules (sulphate ion). K. Rolan (Z. Physik, 1926, 39, 588—600).—A formula is obtained which gives values for the polarisability and distance apart of sulphate ions in sulphate crystals, using the specific frequencies for 9 μ and 16 μ. E. B. Ludlam.

Apparent duplication of the optic axis of calcite with Federov's plate. M. Philibert

(Atti R. Accad. Lincei, 1926, [vi], 4, 300—305).—The apparent double refraction of two separate calcite plates, when examined in conjunction with a Federov plate, is found to be due to double refraction of the glass setting of the crystal. T. H. Pope.

Theory of electrical conductivity in metals. S. Procopiu (Bull. Acad. Sci. Roumaine, 1926, **10**, 93—95).

Resistance of metals and metal crystals at the temperature of liquid helium. W. Meissner (Physikal Z., 1926, **27**, 725—730).—See A., 1926, 1086.

Paramagnetism independent of temperature. [Mlle.] P. Collet (Compt. rend., 1926, **183**, 1031—1032).—The coefficient of atomic magnetisation of manganese as obtained from measurements of the paramagnetism of solid potassium permanganate is $56{\cdot}5\times10^{-6}$ and is independent of temperature from 15° to 150°. The paramagnetism is raised by the presence of impurities. For solutions of this salt a value of 62×10^{-6} is obtained at the ordinary temperature, and this is approximately constant from 17° to 100° (cf. A., 1924, ii, 586). J. Grant.

Longitudinal magneto-resistance effect in single crystals of iron. W. L. Webster (Proc. Roy. Soc., 1926, A, **113**, 196—207).—The change of resistance in a longitudinal magnetic field has been measured for three directions in single crystals of iron. For the (100) axis there is no change in resistance. For the (111) and (110) axes no change in resistance occurs until a magnetic intensity of about 800 c.g.s.u. is reached; the resistance then increases with the field until magnetic saturation is approached, when the value of dR/R tends to limiting values of 0·40% and 0·28% for the (111) and (110) axes, respectively. The change is probably due to the orientation of the atoms. If in unmagnetised iron the axes of the atoms are parallel to a (100) crystal axis, but may point in either direction, then when the iron is magnetised along the (100) axis there will be reversal of some of the atoms, but without change in orientation, and consequently no change in resistance. For other directions, magnetisation produces a change in orientation and hence a change in resistance. No direct connexion exists between the change of resistance and the net change of length, for there is a large increase in length in the direction of the (100) axis (A., 1925, ii, 369). Magneto-striction is regarded as due to one or both of two effects, change of orientation, and change of structure of the atoms in the magnetic field, and the results are interpreted on this hypothesis. W. Hume-Rothery.

Magnetic disturbance of the superconductivity with tin and mercury. W. J. de Haas and G. J. Sizoo (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 947—963; cf. A., 1926, 230, 667).—Existing measurements have been supplemented by an investigation of the hysteresis figures in longitudinal fields. The figures are very similar to those obtained in transverse fields, discontinuities being again present in the descending lines. New measurements confirm the previously given explanation of the discontinuities. The influence of temperature has been investigated. The threshold value ($H\frac{1}{2}$), *i.e.*, the value of the field at which the resistance has half returned, varies with temperature according to equation $(H\frac{1}{2})=h(T_s^2-T^2)$, where h is a constant characteristic of the metal and T_s the "vanishing point" of the metal. J. S. Carter.

Ferromagnetic characteristics of stable iron sesquioxide. H. Forestier and G. Chaudron (Compt. rend., 1926, **183**, 787—789; cf. A., 1925, ii, 1159; 1926, 556).—The coefficient of magnetisation of iron sesquioxide varies with the thermal and magnetic treatment to which the sample is subjected. Starting with an oxide devoid of all magnetisation, the magnetisation–temperature curve shows an increase in the coefficient of magnetisation up to 600°; this is followed by a sharp decrease, which ends at 675°. The magnetisation–temperature curve obtained on cooling is separated from that obtained on heating below 600°, and the coefficient of magnetisation increases on cooling down to the ordinary temperature. On repeating the experiment with the same sample, a curve is obtained which is rigorously reversible and superposable on the cooling curve of the first experiment; moreover, the sample is now polarised. Magnetisation can be destroyed by heating beyond 675° and cooling in a non-magnetic field. Under the same conditions with magnetite and ferrites, a very sharp increase in the coefficient of magnetisation is obtained. M. E. Nottage.

Magnetic susceptibilities of the rare earths. J. Zernike with C. James (J. Amer. Chem. Soc., 1926, **48**, 2827—2831).—The magnetic susceptibilities and their approximate temperature coefficients are recorded for the rare-earth sulphate octahydrates (excluding europium, dysprosium, and thulium). A comparison of the results with those of previous workers indicates that cerium may show different values in the dissolved and solid states, and that the values for holmium, terbium, and ytterbium are still uncertain. It is impossible at present to calculate magneton numbers. S. K. Tweedy.

Optical constants of molybdenite in the ultra-violet. A. W. Meyer (J. Opt. Soc. Amer., 1926, **13**, 557—560).—By means of the crystalliptometer the optical constants of molybdenite have been measured for wave-lengths 500—330 $\mu\mu$. The apparatus and method were in general the same as those used by Weld (*ibid.*, 1922, **6**, 67), Van Dyke (*ibid.*, 917), and Graber (A., 1925, ii, 1041). Observations were made on thin cleavage surfaces of crystals perpendicular to the optical axis, at settings of 65°, 70°, and 76°, and average results for the refractive index, coefficient of absorption, and reflecting power for each wave-length setting are tabulated. The results are in satisfactory agreement with those obtained by Tyndall (Physical Rev., 1925, [ii], **21**, 162) and Coblentz (A., 1924, ii, 716). L. L. Bircumshaw.

Specific heats of hydrocyanic acid. (Mrs.) E. H. Ingold (J.C.S., 1926, 2816—2817; cf. *ibid.*, 1922, **121**, 1604; A., 1926, 231).—A reply to criticisms (Partington and Carroll, A., 1925, ii, 373; Partington, *ibid.*, 1926, 784) of the author's previous communications. M. S. Burr.

Thermal data on organic compounds. IV. Heat capacities, entropies, and free energies of

***n*-propyl alcohol, ethyl ether, and dulcitol.** G. S. Parks and H. M. Huffman (J. Amer. Chem. Soc., 1926, 48, 2788—2793).—The specific heats of the above compounds were determined in the manner previously described (A., 1925, ii, 491) over the approximate temperature range 80—290° Abs. The latent heats of fusion were (g.-cal./g.): *n*-propyl alcohol (m. p. 147·0° Abs.) 20·66; ethyl ether (m. p. 156·8° Abs.) 23·54. The calculated entropies at 25° were (g.-cal./1°) 51·2 and 67·7, respectively, and 59·2 for dulcitol, in agreement with the predicted values (A., 1926, 232, 784). The entropy of *n*-propyl alcohol glass exceeds that of the crystals by 1·89 units/mol. at the absolute zero. The calculated free energies at 25° are −44,100, −33,600, and −228,100 g.-cal., respectively. The first and third values agree with those predicted; the value for ether agrees with that calculated from the equilibrium data of Pease and Yung (A., 1924, i, 363; cf. Clark, Graham, and Winter, *ibid.*, 1926, 45). In the case of isomerides, that compound with the lowest m. p. has the largest entropy and free energy. S. K. Tweedy.

Calculation of the molecular heats of gases from equilibrium constants. W. G. Shilling (Trans. Faraday Soc., 1926, 22, 377—400).—By means of the reaction isochore $d(\log_e K)/dT=Q/RT^2$, where K is the equilibrium constant of a gaseous reaction; Kirchhoff's equation $dQ/dT=\Sigma C_f-\Sigma C_i=\Sigma C'$, where ΣC_f is the sum of the molecular heats of the resultants of the reaction, ΣC_i the sum of the molecular heats of the reactants, and $\Sigma C'$ the difference between these two quantities; and the equation $Q_{\mathrm{T}}=Q_0+\int\Sigma C'dT$, where Q_T is the heat of reaction at a given temperature T, and Q_0 that at the absolute zero, the molecular heats, C_p and C_v, of nitrogen, oxygen, nitric oxide, carbon monoxide, carbon dioxide, and ammonia have been calculated up to 3000° Abs. In some cases, Nernst's formulæ for the heat of reaction have been used. By careful correlation of the equilibria and specific heat data, it was possible to eliminate impossible values. The results obtained were found to be in very good agreement with the values given in Partington and Shilling's "The Specific Heats of Gases."

L. L. Bircumshaw.

Correction for heat exchanges between a calorimeter and its surroundings. P. E. Klopsteg (J. Opt. Soc. Amer., 1926, 13, 589—595).—A description is given of a graphical method, derived from well-known calorimetric principles, for determining the corrected temperature rise in calorimetric experiments, which appears to yield results of greater accuracy than the usual methods employed. The efficiency of the method is illustrated by applying it to a series of determinations of *J* by Puluj's method.

L. L. Bircumshaw.

Solidification of helium. J. E. Verschaffelt (Natuurwetensch. Tijdschr., 1926, 8, 77—81; cf. Keesom, A., 1926, 893).—The m.-p. curve does not meet the b.-p. curve, so that helium seems to have no triple point. S. I. Levy.

M.-p. curves of optical isomerides in the camphor series. J. D. M. Ross and I. C. Somerville (J.C.S., 1926, 2770—2784).—The m.-p. curves of the optical isomerides of a number of compounds belonging to the camphor series have been determined. Members of the three groups described by Roozeboom have been distinguished. Borneol, camphor, camphoric anhydride, bornyl hydrogen phthalate, and camphene belong to the mixed crystal group, pinene forms a simple (*dl*) conglomerate, whilst camphoric acid and *o*-methyl hydrogen camphorate give definite racemic compounds. A mathematical analysis of the curves has been given, and the experimental curves have been compared with the ideal curves based on the formulæ of Washburn and Read (A., 1915, ii, 738), and on the f.-p. laws of van 't Hoff and Raoult. Associating substances show a strong tendency to form racemic compounds, those in which association is only slight form mixed crystals, whilst non-associating substances form either mixed crystals or a *dl*-conglomerate. M. S. Burr.

Thermal conductivity of vitreous silica and crystalline quartz. G. W. C. Kaye and W. F. Higgins (Proc. Roy. Soc., 1926, **A**, **113**, 335—351).—The thermal conductivity of vitreous silica was determined over the range 60—240° by the "divided-bar" method. The value for the conductivity at 100° is 0·00338, increasing with rise of temperature with a mean change of +0·00000185 c.g.s.u. per degree. On the other hand, the thermal conductivity of crystalline quartz decreases with rise of temperature (70—105°) with a mean change of −0·00010 per degree in a direction parallel to the optic axis, and −0·000037 in a direction perpendicular to the optic axis. E. S. Hedges.

Density of fluids. I. Relation between density, temperature, and the latent heat of vaporisation. J. H. Shaxby (Phil. Mag., 1926, [vii], 2, 1127—1136).—From kinetic considerations, it has been shown that the density ρ of a fluid can be represented by the equation $\rho^{1/3}-\alpha T\log\rho^{1/3}=\rho_1^{1/3}-\alpha T\log\rho_0^{1/3}$, where ρ_0 is the maximum density of the substance and ρ_1 and α are constants of which $\alpha=\rho_c^{1/3}/T_c$, where ρ_c and T_c are data at the critical temperatures. It is shown also that $\rho_1^{1/3}=1{\cdot}5\rho_c^{1/3}$ and $\rho_0^{1/3}=e^{1/2}\rho_c^{1/3}$. From these results, a reduced equation of state which contains no constants peculiar to a particular substance has been obtained. The equations hold fairly closely for liquids, but are approximate only for saturated vapours. It is shown that the internal latent heat of vaporisation can be deduced from kinetic considerations and does not depend on any inverse square law for molecular attractions, as assumed by Mills. The molecular diameters of a number of gases have been calculated from the maximum densities. These values are not in good agreement with those determined from viscosity measurements. A. E. Mitchell.

Density of calcium carbonate hexahydrate. J. Hume and B. Topley (J.C.S., 1926, 2932—2934).—The density of crystals of calcium carbonate hexahydrate, prepared by precipitation with carbon dioxide from calcium oxide dissolved in sucrose solutions at 0°, has been obtained by two different methods. When determined dilatometrically, by measuring the expansion on decomposition, the density at 0° is 1·834, with an average deviation of 0·43%.

The value obtained directly, by displacement of the mother-liquor of the crystals in a specific-gravity bottle, is 1·817, with an average deviation of 0·60%. These values are higher than those obtained by any other investigators. By preparing the crystals from a 10% instead of a 20% sucrose solution, no appreciable difference in density is obtained. M. S. Burr.

Vapour pressures, densities, and some derived quantities for acetone. W. A. Felsing and S. A. Durban (J. Amer. Chem. Soc., 1926, 48, 2885—2893).—The vapour pressure of acetone over the range −70° to +65° is expressed, with an accuracy of at least 0·1 mm. of mercury, by the relation $\log_{10} p = -2986{\cdot}21241/T + 20{\cdot}7587806 - 40{\cdot}8472641 \times 10^{-3}T + 42{\cdot}6623920 \times 10^{-6}T^2$, where p is expressed in mm. (1/760 normal atm.), and T in degrees absolute. The density of acetone, between −90° and +52°, is given to within 1 in 3000—4000 by the relation $d = 1{\cdot}091301 - 92{\cdot}722 \times 10^{-5}T - 32{\cdot}331 \times 10^{-8}T^2$. The solubility of carbon dioxide in acetone between −75° and +20° is given by the relation $\log_{10} S = 2615{\cdot}017/T - 18{\cdot}085436 + 66{\cdot}55546 \times 10^{-3}T - 79{\cdot}07114 \times 10^{-6}T^2$, where S is expressed in g.-mol. per 1000 g. of acetone when the partial pressure of carbon dioxide is 760 mm. From the vapour pressure–temperature relation given, the heats of evaporation of acetone at different temperatures can be calculated by means of the Clausius–Clapeyron equation. F. G. Willson.

Vapour pressure of naphthalene at low temperatures. (Miss) M. R. Andrews (J. Physical Chem., 1926, 30, 1497—1500; cf. A., 1923, ii, 327).—The vapour pressure of naphthalene has been determined over the temperature range −50° to 70° by a modification of Knudsen's method (Ann. Physik, 1909, [iv], 29, 179), and also a method involving the use of a vibration gauge in which a quartz fibre is replaced by molybdenum. The results given by the two methods are in fair agreement, and the vapour-pressure curve is represented by the equation $\log_{10} P = -4000/T + 12{\cdot}275$ (mm.), which gives a value of 18,280 g.-cal./mol. for the heat of evaporation. It is concluded that every molecule of naphthalene striking a surface of tungsten carbide is decomposed into carbon and hydrogen (cf. *loc. cit.*).

L. S. Theobald.

Production of high vacua by using metals of low volatility, especially tungsten. (Frl.) M. A. Schirmann (Physikal. Z., 1926, 27, 748—751).—A general review of the conditions governing the production of high vacua by absorbing gases on surfaces of metals of high volatility, produced, *e.g.*, by the distillation of the metal from a glowing filament to the walls of a vessel. The efficiency of tungsten is discussed with reference to the formation of tungstic oxide, tungsten nitride, and tungsten carbonyl, which are solids of low vapour pressure. R. W. Lunt.

Surface tension of liquid neon. A. T. van Urk, W. H. Keesom, and G. P. Nijhoff (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 914—916).—With the same apparatus as used for helium (A., 1926, 568), the surface tension of liquid neon has been examined. The molecular surface tension ψ_M varies linearly with the temperature, Eötvös' constant being 2·1.

J. S. Carter.

Electrocapillary curve near its maximum. O. K. Rice (J. Physical Chem., 1926, 30, 1501—1509).—Theoretical. Previous investigators (Frumkin, A., 1920, ii, 578; Chapman, Phil. Mag., 1913, [vi], 25, 475) in this field have considered the charge to reside on the surface of the mercury, but calculations made on this basis do not agree with experimental results. It is now suggested that there may be a diffuse layer of positive particles and electrons in the mercury as well as the diffuse layer in the solution, and further that, owing to their finite size, ions can approach only within a certain distance of the surface. The difference in surface tension referred to the surface tension of the maximum of the electrocapillary curve may be equal to the sum of the differences which would be caused by the diffuse layer in the solution and that in the mercury for any given *P.D.* across the respective layers. The distribution of the potential drop can also be found. The values of the surface tension calculated in both ways are similar and they agree better with the experimental data. L. S. Theobald.

Viscosity of copper and its alloys. J. Cournot and R. Pagès (Compt. rend., 1926, 183, 885—886).—The viscosities have been determined by a modification of the method previously described (B., 1925, 994) at temperatures up to 700°. It has been verified that there exists a limiting viscosity, and that for slightly greater loads the velocity of flow assumes a constant value, the time required to attain this state being longer the lower the temperature. The experiments at high temperatures have been continued up to the point of rupture, which is preceded by a sudden increase in the rate of flow. The curve limiting viscosity–temperature for the brasses is similar to those for steel; that for copper, however, is approximately rectilinear. S. J. Gregg.

Effect of temperature on the viscosity of air. F. A. Williams (Proc. Roy. Soc., 1926, A, 113, 233—237; cf. A., 1926, 234).—A reply to criticism by Rankine (*ibid.*, 671). The author's low-temperature results were obtained by an extension of the graph for higher temperatures to Millikan's value (Ann. Physik, 1913, 41, 759) for the ordinary temperatures; the high-temperature results are confirmed by the work of Fisher (Physical Rev., 1909, 28, 73). The author's experimental methods are vindicated. W. Hume-Rothery.

Dielectric constants of mixtures of organic liquids. R. N. Kerr (J.C.S., 1926, 2796—2804).—Mixtures of benzene with methyl benzoate, ethyl benzoate, phenetole, ethyl cinnamate, dimethylaniline, chlorobenzene, bromobenzene, aniline, benzaldehyde, nitrobenzene, benzyl alcohol, and *m*-cresol were examined. Those mixtures which approach most closely to ideal solutions obey Silberstein's volumetric rule, viz., $\varepsilon = (\varepsilon_1 v_1 + \varepsilon_2 v_2)/(v_1 + v_2)$, with fair accuracy. The marked deviations shown by the mixtures of benzene with aniline, benzaldehyde, *m*-cresol, benzyl alcohol, and nitrobenzene, which have curves (ε-volumetric composition) convex to the concentration axis, are attributed to association. With several non-associating mixtures (*e.g.*, benzene–dimethylaniline), the values of ε are slightly greater than those required by the volume rule. Calculation, from surface tension data, of the relative internal pressures of the components supports the hypothesis that this divergence is due to the different environment of the molecules in the mixture from that in the pure state. A number of mixtures of ethyl ether with benzene derivatives have also been examined, and in the case of mixtures with aniline and chlorobenzene, the curves are concave to the concentration axis. It is inferred that the effect of association on the dielectric constant depends on the nature of the complex formed, this being determined by the sizes of the dipoles and their geometrical positions in the participating molecules. This view is supported by results obtained with aniline–*m*-cresol and acetone–chloroform mixtures. L. L. Bircumshaw.

Double decomposition in absence of a solvent. A. G. Bergmann (Z. anorg. Chem., 1926, **157**, 83—116).—The heating and cooling curves of various fused binary salt mixtures have been studied. The factors involved in the occurrence of double decomposition in such systems are: the degrees of ionisation and heats of formation of reactants and resultants, the heat of reaction, the formation of complex compounds, and the miscibility of the components. Feebly-ionised salts, such as the mercuric halides, show little tendency to enter into double decomposition. Mixtures of the nitrates with the halides of the metals of the alkalis and alkaline earths apparently behave like reciprocal salt-pairs. The following double salts appear to exist in fused mixtures of their components: $TlNO_3,HgCl_2$; $2TlNO_3,HgCl_2$; $TlNO_3,HgBr_2$; $AgNO_3,HgI_2$; and $2AgNO_3,HgI_2$. The first three compounds can be crystallised from aqueous solutions. R. Cuthill.

Azeotropism, particularly of binary systems with chemically related constituents. M. Lecat (Compt. rend., 1926, **183**, 880—882).—It is shown by reference to a table of data that close chemical relationship between the constituents is unfavourable to, but not exclusive of azeotropism. Both chemical dissimilarity and molecular association are favourable to azeotropism, especially if present in only one constituent; if both factors are present together, the difference between the azeotropic b. p. and that of the less remote constituent may amount to 12°. Various other relationships are briefly discussed. S. J. Gregg.

Preparation and hydrolysis of esters by the distillation method. I. L. Gay, P. Mion, and M. Auméras (Bull. Soc. chim., 1926, [iv], 39, 1329—1349).—A theoretical consideration of mixtures showing a single minimum b. p. R. Brightman.

Internal friction of molten metals and alloys. II. Method of measurement, and internal friction of bismuth–tin alloys and of the alloy Cu_3Sn. F. Sauerwald and K. Töpler (Z. anorg. Chem., 1926, **157**, 117—137).—The experimental method has been improved, as a result of which it is found that the viscosity values previously recorded (A., 1924, ii, 553) are all about 3% too small. Measurements of the internal friction of alloys of bismuth and tin have failed to give any indication of the existence of the compounds $BiSn_2$ and Bi_2Sn mentioned by Plüss (*ibid.*, 1916, ii, 294). The temperature–viscosity curve for both the pure metals and their alloys is convex to the temperature axis, the convexity being least for bismuth. The viscosity of the alloy Cu_3Sn, measured at 804°, is unusually large. R. Cuthill.

Serial solubility of some rare-earth bromates. J. Zernike and C. James (J. Amer. Chem. Soc., 1926, **48**, 2871).—A mixture of some rare-earth bromates was fractionally crystallised at 20—25°, and each fraction separated into the elements of the yttrium and cerium groups. The elements were arranged in the following order of decreasing solubility: erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, gadolinium. The order probably depends on the temperature of crystallisation, and preliminary solubility determinations indicate that below 20—25° neodymium comes between terbium and gadolinium. S. K. Tweedy.

Solubility influences. II. Effect of various salts on the solubility of ethyl acetate in water. S. Glasstone, D. W. Dimond, and E. C. Jones (J.C.S., 1926, 2935—2939; cf. Glasstone and Pound, A., 1926, 18).—The solubility of ethyl acetate has been determined at 25° in aqueous solutions of varying concentrations of sodium, potassium, and ammonium nitrates, ammonium acetate and oxalate, potassium fluoride, chlorate, and chromate, calcium, strontium, barium, and lead nitrates, barium and cupric chlorides, sodium, potassium, magnesium, nickel, copper, and zinc sulphates, and potassium ferro- and ferri-cyanides. Assuming the salting-out power of the iodine ion to be zero, the "hydration numbers" per equivalent of various ions at infinite dilution are deduced. It is found that, in general, the salting-out power of an ion is greater the greater the valency and the smaller the size. It is suggested that the hydration number of an ion is a measure of the intensity of the electrostatic field surrounding the ion, the more intense the electrical field produced by the ions of the added salt the greater being the salting-out power of those ions. Abnormal results are given by nitrates, which have a negligible salting-out power, and, particularly in dilute solutions, tend to increase the solubility of the neutral substance. There appears to be no connexion between the hydration of a salt in solution and its tendency to form stable solid hydrates, since the hydration effect of sodium sulphate in 7·5% solution is the same both below and above the transition temperature of the decahydrate. L. L. Bircumshaw.

Solubility influences. III. Salting-out effect of mixtures on aqueous solutions of ethyl acetate. S. Glasstone, D. W. Dimond, and E. R. Harris (J.C.S., 1926, 2939—2943).—Measurements have been made of the influence of the following mixtures on the solubility of ethyl acetate in water at 25°: dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, sodium and ammonium chlorides, potassium and ammonium chlorides, lithium and sodium chlorides, barium and sodium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates. For small concentrations, the effect of the mixture is almost equal to the sum of the effects of the constituents, taken at a concentration, relative to water, equal to that in the mixture, whilst at higher concentrations each salt has a salting-out capacity which it would have in a pure solution at a concentration corresponding with the sum of the constituents. This is attributed to electrical interaction between the two substances. Erratic values are given by the nitrates (cf. preceding abstract). The results obtained for the mixtures of potassium and cupric chlorides show that, contrary to expectation, salting-out cannot be utilised for the detection of complex-ion formation. L. L. Bircumshaw.

Influence of dissolved salts on the mutual miscibility temperature of the systems ethyl alcohol or methyl alcohol–paraffins. E. J. Howard and W. H. Patterson (J.C.S., 1926, 2787—2791; cf. Carrington, Hickson, and Patterson, A., 1926, 18).—A continuation of previous work. The changes in the temperature of complete miscibility caused by the addition of various salts to the systems (1) ethyl alcohol–paraffin (b. p. 160—180°) and (2) methyl alcohol–hexane are recorded. In (1), the order of the univalent cations is nearly the same as, and in (2) is still nearer, that for aqueous solutions. The order of the anions in (1) is nearly the reverse of that for aqueous solutions, whilst in (2) intermediate values are obtained. For both systems, the effect of the anions is greater than that of the cations. Univalent ions cause a greater rise than bi- or tervalent ions in both systems, although in (2) the effect of uni- and bi-valent ions is almost identical. The tests for complexity or association in aqueous solution are applicable to alcoholic solutions. Abnormality is shown by zinc, cadmium, and mercuric halides and mercuric cyanide. L. L. Bircumshaw.

Miscibility tests of dilute solutions of chromic chloride hexahydrates. J. E. Howard and W. H. Patterson (J.C.S., 1926, 2791—2796; cf. preceding abstract).—Measurements have been made of the rise in critical solution temperature caused by the addition of violet hexa-aquochromic chloride, and green dihydrated dichlorotetra-aquochromic chloride, to the following liquid pairs: water–butyric acid, water–*iso*butyric acid, water–phenol, and ethyl alcohol–paraffin (b. p. 160—180°). Butyric and *iso*-butyric acid systems give identical results. In aqueous solutions up to a concentration of 0·05 g.-mol. of salt per 1000 g. of total solution, the rise in critical solution temperature due to the violet salt is nearly double that due to the green, the ratio becoming gradually less above this concentration. Curves are given showing the rate of change of the green to the violet salt in aqueous solution. In ethyl-alcoholic solutions the green salt causes a greater rise in critical solution temperature than the violet. The results both in aqueous and alcoholic solution support the Werner co-ordination theory, and are at variance with the views of Britton (A., 1925, ii, 1203), who postulates the existence in the green solution of basic aggregates essentially colloidal in nature. L. L. Bircumshaw.

Occlusion of gases by metals and alloys in liquid and solid states. K. Iwasé (Sci. Rep. Tôhoku Imp. Univ., 1926, 15, 531—566).—The occlusion of gases by solid and liquid metals has been studied by direct determinations of the volumes of gas absorbed by the metals at various temperatures and 1 atm. pressure. Hydrogen is absorbed by iron from a relatively low temperature, and the solubility increases linearly with the temperature both for the α- and γ-forms, but there is a marked break in the absorption graph at the transformation temperature (910°), the temperature coefficient being greater for the γ-form. The volume absorbed per 100 g. at $t°$ is given by $V=1{\cdot}685+0{\cdot}016(t-200)$, and $V=13{\cdot}445+0{\cdot}1293(t-910)$, for α- and γ-iron, respectively. With steels and cast irons, the solubility diminishes with increasing carbon content, and increases at the m. p. Hydrogen is also dissolved by copper, zinc, antimony, tin, aluminium, silumin (12% Si, 88% Al), and bronze; the absorption for both liquid and solid states increases linearly with temperature, and increases discontinuously at the m. p. Nitrogen is not dissolved by zinc, tin, antimony, or solid copper. It is soluble in iron, but much less soluble than hydrogen; the general form of the absorption–temperature graphs is the same. Cast iron, on the contrary, dissolves more nitrogen than hydrogen. Liquid copper dissolves nitrogen, but the solubility is much less than that of hydrogen. The solubility of nitrogen in aluminium is about the same as that of hydrogen, but with silumin the solubility of nitrogen is less than that of hydrogen; carbon monoxide and dioxide are not absorbed by zinc, antimony, or tin; with solid copper, the absorption of either gas is slight and increases with temperature, but in liquid copper the solubility is greater and diminishes with rise of temperature. With iron, steel, or cast iron, simple occlusion of these gases does not occur, owing to the reaction $2CO \rightleftharpoons CO_2+C$ taking place. From the equilibrium diagram, the composition of mixtures absorbed without change of composition was determined, and simple occlusion of these mixtures was studied. The solubility of the mixed gas decreases with rise of temperature. W. Hume-Rothery.

Adsorption of alkali chlorides in aqueous solutions by active carbon. N. Zelinsky and A. Balandine (Bull. Soc. chim., 1926, [iv], 39, 1508—1515).—The adsorption of alkali chlorides from solutions ($N/10$—$N/160$) by active carbon at 16—18° follows the order: $HCl>LiCl>NaCl<KCl<RbCl<CsCl$ and $NaCl<RbCl<HCl$. The results conform to Freundlich's adsorption isotherm. Experiments with rubidium chloride show that with a given active carbon the amount of salt adsorbed is greater when the carbon is almost powdered. Calcination of the carbon has little effect on the adsorption of hydrochloric acid from solution. Lithium iodide is adsorbed to a greater extent than the chloride at equivalent concentrations (cf. Schilov and others, A., 1922, ii, 350). The experiments indicate that the adsorptive power of a carbon for these salts is not directly connected with its activity. S. K. Tweedy.

Identity of Langmuir's adsorption equation with the law of mass action. D. I. Hitchcock (J. Amer. Chem. Soc., 1926, 48, 2870).—The simple Langmuir adsorption equation, $q=abp/(1+ap)$, where

q is the amount of gas adsorbed at the equilibrium pressure p, a and b being constants, is deduced from the mass action law, showing that agreement of experimental data with the equation does not determine decisively whether the reaction is one of adsorption or chemical combination. Rinde's conclusion that the reaction between gelatin and hydrochloric acid is not a chemical process is thus rendered invalid (cf. A., 1926, 347). S. K. TWEEDY.

Chemical sorption. II. Sorption and heterogeneous chemical equilibrium. S. LIEPATOV (Z. anorg. Chem., 1926, 157, 22—26).—The results previously obtained (A., 1926, 571) for the sorption of bases from salts can be satisfactorily accounted for by treating the process as the distribution of a base between two acids and applying the mass law. Experiments on the sorption of bases from basic colouring matters by gels of an acid nature yield analogous results. R. CUTHILL.

Manifestation of interfacial forces in dispersed systems. A. DE WAELE (J. Amer. Chem. Soc., 1926, 48, 2760—2776).—A qualitative discussion of the interfacial forces in dispersed systems. Three cases arise according as the "spreading coefficient" (Harkins and Feldman, *ibid.*, 1921, 43, 2665) is positive, zero, or negative. In the first case, the adhesion between the phases is greater than the cohesion, so that the particles of the disperse phase mutually repel. In this case, a positively-held layer is attached to the particles. The second case represents an equilibrium state, the disperse particles having a loosely-held layer. The particles in the last case have no layer, and mutually attract. In a disperse system at rest, the interfacial tension manifests itself in orienting the molecules of the continuous phase normally to the interface. Application of tangential shear to the system causes disturbance of the transversal orientation in a direction tangential to the surface of the dispersed particles, the subsequent rate of re-orientation of the lines of force after removal of the shear being an inverse function of the viscosity of the continuous phase. These ideas are utilised in discussing some well-known phenomena, *e.g.*, lubrication, sintering, sherardising, drying of printers' ink, etc. S. K. TWEEDY.

"Intertraction." N. K. ADAM (Proc. Roy. Soc., 1926, A, 113, 478—479).—The experiments of Wright (A., 1926, 901) have been repeated and some further observations made. The effect described by Wright is produced even more clearly by replacing the albumin by magnesium sulphate, and sodium chloride by hydrochloric acid. The experiments support the former views of Adam and Jessop (*ibid.*, 1925, ii, 772), and indicate that the phenomenon of "intertraction" has not been proved to exist. E. S. HEDGES.

Metal films reduced on the surfaces of silica gel. L. H. REYERSON, O. E. HARDER, and L. E. SWEARINGEN (J. Physical Chem., 1926, 30, 1623—1627).—Metallised silica gels have been examined by X-ray analysis. Whenever adsorbed hydrogen is used for the reduction to metal, as in the method of Latshaw and Reyerson (A., 1925, ii, 412), the deposited films are too thin to give diffraction patterns, but impregnation of the silica gel by metallic salts or acids such as chloroplatinic acid gives metal aggregates, which afford X-ray patterns when reduced by hydrogen or by heating. Photographs of silica gel metallised by platinum, copper, and palladium are reproduced. L. S. THEOBALD.

Electrostatic theory of anomalous liquids. J. J. BIKERMANN (Physikal. Z., 1926, 27, 710—711).—From equations relating surface tension to the electric field at an interface and to the dielectric constant of the medium, the ratio of the potential across the interface to $\varepsilon - 1$ (ε = dielectric constant) is evaluated for methyl, ethyl, and *n*-propyl alcohols at various temperatures. The ratio is independent of temperature for each alcohol, in agreement with the theories of Coehn and Raydt (Ann. Physik, 1909, [iv], 30, 797). R. W. LUNT.

Motion of organic substances on water and other liquid surfaces. C. W. ZAHN (Rec. trav. chim., 1926, 45, 783—791).—The "camphor movements" exhibited by a large number of substances on the surface of water and their influence on the surface tension of the liquid have been examined. The substances which move are all found to lower the surface tension; those which do not move either raise the surface tension or affect it but little. The motion, which never occurs on the surface of a saturated solution of the substance, is attributed to the preliminary formation of a boundary layer on the surface, which spreads with unequal velocities in different directions. Motion does not occur on a liquid–liquid interface where there is already an oriented boundary layer (*e.g.*, *iso*amyl alcohol–water), but it does occur where such orientation is not already present (*e.g.*, ethylene dibromide–water). Substances which move are positively adsorbed, and their molecules are of an unsymmetrical type. G. M. BENNETT.

Sensitive electrical precision apparatus for the determination of the b.-p. elevation. J. N. PEARCE and M. M. HICKS (J. Physical Chem., 1926, 30, 1678—1682).—The apparatus of Washburn and Read (A., 1919, ii, 447) has been modified by the introduction of electrical heating and of a thermocouple to replace the Beckmann thermometer. The curve for naphthalene in benzene (data not given) was identical in form with that obtained by Washburn and Read. L. S. THEOBALD.

Cobalt chloride solutions. III. Absorption spectra. IV. Sodium and cobalt chloride solutions. C. MAZZETTI (Gazzetta, 1926, 56, 589—594, 595—600; cf. A., 1925, ii, 209, 210).—III. Results are given of a spectroscopic examination of aqueous cobalt chloride solutions containing various other chlorides and of solutions of cobalt chloride in methyl, ethyl, propyl, and butyl alcohols. The spectra of the pure aqueous solution and of the solutions containing sodium or barium chloride are characterised by the so-called principal band with its centre at about 5100 Å. For solutions containing hydrogen chloride or aluminium chloride, the spectra show a series of bands in the red with centres at approximately 6120, 6260, and 6580 Å. Intermediate behaviour is shown by solutions containing magnesium or calcium chloride, the principal band being accompanied by a secondary band nearer to the red end of the spectrum. These bands in the red are apparently due to the formation of a complex, probably $CoCl_4^{--}$, more or less solvated.

The higher alcohols examined exhibit the effect known as bathochromy, and show increasing tendency to resolve the principal band into a series of bands. The former effect is connected with the increased mol. wt. of the solvent.

IV. The variations in the conductivity of solutions containing sodium and cobalt chlorides with temperature are said to afford evidence of dehydration, and not of scission of complex compounds. This conclusion is in agreement with that reached from a study of the absorption spectra of these solutions.

T. H. Pope.

Rotatory power of tartaric acid. L. Longchambon (Compt. rend., 1926, **183**, 958—960).—Partly polemical against Vellinger's criticism of the author's theory of the lævo-constituent of tartaric acid (A., 1924, ii, 373). The rotatory powers and dispersions of solutions of tartaric acid over a wide range of concentrations increase with decrease in concentration in the same manner. No limit is attained in the dilute solutions, which indicates that the lævo-constituent still exists in appreciable quantities or that it has a high rotatory power. The dispersion and rotatory power of tartaric acid dissolved in calcium chloride solution increase regularly with decrease in temperature from +43° to −40°.

J. Grant.

Properties of large molecules in solution. N. Marinesco (Compt. rend., 1926, **183**, 964—966).—The mol. wt. of certain substances the molecules of which become surrounded with a perisphere of solvent cannot be measured by application of the gas laws because of the large volume which the molecules occupy. Stokes' law has been found to hold, however, and by means of a diffusion method, values of 544 and 470 for rhodamine-*B* in water and ethyl alcohol solutions, respectively, and of 1130 for rose-Bengal in water have been found. In terms of the current theory (A., 1926, 673), the ratio of the number of fixed dipoles to the surface of the large molecule is a function of the deformability of the molecule, that of a molecule containing a halogen being high.

J. Grant.

Densities of particles in smokes. H. S. Patterson and R. Whytlaw-Gray (Proc. Roy. Soc., 1926, A, **113**, 302—311).—In determining the radii of ultramicroscopic particles from the rate of fall, it is not valid to use the density of the substance in bulk, except for liquids or homogeneous solids. Particles of smoke have a loose structure possessing a density much less than that of the substance in bulk. A method was devised for measuring the density of such particles by an application of Millikan's "oil-drop" method, assuming the electronic charge instead of the density. The mean observed densities of some smokes were as follows: cadmium oxide, 0·51; silver, 0·94; mercuric chloride, 1·27; mercury, 1·7; magnesium oxide, 1·35; compared with the respective normal densities of 6·5, 10·5, 5·4, 13·6, 3·6. The Cunningham equation was used to determine the true radii of spheres having the same volume as the aggregates, and the results show that the particles are in general much larger than previously supposed. Photomicrographs of particles deposited from the clouds are in complete conformity with the results of the density measurements.

E. S. Hedges

Space distribution of colloid particles. R. Zsigmondy (Z. Physikal. Chem., 1926, **124**, 145—154).—The author's views on the number and constitution of secondary particles in colloidal solution are maintained (cf. "Kolloidchemie," 5th ed., Leipzig, 1925), in opposition to opinions incidentally expressed by Pauli and Valkó (A., 1926, 901).

L. F. Gilbert.

Colloidal properties of cellulose nitrate sols in mixed solvents. A. Highfield (Z. physikal. Chem., 1926, 124, 245—269).—Translated from Trans. Faraday Soc. See B., 1926, 579. L. F. Gilbert.

Emulsions. H. Limburg (Rec. trav. chim., 1926, **45**, 772—782).—A theoretical discussion of the conditions for the coagulation of oil emulsions from the point of view of Freundlich's theory concerning the critical velocity of the particles (cf. Smoluchowski, Z. physikal. Chem., 1918, **92**, 129). The conclusion is reached that the stabilising influence of the electric charge on a particle with respect to coagulation must become smaller with increasing conductivity of the medium. The deductions of Powis (J.C.S., 1916, **109**, 734) are rejected, and the significance of the critical point in his stabilisation curves is discussed. A difference in structure (in the widest sense of the term) between the liquid–liquid interface and the bulk of the two phases tends to hinder coagulation.

G. M. Bennett.

Application of the drop-weight method to the determination of the surface tension of colloidal solutions. W. D. Harkins (Nature, 1926, **118**, 732—733).—By modification of the usual apparatus, the accuracy of the method was increased; the drop may be held for many hours without falling.

A. A. Eldridge.

Hydrates and hydrogels. X. Detection of hydroxides in hydrogels. R. Willstätter and H. Kraut (Ber., 1926, 59, [*B*], 2541—2547).—In reply to Gutbier, Hüttig, and Döbling (A., 1926, 798), it is pointed out that the examination of pressure–temperature curves is not a suitable method for investigating the possible existence of hydroxides in gels. The portion of Gutbier's curve for stannic acid gel lying below 100° is greatly influenced by the presence of adsorbed water. Rise of temperature causes chemical changes in the stannic acid on which the presence of adsorbed water has an important influence. Again, the large number of different compounds which may be present in the gel exert a very considerable influence on the nature of the pressure–temperature curves; even in the case of definite hydrates the change of vapour tension accompanying a given change in composition is not independent of the size of the particles (cf. Hagiwara, A., 1923, ii, 234).

H. Wren.

Photophoresis of colloidal particles in aqueous solutions. W. W. Barkas (Phil. Mag., 1926, [vii], 2, 1019—1026).—The action of light and *X*-rays on aqueous suspensions of copper, silver, gold, and gamboge has been examined. The cloud of particles settling under gravitation moves, on the average, towards the light side of the containing vessel. The upper side of the cloud assumes a characteristic form under the action of light, the boundary becoming much more sharply defined. Similar results were obtained with X-rays. The drift velocities for particles near the top of the cloud have been calculated, and are shown to be greater in most cases than those found by Ehrenhaft for particles suspended in gases and illuminated by an intense beam from an ultramicroscope. A suspension of gold particles exposed to light showed an increase of mean radius of from $2{\cdot}3\times10^{-6}$ to $2{\cdot}9\times10^{-6}$ cm. Those exposed to X-rays showed no increase in size. A. E. Mitchell.

Influence of ageing of a sol on its coagulation. S. Ghosh and N. R. Dhar (J. Physical Chem., 1926, **30**, 1564—1570; cf. A., 1925, ii, 386).—Arsenious sulphide becomes unstable on ageing when coagulated by potassium or barium chloride, aluminium nitrate, aniline hydrochloride, or crystal-violet, the instability decreasing in the order: potassium chloride, aniline hydrochloride, crystal-violet, barium chloride, aluminium nitrate. On the other hand, the same sol becomes stable on ageing when coagulated by quinine and by strychnine hydrochlorides. The stability of ferric hydroxide towards potassium chloride, sulphate, or oxalate is unchanged by ageing, but decreases when coagulated by hydrochloric acid or aluminium nitrate. These results are discussed in the light of adsorption of ions by the sol.

L. S. Theobald.

Mechanical coagulation of cupric oxide [and FeO(OH)] sols. H. Freundlich and H. Kroch (Z. physikal. Chem., 1926, **124**, 155—180; cf. A., 1925, ii, 522).—The properties of cupric oxide hydrosol prepared by Bredig's method are described. Vigorous stirring coagulates the colloid particles. This mechanical coagulation is independent of the temperature (0—20°) and proceeds according to the equation $K=(n_0-n)/t$, where K is the velocity coefficient and n_0 and n are the concentrations at the commencement of stirring and after time t, respectively. The rate of coagulation is proportional to the square of the rate of stirring. No change of the ζ potential of the particles was observed during (mechanical) coagulation. Electrolytes, in concentrations less than certain small "threshold" values, do not affect the rate of coagulation. Salts yielding chloride, bromide, and nitrate ions have threshold values of the order of 10^5 times as great as those yielding ferro- and ferri-cyanide ions. The relative differences between these threshold concentrations are greater than those shown by the coagulation values compared against an electrolyte concentration higher than the threshold value. Hydroxyl ions have a greater influence even than ferro- and ferri-cyanide ions, as in water of p_H 7 (or greater) cupric oxide sol cannot be prepared. The p_H of the sols decreases during mechanical coagulation, whilst the conductivity increases somewhat. With electrolyte concentrations only a little higher than the threshold values, coagulation proceeds according to the formula $K=1/t\,.\,\sqrt{n_0/n-1}$. A FeO(OH) sol, prepared by oxidation of iron pentacarbonyl with hydrogen peroxide, was also coagulated mechanically.

L. F. Gilbert.

Coagulation of weakly solvated sols by acids. Wo. Ostwald (Kolloid-Z., 1926, **40**, 201—209).—The mechanism of coagulation of weakly solvated sols differs from that of strongly solvated sols, the Schultze–Hardy rule applying to the former case and the Hofmeister series being applicable to the latter. A study is made of the effect of a large number of acids on the coagulation of various sols by plotting the time for coagulation against the p_H value of the acid. If the hydrogen-ion concentration is the determining factor, every acid should give the same curve, and this is actually the case with gold sol and with Congo-red. With sols of silver sulphide, arsenious sulphide, sulphur, antimony sulphide, vanadium pentoxide, copper ferrocyanide, paraffin, and stearic acid, the curves for different acids deviate from one another, the amount of deviation increasing in the order of sol given. This is also the order of increasing stability towards coagulation by a given acid. It is noteworthy, also, that some weak organic acids have a stronger coagulative effect than an equivalent amount of hydrochloric acid. Hydrogen-ion concentration cannot therefore alone account for the coagulation of the sols, and the effect of the anion must also be considered. E. S. Hedges.

Antagonistic actions of ions in the neutralisation of sols. II. H. B. Weiser (J. Physical Chem., 1926, **30**, 1527—1537; cf. A., 1926, 242).—Ultramicroscopic examination of an arsenious sulphide sol shows that the addition of an amount of sodium chloride which represents but a small fraction of that required for precipitation results in agglomeration of the particles. In spite of the consequent decrease in stability of the sol, the higher precipitation value of barium chloride in the presence of sodium chloride is maintained, and is due mainly to cationic antagonism rather than to the stabilising influence of the chloride ion. The addition of potassium ferrocyanide to a copper ferrocyanide sol increases the stability of the sol towards electrolytes, owing to strong adsorption of the ferrocyanide ion. The precipitation curves for mixtures of (*a*) potassium chloride and ferrocyanide and (*b*) barium chloride and potassium ferrocyanide each show a maximum, which in the former case is very sharp (cf. Sen, A., 1925, ii, 664, 665). Cationic antagonism plays a minor rôle in the latter case.

The antagonistic action of salt pairs on protoplasm is determined by their effect on the permeability of the cell membrane, which it is suggested may have a close resemblance to a reversible colloidal sol (cf. Gurchot, A., 1926, 240). A close analogy between the action of salt pairs towards sols such as copper ferrocyanide and arsenious sulphide and the antagonistic action on the permeability, and hence on the life and growth of living cells, could then exist. L. S. Theobald.

Rhythmic, diurnal bands of gold and platinum in silicic acid gel. E. C. H. Davies and V. Sivertz (J. Physical Chem., 1926, **30**, 1467—1476; cf. Holmes, A., 1918, ii, 392).—Rhythmic, diurnal bands of red, colloidal gold have been obtained in a silicic acid gel containing 10 c.c. of $3N$-hydrochloric acid, 10 c.c. of water-glass (*d* 1·16), 0·8 c.c. of 1% gold chloride, and 0·2 g. of oxalic acid, by exposure to light passing through a grid with rhythmic apertures, followed by several days in the dark. The colour of the gold depends on the age of the gel. Freshly-prepared gel gives red gold, older gel blue, and a still older gel yellow gold. Further, reduction to the red form is more rapid in the gel than in the same mixture before setting. Photochemical after-effects occur in the system gold oxalate–silicic acid gel, light producing changes in the gold before any visible effects can be noticed.

Diurnal bands of platinum were produced in ordinary light when oxalic acid or one of its soluble salts diffused into a gel containing 10 c.c. of $3N$-acetic acid, 10 c.c. of water-glass (*d* 1·16), and 0·8 c.c. of 1% platinic chloride. Continuous illumination for 3 weeks was accompanied by reduction, but no bands were formed. Rhythmic, diurnal bands were formed in a gel of the above composition, but containing, in addition, 0·2 g. of oxalic acid, whenever exposure through a grid with rhythmic apertures was followed by a period in darkness. The bands result from light reduction of alternate zones, followed by diffusion.

L. S. THEOBALD.

Behaviour of silicic acid gel during the drying-up process. K. KRISHNAMURTI (Nature, 1926, **118**, 843).—A question of priority (cf. Fells and Firth, A., 1926, 995). A. A. ELDRIDGE.

Swelling of collagen fibres in acids. I. Mineral acids. A. KÜNTZEL (Kolloid-Z., 1926, **40**, 264—279).—Tendons from rats' tails were used for single collagen fibres. When placed in acid or alkali, these swell and become shortened in length, although in pure water this does not occur. There is a limit to the contraction—viz., 33%—but the amount of contraction in acid is a measure of the extent of swelling. Using hydrochloric, nitric, and sulphuric acids, the swelling curves, obtained by plotting the contraction against the $p_{\rm H}$ of the solution, are quite unlike any previously recorded curves. Instead of a well-defined maximum of swelling at a certain $p_{\rm H}$ value, with these fibres the swelling increases with increasing $p_{\rm H}$, reaches a maximum, at which it remains over a wide range, and then suddenly drops to zero. This sudden break occurs at a concentration of $0\cdot0001N$, more dilute solutions not causing swelling. A factor influencing the type of curve is the excess of liquid in which the substance is immersed. Theories of swelling are discussed. The exponential law does not hold for the above cases. E. S. HEDGES.

Effect of acids and hydrogen-ion concentration on glue and gelatin. O. GERNGROSS (Kolloid-Z., 1926, **40**, 279—286).—A *résumé* of published work, especially on the isoelectric point of gelatin and the firmness of the gels. E. S. HEDGES.

Albumins and acids. WO. PAULI (Kolloid-Z., 1926, **40**, 185—201).—Proteins can be divided into two groups, according to whether the system is stable or unstable at the isoelectric point. A summary is given of the behaviour of albumins in the neighbourhood of the isoelectric point with respect to viscosity, precipitability by alcohol, hydrogen-ion activity, and conductivity. The phenomena are explained on the basis of Bjerrum's theory of "Zwitterions" (A., 1923, i, 444). At the isoelectric point, the acidic properties of albumins are still more in evidence than the basic properties, although this is no longer the case when excess of acid is added. With increasing quantities of hydrochloric acid, the osmotic pressure, viscosity, activity, and conductivity of albumins rise, pass through a maximum, and subsequently fall.

E. S. HEDGES.

Influence of hydrolysis of gelatin on gold numbers and peptisation of other substances. P. B. GANGULY (J. Indian Chem. Soc., 1926, **3**, 177—186).—Gelatin containing gelatose and other earlier products of hydrolysis of gelatin is more efficient in peptising gold sols than is purified gelatin. When gelatin is boiled with water, the gold number falls to a minimum, and then rises again. Dilute gelatin sols prepared at 70° from a 1% gelatin gel gave the same gold numbers, irrespective of the dilution (cf. Elliott and Sheppard, A., 1921, ii, 720). Partly hydrolysed gelatin is also a better peptising agent for silver and lead chromates than pure gelatin. G. M. BENNETT.

Fractures of acraldehyde gels: rhythmic production of furrows. C. DUFRAISSE and P. GAILLIOT (Compt. rend., 1926, **183**, 967—969).—Regular series of lines resembling furrows are produced on the cut surface of an acraldehyde gel. Spectrograms obtained from these furrows show lines at 4358, 5461, and 5769 Å., and indicate that the greater part of the incident light is diffracted. The distances between the furrows vary slightly in a continuous fashion, but sometimes show a regular and rapid decrease, when the furrows finally converge. The nature of the furrows is probably that of fine fissures (less than 0·5 μ long) on a smooth surface. It is suggested that the furrows are present in the gel before fracture, and are part of the gel structure. J. GRANT.

Permeability of collodion membranes. R. E. LIESEGANG (Biochem. Z., 1926, **177**, 239—242).—Collodion membranes possess a much greater permeability than would be expected from the findings of Michaelis and Fujita (A., 1926, 120, 349) when they are dried under tension instead of in a free state.

J. PRYDE.

Stable equilibrium of physico-chemical systems. G. HOMÈS (Bull. Acad. roy. Belg., 1926, [v], **12**, 20—24).—It is shown thermodynamically that if a mixture of perfect gases is in stable equilibrium at constant temperature and pressure, it is also in equilibrium at constant temperature and volume, and *vice versa*. R. CUTHILL.

Comparison of the effects of the electric spark and thermal dissociation. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1926, **183**, 784—786; cf. A., 1926, 586, 680).—The limiting dissociation of carbon dioxide depends on the pressure and on the capacity of the condenser. So long as the capacity exceeds 0·1 microfarad, an increase in pressure, or diminution in capacity, lowers the degree of dissociation, and the mode of discharge is of the symmetrical, continuous type. Under a low pressure and with a small capacity, the mode of discharge is of the unsymmetrical type with dark spaces, and it corresponds with a small dissociation. As the pressure increases even when the capacity is still small, the symmetrical type of discharge reappears, and this is accompanied by an increase in the dissociation. A given volume of carbon dioxide at a pressure p can be brought to a degree of dissociation α by the passage of a large number of discharges of a condenser of capacity c, or by heating the gas to a certain temperature T. Consequently, any point on the diagram (p α T) corresponds with a point (p α c), and therefore a given capacity c corresponds with a temperature T on the thermal diagram, which may be called the apparent temperature of the spark. The following results may be deduced from the diagram (p α c). (1) At all pressures the apparent temperature of the spark increases with the capacity. (2) When the capacity is at least 0·1 microfarad the apparent temperature of the spark is practically independent of the pressure. For a capacity of 10 microfarads it is about 3000° Abs. (3) When the capacity is very small, the apparent temperature of the spark is much lower, but still above 2000° Abs.; its variations are not a simple function of the pressure. (4) With an average capacity, the two types of discharge alternate with one another, but for any given capacity the symmetrical type is more frequent when the pressure of the gas is greater. M. E. NOTTAGE.

Methane equilibrium. I. R. C. CANTELO (J. Physical Chem., 1926, 30, 1641—1645; cf. A., 1926, 798).—The equilibrium constants for the system $C+2H_2 \rightleftharpoons CH_4+21,730$ g.-cal. have been calculated for temperatures between 500° and 1100°, using the equation of Saunders (A., 1924, ii, 836), and from these, the equilibrium concentrations of methane and hydrogen for the same temperature range. These values reconcile the apparent disagreement of previous investigators (Coward and Wilson, J.C.S., 1919, **115**, 1380). Experiments at 565°, 670°, and 770° with methane as the initial system and a specially-prepared nickel catalyst are also described. L. S. THEOBALD.

Electrochemical resonance. W. A. PLOTNIKOV (Z. physikal. Chem., 1926, **124**, 236—244).—From the point of view of the Nernst–Thomson rule and related theories, apparent anomalies in the degree of ionisation of electrolytes in solution are discussed. It is suggested that conditions favourable to ionisation are: (1) resonance between the oscillations of molecules or portions of molecules of solvent with those of solute; (2) resonance of the oscillations of the (potential) ions of solute molecules with those of solvent molecules. Ionisation will occur when $A=\nu h$, where A is the work of ionisation permolecule, ν is the frequency of the radiation emitted by the ionising medium, and h has the usual significance. L. F. GILBERT.

Experimental methods for determining acid concentration, hydrogen-ion concentration, and acid activity. A. LOTTERMOSER (Kolloid-Z., 1926, **40**, 180—185).—A description of electrometric and colorimetric methods of measurement at present in use. E. S. HEDGES.

Actual acidity, potential acidity, and buffering. K. TÄUFEL and C. WAGNER (Kolloid-Z., 1926, **40**, 174—180).—The complete acid properties of a system can be summed up in terms of (1) "actual acidity," or hydrogen-ion concentration, (2) "potential acidity," or titration value, and (3) buffering effect. Typical titration curves are discussed, and the properties of buffer solutions are considered, particularly with reference to the control of the taste of beers and wines. E. S. HEDGES.

Hydrogen-ion concentration, hydrogen-ion activity, and the newer solution theories. L. EBERT (Kolloid-Z., 1926, **40**, 169—173).—A critical review of theories of solution. E. S. HEDGES.

Hydrogen-ion concentration and pharmacological effect. A. JARISCH (Kolloid-Z., 1926, **40**, 259—264).—A *résumé* of the literature concerning the influence of the hydrogen-ion concentration of the medium on pharmacological effect. A comprehensive bibliography is included. E. S. HEDGES.

Importance of hydrogen-ion concentration in pathology. H. SCHADE (Kolloid-Z., 1926, **40**, 252—258).—A discussion of the changes of p_H value in blood in pathological cases. E. S. HEDGES.

Hydrogen-ion concentration and plasmolysis. S. PRÁT (Kolloid-Z., 1926, **40**, 248—251).—The plasmolysis of plant cells (mainly epidermis of *Allium cepa*) was studied in sea-water of varying hydrogen-ion concentration. Natural sea-water has p_H 8·2, but by addition of acid or alkali this medium lends itself to plasmolytic investigations over the range of p_H 2—10. The results show that with sea-water of p_H 2—4 the contents of the cells were coagulated in 3—5 hrs., yet in neutral or very feebly acid solution the process took several days, or even weeks. The appearance of the precipitated mass also varies with the hydrogen-ion concentration. Hydrochloric acid and sulphuric acid are similar in their effect, but some organic acids differ. Causes affecting the influence of hydrogen-ion concentration are the previous history of the material and the presence of substances of high surface activity. E. S. HEDGES.

Acid taste and hydrogen-ion concentration. R. DIETZEL (Kolloid-Z., 1926, **40**, 240—248).—A discussion of previously published work on the methods of comparing taste, and the relation between the sour taste of acids and their hydrogen-ion concentration. The sour taste is not quantitatively proportional to the strength of the acid, although the two are parallel in a qualitative way. It has been sought to relate the difference to surface tension, volatility, and effect on swelling. E. S. HEDGES.

Fermentation and hydrogen-ion concentration. A. FODOR (Kolloid-Z., 1926, **40**, 234—240).—A discussion of previously published work on the effect of hydrogen-ion concentration on the rate of fermentation, and the variation of the optimum hydrogen-ion concentration with the nature of the substrate. The author's former theoretical views (A., 1922, i, 92) are further developed. E. S. HEDGES.

Effect of acids and hydrogen-ion concentration in physiology. R. MOND (Kolloid-Z., 1926, **40**, 228—233).—A review of the advances made in physiology through the study of hydrogen-ion concentration in colloid systems. The buffer solutions of the blood are considered in particular. E. S. HEDGES.

Amphoteric behaviour of complex systems. I. Theoretical. II. Titration of sulphanilic acid–glycine mixtures. A. E. Stearn (J. Gen. Physiol., 1926, **10**, 313—323, 325—336).—Systems consisting of two amphoteric substances in aqueous solution are discussed mathematically, and it is shown that there exists a p_H value between the isoelectric points of the separate components which is virtually the isoelectric point for the complex system. Electrometric titrations of solutions containing both glycine and sulphanilic acid give curves and virtual isoelectric points agreeing with the theoretical. General agreement is also found between experimental and theoretical results in the case of lysine–sulphanilic acid and of glycine–lysine mixtures.

W. O. Kermack.

Hydration of dissolved sucrose and the expression of the concentration in measuring the activity of ions. I. M. Kolthoff (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 885—898).—Colorimetric determinations and measurements of the *E.M.F.* of cells containing sucrose show that the apparent hydrogen-ion concentration of solutions of hydrochloric acid is increased appreciably on addition of sucrose. Assuming that hydrogen ions are hydrated and that the hydrogen electrode measures the concentration of anhydrous ions only, a possible explanation is that sucrose has a dehydrating effect on the hydrated ions. Since the colorimetrically and electrometrically determined hydrogen-ion concentrations are in excellent agreement, this explanation involves the further assumption that colour indicators are sensitive only to anhydrous ions. The fact that a corresponding increase in acidity is not observed with solutions of organic acids and that the p_H value of a buffer-mixture is practically uninfluenced by sucrose, renders the proposed explanation untenable. A more plausible suggestion is that sucrose displaces water in the solution, *i.e.*, the quantity of free water is diminished and the concentration of solute is increased. All concentrations should therefore be expressed in mols. of solute (n) in mols. of solution ($n+N$), N being the number of mols. of solvent. Expressing concentrations in this way, a slight increase in the activity of the hydrogen ion is found, which is attributed to the withdrawal of water from the system by hydration of the dissolved sucrose. The calculated hydration of sucrose, 8 ± 2 mols. of water per mol. of sucrose in M-solution, is of the same order of magnitude as that calculated from existing data on the viscosities, osmotic properties, solvent power, and rates of inversion of sucrose solutions. It is unlikely that definite hydrates exist, and it is suggested that, by reason of the affinity of sucrose for molecules of water, some of the latter are retained within the sphere of influence of sucrose molecules, the quantity of free water which remains being consequently decreased.

J. S. Carter.

Activity coefficients of aqueous hydrochloric acid at extreme dilutions. G. Nonhebel (Phil. Mag., 1926, [vii], **2**, 1085—1090).—The *E.M.F.* at 25° of the combination $H_2|HCl\ aq.|AgCl|Ag$ have been measured over the concentration range 0·00015 — 0·04M. The results are in good agreement with those of Linhart (A., 1919, ii, 444). The most probable value of E_0 derived from the results is $0{\cdot}2228\pm0{\cdot}0001$ volt, in agreement with the conclusion of Nonhebel and Hartley (*ibid.*, 1925, ii, 1061). The results indicate that the relationship between the activity coefficient and the concentration up to 0·003M is given by the equation $-\log\gamma=A\sqrt{M}$, in which the constant A is equal to 0·39. The value of the constant is thus smaller than that demanded by the equation of Debye for the interionic attraction in the strong electrolyte.

A. E. Mitchell.

Law of neutral salt action in concentrated solutions. II. G. Schmid and R. Olsen (Z. physikal. Chem., 1926, **124**, 97—114).—A general discussion of the salt effect from the points of view of the Brönsted and Debye–Hückel theories is given. The velocity of hydrolysis of cyanamide to carbamide by 0·25N-nitric acid has been measured in presence of potassium, sodium, calcium, and magnesium nitrates at concentrations up to 6N, at a number of temperatures. The equation defining specific neutral salt effect given in the first paper (A., 1926, 474) is found to hold at all the temperatures and concentrations employed. Further, the salt effect is shown to be independent of temperature, which is not compatible with the explanation obtained by assuming it to be due to dehydration of the hydrogen ion.

H. F. Gillbe.

New transformation of cobalt, and the equilibrium diagrams of nickel–cobalt and iron–cobalt. H. Masumoto (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 449—477).—Measurements of electrical conductivity, thermal expansion, heat evolution, and magnetisation have been made, and show that cobalt undergoes a transformation between 400° and 500°. With the purest cobalt available, the change occurred at about 477° on heating and 403° on cooling, but these temperatures are depressed considerably by traces of impurity. X-Ray analysis shows that below the transformation point cobalt has a close-packed hexagonal structure, and above it a face-centred cubic structure, both forms being ferromagnetic. On the temperature–magnetisation curves, the transformation is shown only when weak fields are used; the cause of this is discussed. Similar measurements with nickel–cobalt and iron–cobalt alloys have been made, and the equilibrium diagrams constructed for the solid state. In each case, the addition of the second metal lowers the transformation point of cobalt.

W. Hume-Rothery.

Separation of pure ice. J. J. van Laar (Chem. Weekblad, 1926, **23**, 551—552).—The purity of a solid phase separating from a system of two components is determined by the interval separating the critical pressures; if this is small, the two separate together; if it is great, one component separates in the pure condition over a wide temperature range.

S. I. Levy.

Apparatus for the dynamic determination of dissociation pressures. Dissociation of silver carbonate. M. Centnerszwer and J. Krustinson (Z. physikal. Chem., 1926, **124**, 225—244; cf. A., 1926, 1107).—An improved apparatus for the determination of dissociation pressures by the dynamic method is described (cf. A., 1925, ii, 803). The dissociation pressures of silver carbonate between 180° and 250° have been measured and are in good agreement with Colson's results (*ibid.*, 1901, ii, 238; 1905, ii, 304). Values calculated from the Nernst formula agree closely with those observed. The dissociation pressure of silver carbonate is influenced by the grain size. L. F. Gilbert.

Equilibrium in the binary systems diphenylamine–*p*-nitroanisole and phenol–*p*-toluidine at atmospheric and at higher pressures. N. A. Pushin (Z. physikal. Chem., 1926, **124**, 217—224; cf. A., 1913, ii, 852).—The temperature–pressure curves for the eutectic point in the system diphenylamine–*p*-nitroanisole and the second eutectic point in the system phenol–*p*-toluidine (75 mol. % of phenol at 1 atm.) have been investigated at pressures up to 3500 kg./cm.^{2}, by means of a method previously described (A., 1925, ii, 38). No changes in the compositions of the eutectic mixtures were observed. A thermal investigation, at atmospheric pressure, of the system phenol–*p*-toluidine confirms the existence of two forms of the compound *p*-$C_6H_4Me{\cdot}NH_2,Ph{\cdot}OH$, as reported by Philip (J.C.S., 1903, **83**, 814), but in contradistinction to Kremann (A., 1906, ii, 266). L. F. Gilbert.

Mixtures of antipyrine with phenylurethane and with thiosinamine [allylthiocarbamide]. C. Mazzetti (Gazzetta, 1926, **56**, 606—611).—Investigation of these systems by the f.-p. method has proved unsuccessful owing to gaps in the crystallisability. By measurements of the viscosity, however, it is shown that antipyrine forms no molecular compound with phenylurethane, whereas, in accordance with cryoscopic determinations (A., 1919, i, 524), it forms at least one additive compound with thiosinamine (cf. Garelli and Barbieri, *ibid.*, 1906, i, 985). T. H. Pope.

Systems sodium iodide–acetone and sodium iodide–methyl ethyl ketone. A. E. Wadsworth and H. M. Dawson (J.C.S., 1926, 2784—2786).—The solubility relations underlying the sodium iodide method for the purification of acetone have been examined, and results obtained in agreement with those of Macy and Thomas (A., 1926, 799). At low temperatures, the stable solid phase is the complex $NaI,3Me_2CO$, which is converted into the simple iodide at 25·7°. The solubility of the complex increases rapidly with rise of temperature, whilst that of the simple salt shows a rapid fall. Methyl ethyl ketone forms a similar complex with sodium iodide, with a transition point at about −30°. The system shows great similarity to the acetone system. The conditions for purifying methyl ethyl ketone by means of sodium iodide, as deduced from the solubility curves, differ widely from those prescribed by Lochte (A., 1924, i, 1166), and it is suggested that the crystalline substance which separates out in Lochte's recommended process is really hydrated sodium iodide. L. L. Bircumshaw.

Transition temperature and solubility of sodium sulphate in presence of sodium chloride or sodium bromide. F. J. Norton and J. Johnston (Amer. J. Sci., 1926, **12**, 477—483; cf. *ibid.*, 467).—The lowering of the transition temperature of sodium sulphate by sodium chloride and sodium bromide of varying concentration has been determined, and also the composition of the liquid phase at the different temperatures. Equimolecular concentrations produce equal lowering, although the reduction in solubility of sodium sulphate is not the same. By comparison with the data obtained by other investigators, it is found that sodium iodide and dextrose exhibit the same behaviour. In the case of the sodium salts, this probably means that only one new ionic species, the halide ion, has been added to a completely ionised solution. The variable effect on solubility is probably due to variations in the attraction of the added solute for water. Alcohol, sodium hydroxide, sodium phthalate, and sodium nitrate are variable in their influence on the transition temperature as well as on the solubility. Addition of sulphuric acid produces approximately the same effect on the transition temperature as addition of sodium chloride or bromide of double the molecular concentration. M. S. Burr.

System sulphuric acid–sodium sulphate–water. O. Faust and P. Esselmann (Z. anorg. Chem., 1926, **157**, 290—298).—The composition of the solid and liquid phases in the above system at 0°, 29·5°, 46°, 60°, and 82·5° has been determined, the solutions containing up to 80% of sulphuric acid. The results are in fair agreement with those of Pascal and Ero (A., 1919, ii, 154). R. Cuthill.

Solutions of the bi-ternary mixture of the chlorides and nitrates of sodium, potassium, and magnesium. F. Frowein and E. von Mühlendahl (Z. angew. Chem., 1926, **39**, 1488—1500).—A phase-rule study at 0°, 20°, 40°, 60°, and 80° with special reference to the manufacture of potassium nitrate. R. Cuthill.

Systems $CoCl_2$–$NaCl$–H_2O, $CoCl_2$–KCl–H_2O, and $CoCl_2$–$BaCl_2$–H_2O at 20°. C. Mazzetti (Gazzetta, 1926, **56**, 601—605; cf. A., 1925, 209, 210).—In no case are double salts formed which can exist in equilibrium with the saturated aqueous solutions at 20° (cf. Engel, A., 1890, 106). T. H. Pope.

Equilibria in systems containing phases separated by a semi-permeable membrane. XVII. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 964—974).—Mathematical. Ternary systems with vapour phases are considered. J. S. Carter.

Heat of oxidation of beryllium. C. Matignon and (Mlle.) G. Marchal (Compt. rend., 1926, **183**, 927—929).—The mean values of the heats of solution of beryllium containing negligible quantities of impurities in hydrofluoric and hydrochloric acids are 94·25 and 87·90 g.-cal., respectively. From the heats of solution of beryllium oxide in these acids, a mean value for the heat of formation of this compound is found to be 140·15 g.-cal. A list of modified thermochemical data for beryllium is appended. J. Grant.

Correction of thermochemical data. W. Swientoslawski and (Mlle.) H. Starczewska (J. Chim. phys., 1926, **23**, 821—822).—The data of Valeur

(A., 1901, i, 154) have been recalculated using accurate atomic weights, and applying the corrections previously enumerated (*ibid.*, 1925, ii, 1139).

R. Cuthill.

Heats of mixture of partly miscible couples. System methyl alcohol–*cyclo*hexane. P. Mondain-Monval (Compt. rend., 1926, 183, 1104—1106).—The heats of mixture of various proportions of methyl alcohol and *cyclo*hexane have been measured at 18°, 29°, 40°, and 52°, the critical temperature (above which the liquids are miscible in all proportions) being 49·1°. At 52°, the curve obtained is continuous and similar to those for systems in which total miscibility occurs at all temperatures. At temperatures below 49·1°, where two layers separate for certain proportions of the constituents, discontinuous curves result. The specific heats of the mixtures are greater than those obtained by calculation from the rule of mixtures, and are 0·64 and 0·43 for methyl alcohol and *cyclo*hexane, respectively.

J. Grant.

Heat of adsorption of carbon monoxide on a copper catalyst. R. A. Beebe (J. Physical Chem., 1926, 30, 1538—1544).—The integral and differential values for the heat of adsorption of carbon monoxide on a copper catalyst have been found by the method previously employed (Beebe and Taylor, A., 1924, ii, 159). The values of the former vary from 11,200 to 12,200 g.-cal. per mol. The differential values are much higher for the initial than for the later amounts of carbon monoxide adsorbed, but never less than 8000 g.-cal. per mol. Accidental poisoning of the catalyst by an unknown substance resulted in decreased adsorptive capacity, but the integral heat of adsorption increased. A similar result was obtained with hydrogen and nickel (*loc. cit.*), although Foresti (A., 1925, ii, 692) found no increase in heat of adsorption with decreasing adsorptive capacity.

It is questionable whether the points of highest energy level and greatest unsaturation in a metal surface are always the most active catalytically for every reaction.

L. S. Theobald.

Theory of electrolytic ions. XXXIV. Application of extrapolation method of Lorenz and Landé. R. Lorenz and J. Westenberger (Z. anorg. Chem., 1926, 157, 313—318; cf. A., 1926, 1008).—The relations between ionic mobilities discovered by Lorenz and Landé (A., 1923, ii, 9) receive further confirmation from the results of recent measurements (*ibid.*, 1926, 910).

R. Cuthill.

Electrical conductivity of solid oxide mixtures. P. Fischer (Z. Elektrochem., 1926, 32, 538—543).—Previous work on salt mixtures (A., 1926, 478) has been extended to include metallic oxides. The systems examined fall into three groups: (1) salt mixtures: no regular variation of conductivity with percentage composition; (2) oxide–salt mixtures, *e.g.*, manganese dioxide and potassium bromide: the conductivity–composition curve shows a maximum; (3) oxide mixtures, *e.g.*, cupric oxide and manganese dioxide: continuous increase or decrease of conductivity with composition. Whereas in group (1) values obtained with direct current and with alternating current often show wide divergences, they agree fairly closely in the other groups.

H. J. T. Ellingham.

Conductivity of stable aqua regia. E. Briner, R. Heberlein, and A. Rothen (Helv. Chim. Acta, 1926, 9, 951—956).—The conductivity of the aqueous phase in the equilibrium $HNO_3+3HCl \rightleftharpoons NOCl+2H_2O+Cl_2$ (cf. Briner, A., 1916, ii, 231) has been measured, using pure iridium electrodes, equilibrium being maintained by the use of a closed cell. The values of K, 0·326—0·324 and 0·465 ohm^{-1} at 0° and 20°, respectively, are independent of the proportions and concentration of the acid mixture.

J. W. Baker.

Electrical conductivity of mixtures of hydrochloric and sulphuric acids with orthophosphoric acid prepared in various ways. A. Kailan and J. Schroth (Monatsh., 1926, 47, 1—10; cf. Pessel, A., 1923, ii, 396).—The low conductivity found for solutions of hydrochloric or sulphuric acid with orthophosphoric acid prepared from lead pyrophosphate is shown to be due to phosphates present as impurities, the observed values agreeing with those calculated from the content of sodium salt found to be present. When the orthophosphoric acid is prepared from pure pyrophosphoric acid, the results agree with those obtained with the ortho-acid from phosphorus pentoxide. Pessel's observations on the velocities of hydration are confirmed.

G. M. Bennett.

Potential differences at phase boundaries at which partition equilibria exist. E. Baur and E. Allemann (Z. Elektrochem., 1926, 32, 547—550).—Improved methods are described for setting up cells of the types previously described (A., 1925, ii, 1164), whereby errors due to the presence of membranes are avoided. Revised values for these phase-boundary potentials are recorded. Measurements have now been made on cells of the type: Hg, HgCl|*N*-KCl in water (1)|*N*-KCl in amyl alcohol (2)|salt AB in amyl alcohol (3)|salt AB in water (4)|3·5*N*-KCl in water (5)|*N*-KCl in water (6)|HgCl, Hg. The *P.D.* between (2) and (3) is made zero by using a solution of the salt in (3) of such a concentration that it has the same electrical conductivity as (2). When the salt AB is a chloride, (5) and (6) are omitted. The *P.D.* at the various junctions are now either zero or capable of determination, except that between (3) and (4), which can thus be obtained from a measurement of the *E.M.F.* of the complete cell. The results are true "ionic partition potentials," and a comparison of their values for various salts suggests that each ion makes a specific contribution to such a potential, although this rule is probably not exact. The significance of these potentials is discussed.

H. J. T. Ellingham.

Potential of the fluorine electrode from thermal data. W. M. Latimer (J. Amer. Chem. Soc., 1926, 48, 2868—2869).—From recent thermal data of von Wartenberg (A., 1926, 476) the potential of the normal fluorine electrode is calculated to be 2·85±0·04 volts at 25°.

S. K. Tweedy.

Reduction–oxidation potentials. II. Colorimetric determination of reduction–oxidation potentials. P. Hirsch and R. Rüter (Z. anal.

Chem., 1926, 69, 193—232; cf. A., 1926, 930).—The reduction–oxidation (R–O) potential of a solution containing a substance and its oxidation or reduction product is shown from theoretical considerations based on the ionic hypothesis and the mass action law to be a function of the ratio of the two substances present; *i.e.*, for the reversible R–O process $E_h = E_0 + (0{\cdot}0577/n)\log([O]/[R])$ at 18°. Certain substances which undergo colour changes in the presence of oxidising or of reducing agents may be used as indicators for R–O potentials in the same way that certain dyes act as indicators of p_H; similarly, R–O buffer solutions of well-defined potential may be prepared for standardising the indicator solutions. The most suitable buffer solutions are mixtures of cuprous and cupric chlorides in potassium chloride solution when the acidity is greater than p_H 2·2, ferrous–ferric oxalate in sodium oxalate–oxalic acid solutions for p_H 2·7—4·2, and ferrous–ferric oxalate in citric acid–trisodium citrate solutions for p_H 5·2—6·0. The colour of methylene-blue in these buffer solutions has been fully investigated; the system methylene-blue–leuco-base is reversible in all solutions more acid than p_H 7. For a 50% reduction at 20°, the R–O potential of a methylene-blue solution decreases from +0·4206 volt at p_H 1·2 to +0·0920 volt at p_H 5·2, measured against the normal hydrogen electrode, and this fall is directly proportional to increase of p_H. A temperature change of 1° causes a change of 1 millivolt in the potential and a change of 2% in the depth of colour. To determine the R–O potential of a solution by means of the methylene-blue indicator, the p_H is first determined colorimetrically or otherwise; to 20 c.c. of the solution is added 1 c.c. of a 0·045% solution of methylene-blue, and the volume of water required to be added to a further 1 c.c. of the indicator solution to match the colour of the test solution is then determined. From this result, the colour intensity, $f/(1-f)$, is calculated and the value of A_h (a constant depending on the p_H of the solution) is read from a graph. Then the R–O potential of the solution is calculated from the equation $E_h = A_h + 0{\cdot}02935 \log f/(1-f)$; the result is the potential for 23°. The work of Clark and his collaborators on reduction potentials of certain dyes in equilibrium with their reduction products is discussed at length and shown to be in agreement with the theories recorded in this paper.

A. R. POWELL.

Electrochemical investigations on the metallic properties of iodine. W. FINKELSTEIN (Z. physikal. Chem., 1926, 124, 285—298; cf. A., 1925, ii, 546).—Measurements of the decomposition potentials of solutions of iodine trichloride, chloride, and bromide, and of the potentials of iodine electrodes in these solutions, have been made. The results are in accordance with the existence of iodine cations ($I^{\cdots}$ and $I^{\cdot}$). Other considerations support this view.

L. F. GILBERT.

Influence of traces of alkali or alkaline-earth metals on the normal cathode fall of potential of mercury. A. GÜNTHER-SCHULZE (Z. Physik, 1926, 39, 491—494).—The cathode fall of potential is greatly reduced by minute quantities of metals of the alkalis or alkaline earths.

E. B. LUDLAM.

Electrometric determination of small amounts of ferric iron. J. F. KING and R. N. WASHBURNE (J. Physical Chem., 1926, 30, 1688—1697; cf. Hostetter and Roberts, A., 1919, ii, 480).—A method is described for the determination of 0·0003—0·0005 g. of ferric iron by electrometric titration with titanous sulphate with an error of less than 0·1%. The apparatus includes an electrode of fine platinum wire (0·0085 mm. diameter) for use in hot solutions and a satisfactory means of storage of 0·0003*N*-titanous sulphate. Titrations are best carried out in 20% sulphuric acid solution and at the b. p. of the solution.

L. S. THEOBALD.

Overvoltage. I. Hydrogen overvoltage. T. ONODA (J. Fac. Sci. Tokyo, 1926, 1, 223—247).—The overvoltage of hydrogen at electrodes of platinum, gold, copper, or nickel depends to a considerable extent on the previous treatment of the electrode. After anodic polarisation, the value is a minimum, which is characteristic of the metal employed. With rise of temperature, this minimum decreases in a linear manner.

R. CUTHILL.

Apparatus for determining oxidation–reduction potentials. J. M. ORT (J. Opt. Soc. Amer., 1926, 13, 603—608).—By means of a reduction flask and a movable burette, solutions can be reduced, stored, and transferred to the electrode chamber without contact with air during the run. Active gases are removed by flushing with nitrogen. The electrode chamber is a large pyrex test-tube, closed with a rubber stopper, and provided with a gas outlet through a mercury trap. Extending nearly to the bottom of the chamber are the platinum electrodes, the glass tube of the nitrogen inlet, and the glass tube leading to the salt bridge. The latter tube dips into a beaker of saturated potassium chloride, into which three saturated calomel electrodes also dip. At any time during a run, the electrode chamber can be raised out of, or lowered into, the oil thermostat in which readings are taken. Full details of the method of using the apparatus are given.

L. L. BIRCUMSHAW.

Electrolytic polarisation. IV. Electrodeposition potentials of iron, cobalt, and nickel. V. Electrodeposition potentials of alloys of iron, cobalt, and nickel. S. GLASSTONE (J.C.S., 1926, 2887—2897, 2897—2902).—IV. Measurement of the initial deposition potentials of iron, cobalt, and nickel, at temperatures ranging from 15° to 95°, and in a series of solutions of known hydrogen-ion concentration, ranging roughly from p_H 2 to 6, shows that for each temperature the deposition potential has a definite value, depending only on the concentration of metal in the solution, and independent of the p_H of the electrolyte and of the nature of the anions present. The presence of a depolariser (*e.g.*, hydrogen peroxide) causes scarcely any change in the deposition potential. In each case, a considerable overvoltage is required to cause the initial deposition of metal, after which increase of current density produces only slight increase of polarisation. The results obtained do not appear to be in agreement with any of the theories previously advanced to account for the retarded deposition of the metals of the iron group. As an alternative hypothesis, it is suggested that the metals are primarily deposited in a metastable form which has a different electronic arrangement from the ordinary form (perhaps 2, 8, 16, 2, as compared with 2, 8, 17, 1 for the normal form), and a different deposition potential.

V. By means of the commutator–extrapolation method of measuring the potentials of polarised electrodes, the initial deposition potentials of alloys of iron, nickel, and cobalt, in pairs or all together, from solutions of various metallic and hydrogen-ion concentrations, have been measured at 15°, 55°, and 95°. Acetate buffer solutions were used to maintain a definite p_H. The initial deposition potential is independent of the p_H, but decreases with rising temperature, and with decreasing iron ratio (in the case of the iron alloys) or cobalt ratio (in the case of nickel–cobalt alloys) in the electrolyte. With iron–cobalt and iron–nickel alloys, the deposition potential is much closer to that of pure iron than would be expected. Applying this fact to the theory previously advanced to account for the retardation of the deposition of the iron-group metals, it is shown that for a given electrolyte the proportion of iron in the deposit should increase at first rapidly with increasing current density, then more slowly, and finally reach an almost constant value. L. L. Bircumshaw.

Periodic electrochemical passivity of iron, cobalt, nickel, and aluminium. E. S. Hedges (J.C.S., 1926, 2878—2887; cf. A., 1926, 807, 1213).—A study has been made of the periodic passivation of anodes of iron in sulphuric acid, nitric acid, and phosphoric acid, of cobalt in sulphuric acid, of nickel in sulphuric acid, and of aluminium in nitric acid and in sodium hydroxide. Experiments in which a passivated anode is progressively activated, (*a*) by raising the temperature, (*b*) by diluting the reagent, and (*c*) by addition of some agent favouring the active state (*e.g.*, ammonium chloride to an ammonium sulphate solution in which a nickel anode has been made passive), support the view that periodicity ensues whenever the anode is given equal opportunities of existing in the active or passive state. Evidence in favour of the suggestion that passivity is a special case of film formation is drawn from a comparison of the behaviour of a nickel anode in 5% sulphuric acid with that of a zinc anode in sodium hydroxide. In every case investigated, passivation is immediately preceded by the formation of a visible film on the metal, which disappears at the moment the electrode assumes the passive state. L. L. Bircumshaw.

Electrolysis of molten alloys. XVII. Zinc with lead, bismuth, and cadmium, antimony with lead and bismuth, and cadmium with lead and bismuth. R. Kremann and A. Troster (Monatsh., 1926, 47, 285—293).—Experimental difficulties were met with in all cases specified except that of the bismuth–cadmium alloys. Electrolysis of these mixtures containing 25, 50, and 75 atomic-% of bismuth was maintained for 20 hrs. The exceptionally large electrolytic effect, involving accumulation of bismuth near the anode, increased with rising current density up to 5—6 amp./mm.^{2} The maximum effect, obtained with an alloy containing 50 atomic-% of bismuth, produced a difference of concentration of 65·5% of bismuth. G. M. Bennett.

Electrolysis of molten alloys. XVIII. Summary of preceding papers. R. Kremann (Monatsh., 1926, 47, 295—306; cf. A., 1924, ii, 723; 1925, ii, 132, 312, 678, etc.).—The accumulation of one constituent metal of a molten alloy in a higher concentration near the cathode during electrolysis is compared with the analogous case of gas mixtures (Skaupy, A., 1916, ii, 466, 469). For a given alloy, this effect is remarkably constant when the temperature is varied over a range of several hundred degrees, which indicates that the electrolytic transport increases with rise of temperature to the same extent as the opposed diffusion. The relatively small effect observed in certain alloys (*e.g.*, Bi–Pb) studied at high temperatures is to be attributed to the specific character of the individual metals rather than to the influence of increased diffusion. For production of the maximum effect, an alloy containing 50 atomic-% of each metal must be electrolysed with a current density of an upper limiting value for 3—24 hrs. The following series shows in descending order the tendency to migrate to the cathode: He, Ne, A, Bi, Sb, Hg, Pb, Sn, Zn, Cd, Cu, Ag, Al, Na, K. This series gives approximately the order of diminishing ionisation potentials, but the difference between the ionisation potentials of two metals is not a quantitative indication of the magnitude of the electrolytic effect. The current is carried both by liberated electrons and by the metal ion M^+. The positions of aluminium and lead in the above series are not in accord with their positions in the series of ionisation potentials, which may be due partly to the liberation of a second electron from the metal and partly to the electrolysis of intermetallic compounds $M_1M_2 \rightleftharpoons M_1^+ + M_2^-$. Wherever one constituent of the alloy is of markedly metalloid character (*e.g.*, Bi, Sb), the effect of electrolysis is large. G. M. Bennett.

Electrolysis of glass. I. H. Hurter (Helv. Chim. Acta, 1926, 9, 1069—1073).—The quantity of sodium (as measured by the increase in weight of the lamp) introduced into the high vacuum of an electric light bulb in accordance with the method of Burt (A., 1925, ii, 921) is in exact agreement with Faraday's laws. Contrary to the conclusion of Burt, substitution of potassium for sodium ions occurs when the bulb is immersed in a bath of molten potassium nitrate during the passage of the current, the substitution again being in agreement with Faraday's laws; both the red potassium lines are shown by the spectrum. J. W. Baker.

Electrolysis of dichromic acid under a mercury vapour lamp of high intensity. G. S. Forbes and P. A. Leighton (J. Physical Chem., 1926, 30, 1628—1633).—Electrolysis of 0·006—0·05N-chromate solutions in N- and 3N-sulphuric acid between platinum electrodes has been carried out at different current densities, and the electrochemical yields in light and in the dark compared. At the illuminated cathode, 0·5% greater efficiency was observed, but part or all of this can be attributed to local heating in the thin diffusion layer at the cathode. The curves obtained by plotting electrochemical yields against current densities show maxima and minima, explicable, for the most part, in terms of the formation of hydrogen and of hydrogen peroxide.

A quartz–mercury lamp, consuming 1500 watts and intensely illuminating a horizontal surface, is described. L. S. Theobald.

Apparently unimolecular reaction. Homogeneous decomposition of gaseous propaldehyde. C. N. Hinshelwood and H. W. Thompson (Proc. Roy. Soc., 1926, A, **113**, 221—229).—The decomposition of propaldehyde has been studied between 722° and 877° Abs. Carbon monoxide is removed from the molecule in almost theoretical amount, and the residual fragments give rise to a mixture consisting principally of methane and ethane, with small amounts of more highly-condensed products, whilst about 2% of carbon dioxide and ethylene are also formed. The relative proportion of methane increases with rise of temperature. The decomposition is a homogeneous reaction which is very nearly unimolecular at pressures above 100 mm. The velocity coefficients rise from $0{\cdot}052\times10^{-3}$ at 722° to $39{\cdot}4\times10^{-3}$ at 877° Abs. The heat of activation is 55,000 g.-cal. At 800° Abs., the number of molecules reacting is approximately 2×10^{16} per c.c. per sec. at 760 mm., whilst the number of collisions is only about 5×10^{13}. At low pressures, the unimolecular velocity coefficients appreciably diminish, but not in the manner characteristic of a bimolecular reaction (cf. following abstract). W. Hume-Rothery.

Theory of unimolecular reactions. C. N. Hinshelwood (Proc. Roy. Soc., 1926, A, **113**, 230—233).—It is usually supposed that the energy of activation is confined to a few degrees of freedom, in which case the chance that a molecule possesses energy in excess of E is $e^{-E/RT}$. The rate of bimolecular reactions is adequately expressed by the equation, number of molecules reacting$=Ze^{-E/RT}$, where Z is the number entering into collision. If molecules are activated by collision in unimolecular reactions and Lindemann's mechanism (Trans. Faraday Soc., 1922, 17, 599) operates, the energy E ought in unit time to be communicated to more molecules than the number reacting, but actually many more molecules react than the expression $Ze^{-E/RT}$ allows for (cf. preceding abstract). Lindemann suggested (private communication) that there might be enough collisions for unimolecular reactions if the total energy E could be made up by any distribution among a number of degrees of freedom. Calculation shows that for propaldehyde (cf. preceding abstract) from 12 to 14 degrees of freedom would be required for this mechanism to operate; for acetone and nitrogen pentoxide, even more degrees of freedom would be required. The mechanism is thus possible only in the case of molecules of complex internal structure, in agreement with the fact that all known unimolecular changes involve molecules of complex structure, whilst bimolecular reactions, where the simple activation theory holds, usually involve simpler molecules. W. Hume-Rothery.

Supposed law of flame speeds. W. A. Bone (Nature, 1926, **118**, 837).—Experiments with acetylene–hydrogen–oxygen and ethylene–hydrogen–oxygen mixtures do not support the claim that Wheeler and Payman's law of flame speeds is of universal application. A. A. Eldridge.

Effect of hydrogen-ion concentration on the rate of hydration of sodium pyrophosphate. S. J. Kiehl and W. C. Hansen (J. Amer. Chem. Soc., 1926, **48**, 2802—2814).—The rate of hydration of sodium pyrophosphate, $Na_4P_2O_7+H_2O \rightleftharpoons 2Na_2HPO_4$, was followed by hydrogen-ion concentration measurements in 0·125, 0·175, and 0·225*M*-solutions, each containing 0·350, 0·425, and 0·500*M*-hydrochloric acid. When the hydration exceeded 50%, the orthophosphate was determined by a gravimetric method with the aid of "magnesium chloride mixture." The results indicate that pyrophosphoric acid is more active than orthophosphoric acid. S. K. Tweedy.

Inversion of sucrose by acids. H. Colin and A. Chaudun (J. Chim. phys., 1926, **23**, 808—813; cf. A., 1925, i, 233).—Addition of glycerol or increase in the concentration of sugar raises or lowers the velocity coefficient of the above process according as the catalyst is a strong or a weak acid. For weak acids, the ratio of the velocity coefficients for two concentrations of acid and a fixed initial concentration of sugar is nearly equal to the ratio of the conductivities of the solutions; with strong acids, the former value is the greater. The velocity coefficient is increased by the addition of a salt of an acid other than the catalyst, whether the latter is a strong acid or a weak acid. These facts can be accounted for on the basis of the mechanism previously suggested for the inversion (A., 1926, 580). R. Cuthill.

Esterification of malonic acid by glycerol and hydrogen chloride. A. Kailan and J. Schroth (Monatsh., 1926, **47**, 63—81; cf. A., 1914, ii, 41; 1925, i, 880, ii, 49).—The esterification of malonic acid in a glycerol solution of hydrochloric acid with or without the addition of water (2/3 and 4/3 mols. per litre) proceeds according to a unimolecular law with a velocity which is proportional to the concentration of hydrochloric acid. The variation of the velocity coefficient with the varying concentration of acid and of water at 25° and 35° follows a relation of the simple type previously used for the values for malonic acid in ethyl alcohol. The effect of water in depressing the reaction velocity is much less in glycerol than in ethyl alcohol. The values of the coefficient decrease more than can be accounted for by the effect of the water produced in the reaction; this is attributed to a velocity of esterification of the first carboxyl group somewhat higher than that for the second. G. M. Bennett.

Stability of benzenediazonium chloride solutions. II. Reaction of benzenediazonium chloride with certain organic hydroxy-substances. H. A. H. Pray (J. Physical Chem., 1926, **30**, 1477—1486; cf. A., 1926, 1214).—The velocity of reaction of benzenediazonium chloride with various alcohols and organic acids has been determined at 20°, 30°, 40°, and 50°. The reactions are unimolecular or pseudo-unimolecular, and the values of $0{\cdot}4343k \times 10^{1}$ at 30° and 40°, respectively, are for the alcohols as follow: methyl, 53·5, 227; ethyl, 53·5, 218; *n*-propyl, 52·0, 204·2; *iso*propyl, 69·0, 288; *n*-butyl, 50, 201; *iso*butyl, 54, 208; amyl, 46·3, —; allyl, 41·7, —; benzyl, —, 153·0; and for the acids: formic, 18·6, 73·1; acetic, 18·7, 82·0; propionic, 18·9, 82·0; butyric, 23·0, 102·0; dichloroacetic, —, 53·1, and for water, 25·0, 107·0. The temperature coefficients vary markedly with temperature. The rate of reaction of benzenediazonium chloride in methyl alcohol–water mixtures is an additive function of the mol. percentage of the components of the solvent. Benzenediazonium chloride is insoluble in a large number of organic liquids with which it does not react. It is slightly soluble in furyl alcohol, pyridine, and quinoline, but the addition of water or alcohol does not cause the liberation of nitrogen in these cases. Selenium and phosphorus oxychlorides and arsenic trichloride dissolve and decompose the diazo-compound, and in the last-named case the rate of decomposition is the same as in water. Collodion has no effect on the velocity of reaction between benzenediazonium chloride and ethyl alcohol.

The theory of the mechanism of diazo-decomposition of Hantzsch is inadequate for the above results, and further, there is no simple relation between the physical properties of the solvent and the velocity of decomposition. L. S. Theobald.

Velocity of hydrolysis of pentaerythritol tetra-acetate. A. Skrabal and M. Zlatewa (Monatsh., 1926, 47, 39—56).—The hydrolysis of pentaerythritol tetra-acetate is an apparently bimolecular reaction in both acid and alkaline solution. The velocity coefficients at 25°, referred to molar concentrations of hydrogen and hydroxyl ions, respectively, are 0·00432 and 20·5. The latter figure was determined in sodium carbonate solution; the value for the reaction in sodium hydroxide solution is computed to be 26·6. The reason for the simple course of the hydrolysis of the esters of glycol, glycerol, and pentaerythritol is discussed. The following influences are distinguished, which together determine the velocity of such reactions: (*a*) depressing effect of steric hindrance, (*b*) increase of velocity with any increase of acid character of either the acid or the alcohol component of the ester, (*c*) mutual reinforcement of active groups in the molecule, and (*d*) a depression with increasing symmetry of the molecule. The case of glyceryl esters with one group in a less favourable position than the others involves a diminishing velocity of reaction, particularly in alkaline solution. The effect of migration of acyl groups is discussed. G. M. Bennett.

Influence of the alcohol component on velocity of hydrolysis of acetic esters. A. Skrabal and A. M. Hugetz (Monatsh., 1926, 47, 17—38; cf. A., 1924, ii, 842; 1926, 1010).—The following velocity coefficients for alkaline hydrolysis (k_a) and for acid hydrolysis (k_s), respectively, have been found at 25°, the values being expressed in minutes and referred to unit molar concentration of hydrogen or hydroxyl ions: *iso*propyl acetate, 1·57, 0·00360; *tert.*-butyl acetate, 0·090, 0·00758; phenyl acetate, 82·0, 0·00469; benzyl acetate, 11·8, 0·00654. The alkaline hydrolysis of phenyl acetate was carried out with sodium phenoxide. The general question of the variation of the velocity of hydrolysis of esters with the nature of the alcohol component is discussed, and the results are compared with those obtained in the study of other reactions. G. M. Bennett.

Velocity of saponification of mono- and di-substituted chloro- and methoxy-derivatives of ethyl benzoate. W. Blakey, H. McCombie, and H. A. Scarborough (J.C.S., 1926, 2863—2868).—The velocities of saponification of ethyl benzoate, *o*-, *m*-, and *p*-methoxy- and -chloro-benzoate, 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, 3 : 5-dimethoxy- and -dichloro-benzoate have been determined in 95% and 70% alcohol–water mixtures. With one exception, the *m*-chloro- and *m*-methoxy-esters are the more reactive. The values for *k* for the dimethoxy-esters bear a definite relation to those of the monomethoxy-esters; for the dichloro-esters, no relationship was observed. Change of solvent changes the order of the velocity coefficients for the monomethoxy-esters. W. Thomas.

Initial stages of dehydrogenation and isomeric change of allyl alcohol. F. H. Constable (Proc. Roy. Soc., 1926, **A**, 113, 254—258).—When the vapour of allyl alcohol is passed over a heated copper catalyst, two simultaneous reactions occur, producing respectively propaldehyde and a mixture of acraldehyde and hydrogen. A study of the two reactions was made over the temperature range 245—280°. The rate of dehydrogenation is approximately equal to that of ethyl alcohol, and has a temperature coefficient of 1·5, whilst the isomeric change to propaldehyde is considerably faster, but has a diminished temperature coefficient of 1·16. The isomeric change is more easily catalysed by sintering the catalyst than is the dehydrogenation. It appears that there are two sets of centres of activity, one characteristic of each reaction, and it is therefore considered that true isomeric change occurs, and not rehydrogenation. E. S. Hedges.

Corrosion of steel by acids. V. Duffek.—See B., 1926, 949.

Acid and salt effects in catalysed reactions. II. Minimum reaction velocities for acid–salt mixtures. H. M. Dawson and N. C. Dean (J.C.S., 1926, 2872—2878).—The significance of the reaction velocity minimum for acid–salt mixtures of the type $C\cdot HA - x\cdot MA$ is discussed. The hydrogen-ion concentration of the minimum velocity mixture depends on the catalytic coefficients of the hydrogen and acid ions, on the dissociation constant of the acid, and on its concentration. The velocity–p_H curve is symmetrical with respect to the minimum velocity point. Results indicate that salts in aqueous solutions are completely ionised, and that the catalytic activity of a catalyst is proportional to its concentration and has no apparent connexion with the thermodynamic activity. The results are confirmed by the study of the catalytic effect of $0\cdot05N$-acetic acid$+xN$-sodium acetate on the rate of interaction of iodine and acetone. W. Thomas.

Dehydration by means of acetic anhydride. J. B. Menke (Chem. Weekblad, 1926, 23, 552—553).—The reaction between acetic anhydride and water is accelerated by mineral acids and their salts;

hydrated salts may be rapidly and completely freed from water by addition of the anhydride.
S. I. Levy.

Rôle of certain metallic ions as oxidation catalysts. S. F. Cook (J. Gen. Physiol., 1926, **10**, 289—312).—Measurements have been made of the rate at which pyrogallol is oxidised by hydrogen peroxide in the presence of an iron or a copper salt as catalyst. The reaction is also catalysed, but less strongly, by salts of silver, gold, cobalt, and nickel. In the case of silver and gold salts, the reaction rate suddenly decreases and at the same time the metal separates from the solution. Although gold salts act as catalysts, colloidal gold is inert. It is concluded that the activity of metal catalysts depends on their ability to form metallic peroxides and at the same time to remain in solution. W. O. Kermack.

Autoxidation and anti-oxygens. XX. Catalytic action of another series of nitrogen compounds. General observations on nitrogen compounds. C. Moureu, C. Dufraisse, and M. Badoche (Compt. rend., 1926, **183**, 823—826).—The action of 37 nitrogen compounds in exalting or diminishing the autoxidation of acraldehyde, benzaldehyde, and styrene has been studied. The nitroso-bases are the most frequently inactive or only slightly active, but the other results are difficult to summarise. Although 177 substances have so far been investigated, few general rules can yet be given. However, the presence of nitrogen in a molecule usually confers an exalting or a diminishing action with respect to autoxidation reactions. It might be thought that this would be of great importance biologically, but actually the effect is not large, owing to the simultaneous presence of carboxyl groups, which tend to diminish the activity of the amino-groups, and also to the fact that the nitrogen is often combined in the inactive amido-form. S. J. Gregg.

Catalytic activity of contact substances. IV. H. Remy (Z. anorg. Chem., 1926, **157**, 329—338).—The results previously obtained (cf. A., 1926, 134) for the catalysis of the combination of hydrogen and oxygen are examined in the light of Bodenstein's theory (*ibid.*, 1925, ii, 216) that in heterogeneous catalysis the molecules are rendered active by being deformed by the unsaturated surfaces of crystalline substances. If, as Hofmann and Ebert suppose (*ibid.*, 1917, ii, 25), the catalyst first activates both the hydrogen and the oxygen, its activity will depend on its affinity for oxygen as well as on its solvent power for hydrogen. If the former quantity be small but the latter great, then on charging the catalyst with oxygen the small amount that it takes up will be in a highly reactive state, whilst the affinity for hydrogen will still be great. On the other hand, the catalyst charged with hydrogen will have little activating effect on oxygen, so that the catalytic activity will be small. As would therefore be expected, the results show that if the pure metals examined are arranged in order of increasing solvent power for hydrogen and increasing affinity for oxygen, a metal which occurs earlier in the first series than it does in the second is more active when charged with hydrogen than when charged with oxygen, and *vice versa.* Alloys of metals of the eighth group of the periodic classification behave in a similar manner, except those composed of metals of the iron group. The catalytic activity is also dependent on the readiness with which the deformed molecules combine with the catalyst. If this be assumed, for oxygen, to run parallel with the heat of formation of the oxides, metals the oxides of which have large heats of formation would be expected to be relatively poor catalysts; this probably accounts for the small catalytic activity of metals of the iron group. R. Cuthill.

Catalytic oxidation of carbon monoxide in contact with quartz glass. A. F. Benton and T. L. Williams (J. Physical Chem., 1926, **30**, 1487—1496).—Langmuir's explanation (A., 1917, ii, 19) of the results obtained by Bodenstein and Ohlmer (*ibid.*, 1905, ii, 692) has been examined by measuring the amount of carbon monoxide, and oxygen in certain cases, adsorbed by powdered quartz glass at 760 mm. and at 0°, 25°, 218°, 300°, and −79°, and also at low pressures. The adsorption is practically immeasurable and certainly less than 3% of the surface is involved.

Measurements of reaction velocity showed that quartz glass, when carefully freed from impurities, is a poor catalyst, and although the surface of the catalyst was greater, the rates of reaction found at 500° were smaller than those obtained by Bodenstein and Ohlmer (*loc. cit.*). This difference is attributed to the presence of impurities in the latter case. Further, the retarding influence of carbon monoxide found by the last-named workers was not confirmed. The reaction velocity is directly proportional to the pressure of the oxygen and to the square root of the pressure of the carbon monoxide, but quantitative results are difficult to reproduce.
L. S. Theobald.

Mechanism of activation of catalytic surfaces. H. S. Taylor (Proc. Roy. Soc., 1926, **A**, **113**, 77—86).—The mechanism of catalytic activation is discussed with special reference to recent experimental work indicating that the activation of diatomic molecules at metallic surfaces involves the production of adsorbed atoms. The following explanations are given of the unimolecular decomposition of hydrogen iodide and of ammonia at platinum surfaces discovered by Hinshelwood and Burk (A., 1925, ii, 691). In the gaseous phase, the unimolecular and bimolecular decompositions of hydrogen iodide involve the following amounts of energy: $HI=H+I-68$ kg.-cal. and $2HI=H_2+I_2-3$ kg.-cal. Since the bimolecular critical increment is only 44,000 g.-cal. per 2 mols., the gaseous decomposition is bimolecular. At the platinum surface, it is assumed that the first stage is the adsorption of hydrogen iodide on the platinum and its decomposition to give a free iodine atom, and an adsorbed hydrogen for which the thermal change is $Pt+HI=Pt(H)+I-15$ kg.-cal. The adsorbed hydrogen atom is then struck by a hydrogen iodide molecule, when the following changes occur: (i) $Pt(H)+HI=Pt(H_2)+I+x$ kg.-cal., (ii) $Pt(H_2)=Pt+H_2+y$ kg.-cal., where y lies between −10 and −25 kg.-cal., and x between −8 and +7 kg.-cal., according to different workers. By this mechanism, the unimolecular decomposition is changed from a single stage requiring 68 kg.-cal., to a series of changes none of which requires more than 25 kg.-cal., so that the energy of activation is probably reduced and the catalytic action is understood. The decomposition of ammonia is somewhat similarly explained, but the removal of adsorbed hydrogen atoms with colliding ammonia is not possible. The adsorbed hydrogen atoms are removed by evaporation or reaction with adjacent atoms, in agreement with the observation of Hinshelwood and Burk (*loc. cit.*) that the surface is poisoned by hydrogen atoms.

W. Hume-Rothery.

Dissociation of methane. F. E. C. Scheffer, T. Dokkum, and J. Al (Rec. trav. chim., 1926, 45, 803—816; cf. Mayer and Altmayer, A., 1907, i, 457; Coward and Wilson, J.C.S., 1919, 115, 1380).—Determinations have been made of the compositions of mixtures of hydrogen and methane brought to equilibrium at 480—680° and atmospheric pressure by continuous circulation over finely-divided carbon and catalytic nickel. The mixture contains 59% of methane at 480°, falling to 18% at 680°, similar figures being obtained when the equilibrium is approached from either direction. The reaction involved is $C+2H_2=CH_4+18\cdot8$ kg.-cal. (at constant pressure). At lower temperatures, a carbide of nickel is involved which is exothermic and stable between 340° and 420°, and also occurs in a metastable state at higher temperatures. The carbide produces methane by the following reaction: $Ni_xC+2H_2=xNi+CH_4+11\cdot4$ kg.-cal. G. M. Bennett.

Poisoning action of oxygen on iron catalysts for ammonia synthesis. J. A. Almquist and C. A. Black (J. Amer. Chem. Soc., 1926, 48, 2814—2820).—The effect of oxygen (0·02—0·24 vol.-%) on the reaction $N_2+3H_2=2NH_3$ at 444° and 1 atm., in presence of promoted and unpromoted iron catalysts is to diminish the yield of ammonia to a constant amount, which is the lower the higher is the oxygen content, and for a given oxygen concentration is lower for the less active catalysts. Similar results are obtained when the oxygen is replaced by water vapour, which bears out the results obtained previously, *i.e.*, that the poisoning action of oxygen compounds is proportional to the oxygen content in those cases in which the oxygen is converted into water under the conditions of the experiment. Oxygen is retained by the catalyst during the reaction, probably in the form of an iron oxide. S. K. Tweedy.

Nature of the catalyst surface and the effect of promoters. J. A. Almquist (J. Amer. Chem. Soc., 1926, 48, 2820—2826; cf. preceding abstract).—A consideration of the previous results indicates that iron catalysts contain atoms of various degrees of unsaturation capable of catalysing the ammonia synthesis and of forming oxide in presence of water vapour at low concentrations (cf. Kubota and Yoshikawa, A., 1925, ii, 1174). Calculations based on the amounts of oxygen retained by the iron in the above experiments show that in pure iron about 1 atom in 2000 atoms is active and in iron promoted with alumina about 10 times this number.

S. K. Tweedy.

Influence of added substances on the mode of fixation of nitrogen by mixtures of barium carbonate and carbon. P. Askenasy [with J. Bring].—See B., 1926, 978.

Negative catalysis in the oxidation of benzaldehyde. O. M. Reiff.—See this vol., 57.

Reversal of chemical reactions by electrolysis. R. Saxon (Chem. News, 1926, 133, 342).—An attempt to reverse certain precipitation reactions. A porous pot surrounds a carbon anode, and in this anode chamber are placed ammonium chloride solution and a sparingly soluble or an insoluble salt (gypsum, Iceland spar, calamine, etc.). Using high voltages, it is found that the metallic salt undergoes partial decomposition, appreciable quantities of the corresponding chloride being found in the solution.

J. S. Carter.

Electrolytic preparation of sodium perborate. U. Sborgi and D. Lenzi.—See B., 1926, 985.

Decomposition of nitrogen pentoxide by light. C. S. Fazel and S. Karrer (J. Amer. Chem. Soc., 1926, 48, 2837—2839).—Previously recorded results on the decomposition of nitrogen pentoxide and dioxide mixtures by light are accounted for if the energy absorbed by the dioxide molecules is transferred to the pentoxide molecules by collisions of the second type (cf. Klein and Rosseland, A., 1921, ii, 291; Dickinson, *ibid.*, 1924, ii, 841). The dioxide molecules absorb light of wave-length 0·460 μ and transfer this energy to, and so cause decomposition of, the pentoxide molecules, which are unable to absorb light corresponding with their critical energy increment. S. K. Tweedy.

Colour produced by the action of light on concentrated solutions of ammonium thiocyanate. E. A. Werner and K. C. Bailey (J.C.S., 1926, 2970—2971).—The pink coloration developed in ammonium thiocyanate or its concentrated solution on exposure to light is believed to be due to the dissociation of the salt into ammonia and thiocyanic acid, and not to the formation of sub-microscopic sulphur (Holmes, A., 1926, 920). The possibility of the colour being due to traces of iron is being investigated. W. Thomas.

Photochemical decomposition of aqueous formic acid solutions. A. J. Allmand and L. Reeve (J.C.S., 1926, 2852—2863).—Light of wave-length 250—300 μμ decomposes formic acid according to the two primary reactions $H\cdot CO_2H \longrightarrow CO_2+H_2$, and $H\cdot CO_2H \longrightarrow CO+H_2O$, the former taking place to the extent of about six times the latter, and this relative occurrence is not dependent on wave-length (cf. Berthelot and Gaudechon, A., 1910, ii, 814). With concentrated solutions, the greater part of the nascent hydrogen and carbon monoxide molecules, especially the former, reduce the formic acid to formaldehyde and other more highly-reduced products. For 0·11—2·4*M*-solutions, the quantum efficiencies for formic acid decomposition are of the order 1·0 for 300, and 2·7 for 260 μμ. W. Thomas.

Photochemical decomposition of aqueous oxalic acid solutions. A. J. Allmand and L. Reeve (J.C.S., 1926, 2834—2851).—The initial stages of the photolysis of aqueous oxalic acid have been quantitatively investigated by specially developed experimental methods. Monochromatic light of wave-length between 254 and 365 μμ was employed, the extent and nature of the decomposition being followed by measurement and analysis of the evolved gases. Contrary to the statements of Berthelot and Gaudechon (A., 1914, ii, 602), there is, under these conditions, only one primary reaction: $C_2H_2O_4 \longrightarrow H{\cdot}CO_2H+CO_2$. Neither hydrogen nor carbon dioxide is produced. Formaldehyde (the vapour of which is liable to be analysed as a mixture of carbon monoxide and hydrogen) is formed in small quantity, probably by the interaction between nascent carbon dioxide molecules and water. The amount of formaldehyde formed increases with the frequency of light used, and increases with dilution of the oxalic acid. For solutions of concentration 0·6—0·7*M*, the numbers of quanta required for the decomposition of 1 mol. of oxalic acid are as follows: 265 μμ, 100; 300 μμ, 245; 365 μμ, 1060. Quantum efficiencies are probably greater for solutions of concentration 0·01*M* and particularly 0·001*M*. This is interpreted by assuming a finite life for the photo-activated oxalic acid molecules before decomposition, coupled with deactivation from collision with another oxalic acid molecule (cf. Ghosh and Mukherjee, A., 1925, ii, 1179).

W. Thomas.

Photochemical studies. IV. Thermal decomposition of anhydrous oxalic acid and its relation to photochemical decomposition. D. E. Wobbe and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1926, 48, 2856—2868).—The thermal decomposition of anhydrous oxalic acid (d^{25} 1·873) between 130° and 170°, $(CO_2H)_2=H{\cdot}CO_2H+CO_2$, is nearly of zero order, the constants being given by the equation $\log_{10}k=22{\cdot}548-11227/T$. The reaction probably takes place on the surface of the crystals. The progressive increase of k with time at the lower temperatures indicates adsorption of the reaction products by the glass and by the acid itself. The results confirm those published previously (Noyes and Kouperman, A., 1923, ii, 527). The critical increment is about 51,400 g.-cal. The photochemical decomposition of the acid is brought about by radiation of wave-length 0·250 μ or less, the wave-length predicted by the radiation hypothesis, viz., 0·550 μ, being without measurable effect. The suitability of the reaction for testing the radiation hypothesis is queried.

S. K. Tweedy.

Chemical action of cod-liver oil and of adrenaline on the photographic plate. P. Niederhoff (Biochem. Z., 1926, 176, 478—482).—The action of cod-liver oils from various sources and of adrenaline on photographic plates is a purely chemical effect comparable with the darkening action of resins, oils, and hydrogen peroxide on silver bromide and is not due to radiation. C. Rimington.

Chemical reactions of hydrogen atoms. H. S. Taylor (J. Amer. Chem. Soc., 1926, 48, 2840—2848).—Two simple quartz mercury arcs suitable for the preparation of atomic hydrogen are described. The chemical properties of atomic hydrogen prepared by the methods of Wood (A., 1922, ii, 759) and of Cario and Franck (*ibid.*, ii, 809) are detailed, and the preliminary results of some investigations by the author and co-workers are mentioned. Thus hydrogen atoms react with oxygen to form hydrogen peroxide as an initial product, which decomposes to water in ultra-violet light. Ethylene is quantitatively reduced to ethane. Contrary to the results of Hirst (*ibid.*, 1926, 583), and in agreement with those of Bonhoeffer (*ibid.*, 583, 586), no reaction occurs with nitrogen. Carbon dioxide reacts slowly, forming the monoxide and oxygenated organic compounds. Rideal and Hirst's suggestion (*ibid.*, 486) that excited hydrogen molecules, and not atomic hydrogen, cause certain reactions attributed to the latter is considered to be improbable in the light of published results (Senftleben, *ibid.*, 1925, ii, 883). The presence of hydrogen atoms at cathodes during electrolysis, as well as in oxy-hydrogen flames, is indicated. Experiments by Compton and Turner (A., 1924, ii, 639) point to the mechanism $Hg'+H_2=HgH+H$ for the production of atomic hydrogen by the Cario–Franck method (cf. Taylor and Marshall, A., 1925, ii, 1078). S. K. Tweedy.

Displacement of metals from solutions of their salts by less electropositive elements. III. Action of liquid ammonia solutions of salts of the alkali and alkaline-earth metals on magnesium and other elements. F. W. Bergstrom (J. Amer. Chem. Soc., 1926, 48, 2848—2856; cf. A., 1925, ii, 885).—The extremely slow reaction $Mg+2NH_3=Mg(NH_2)_2+H_2$ is catalysed by salts of the alkali and alkaline-earth metals (excluding cæsium chloride, sodium tetrasulphide, strontium and barium iodides, and sodium nitrate): $2NaCl+Mg \rightleftharpoons MgCl_2+2Na$; $2Na+2NH_3=2NaNH_2+H_2$; $2NaNH_2+MgCl_2=Mg(NH_2)_2+2NaCl$. When heated at 350—400° in a vacuum, magnesium amide yields light yellow deammonation products. Sodium chloride or potassium cyanide in liquid ammonia has little or no action on metals less electropositive than magnesium. Potassium thiocyanate in liquid ammonia removes all trace of magnesium from its amalgam, forming soluble magnesium thiocyanate and potassium amalgam. The ultimate product of the action of potassium amide on magnesium in ammonia solution is the sparingly soluble potassium ammonomagnesiate, which is also produced by the action of a solution of potassium on magnesium. The sodium salt reacts with water to form sodium and magnesium hydroxides and ammonia. It reacts with magnesium to form magnesium amide; the latter is also formed by the action of amides of lithium and sodium and a solution of sodium in ammonia on magnesium. By analogy, the reaction between magnesium and sodium iodide in aqueous solution, in so far as it is exclusive of electrochemical influences, may be represented: $2NaI+Mg \rightleftharpoons MgI_2+2Na$; $2Na+2H_2O=2NaOH+H_2$; $2NaOH+MgI_2=Mg(OH)_2+2NaI$. S. K. Tweedy.

Dehydration of metallic salt hydrates. I. Sodium borate, carbonate, and sulphate. M. A. Rakusin and D. A. Brodski.—See B., 1926, 1011.

Basic sulphate of copper. H. T. S. Britton (J.C.S., 1926, 2868—2872).—A criticism of Fowles' paper (A., 1926, 922). Phase-rule studies at 25° and 100° indicate that the compound $4CuO,SO_3,4H_2O$ is the only basic sulphate of copper. W. Thomas.

Changes in heterometallic complex compounds on heating. A. Grünberg and N. Pschenitzin (Z. anorg. Chem., 1926, 157, 173—189).—*Triethylenediaminezinc chloroplatinite*, $[Zn(en)_3][PtCl_4]$ (red), and *triethylenediaminecadmium chloroplatinite*, $[Cd(en)_3][PtCl_4]$ (red), have been prepared by the action of potassium chloroplatinite on the complex triethylenediamine sulphate. The corresponding copper *compound*, $[Cu(en)_3][PtCl_4]$ (lilac), is obtained by adding potassium chloroplatinite to an aqueous solution of copper sulphate saturated with ethylenediamine. When these salts and the analogous nickel salt are heated, part of the ethylenediamine is driven off, and the remainder wanders to the platinum atom, so that the residue consists of the chloride of the particular metal concerned and the compound $[Pt(en)_2]Cl_2$. With the zinc and cadmium salts these combine to form the *compounds* $[Pt(en)_2]Cl_2,ZnCl_2$ and $[Pt(en)_2]Cl_2,CdCl_2$, respectively. In the case of the copper compound, *diethylenediaminecopper chloroplatinite*, $[Cu(en)_2][PtCl_4]$ (reddish-violet), is an intermediate product. The temperatures at which the above migration occurs increase in the order: copper, zinc, cadmium, nickel. The compound $[Ag(en)]_2[PtCl_4]$ behaves when heated in the same way as the above, except that no ethylenediamine is given off.

R. Cuthill.

Displacement reactions of complex compounds. A. Grünberg (Z. anorg. Chem., 1926, 157, 201—210).—The equilibrium $[M(en)_3]X_2+2nH_2O \rightleftharpoons [M(en)_{3-n}(H_2O)_{2n}]X_2+n\,\mathrm{en}$, where M is a metal and X an acid radical, seems to exist in aqueous solutions of the triethylenediaminates of bivalent metals. If to a solution of triethylenediaminezinc sulphate there is added nickel sulphate, the ions $[Ni(en)_3]^{\cdot\cdot}$ and $[Ni(en)_2]^{\cdot\cdot}$ are formed, the amine passing to the metal capable of forming the more stable complex ion. Analogous results are obtained if the zinc salt is replaced by the corresponding cadmium compound, or if copper sulphate is used instead of nickel sulphate. R. Cuthill.

Precipitation of metals from non-aqueous solutions. II. Reactions of zinc and cadmium with nickel and cobalt chlorides in absolute ethyl alcohol. R. Müller and F. R. Thois (Z. anorg. Chem., 1926, 157, 349—370; cf. A., 1926, 1016).—The precipitation of nickel and cobalt from solutions of their chlorides in absolute alcohol by zinc and cadmium at the ordinary temperature is slow and incomplete, the precipitated metal being in the form of a loose powder. If even minute traces of water are present, some hydroxide is produced in the process. The general phenomena observed are very similar to those previously recorded (*loc. cit.*) for solutions in 98% alcohol. After being annealed by heating at 150°, the precipitates have an electrode potential equal to that of the precipitating metal.

R. Cuthill.

Element 61. L. Rolla and L. Fernandes (Z. anorg. Chem., 1926, 157, 371—381).—A claim for priority over Harris and Hopkins (A., 1926, 810) in the discovery of the above element. By fractional crystallisation of the double thallium, ammonium, and magnesium nitrates of the constituents of commercial didymium oxide, solutions were obtained the absorption spectra of which showed irregularities ascribed to the presence of a new element. Confirmatory evidence was afforded by the application of *X*-ray methods. R. Cuthill.

Germanium. III. Salts of germanic acid. W. Pugh (J.C.S., 1926, 2828—2832).—The rate and extent of displacement of carbon dioxide from the carbonates of lithium, sodium, and potassium by germanium dioxide are parallel with the extent to which the various carbonates lose carbon dioxide by dissociation. The salts $Na_2GeO_3,7H_2O$ and $Li_2GeO_3,\frac{1}{3}H_2O$ have been crystallised from water; the potassium salt is too soluble to be crystallised. Metagermanates of lithium, barium, lead, and silver have been prepared by precipitation with sodium metagermanate. W. Thomas.

Oxidation of stannous to stannic salts. S. Komaretzkyj (Z. anal. Chem., 1926, 69, 257—260).—When a solution of stannous chloride is boiled with sodium thiosulphate, the pale brown precipitate obtained consists of monothio-β-stannic acid, $SnS(OH)_2$, which is decomposed by dilute hydrochloric acid into stannic chloride and stannic sulphide. Addition of thiosulphate to a hot acid solution of stannous chloride results in the direct formation of stannic chloride according to the equation $SnCl_2+Na_2S_2O_3+4HCl=SnCl_4+2NaCl+H_2O+H_2S+SO_2$. Similar reactions occur when stannous chloride is boiled with ammonium or potassium disulphide, and it is shown that the oxidising agent in all cases is the colloidal sulphur first produced by the decomposition of the precipitant by the acid formed in the hydrolysis of the stannous salt or originally present in the solution.

A. R. Powell.

Action of molecular oxygen and hydrogen on sodium azide. K. A. Hofmann and U. Hofmann (Ber., 1926, 59, [*B*], 2574—2579; cf. A., 1926, 370).—Sodium azide when rendered unstable thermally in an atmosphere of oxygen is converted almost quantitatively into sodium nitrite and oxygen. Catalysts or carriers are unnecessary, but the presence of free alkali is essential to delay the transformation $3NaN{:}{=}$ into Na_3N+N_2 until the oxygen molecule can penetrate the nitrogen zone. Oxidising agents such as copper oxide, manganese dioxide, and lead dioxide merely facilitate the removal of nitrogen by oxidising the sodium, whereas peroxides such as barium peroxide have the same effect as gaseous oxygen, since they furnish molecular oxygen. It therefore appears probable that the direct combustion of ammonia to nitrite and subsequently to nitrate at a basic contact depends on an unstabilising of the molecule, previously to thermal dissociation, which may be represented by the scheme $HN\longleftrightarrow H_2$; molecular oxygen then penetrates the molecule and displaces hydrogen, which is subsequently oxidised to water. In a similar manner, hydrogen converts sodium azide into hydrogen and sodamide, the greater velocity of diffusion of hydrogen allowing it to penetrate the nitrogen zone so rapidly that the presence of alkali is not necessary to prevent the transformation $3NaN\equiv\longrightarrow Na_3N+N_2$. If sodium azide is decomposed in an atmosphere of carbon dioxide, the $NaN\equiv$ residues unite with loss of nitrogen and production of sodium azoimide, which is very readily hydrolysed to sodium hydroxide and ammonia, even when the concentration of aqueous vapour is very low. H. WREN.

Tervalent vanadium. II. J. MEYER and E. MARKOWICZ (Z. anorg. Chem., 1926, **157**, 211—250; cf. A., 1924, ii, 558).—Pure ammonium vanadium alum is blue in colour, the red variety described by Bültemann (A., 1904, ii, 266) owing its colour to the presence of traces of vanadic oxide or hydroxide. By electrolysis of a solution of ammonium metavanadate in dilute sulphuric acid after reduction with sulphur dioxide, a *compound*, $NH_4V(SO_4)_2,4H_2O$, is obtained as a green powder (cf. Brierley, J.C.S., 1886, **49**, 823). Using excess of sulphuric acid, the ammonium *salt* of Stähler and Wirthwein's acid, $HV(SO_4)_2,6H_2O$ (A., 1906, ii, 33), is formed. If a suspension of vanadium pentoxide in glacial acetic acid is reduced with hydrazine, and the resulting solution of vanadic acetate treated with fuming sulphuric acid, a mixture of *acids* of the formula $HV(SO_4)_2,nH_2O$, where n is 5, 6, or 8, is obtained. The ammonium salt $NH_4V(SO_4)_2,4H_2O$ and the *salt* $NH_4V(SO_4)_2,5H_2O$ are prepared by substituting ammonium metavanadate for vanadium pentoxide. Addition of 60% sulphuric acid to a vanadic acetate solution yields a number of dark green *hydrates* of vanadic sulphate, $V_2(SO_4)_3,nH_2O$, where n is 9 or 10—11. A yellowish-green *trihydrate* and a pale green *dihydrate* are obtained by the action of concentrated sulphuric acid on solid vanadic acetate. A *monohydrate* is formed when excess of concentrated sulphuric acid is added to a vanadic acetate solution and the acetic acid then evaporated off. If only part of the acetic acid is removed and pyridine is then added, green crystals of *triaquopyridinemonosulphatovanadic hydrogen sulphate*, $[V(H_2O)_3(C_5H_5N)(SO_4)]HSO_4$, appear. When this is heated at 300°, yellow *monoaquopyridinevanadic sulphatesulphuric acid*, $[V(H_2O)(C_5H_5N)(SO_4)_2]H$, results. The vanadic sulphates and sulphatesulphuric acids are able to give three kinds of solutions, two green in colour and one yellow. These seem to correspond with the various solutions of chromic sulphate. By addition of selenic acid to a solution of vanadic acetate, three *acetatovanadic selenates*, $V_3(CH_3{\cdot}CO_2)(SeO_4),nH_2O$, ($n$=10, 14, or 18), have been prepared.

R. CUTHILL.

Tantalum and niobium and their mineral associates. VI. Precipitation of the earth acids by sodium compounds. W. R. SCHOELLER and C. JAHN (Analyst, 1926, **51**, 613—620).—If tantalic and niobic oxides are fused with potassium carbonate until the product is clear, and a fragment of potassium hydroxide is added to the cooled mass, the whole dissolved in hot water, and an excess of solid sodium chloride gradually added, dense micro-crystalline precipitates of 4 : 3 sodium tantalate and of 7 : 6 sodium niobate, respectively, are formed. The small amount of non-precipitated earth acid contained in the filtrates may be substantially recovered by partial neutralisation to the hydrogen carbonate stage and digestion on the water-bath, when hydrolytic dissociation takes place and precipitation of the earth acid. The salts are decomposed by dilute acids and the volume of hydrochloric acid required is proportional to the quantity of alkali in the precipitates. The application of the reaction to the volumetric determination of the earth acids was attempted.

D. G. HEWER.

Formation of sulphur trioxide during the burning of sulphur. J. CORNOG, W. DARGAN, and P. BENDER (J. Amer. Chem. Soc., 1926, **48**, 2757—2760).—Sulphur sealed in a tube with a capillary orifice was vaporised at 460° and the vapour burned at the orifice in a current of oxygen. The effluent gases were passed through $0{\cdot}1N$-iodine solution, potassium iodide solution, and a Hawley filter, and contained about 3·6% of sulphur trioxide. In absence of the filter, inconsistent results were obtained, some of the trioxide escaping unabsorbed. Blank experiments with sulphur dioxide–oxygen mixtures indicated that the catalytic action $2SO_2+O_2=2SO_3$ does not occur. S. K. TWEEDY.

Compound of sulphur trioxide with nitric oxide. Theory of the lead chamber process. W. MANCHOT [with J. KÖNIG and S. REIMLINGER] (Ber., 1926, **59**, [*B*], 2672—2681).—Nitric oxide readily reacts with sulphur trioxide at 60°, yielding the *product*, $2SO_3,NO$, m. p. 215—220° after darkening and softening at 180°, b. p. 275°/715 mm. The substance is readily decomposed by water into sulphuric acid and nitric oxide, but does not react with ferrous sulphate or cupric sulphate dissolved in concentrated sulphuric acid. When heated, it becomes decomposed into sulphur dioxide and nitrogen peroxide, from which it may be prepared at 200—300°. If, however, the gases are moist, nitrosylsulphuric acid is formed in which drops of "blue acid" appear after some time (cf. Manchot, A., 1912, ii, 637). The "acid" is regarded as an oxide of nitrogen intermediate between $NO_{1.5}$ and NO. Raschig's conception that "blue acid" has the composition H_2SNO_5 is rendered improbable by the observation that its absorption spectrum does not resemble those of the compounds $CuSO_4,NO$ and $FeSO_4,NO$. The production of the "copper salt of the blue acid" throws no light on its constitution, since the formation of copper–nitric oxide compounds by the action of "blue acid" on copper sulphate depends on the "acid" serving simply as a source of nitric oxide. H. WREN.

Sulphurous acid and its salts. IV. Action of sulphites on polythionates. F. FOERSTER and K. CENTNER (Z. anorg. Chem., 1926, **157**, 45—82; cf. A., 1925, ii, 120).—The reaction between equivalent quantities of sulphite and tetrathionate or pentathionate leads to the equilibria $S_5O_6''+SO_3''\rightleftharpoons S_4O_6''+S_2O_3''$, and $S_4O_6''+SO_3''\rightleftharpoons S_3O_6''+S_2O_3''$ being set up. If, however, a slight excess of sulphite is present, both reactions occur practically to completion to the right in accordance with the ordinary bimolecular law, the speed of the former reaction being much greater than that of the latter. When hydrogen sulphite acts on pentathionate and tetrathionate, the equilibria $S_5O_6''+HSO_3'\rightleftharpoons S_4O_6''+S_2O_3''+H^{\cdot}$ and $S_4O_6''+HSO_3'\rightleftharpoons S_3O_6''+S_2O_3''+H^{\cdot}$

are slowly established, the reactions probably being brought about entirely by the sulphite ions present in the hydrogen sulphite solutions. The second equilibrium is disturbed by the decomposition of the trithionate, according to the equation $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$, and by its re-formation from hydrogen sulphite and thiosulphate, $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$. As a result of these reactions, the hydrogen-ion concentration increases until sulphur is deposited by the reaction $S_2O_3''+H^{\cdot}\rightleftharpoons HSO_3'+S$. Finally, a stationary state is reached, and sulphate and free sulphur are formed from thiosulphate and sulphite, corresponding with the equation $S_2O_3''+2HSO_3'=2SO_4''+2S+H_2O$. Since hydrogen sulphite and free sulphur can be obtained from thiosulphate by the action of acids, thiosulphate itself can, under suitable conditions of acidity, be converted into sulphate and sulphur.

R. Cuthill.

Decomposition of ammonium thiocyanate into carbon disulphide and "mellon," and decomposition of "mellon" into ammonia and carbon dioxide. W. Gluud, K. Keller, and W. Klempt. —See B., 1926, 1011.

Action of gaseous hydrogen chloride on tungsten compounds. V. Spitzin and L. Kaschtanoff (Z. anorg. Chem., 1926, **157**, 141—164).—If tungsten trioxide is heated in hydrogen chloride, the dioxydichloride commences to be formed at 300°. The sodium tungstates gradually lose tungstic oxide, which is converted into the dioxydichloride and volatilised, and finally sodium chloride remains; in no case are lower tungstates formed as intermediate products. Metallic tungsten is not attacked at 500—600°. The dioxide and the pentoxide form the dioxydichloride, and leave a residue of the metal; it is concluded that their structures are $W(WO_3)_2$ and $W(WO_3)_5$, respectively. Tungsten bronzes form the dioxydichloride, and leave a residue of sodium chloride and the metal, the results indicating that their formula is $(Na_2W_2O_6)_3$ rather than the single formula.

R. Cuthill.

Hydrogenomolybdotungstates. L. Fernandes (Gazzetta, 1926, 56, 655—681).—Derivatives of definite hetero-poly-acids are obtained by (1) neutralisation of a solution containing a molybdate and a tungstate in stoicheiometric proportions by addition of acetic acid, followed by crystallisation, (2) addition of molybdic anhydride to a boiling solution of a tungstate, or (3) mixing solutions of a polymolybdate and a polytungstate. Guanidine derivatives may be obtained by adding a soluble salt of the base to a boiling alkali molybdotungstate solution. Addition of concentrated hydrochloric acid to aqueous solutions of the salts results in the precipitation of the free tungstomolybdic acids as white, amorphous powders, and repeated treatment with hydrochloric acid fails to effect separation of the two acids; the barium salts form sparingly soluble white, microcrystalline precipitates.

The following compounds were prepared and analysed: $2WO_3,4MoO_3,2K_2O,12H_2O$;
$2WO_3,3MoO_3,2K_2O,10H_2O$;
$3WO_3,3MoO_3,3K_2O,9H_2O$;
$3WO_3,3MoO_3,3K_2O,3H_2O$;
$5WO_3,MoO_3,3K_2O,5H_2O$;
$3WO_3,MoO_3,2K_2O,4H_2O$;
$4WO_3,2MoO_3,3K_2O,11H_2O$;
$10WO_3,MoO_3,5K_2O,12H_2O$;
$4WO_3,MoO_3,2K_2O,9H_2O$;
$WO_3,10MoO_3,3Gu_2O,7H_2O$;
$WO_3,5MoO_3,2Gu_2O,6H_2O$;
$4WO_3,MoO_3,2{\cdot}5Gu_2O,6{\cdot}5H_2O$;
$2WO_3,4MoO_3,3Gu_2O,11H_2O$;
$2WO_3,3MoO_3,2{\cdot}5Gu_2O,H_2O$;
$3WO_3,3MoO_3,3Gu_2O,5H_2O$;
$4WO_3,2MoO_3,3Gu_2O,5H_2O$.

The constitution of these compounds is discussed.

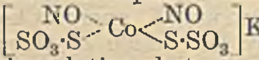
T. H. Pope.

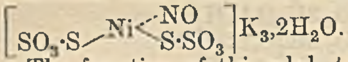
Heterotriphosphates. III. Tungstovanadophosphates. G. Canneri (Gazzetta, 1926, **56**, 642—651).—The tungstovanadophosphates, which are perfectly analogous in constitution and behaviour to the tungstovanadoarsenates (A., 1926, 258), form a continuous series of mixed crystals, the miscibility in the solid state taking place in every case between definite chemical species of analogous molecular constitution. Solutions especially rich in tungstic acid yield red crystals of type (1) (*loc. cit.*), whilst solutions somewhat enriched in vanadic acid give ruby or wine-red crystals of type (2), and those still richer in vanadic acid yield reddish-brown or pitch-black crystals of type (3).

T. H. Pope.

Tervalent manganese. VI. J. Meyer and W. Schramm (Z. anorg. Chem., 1926, **157**, 190—200; cf. A., 1924, ii, 555).—If manganic hydroxide is added to a concentrated solution of oxalic acid at 0°, a reddish-violet solution results which probably contains *trioxalatomanganic acid*, $H_3[Mn(C_2O_4)_3]$. The normal *thallous* salt appears to be formed when manganese dioxide is treated with thallous tetra-oxalate in a freezing mixture. *Sodium diaquodioxalatomanganate*, $Na[Mn(H_2O)_2(C_2O_4)_2]$, is precipitated as green crystals when alcohol is added to a solution of manganese dioxide in sodium tetra-oxalate solution at a low temperature. The free *acid*, $H[Mn(H_2O)_2(C_2O_4)_4]$,aq. (green), is obtained by adding manganic hydroxide to cooled oxalic acid. Both the oxalatomanganic acids form salts with organic bases, but only the *quinoline* salt, $(C_9H_7N)_3,H_3[Mn(C_2O_4)_3]$,aq. (black), has been isolated.

R. Cuthill.

Univalent iron, cobalt, and nickel. W. Manchot (Ber., 1926, 59, [*B*], 2445—2453; cf. A., 1926, 453).—The action of nitric oxide at 0° on a concentrated aqueous solution of cobalt acetate and a large excess of potassium thiosulphate leads to the separation of the *salt*,  $\left[\begin{array}{c}NO\\SO_3{\cdot}S\end{array}\!\!>Co<\!\!\begin{array}{c}NO\\S{\cdot}SO_3\end{array}\right]K_3$, which is somewhat unstable in solution, but may be preserved for some days in the solid state. In more dilute solution, the corresponding *dihydrate* is produced. A similar reaction occurs in the presence of potassium sulphide or ethyl mercaptan. Bivalent nickel does not appear to give compounds with nitric oxide, which readily combines with salts containing univalent nickel such as red potassium nickelocyanide (cf. Bellucci, A., 1919, i, 526; 1920, i, 296). Nickel acetate in presence of potassium thiosulphate and nitric oxide in aqueous-alcoholic solution suffers reduction with formation of the *salt*,



$$\left[\mathrm{SO_3{\cdot}S{-}Ni}\begin{smallmatrix}\cdots\mathrm{NO}\\ \diagdown\mathrm{S{\cdot}SO_3}\end{smallmatrix}\right]\mathrm{K_3,2H_2O}.$$

The function of thiosulphate during the reduction of cobalt by nitric oxide of which 3 mols. are necessary lies in the removal of oxidised nitric oxide, but an excess of the substance above that required for this purpose is highly advantageous. With iron and nickel, reduction is less complete than with cobalt.

The nickel compound is transformed by potassium cyanide without evolution of nitric oxide into the *compound*, $(NO)Ni(CN)_3K_2$, obtained also from red potassium nickelocyanide and nitric oxide. The cobalt salt appears to act similarly with dilute potassium cyanide solution, whereas the iron compound evolves nitric oxide vigorously when treated with concentrated potassium cyanide, but reacts without liberation of gas from the cold, dilute solution.

The proof of the actual existence of compounds containing univalent iron permits the constitution $\begin{smallmatrix}\mathrm{NO}\\ \mathrm{NO}\end{smallmatrix}\!\!>\!\mathrm{Fe^{I}{-}SK}$ to be assigned to the red series of Roussin's salts (in which nitric oxide is regarded as neutral portion without effect on the valency of iron) and the structure $\left[\begin{smallmatrix}\mathrm{Fe^{I}(NO)_2S}\\ \mathrm{Fe^{I}(NO)_2S}\end{smallmatrix}\!\!>\!\mathrm{Fe^{II}}\!<\!\begin{smallmatrix}\mathrm{SFe^{I}(NO)_2}\\ \mathrm{NO}\end{smallmatrix}\right]\mathrm{K}$ to be given to the black series. H. WREN.

Oxidation by alkaline ferricyanide and composition of higher oxides of cobalt. D. BHADURI and P. RÂY (J. Indian Chem. Soc., 1926, **3**, 213—228; cf. Howell, J.C.S., 1923, **123**, 65).—The oxidation of freshly-precipitated cobaltous hydroxide by ferricyanide in solutions of various concentrations of alkali has been followed by titrating with permanganate the ferrocyanide produced. The amount of available oxygen used up is plotted against the increasing amounts of either ferricyanide or potassium hydroxide present. The oxidation rapidly affords the oxide Co_2O_3, and, further, a small amount of peroxidation may occur, especially in the presence of large excesses of alkali. A slight discontinuity in one of the curves is interpreted as indicating the formation of the compound Co_3O_4. Direct analysis of the precipitate, carried out in only one series of experiments, indicates that somewhat less available oxygen is combined than was deduced from the indirect measurements. Nickel and iron salts retard the oxidation of cobalt hydroxide. Nickel hydroxide is not oxidised readily to a higher oxide by a similar method. G. M. BENNETT.

Mol. wts. of the isomeric platinous salts. A. GRÜNBERG (Z. anorg. Chem., 1926, **157**, 299—310).—By the action of thiocarbamide on the two isomeric dithiocyanatodiammineplatinums, the *compounds* $[Pt,4CS(NH_2)_2]Cl_2$ (yellow) and $[Pt(NH_3)_2,2CS(NH_2)_2]Cl_2$ (white) have been prepared. On the basis of Kurnakov's rule (J. Russ. Phys. Chem. Soc., 1893, **25**, 585), it is therefore concluded that the latter compound is derived from the *trans*-isomeride and the other one from the *cis*-isomeride. The mol. wt. of both isomerides in acetone solution corresponds with the single formula $[Pt(NH_3)_2(CNS)_2]$, and the solutions are very poor conductors, as Werner's theory requires. It seems, by analogy, that Peyronne's chloride and the chloride of Reiset's second base are geometrical isomerides, and that they do not differ in mol. wt., as Reihlen and Nestle have suggested (A., 1926, 699). R. CUTHILL.

Platinum metals. VI. Rôle of carbon monoxide in the preparation of ruthenium trichloride by direct union of its elements. H. REMY and T. WAGNER (Z. anorg. Chem., 1926, **157**, 339—344; cf. A., 1924, ii, 770).—Ordinary metallic ruthenium is only partly attacked by pure chlorine, but in presence of carbon monoxide and at temperatures above red heat the reaction is complete. If the product is reduced again to the metal, it can be completely chlorinated with chlorine alone, in absence of carbon monoxide. It is therefore concluded that, as Manchot and König have suggested (A., 1925, ii, 149), carbon monoxide promotes the reaction by exerting a disintegrative effect on the solid phases. If oxygen is present in the chlorine, the trichloride first formed is converted into the dioxide, but carbon monoxide, by itself combining with the oxygen, prevents this. R. CUTHILL.

Preparation of cyanides from calcium cyanamide and dicyanodiamide. A. E. KRETOV.—See B., 1926, 1012.

Kuhlmann micro-balance, and use of porcelain, quartz, and glass filters in quantitative micro-chemical analysis. E. SCHWARZ-BERGKAMPF (Z. anal. Chem., 1926, **69**, 321—341).—Close examination of the variations of the balance with temperature and atmospheric conditions showed that a hitherto unobserved cause of variation is the differential expansion of the knife-edge supports, a metastable temperature equilibrium being established in the interval between weighings. The balance should be kept in a room maintained at about 18—20°, with a maximum difference of 1°, and after being so maintained for several days, may be used without correction, save for pressure variations, for weighings made on the same day; the necessary precautions are described. A porcelain micro-filter which suffers no change in weight after treatment with hot concentrated hydrochloric acid, or with ammonia, or after ignition in a Teclu burner, is described, and details of micro-chemical analyses carried out with it are given. Suitable quartz filters are also described, but are found slower in operation; glass filters are satisfactory, and are more rapid. The use of a new glass filter vessel is described. S. I. LEVY.

Temperature correction in volumetric analysis. W. J. COUVÉE (Chem. Weekblad, 1926, **23**, 550—551; cf. Schlösser, Chem.-Ztg., 1905, 29, 510).—A volume-correction table for reduction of burette readings to a standard temperature of 20° is given. Temperatures should be read in the burette itself after reading, by means of a thermometer suspended from a soda-lime or an empty tube. S. I. LEVY.

Hydrogen electrode. J. M. LEWIS (Austral. J. Exp. Biol., 1926, **3**, 189—191).—A modification of Michaelis' apparatus whereby the usual tape or wick completing the chain between the hydrogen and calomel electrodes is replaced by the column of fluid lying between a lightly-fitting, ungreased glass stopper and the neck of the containing vessel. W. Robson.

Electrolytic preparation of calomel for use in the calomel electrode. S. W. Pennycuick and R. J. Best (Austral. J. Exp. Biol., 1926, 3, 173—176).—A mercury dropping electrode forms the anode, and the calomel is precipitated on the falling stream of mercury which carries down the finely-divided calomel and simultaneously presents a new mercury surface to the current. Introducing the product into the chain H_2, Pt, 0·1N-HCl, sat. KCl, N-KCl, Hg_2Cl_2Hg gave an *E.M.F.* value of 0·3483 volt. Of the substances required in the preparation, only the potassium chloride and mercury need be pure. A method for purifying mercury is detailed. W. Robson.

Graphical interpretation of electrometric titration data. H. S. Simms and P. A. Levene (J. Biol. Chem., 1926, **70**, 319—325).—The titration curve of an unknown or complex substance, obtained by plotting corrected equivalents of base, b', against p_H, is compared with the curve of a known compound of similar constitution; a third " comparison " curve is then constructed, by subtracting values of b' for the known curve from those of the unknown, from which may be deduced the properties of the unknown compound. C. R. Harington.

Method of differential potentiometric titration. D. A. MacInnes and P. T. Jones (J. Amer. Chem. Soc., 1926, 48, 2831—2836).—A method of potentiometric titration described previously (Cox, A., 1925, ii, 999) is improved by inserting the two electrodes in the same solution and temporarily isolating the solution round one of the electrodes while the next small increment of titrating agent is added to the bulk of the solution. A simple device for isolating the solution is described. The improved method is very accurate. S. K. Tweedy.

Buffering in homogeneous and heterogeneous systems. K. Täufel and C. Wagner (Biochem. Z., 1926, **177**, 389—399).—The reciprocal of the buffering capacity of a system in heterogeneous equilibrium equals the sum of those of the participants in the equilibrium multiplied by 0·4343. Formulæ for the determination of changes of p_H of systems of known buffering capacity on addition of weak acids and bases and for the calculation of the p_H of mixtures of buffer systems are deduced. P. W. Clutterbuck.

Titration acidity and true acidity. W. Mang (Chem.-Ztg., 1926, 50, 781).—The true acidity of a solution is measured by the hydrogen-ion concentration, and as this may be reduced by the presence of a neutral salt of the acid radical in the solution, it is possible for the acidity as determined by titration with an alkali to appear to be much higher than it really is. This difference may cause serious errors in work involving colloidal phenomena, *e.g.*, in determining the conditions under which flocculation of colloidal solutions takes place. In all such cases, determinations of the p_H of the solution should be made in preference to titrations with alkalis. A. R. Powell.

Potassium di-iodate as a standard in alkalimetric and iodometric titrations. I. M. Kolthoff and L. H. van Berk (J. Amer. Chem. Soc., 1926, 48, 2799—2801).—Pure potassium di-iodate, prepared according to the method of Shaffer and Hartmann (A., 1921, ii, 417), and crystallised two or three times from water, is a suitable substance for the standardisation of thiosulphate and, because of its high mol. wt., especially of alkali. Indicators showing a colour change between dimethyl-yellow and phenolphthalein may be used in the latter case. S. K. Tweedy.

Detection and rapid determination of chlorides in presence of bromides and iodides. R. Berg (Z. anal. Chem., 1926, 69, 342—348).—On treatment of the acidified solution with bromic acid in presence of acetone, the chloride remains unoxidised in the solution, whilst the liberated bromine and iodine attack the acetone, forming derivatives from which the halogen is not precipitated by means of silver nitrate. The chloride is determined gravimetrically, or, after removal of the excess of bromic acid by addition of a ferrous salt, by Volhard's method. S. I. Levy.

Determination of silicic acid and fluorine in fluorspar, sand, and silicates. H. Dubiel.—See B., 1926, 978.

Complete analysis of fluorspar. E. Bailleux. —See B., 1926, 1012.

Micro-analytical determination of sulphur and the halogens. A. Récsei (Chem.-Ztg., 1926, **50**, 785).—For the determination of sulphur in organic substances that are not too easily volatile, 2—8 mg. of the substance are heated in a nickel crucible with 0·2—0·8 g. of a mixture of potassium sodium carbonate and sodium peroxide in the ratio 2 : 1. The fused mass is dissolved in water, the solution acidified with hydrochloric acid and boiled with a few drops of bromine water, and the sulphur precipitated by addition of 1—2 c.c. of 0·5N-barium chloride solution. The halogens may be determined in a somewhat similar manner; the fusion is conducted as before, the solution of the mass boiled with a little sodium sulphite, acidified with nitric acid and treated with 1 c.c. of 0·5N-silver nitrate solution, and the precipitate collected on a filtering crucible, washed successively with very dilute nitric acid and alcohol, dried at 125°, and weighed. A. R. Powell.

Use of the potassium iodide and iodate method for the titration of Kjeldahl distillates. H. F. Wilson and F. Mattingley (Analyst, 1926, 51, 569). —Carbonic acid seriously interferes with the iodide–iodate method of titration of Kjeldahl distillates by retarding the end-point, and since it is almost certain to be present in such distillates, the latter should be boiled. D. G. Hewer.

Spectrometric determination of nitrates and nitrites by diphenylamine sulphate. E. Tassilly and R. Savoire (Compt. rend., 1926, 183, 887—888).—The reagent was prepared by dissolving 0·2 g. of diphenylamine (recrystallised from alcohol) in 1 litre of pure sulphuric acid. A mixture of 15 c.c. with 3 c.c. of nitrite solution of known titre, added drop by drop with cooling, was poured into one cell of Féry's spectrometer, the other being filled with 15 c.c. of reagent together with 3 c.c. of water, the reading being taken after 15 min. Absorption varied linearly with concentration. The lower limit of sensibility of the method is 0·1 mg. and freshly-prepared reagent is essential. With nitrates, there is intermediate formation of nitrite, since the characteristic blue colour was not formed in the presence of carbamide. S. J. Gregg.

Determination of arsenic in small quantities of organic compounds. O. Wintersteiner and H. Hannel.—See B., 1926, 994.

Thiele's test for arsenic with sodium hypophosphite. H. Matthes (Pharm. Ztg., 1926, **71**, 1509).—Although this material for detection of arsenic is frequently known as Bougault's reagent, it was first employed by Johannes Thiele in 1890. S. I. Levy.

Apparatus for the direct determination of carbon dioxide. J. E. Underwood.—See B., 1926, 977.

Colorimetric determination of minute amounts of compounds of silicon, phosphorus, and arsenic. W. R. G. Atkins and E. G. Wilson (Biochem. J., 1926, 1223—1228).—The amounts of phosphate and arsenate usually present in natural waters do not interfere with Diénert and Wandenbulcke's method for the determination of silicate (A., 1923, ii, 507; 1924, ii, 253), nor does the reagent used by these authors give any colour with moderate quantities of phosphate, arsenate, or arsenite. Denigès' methods for phosphates and arsenates (*ibid.*, 1920, ii, 770; Compt. rend. Soc. Biol., 1921, **84**, 875) are satisfactory. Bell and Doisy's method (Briggs' modification, cf. A., 1922, ii, 659; 1924, ii, 498) is not as convenient and delicate as Denigès' method. The amounts of silicate ordinarily found in natural waters do not interfere with the accuracy of the latter method. Glycerophosphate, triphenyl phosphate, and tritolyl phosphate do not react with Denigès' reagent, the last one not even after hydrolysis, nor do vanadates, tungstates, or phosphotungstates. Pouget and Chouchak's reagent for phosphates (*ibid.*, 1909, ii, 266; 1911, ii, 823) reacts definitely with arsenates on heating, but only faintly in the cold. It does not react with arsenites. S. S. Zilva.

Sensitive reagent for sodium ions. Possible differentiations and separations among the alkali and alkaline-earth metals. F. Díaz de Rada (Anal. Fis. Quím., 1926, **24**, 442—451; cf. Gaspar y Arnal, A., 1926, 591).—Lithium ferrocyanide (0·13—0·26%) in aqueous ethyl alcohol solutions gives precipitates with solutions of the chlorides of alkali and alkaline-earth metals. Using the chlorides in 1% solution, precipitates are obtained at the following concentrations of ethyl alcohol: ammonium, 90%; sodium, 84%; potassium, 78%; rubidium, 72%; cæsium, 62%; magnesium, 83%; calcium, 68%; strontium, 61%; barium, 51%. With the alkali metals, at least, the precipitates consist of the corresponding ferrocyanides. Each ferrocyanide can serve as a precipitating reagent for those ions which follow it in the above series. If to a solution of lithium ferrocyanide in 72·8% alcohol as much magnesium chloride be added as will just fail to give a precipitate, the resulting solution is a very sensitive reagent for sodium, yielding sodium magnesium ferrocyanide. Potassium and sodium may also be distinguished by the precipitate obtained on adding dilute copper sulphate solution to a solution of lithium ferrocyanide in 80% alcohol, containing a small quantity of one of their salts. Sodium gives a dense dark precipitate which settles, leaving a clear supernatant liquid, whilst potassium affords a light pink, flocculent precipitate, and the supernatant liquid is turbid and light yellow. G. W. Robinson.

Detection and determination of minute quantities of beryllium. H. Fischer (Wiss. Veröff. Siemens-Konz., 1926, **5**, 99—117).—Addition of a violet alkaline solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone (quinalizarin) to a neutral solution of a beryllium salt produces a pure blue colloidal solution of a complex in which 1 mol. of quinalizarin appears to be united to 2 atoms of beryllium. Phosphates and tartrates do not interfere with the test, but magnesium produces a similar blue colour. Sufficient sodium hydroxide must be present to retain any aluminium in solution, and sufficient tartaric acid to prevent precipitation of iron. Much iron produces a yellow solution in which the violet to blue colour change cannot be detected. If the test is carried out by the addition of an ammoniacal solution of the reagent to the neutral beryllium solution, the addition of bromine water to the blue liquid causes flocculation of the complex; in the case of the magnesium compound, addition of bromine completely destroys the colour, hence beryllium may be detected by this means in the presence of a great excess of magnesium. The delicacy of the reaction is such that 1·5 μg. of beryllium per c.c. may be detected in a solution containing 2 mg. of magnesium or 6 mg. of aluminium per c.c. For the determination of minute amounts of beryllium in a solution free from other metals, 1 g. of ammonium nitrate is added per 10 c.c. of solution, followed by an excess of a 0·05% solution of quinalizarin in 2*N*-ammonia. After centrifuging, the precipitate is collected in a filtering crucible, washed with slightly ammoniacal 3% ammonium nitrate solution, and dissolved in 25 c.c. of 0·5*N*-sodium hydroxide. The blue colour is compared with that of freshly-made standards prepared in the same way from a beryllium solution of known strength. Beryllium may also be determined by direct titration with a 0·05% solution of the dye in 0·25*N*-sodium hydroxide if the solution is first treated with sodium hydroxide until it is 0·25*N*-alkali. The end-point is marked by the appearance of a violet tint in the previously blue liquid, and may most easily be discerned by comparison with the blue tint of a beryllium solution of approximately equal concentration containing a slight deficiency of the reagent. Aluminium does not interfere in this method. Equally good results may be obtained by adding an excess of the quinalizarin solution to obtain a violet tint and titrating back to blue with standard beryllium nitrate. A. R. Powell.

Co-ordination studies on the analytical behaviour of heavy metal sulphides. II. F. Feigl (Z. anorg. Chem., 1926, **157**, 251—268; cf. A., 1925, ii, 70).—A reply to the criticisms of Ruff and Hirsch (A., 1926, 345). It is pointed out that since certain properties, and particularly the value of the solubility product, of metallic sulphides prepared in the wet way depend on the mode of preparation and their age, their formation is not entirely represented by the equation $M^{\cdot\cdot}+S''=MS$; and indeed instances are known of such sulphides being formed in solution from their un-ionised components. The ordinary insoluble coloured sulphides are probably polymerides of soluble colourless sulphides, corresponding in composition with the usually accepted formulæ, polymerisation being effected by the residual affinity of the sulphur atoms. In some cases, mixed sulphides may be formed in a similar way, this being a probable explanation of the "induced precipitation" of one sulphide by another. R. Cuthill.

Co-ordination studies on the analytical behaviour of heavy metal sulphides. III. F. Feigl [with H. Gleich and R. Schacherl] (Z. anorg. Chem., 1926, **157**, 269—289; cf. preceding abstract).—The suggestion of Ruff and Hirsch (A., 1926, 345) that the partial insolubility in acids of manganous sulphide when precipitated along with mercuric sulphide is due to the protective action of a coating of the latter sulphide seems to be incorrect. Thus barium carbonate is not protected from the action of acetic acid by having mercuric sulphide precipitated on its surface, and manganous sulphide coated with mercuric sulphide by treatment with mercuric chloride does not resist acids as well as when it is itself precipitated on the surface of the mercuric sulphide. Similar experiments show that reduction of the solubility of mercuric sulphide in sodium sulphide when co-precipitated with manganous sulphide is not attributable to a protective action of the latter. Further, there is no evidence that manganous sulphide is oxidised when heated with ammonium sulphide solution, as Ruff and Hirsch have claimed. All the experimental facts can, however, be satisfactorily explained by the hypothesis that mixed sulphides are formed. R. Cuthill.

Determination and separation of rare metals from other metals. VII. Determination of tungsten and its compounds by distillation in a current of air and carbon tetrachloride vapour. L. Moser and K. Schmidt (Monatsh., 1926, **47**, 313—326).—The method of Jannasch and Leiste (A., 1918, ii, 460) is modified by the substitution of air for carbon dioxide as a carrier for the carbon tetrachloride vapour, this mixture being more active. Amorphous tungsten requires to be oxidised to the oxide before volatilising it as chloride, but provided that the gas mixture is rich enough in air, a separate preliminary oxidation is unnecessary. Drawn tungsten wire, however, requires heating for 1 hr. in oxygen, followed by 0·5 hr. in hydrogen before it is subjected to the distillation. The distillate may be collected in water, the solution boiled and made alkaline with ammonia, and the tungsten precipitated in the presence of a little sulphuric acid as benzidine tungstate and weighed as the trioxide. The application of the method to various tungstates is described. Where iron is present, the tungstic anhydride, obtained by evaporation with nitric acid, contains ferric oxide, which is quantitatively removed by heating at 300° with a mixture of equal parts of ammonium chloride and bromide. G. M. Bennett.

Acidimetric determination of nickel as the dicyanodiamidine salt. P. Fluch (Z. anal. Chem., 1926, **69**, 232—243).—The precipitate of nickel dicyanodiamidine obtained by Grossmann's method (A., 1906, ii, 903), after washing with 2·5% ammonia, then with 95% alcohol, dissolves readily in 0·2*N*-hydrochloric acid, with the formation of nickel chloride and dicyanodiamidine hydrochloride, both of which react neutral towards methyl-red. The excess of acid is therefore readily determined by titration with 0·2*N*-potassium hydroxide, provided that less than 0·2 g. of the nickel compound is present per 200 c.c. of acid solution; 1 c.c. of acid=0·002934 g. of nickel. Precipitation is carried out in ammoniacal tartrate solution if iron is present, or the iron may be separated by the basic acetate or barium carbonate methods. Copper interferes and is best separated by electrolysis. The method is applicable to the determination of nickel in ores and alloys, examples of which are given. A. R. Powell.

Two sources of error in the electrolytic determination of nickel in presence of iron. C. Marie and J. Bertheloot (Compt. rend., 1926, **183**, 793—795).—In the determination of nickel in presence of iron by the electrolysis of an ammoniacal solution of the sulphates, two sources of error occur: (1) The precipitate of hydrated iron sesquioxide retains nickel; this adsorption may be reduced to a minimum by displacement of the adsorbed nickel ions by means of magnesium ions (cf. Charriou, A., 1926, 899). (2) The hydrated iron sesquioxide is reduced at the cathode and deposited with the nickel; this source of error may be suppressed by preventing the hydrate from coming into contact with the cathode by means of a diaphragm (a sheath of filter-paper). When the nickel content is small, a preliminary separation in the presence of magnesium is necessary; this gives an impure nickel compound which can be reduced and electrolysed. M. E. Nottage.

Oxidation of chromic salts in acid solution with chlorine and bromine in presence of silver salts. E. Posner (Z. anorg. Chem., 1926, **157**, 311—312).—If a solution of chrome alum containing sulphuric acid and silver nitrate is treated with chlorine or bromine, and boiled, it becomes orange-yellow in colour, due to the formation of chromate, which is precipitated as the silver salt when the solution is neutralised. This reaction may be used to detect 1 part of chromium in 100,000 parts of water. R. Cuthill.

Apparatus for vacuum sublimation. E. Tiedemann (Wiss. Veroff. Siemens-Konz., 1926, **5**, 229—232).—The apparatus consists of a thick-walled glass tube 8 cm. in diameter and 35 cm. long blown into a slight bulb at the lower end, and provided with side tubes for connexion to the vacuum pump and for the insertion of a thermometer. The upper end of the tube is closed with a rubber stopper carrying a wide tube ending in a bulb, and provided with an inner tube for the circulation of water, so as to cause the sublimed substance to condense on the bulb. The outer tube is heated either electrically or by immersion in an oil-bath. The sublimation temperature of naphthalene in this apparatus is 100° (0·05 mm.), of 1 : 5-dihydroxynaphthalene 270° (1 mm.), of "1-hydroxy-5-tetralone" 220° (1 mm.), of "α-diphenol" 280° (0·025 mm.), of "α-dinaphthol" 320° (0·025 mm.), and of salicylic acid 140° (0·05 mm.). No decomposition takes place in subliming any of these substances, and the products obtained are very pure. A. R. Powell.

Arrangement for alternating-current electrolysis. H. J. S. Sand and W. V. Lloyd (J.C.S., 1926, 2971—2973).—The circuit makes use of a source of continuous current and a revolving three-point commutator. The ammeter may be a direct-current instrument. To measure electrode potentials during each pulse, a second two-point revolving commutator is mounted on the same shaft as the first. W. Thomas.

[Laboratory] filtering devices. H. B. Gordon. —See B., 1926, 967.

Flask for recovery of volatile liquids. M. Nierenstein (Analyst, 1926, **51**, 569).—Volatile solvents may be recovered with a loss of about 5% by means of a round-bottomed flask with a bent-over neck for attachment to the condenser, and with a vertical arm from the bend of the neck to carry a reflux condenser. D. G. Hewer.

Rapid dialyser. A. Gutbier and R. Fahr (Z. anorg. Chem., 1926, **157**, 345—348).—A new model of the well-known apparatus. R. Cuthill.

Vacuum dryer for laboratory work. A. Rieche (Chem.-Ztg., 1926, **50**, 891).—A simple glass apparatus for keeping the drying tube at any desired temperature by means of a liquid of suitable b. p. is described. S. I. Levy.

Duplex m.-p. apparatus. F. J. F. Muschter (Chem. Weekblad, 1926, **23**, 552).—A simple apparatus is described by which two or more thermometers may be employed in different parts of the apparatus, which may be heated separately or together. It consists of two or more wide vertical tubes connected by narrower tubing so arranged as to permit the desired heating. S. I. Levy.

Titration apparatus. Baader (Chem.-Ztg., 1926, **50**, 891).—The titration is carried out in a wide-mouthed conical flask provided with a narrow glass side tube sealed in at the top and bottom, which facilitates observation of colour changes. S. I. Levy.

Mineralogical Chemistry.

Constitution of the chalcedons and quartzines. L. Longchambon (Compt. rend., 1926, **183**, 1116—1118).—The identity of quartzine (occurring in crystalline, fibrous form in chalcedons) with quartz has been established by means of dilatometric analysis, radiograms, and density determinations of the constituents of pure chalcedons. The chalcedons consist of opal and crystalline silica in a fibrous form, chalcedony itself containing 4% and 96% of the former and latter, respectively. Its high degree of hydration (50%) accounts for its permeability. The quartzine fibres are agglomerated by the opal. J. Grant.

Relation between kaolin and clays. G. Calsow (Chem. Erde, 1926, **2**, 415—441).—Partial analyses are given of eight samples of kaolin, montmorillonite, and other clays. These materials were heated under 4 mm. pressure, and curves show the loss of water with rise of temperature. Kaolin loses the bulk of its water between 400° and 450°. L. J. Spencer.

Relation between kaolin and clays. G. Linck and G. Calsow (Chem. Erde, 1926, **2**, 442—445; cf. preceding abstract).—From the amount of water lost between 400° and 450° the amount of crystalline kaolin present in the clays examined is calculated, the remainder being assumed to be amorphous clay material. L. J. Spencer.

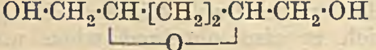
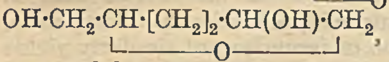
Noteworthy Vesuvian sublimates. G. Carobbi (Atti R. Accad. Lincei, 1926, [vi], **4**, 306—311).—A deposit from a boric acid fumarole on Vesuvius contained appreciable traces both of soluble vanadium compounds and of soluble titanium compounds. T. H. Pope.

Application of X-rays to chemical analysis. I. Analysis of molybdenite from Zovon. G. Natta (Gazzetta, 1926, **56**, 651—654).—Deformed laminæ, weighing in some cases as little as 0·02 mg., found in trachite from Zovon, are identified as molybdenite by the rotating crystal method of X-ray analysis. For the side of the base of the crystal unit the value 12·22 Å. is obtained. T. H. Pope.

Organic Chemistry.

Stereochemistry of ethylene derivatives. J. A. Le Bel (Compt. rend., 1926, **183**, 889).—The existence of three isomeric forms of a substance of the type $CHR':CR''R'''$ (Dufraisse and Gillet, this vol., 58), which cannot be explained by the classical theory, may be ascribed to the possibility of three equilibrium positions of the molecule under the mutual attractions and repulsions of the four different radicals. H. E. F. Notton.

Δ^{α}-Hexene. H. van Risseghem (Bull. Soc. chim. Belg., 1926, **35**, 387).—Δ^{α}-Hexene obtained by Brooks and Humphrey's method is contaminated with a halogen derivative, probably allyl bromide. The following constants are given for pure Δ^{α}-hexene : b. p. 63·35°/760 mm. (±0·05°), d_4^{15} 0·67875, m. p. −139°, and for αβ-dibromohexane, b. p. 87°/16 mm. (±0·2°), d_4^{15} 1·5872 (cf. Kirrmann, A., 1926, 934). R. Brightman.

Action of perbenzoic and peracetic acids on unsaturated substances. J. Böeseken (Rec. trav. chim., 1926, 45, 838—844).—When the double linking in an organic substance is conjugated with the carbonyl group, either free, as an acetal, or in the carboxyl group, it is not attacked. Thus ethyl fumarate and maleate on treatment with perbenzoic acid yield only polymerides. Diallyl on treatment with the peracid in chloroform solution yields the dicyclic oxide, which was not isolated, since it is completely volatile in chloroform, and on hydrolysis with dilute sulphuric acid yields an undistillable *substance*, d_4^{20} 1·2332, n_D^{20} 1·4845, which is probably the furan derivative  $OH{\cdot}CH_2{\cdot}CH{\cdot}[CH_2]_2{\cdot}CH{\cdot}CH_2{\cdot}OH$ or  $OH{\cdot}CH_2{\cdot}CH{\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CH_2$, but is not the expected hexane-αβεζ-tetrol, since it does not form a cyclic derivative with acetone. On oxidation with potassium permanganate in neutral solution at −45°, diallyl yields Δ^{α}-hexene-εζ-diol (b. p. 60—85° in an absolute vacuum) and hexane-αβεζ-tetrol, which yield the cyclic iso*propylidene ethers*, b. p. 166—167°/760 mm., and m. p. 65°, respectively. γ-Methyl-Δ^{α}-butene on oxidation with perbenzoic acid yields the cyclic *oxide*; this on hydrolysis yields γ-methylbutane-αβ-diol, b. p. 97—98°/18 mm., which on treatment with a 1% solution of hydrochloric acid in acetone yields the iso*propylidene ether*, b. p. 136—137°/760 mm., n 1·4110. β-Methyl-Δ^{α}-butene on oxidation with peracetic acid yields β-methylbutane-αβ-diol, b. p. 187°/760 mm. (after liberation from the *diacetate*, which is originally formed), which with acetone yields the corresponding iso*propylidene ether*, b. p. 129°/760 mm. J. W. Baker.

$\Delta^{\alpha\eta}$-Octadi-inene. R. Lespieau and Deluchat (Compt. rend., 1926, 183, 889—891).—βδ-Dibromo-Δ^{α}-butene reacts with magnesium in ethereal solution, forming βη-*dibromo*-$\Delta^{\alpha\eta}$-*octadiene*, b. p. 112—114°/11 mm., d^{15} 1·517, n_D^{15} 1·525, together with a magnesium compound which is converted by chloromethyl ether into (?) β-*bromo*-ε-*methoxy*-Δ^{α}-*pentene*, b. p. 63·5°/11 mm., d^{19} 1·3089, n_D^{19} 1·474. The dibromo-octadiene is converted by alcoholic potassium hydroxide into $\Delta^{\alpha\eta}$-*octadi-inene*, b. p. 135—136°, d^{21} 0·8169, n_D^{21} 1·453 (*silver* salt, $C_8H_8Ag_2,2AgNO_3$), which readily absorbs atmospheric oxygen. H. E. F. Notton.

Preparation of β-chloroallyl chloride. L. Bert and P. C. Dorier (Bull. Soc. chim., 1926, [iv], 39, 1573—1575).—Substitution of technical glycerol αγ-dichlorohydrin for the purified material in Hill and Fischer's process (A., 1923, i, 8) gives 470 g., as against 312 g., of pure β-chloroallyl chloride per kg. of crude dichlorohydrin. Certain experimental precautions are described. M. Clark.

Nitrosyl derivatives of bivalent sulphur. II. Nitrosylethylmercaptide [ethyl thionitrite]. H. Lecher and W. Siefken (Ber., 1926, 59, [*B*], 2594—2601; cf. A., 1926, 819; Tasker and Jones, J.C.S., 1909, 95, 1917).—Even at very low temperatures, nitrosyl chloride and ethyl mercaptan react violently, giving mainly hydrogen chloride, nitric oxide, and diethyl disulphide, with a little hydroxylamine hydrochloride and ethyl thionitrite. In the presence of decahydronaphthalene at −50°, ethyl thionitrite is formed in 80% yield, but its isolation is accompanied by very considerable loss, so that the method is less convenient than that starting from ethyl nitrite and ethyl mercaptan. Ethyl thionitrite is very stable towards alcoholic potassium hydroxide, probably owing to the inability of the $-N{:}O$ group to add water or alkali hydroxide. This inability explains the ready formation of ethyl thionitrite from ethyl mercaptan and ethyl nitrite according to the scheme: $EtO{\cdot}N{:}O+HSEt \rightleftharpoons EtO{\cdot}N(OH){\cdot}SEt \longrightarrow EtOH+O{:}N{\cdot}SEt$, and the failure of the thionitrite at its b. p. to react with amyl alcohol. The remarkable colour of the thionitrites is attributed to the loosely-united valency electrons between the sulphur and nitrogen atoms, and not to the nitrosyl group, which, in these compounds, is an unusually stable complex. The formation of thionitrite from ethyl or amyl nitrite may be used as a colour test for mercaptans, but the method is less sensitive than the mercuric chloride test.

Ethyl nitrite and triphenylthiolmethane afford triphenylmethyl thionitrite, m. p. 99° (decomp.) after darkening at 95° when slowly heated, in theoretical yield. H. Wren.

Dihalogenomethanesulphonic acids. H. J. Backer (Rec. trav. chim., 1926, 45, 830—837).—Dihalogenomethanesulphonic acids have been prepared in good yields by the action of the halogen (or an acidified mixture of the barium halide and halate) on barium sulphoacetate in sealed tubes at 159—210°, according to the individual case. All the acids obtained are extremely deliquescent, but lose a portion of their water of crystallisation on exposure to phosphoric oxide in a vacuum. They are best purified by crystallisation of their barium salts, the solubilities of which have been determined. The following acids have been prepared (the solubility data refer to g. of anhydrous salt per 100 g. of aqueous solution at 25°): dichloromethanesulphonic acid $+1H_2O$, m. p. 70° (*barium* $+1H_2O$, solubility 47·86 g., anhydrous, 91·79 g., and *potassium* salts); dibromomethanesulphonic acid $+1H_2O$, m. p. 73° (barium $+1H_2O$, solubility 33·30 g., anhydrous, 49·92 g.; *potassium*, *sodium*, and *thallous* salts); *di-iodomethanesulphonic acid* $+2H_2O$, m. p. 61° (*barium* $+2H_2O$, $+3H_2O$, and $+6H_2O$, solubility of last-named 14·70 g., anhydrous 17·23 g.; *potassium* and *sodium* salts); chlorobromomethanesulphonic acid $+1H_2O$, m. p. 63° (barium $+1H_2O$, solubility 42·88 g., anhydrous 75·07 g.; *potassium*, *sodium*, and *thallous* salts); chloroiodomethanesulphonic acid $+2H_2O$, m. p. 64° (*barium* $+1H_2O$, solubility 45·40 g., anhydrous 83·15 g., and *sodium* salts); *bromoiodomethanesulphonic acid* $+1H_2O$, m. p. 87° (*barium* salt $+1H_2O$ and $+3H_2O$, solubility of the latter 35·11 g.; anhydrous 54·11 g.). J. W. Baker.

[Decomposition of formic acid by ultra-violet light.] A. Kailan (Ber., 1926, 59, [*B*], 2493; cf. A., 1920, ii, 576).—A claim for priority against Müller and Hentschel (A., 1926, 1124). H. Wren.

Manufacture of acetic anhydride. H. Dreyfus.—See B., 1926, 995.

Separation of fatty acids. A. H. Lewis (Biochem. J., 1926, 20, 1356—1363).—Saturated and unsaturated fatty acids and their triglycerides form phenylhydrazides, but these are unsuitable as a means of separating fatty acids owing to the similarity of their solubility in various media. Hydroxylamine in the presence of sodium ethoxide reacts with the triglycerides of the fatty acids to give hydroxamic acids. The sodium salts of the hydroxamic acids from palmitic and stearic acids are completely insoluble in alcohol, but with decrease of mol. wt. the solubility increases. The lauric acid derivative is appreciably soluble, whilst that of heptoic acid is totally soluble in alcohol. The sodium salts of the hydroxamic acids from unsaturated fatty acids and from the hydroxy-fatty acids are completely soluble in alcohol. The above groups of fatty acids can therefore be separated by this method when present as glycerides in natural oils. S. S. Zilva.

Use of phosphorus pentachloride in the preparation of glycerides. R. K. Newman, V. M. Trikojus, and G. Harker (J. Proc. Roy. Soc. New South Wales, 1925, 59, 293—300).—Glycerides are readily obtained by heating glycerol with phosphorus pentachloride (1 mol.) and the sodium salt of a fatty acid (5½ mols.) at 200° for 9 hrs. Tributyrin (yield 93%) has b. p. 310° (corr.) and 192—196°/26 mm., d_4^{20} 1·0350, n_D^{20} 1·43585. Tri*iso*valerin, b. p. 330·5°, 209·5—210·5°/27 mm., d_4^{20} 0·9984, n_D^{20} 1·43535. The method is also general for the preparation of esters, ethyl acetate being obtained from phosphorus pentachloride (1 mol.), ethyl alcohol (3 mols.), and sodium acetate (4 mols.). Tributyrin results from heating glycerol with butyric acid (6 mols.), so that the water produced is continuously fractionated away (yield 80%). G. M. Bennett.

Undecenoic acid and its homologues. I. P. Chuit, F. Boelsing, J. Hausser, and G. Malet (Helv. Chim. Acta, 1926, 9, 1074—1093).—The action of dry hydrogen bromide on undecenol (*acetate*, b. p. 125—127°/7 mm., d^{15} 0·8858; *undecenoate*, b. p. 225°/8 mm., d^{15} 0·877) at 130°, yields mainly *undecenyl bromide*, $CH_2\dot{:}CH\cdot[CH_2]_8\cdot CH_2Br$, b. p. 117—118°/8 mm., d^{15} 1·070, which on treatment with ozone yields *ι-bromodecoic acid*, m. p. 39·5—40·5°, b. p. 160°/1 mm. (*methyl* ester, b. p. 161—163°/12 mm., 135—136°/1·5 mm., d^{15} 1·177), and the corresponding *aldehyde*, b. p. 128—130°/3 mm., d^{15} 1·22 (*semicarbazone*, m. p. 85·5—86·5°), which rapidly oxidises in the air. When the bromo-acid is boiled with potassium acetate and glacial acetic acid, it yields the acetyl derivative, m. p. 36—37°, b. p. 172—174°/2 mm., of ι-hydroxydecoic acid, m. p. 75·5—76·5° (methyl ester, m. p. 15°, b. p. 165—166°/13 mm.; cf. Grün and Wirth, A., 1922, i, 804). The action of hydrogen bromide on undecenol in a freezing mixture yields *κ-bromoundecan-α-ol*, b. p. 168—169°/15 mm., d^{15} 1·152, which on treatment with acetic acid and potassium acetate and subsequent hydrolysis yields *undecane-ακ-diol*, m. p. 48—48·5°, b. p. 168—169°/8 mm. [*diphenylurethane*, m. p. 93—94°, not identical with the phenylurethane of undecane-αλ-diol (Chuit, A., 1926, 499), m. p. 139—140°], together with iso*undecenol*, $CHMe\dot{:}CH\cdot[CH_2]_7\cdot CH_2\cdot OH$, b. p. 124—125°/8 mm., d^{15} 0·8507, n_D^{19} 1·4535 (*acetate*, b. p. 127—128°/7 mm., d^{15} 0·8841; *phenylurethane*, m. p. 65—66°). The action of hydrogen bromide under either of the conditions mentioned above yields also *ακ-dibromoundecane*, b. p. 164—165°/8 mm., d^{15} 1·323, which on treatment with acetic acid and potassium acetate and subsequent hydrolysis yields the ακ-diol. This glycol, on oxidation with chromic acid in acetic acid solution, yields *κ-ketoundecan-α-ol*, m. p. 42—43°, b. p. 175—176°/16·5 mm. (*acetate*, b. p. 167—168°/11 mm., 135°/1 mm.; *semicarbazone* of the acetate, m. p. 100—100·5°), and *ι-ketoundecoic acid*, m. p. 58·5—59·5°, b. p. 166—167°/1 mm. (*methyl* ester, m. p. 17°, b. p. 163—164°/13·5 mm., d^{20} 0·959). Oxidation of undecenol with sodium dichromate yields undecoic acid (chief product) and sebacic acid, which is also obtained when undecenoic acid is oxidised with chromic acid, potassium permanganate, or ozone. Oxidation of *iso*undecenol similarly yields *iso*undecenoic acid (Krafft and Seldis, A., 1901, i, 115) and azelaic acid, which is also obtained by the oxidation of *iso*undecenoic acid. Attempts to prepare *iso*undecenoic acid (1) by the action of potassium hydroxide at 220—240° on undecenoic acid or (2) by the dehydration of ι-hydroxyundecoic acid (below) with β-naphthalenesulphonic acid yield a mixture of *iso*undecenoic acid (80%) and undecenoic acid, together with a little of the *allo*-form of the former, which lowers the m. p. of the mixture below the eutectic mixture of the main products. Treatment of methyl ι-bromoundecoate (obtained by the action of hydrogen bromide on undecenoic acid at 0°) with potassium acetate and acetic acid yields the *acetyl* derivative of the methyl ester, b. p. 178°/15 mm., d^{15} 0·960, of *ι-hydroxyundecoic acid*, m. p. 49·5°, which is liberated on hydrolysis (*methyl* ester, m. p. 21·5°, b. p. 152°/8 mm.). On oxidation, this acid yields ι-ketoundecoic acid, and on reduction it gives undecane-ακ-diol. J. W. Baker.

Preparation of α-substituted valerolactones. G. Darzens (Compt. rend., 1926, 183, 1110—1112).—The conversion of β-phenyl-α-allylpropionic acid into methyltetrahydronaphthalenecarboxylic acid by the action of 80% sulphuric acid at 90° (A., 1926, 1239) is accompanied by the formation of *α-benzylvalero-γ-lactone*, b. p. 188—190°/20 mm., which is not itself convertible into the tetrahydronaphthalene derivative. The reaction is general for α-alkyl-α-allylacetic acids, and thus are obtained α-iso*butylvalerolactone*, b. p. 119—120°/16 mm., and α-iso*octylvalerolactone*, b. p. 165—170°/18 mm.

J. W. Baker.

Carbon suboxide. O. Diels and K. Hansen (Ber., 1926, 59, [*B*], 2555—2560; cf. Diels and Lalin, A., 1908, i, 939).—Carbon suboxide reacts with sulphur dioxide at a low temperature in the presence of minute traces of rubber or sulphur, yielding a colourless solid substance which is very unstable and sensitive to air. Its composition has not been established with certainty, but, since its formation is attended by production of carbon dioxide, the constitution $CO\dot{:}C\dot{:}SO$ is suggested. Carbon suboxide gives yellow to orange, amorphous additive compounds with tertiary bases. The mode of union is not established, but does not appear very intimate. The following *compounds* are described: with *iso*-

quinoline, C_9H_7N,C_3O_2, m. p. 112—115° (decomp.) after darkening at 100°; with quinoline, $C_9H_7N,2C_3O_2$, m. p. about 115° (decomp.), which is converted by phenylhydrazine into the *compound*, $C_9H_7N,2C_3O_2,NHPh{\cdot}NH_2$; with 2-methylquinoline, $C_{10}H_9N,2C_3O_2$; with nicotine, $C_{10}H_{14}N_2,3C_3O_2$, m. p. about 100°; with codeine, $C_{18}H_{21}O_3N,5C_3O_2$, m. p. 155—160° (decomp.); with atropine, $C_{17}H_{23}O_3N,5C_3O_2$, m. p. 115—120° after darkening; with quinine, $C_{20}H_{24}O_2N_2,7C_3O_2$, m. p. 135° (decomp.). Triethylphosphine (1 mol.) and carbon suboxide (4 mols.) give an amorphous additive compound.

H. Wren.

Addition of alkali alkoxide to esters. II. F. Adickes (Ber., 1926, **59**, [*B*], 2522—2533; cf. A., 1925, i, 1378).—Esters of oxalic acid are not able to add more than 1 mol. of alkali alkoxide. The formation of additive compounds is not observed with esters of formic, carbonic, benzoic, acetic, mono-, di-, or tri-phenylacetic acids. Trichloroacetic esters and sodium ethoxide immediately yield sodium chloride. Ethyl malonate immediately gives ethyl sodiomalonate (conveniently prepared by treating sodium with a slight excess of ethyl malonate dissolved in ether and addition of light petroleum to the solution); the possibility of intermediate formation of an additive compound is not excluded. Ethyl diethylmalonate does not unite with sodium ethoxide. Reaction is not observed with compounds in which the carboxyl groups are separated by a greater number of carbon atoms (succinic and phthalic esters). If, however, the carboxyl groups are united by an aliphatic ·C:C· linking, reactivity is again observed, as instanced by ethyl fumarate. In general, addition of sodium alkoxide appears invariably possible with molecules containing the system R·CO·CO·R′, even when neither R nor R′ is a carboxyl group. Thus benzil unites with sodium ethoxide, as apparently do also ethyl glyoxylate and ethyl mesoxalate. Ethyl pyruvate combines very readily with 1 mol. of sodium alkoxide, but the constitution of the additive compound could not be established with certainty by reason of its great reactivity. It is, however, highly probable that addition occurs at the carboxyl, and not at the carbonyl group, since pyruvic acid is present in the additive compound in polymerised form, and, further, the compound is not converted by ethyl iodide into diethoxypropionic ester, as would be expected if reaction had occurred at the carbonyl group. The second necessary C:O double linking can be replaced by the aliphatic C:C linking, as shown by the reactivity of acrylic, crotonic, and cinnamic esters.

Arguments are advanced against the constitution, $COMe{\cdot}CH_2{\cdot}C(OEt)_2{\cdot}ONa$, assigned by Scheibler and Voss (A., 1920, i, 366) to the intermediate product of the acetoacetic ester synthesis. The assumption of the formation of an additive product from ethyl acetate and sodium ethoxide does not appear to be supported by experimental evidence. H. Wren.

Stereochemistry of the tetrahedral carbon atom. IV. Isomerism of the chloromalic acids. R. Kuhn and R. Zell (Ber., 1926, **59**, [*B*], 2514—2521; cf. A., 1925, i, 780; 1926, 505).—(—)-*trans*-Oxidoethylene-αβ-dicarboxylic acid is conveniently prepared by treating methyl monoacetyl-*d*-tartrate with thionyl chloride in pyridine solution, followed by successive treatment of the product with acid and alkali hydroxide. The mixture of (—)-*trans*-oxidoethylene-αβ-dicarboxylic acid (96%) and chloromalic acid-II is separated into its components by means of the barium salts. (—)-*trans*-Oxidoethylene-αβ-dicarboxylic acid, m. p. 180° (corr. decomp.), $[\alpha]_D^{18}$ —100° in water, gives a *potassium hydrogen* salt ($+H_2O$), $[\alpha]_D^{18}$ —100° in water, normal *calcium* salt ($+H_2O$), and anhydrous *barium* salt. The mother-liquors from the barium (—)-*trans*-oxidoethylene-αβ-dicarboxylate when treated with an excess of alkali hydroxide afford *cis*-oxidoethylene-αβ-dicarboxylic acid, thus confirming the conclusion of Freudenberg and Brauns (A., 1922, i, 623) that partial inversion occurs during the replacement of the hydroxyl group of methyl monoacetyltartrate by chlorine by means of thionyl chloride. Hydrolysis of (—)-*trans*-oxidoethylene-αβ-dicarboxylic acid affords *d*-tartaric acid mixed with a little *meso*tartaric acid. Ethereal hydrogen chloride transforms it quantitatively into (—)-chloromalic acid-I, m. p. 165—166° (decomp.), $[\alpha]_D^{18}$ —8·0° in water, $[\alpha]_D^{22}$ —31·1° in ethyl acetate, $[\alpha]_D^{18}$ —11·5° in 96% alcohol [Sonn and Rosinsky (A., 1925, i, 1237) give m. p. 153°]; the *potassium hydrogen*, *barium* ($+3H_2O$), and *calcium* salts, the *dimethyl* ester, b. p. 140°/14·5 mm., d_4^{20} 1·3598, n_D^{20} 1·4594, $[\alpha]_D^{22}$ —22·05°, and *diethyl* ester, b. p. 147°/11 mm., d_4^{20} 1·2366, n_D^{20} 1·4524, $[\alpha]_D^{25}$ —16·82°, are described. The optical homogeneity of (—)-chloromalic acid-I is established by its quantitative reconversion into (—)-*trans*-oxidoethylene-αβ-dicarboxylic acid. Reduction of (—)-chloromalic acid-I affords *d*-malic acid, whilst hydrolysis converts it into *d*-tartaric acid mixed with a little *meso*-acid, thus confirming the configurative relationship of *d*-malic and *d*-tartaric acids (cf. Freudenberg and Brauns, *loc. cit.*).

Chloromalic acid-II is conveniently resolved into its optical antipodes by fractional crystallisation of the morphine hydrogen salt from 96% alcohol. (+)-*Chloromalic acid*-II has m. p. 166—167° (decomp.), $[\alpha]_D^{20}$ +9·35±1·5° in water (*morphine hydrogen* salt, $[\alpha]_D^{20}$ —72·6° in water); it is slowly converted by boiling water into *meso*tartaric acid. (—)-*Chloromalic acid*, m. p. 166—167° (decomp.), is reduced to *l*-malic acid. H. Wren.

Properties of molybdomalic complexes. II. Action of bases. E. Darmois (Bull. Soc. chim., 1926, [iv], 39, 1515—1527; cf. A., 1926, 559, 723).—The action of bases (ammonium, barium, and sodium hydroxides, aniline, etc.) on α-ammonium *d*-dimolybdomalate is studied by polarimetric and other methods. On progressive addition of a base to a dilute solution of the complex, the latter tends towards a feeble lævorotation; with concentrated solutions, however, this state is attained more rapidly, and the solution then becomes dextrorotatory again, passing through a maximum. The base probably combines with a part of the molybdic acid, forming, in the case of ammonia, the lævo-compound $MoO_3,2C_4H_4O_5(NH_4)_2$, which, in very dilute solution, hydrolyses to the less lævorotatory ammonium malate. In concentrated solutions, the complex *compound*,

$4MoO_3,5C_4H_6O_5,11NH_3,5H_2O$, exists, intermediate to $4MoO_3,2C_4H_6O_5$ (dextro) and $MoO_3,2C_4H_6O_5$ (lævo). It is formed together with basic molybdates. An explanation of the observed maximum dextrorotation is offered. Molybdomalates are considered to be derived from $[Mo_4O_{11}]H_4$, and structures are suggested for the compounds $4MoO_3,2C_4H_4O_5(NH_4)_2$ and $MoO_3,2C_4H_5O_5NH_4$ (cf. A., 1926, 457). The complex $MoO_3,2C_4H_4O_5K_2$ is decomposed by potassium hydroxide into the normal malate without the formation of an intermediate complex. The work of Gernez is explained with the aid of the results (cf. A., 1891, 291, 545). S. K. Tweedy.

Sapogenins of quillaic acid. A. Windaus, F. Hampe, and H. Rabe (Z. physiol. Chem., 1926, **160**, 301—307).—Sthamer's saponin, when heated with dilute sulphuric acid, yields *prosapogenin*, probably a dibasic acid, $C_{35}H_{56}O_{12}$, m. p. 206—207° (decomp.) [*potassium* salt]. It gives an *oxime*, $C_{35}H_{57}O_{12}N$, m. p. 258°, and when treated with concentrated hydrochloric acid yields furfuraldehyde (1 mol.) and carbon dioxide (1 mol.), thus probably containing either glycuronic or galacturonic acid. The saponin, when heated with dilute sulphuric acid at 140—145°, yields *endsapogenin*, a monobasic acid, $C_{29}H_{46}O_5$, m. p. 294° (decomp.); the *potassium* salt, *monomethyl* ester, m. p. 225°, *monoxime*, m. p. 282°, *semicarbazone*, m. p. 288°, *diacetyl* derivative, m. p. 250°, and *methyl ester oxime*, m. p. 238°, are described. It does not contain a double linking, and on oxidation with nitric acid yields a trinitrodicarboxylic acid, $C_{25}H_{35}O_{10}N_3$, m. p. 240° (decomp.) [*dimethyl* ester, m. p. 197° (decomp.)]. Endsapogenin of quillaic acid, is, therefore, a dihydroxyketocarboxylic acid, and is not closely related to bile acid, as was supposed, and cannot, like bile acid, be a decomposition product of sterols. P. W. Clutterbuck.

$\beta\gamma$-Dihydroxy-Δ^{β}-butene-$\alpha\delta$-dicarboxylic acid, the so-called "dihydroxymaleic acid." H. Schmalfuss and H. Barthmeyer (Z. physiol. Chem., 1926, **160**, 196—213).—Dihydroxymaleic acid may be characterised as its dimercurous salt, which is, however, very unstable, 1 mol. yielding, on treatment with water at 70°, tartronic acid (1 mol.), carbon dioxide (1 mol.), and mercury (2 atoms). Dihydroxymaleic acid (1 mol.), on treatment with excess of mercurous nitrate, yields at 70° nitric acid (8 mols.), carbon dioxide (4 mols.) and mercury (8 atoms). Several methods for the determination of the acid are described, and its possible importance in the metabolism of *Glaucium luteum*, Scop., in which it is found, is discussed. The limits of the qualitative test with ferric chloride and potassium hydroxide are 0·05 mg., and of the titanium salt test 0·01 mg. of dihydroxymaleic acid. P. W. Clutterbuck.

Double citrates of quadrivalent vanadium. G. Canneri (Gazzetta, 1926, **56**, 637—642).—Addition of citric acid to the solution of a vanadyl salt and neutralisation of the liquid with ammonia gives a deep blue liquid, further addition of ammonia then giving a precipitate which partly redissolves to form a brown solution. In the dilute solutions, ammonia or an alkali hydroxide causes change in colour from blue to brown, but the alkali carbonates do not alter the colour. This behaviour differs sharply from that of the analogous solutions containing tartaric acid, which, with ammonia or an alkali carbonate, give a purplish-violet solution owing to the formation of complex ions corresponding with violet vanadyltartrates. Evaporation of the neutralised citric solutions of vanadyl salts yields turquoise-blue crystals of double citrates, which may be obtained also either by dissolving hydrated vanadium dioxide in citric acid and neutralising with alkali, or from vanadates and excess of citric acid. These salts dissolve readily in water and respond to all the characteristic reactions of ordinary vanadyl salts, and their constitution, unlike that of the vanadyltartrates, in which the appearance of the force of co-ordination is indicated by their colour reaction, seems to be
$OH\cdot C(CH_2\cdot CO_2R)_2\cdot CO_2\cdot VO\cdot VO\cdot CO_2\cdot C(CH_2\cdot CO_2R)_2\cdot OH$. Thus, the presence in the citric acid molecule of a carboxyl and a hydroxyl group united to the same carbon atom is not a sufficient condition for the formation of internal complex salts. The double citrates of vanadyl and *ammonium*, $(NH_4)_4(VO)_2(C_6H_5O_7)_2$, *potassium* ($+6H_2O$), and *sodium* ($+12H_2O$) were analysed. T. H. Pope.

Products of the bromination of paracetaldehyde. II. A. Stepanov, N. Preobraschenski, and M. Schtschukina (Ber., 1926, **59**, [*B*], 2533—2538; cf. A., 1925, i, 1240).—The action of bromine (1 mol.) on paracetaldehyde at −15° gives *bromoparacetaldehyde*, b. p. 77·5°/8 mm., 82·5°/10 mm., m. p. 27·5°, with dibromoparacetaldehyde and unchanged paracetaldehyde. The monobromo-compound decomposes smoothly at 130° into bromoacetaldehyde and acetaldehyde, from which it can be regenerated under the influence of hydrogen bromide. Paracetaldehyde and bromine (2 mols.) afford dibromoparacetaldehyde in 89—94% yield with very little tribromoparacetaldehyde. Complete action between paracetaldehyde and bromine (3 mols.) is very slow, and is complicated by the action of hydrogen bromide on the aldehyde, resulting in the production of tetrabromobutaldehyde. Attempts to remove the liberated hydrogen bromide by operating in the presence of calcium carbonate show the acid to have a very pronounced accelerating effect on the action.

The action of bromine on paracetaldehyde is accompanied by only slight evolution of hydrogen bromide. The course of the change is explained on the hypothesis that paracetaldehyde is in equilibrium with a small proportion of acetaldehyde which, under the influence of bromine, becomes enolised to vinyl alcohol; the latter substance combines with bromine, yielding the very unstable $\alpha\beta$-*dibromoethyl alcohol*, b. p. 31°/17 mm., d_4^{20} 2·1782, n_D^{20} 1·5492, which passes into tribromoparacetaldehyde and hydrogen bromide. The liberated acid combines with acetaldehyde or vinyl alcohol, yielding α-bromoethyl alcohol, which, with $\alpha\beta$-dibromoethyl alcohol, gives a mixture of mono- and di-bromoparacetaldehyde. H. Wren.

Ester condensation: replacement of functional groups under the action of aluminium ethoxide. R. Dworzak (Monatsh., 1926, **47**, 11—16; cf. A., 1925, i, 783, 1239).—Chloral is converted by aluminium ethoxide in benzene solution into trichloroethyl alcohol (33% yield) together with small quantities of acetaldehyde, paracetaldehyde, and ethyl and trichloroethyl trichloroacetates. The relation of the Tischtschenko reaction to this conversion of an aldehyde into its alcohol is discussed and a scheme of connected, reversible reactions is given in which the production of the two possible aldehydes and the four possible esters is accounted for. G. M. BENNETT.

Process of making aldols. C. J. HERRLY.—See B., 1926, 995.

Action of alkali hydroxide on the sodium salt of enolic glutacondialdehyde. Sorbaldehyde. P. BAUMGARTEN and G. GLATZEL (Ber., 1926, 59, [*B*], 2658—2665; cf. A., 1926, 844).—Treatment of a solution of the enolic form of glutacondialdehyde in 7·5% sodium hydroxide with steam yields much resin, formic acid, acetaldehyde, crotonaldehyde, and two aldehydes, C_6H_8O and $C_8H_{10}O$. The former of these is identified as sorbaldehyde, b. p. 76°/30 mm. (*semicarbazone*, m. p. 203°), since it is oxidised by silver oxide to sorbic acid and adds 4 atoms of bromine; it is smoothly hydrogenated in aqueous suspension in the presence of palladium to a saturated aldehyde converted by silver oxide into *n*-hexoic acid. The aldehyde, $C_8H_{10}O$, b. p. 79°/1 mm., appears to be a cyclic compound, since it reacts with bromine with evolution of hydrogen bromide; its constitution could not be established. H. WREN.

Olefinic terpene ketones from volatile oil of flowering *Tagetes glandulifera*. II. T. G. H. JONES (J.C.S., 1926, 2767—2770).—Ethyl *iso*valerylacetate condensed with *sec.*-butyl iodide in presence of sodium ethoxide gives *ethyl* sec.*-butylisovalerylacetate*, b. p. 133°/24 mm., which on hydrolysis with alcoholic potassium hydroxide yields *γη-dimethyloctan-ε-one*, b. p. 187°/760 mm., $a^{15\cdot5}$ 0·8190, n_D^{20} 1·4190. Under similar conditions, ethyl *iso*valerylacetate and ethyl α-iodopropionate give α-methyl-β-*iso*valerylpropionic acid, m. p. 166°, identical with the acid obtained by oxidising *γη*-dimethyl-Δ^{α}-octen-ε-one. Hot 70% sulphuric acid converts *γη*-dimethyl-Δ^{α}-octen-ε-one into *iso*valeric acid, methyl ethyl ketone, and methyl *iso*butyl ketone, the latter substance being produced also when tagetone is decomposed by boiling alcoholic potassium hydroxide. Tagetone is probably represented by the tautomeric systems $\cdot CO\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2 \rightleftharpoons \cdot C(OH):CH\cdot C(:CH_2)\cdot CH:CH_2 \rightleftharpoons \cdot CO\cdot CH:CMe\cdot CH:CH_2$. The compound $C_{10}H_{18}O$ (see A., 1926, 72), obtained by the reduction of tagetone with sodium in moist ether or with zinc dust and acetic acid, is named *tagetol*. H. BURTON.

Interaction of amino-compounds and carbohydrates. III. Action of nitrous acid on certain nitrogenous sugar derivatives and related compounds. A. HYND and M. G. MACFARLANE (Biochem. J., 1926, 20, 1264—1272).—Amino-compounds reacting with nitrous acid can be subdivided into three groups. Compounds such as glycine and glucosimine are representatives of one group in which the nitrogen is liberated readily on reaction with nitrous acid in the presence of a weak acid. In the second group, which is represented by substances like carbamide, glucose ureide, and glucosamine, the liberation of nitrogen proceeds slowly in presence of weak acid, but rapidly in presence of a strong acid. Urethane, guanidine, and creatine are typical of the third group of compounds, which require the presence of a strong acid for the above reaction. A number of compounds have been investigated on these lines, and structural formulæ are assigned to these substances in the light of the results obtained (cf. Plimmer, A., 1926, 156). S. S. ZILVA.

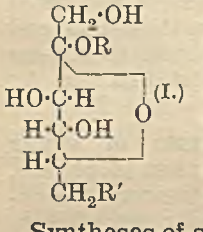
Carbohydrates. V. Bitter taste of sugar derivatives. P. BRIGL and W. SCHEYER (Z. physiol. Chem., 1926, 160, 214—233).—Nineteen sugar derivatives of solubilities at the ordinary temperature varying between 4% and 0·00125% and of differing bitterness to taste (when compared with glucose penta-acetate as standard) are investigated stalagmometrically, and it is shown that there is no direct relationship between surface activity and degree of bitterness. Introducing groups which decrease the solubility in water and increase solubility in organic solvents tends to augment the bitterness, but no parallel could be drawn between solubility and bitterness. Sucrose octa-acetate possesses the greatest degree of bitterness, 34×10^{-6} g. being detectable by taste. There appears to be a relationship, however, between configuration and taste, since all the derivatives of β-glucose are more bitter than those of α-glucose. P. W. CLUTTERBUCK.

Oxygen bridges in the sugars. II. Position of the oxygen bridge in dextrose. F. MICHEEL and K. HESS (Annalen, 1926, 450, 21—29; cf. A., 1926, 1230).—Methylation of *iso*propylideneglucose with methyl sulphate and sodium hydroxide yields the trimethyl ether, which by treatment with 0·5% aqueous methyl-alcoholic hydrochloric acid (40% water) is converted into 3 : 5 : 6-trimethylmethylglucoside. This is methylated further to 2 : 3 : 5 : 6-tetramethylmethylglucoside, b. p. 105—107°/2 mm., α_D^{20} −9·24° (in water), from which by hydrolysis with 0·3% hydrochloric acid 2 : 3 : 5 : 6-tetramethylglucose, m. p. a little above 0°, b. p. 117—120°/1 mm., α_D^{20} −11·1° (in water), n_D^{20} 1·4525, results. Since *iso*propylideneglucose is readily obtained from and converted into di*iso*propylideneglucose under very mild conditions and differs little from it in rotatory power, it contains the same oxygen bridge. The tetramethylglucose <1 : 4> obtained from it is identical with that prepared from γ-methylglucoside (Irvine, Fyfe, and Hogg, J.C.S., 1915, 107, 524) and from 2 : 3 : 6-trimethyl-γ-methylglucoside (Schlubach and Bomhard, A., 1926, 600), and differs greatly from 2 : 3 : 4 : 6-tetramethylglucose <1 : 5> (Purdie and Irvine, J.C.S., 1904, 85, 1049). It follows that γ-glucose has a 1 : 4-oxygen bridge, normal glucose a 1 : 5. The formation of di*iso*propylideneglucose only from β-glucose is explained as due to migration of the 1 : 5- to a 1 : 4-ring only in β-glucose under the conditions.

The *iso*propylidenedioxy-groups are shown to be partly hydrolysed during Zeisel determinations, causing an error of +2 to 3% in the methoxyl value. C. HOLLINS.

Occurrence of gentiobiose in the products of the commercial hydrolysis of corn [maize] starch. H. Berlin.—See B., 1926, 992.

[Degradation of reducing bioses. IV. Constitution of turanose and melezitose.] G. Zemplén (Ber., 1926, 59, [*B*], 2539—2540; cf. A., 1926, 1229).—In conformity with the observation of Haworth and Hirst that sucrose contains a butylene oxidic grouping, the amended constitution (I) is suggested for turanose (R=H, R′=glucose residue) and melizitose (R=R′=glucose residue). H. Wren.



Syntheses of sugars. VI. 6-β-*d*-Galactosido-α-glucose. Constitution of melibiose. B. Helferich and H. Rauch (Ber., 1926, **59**, [*B*], 2655—2657).—1 : 2 : 3 : 4-Tetra-acetylglucose is converted by acetobromogalactose and silver oxide in chloroform solution into 6-β-d-*galactosido-α-glucose octa-acetate*, m. p. 166° (corr.), $[\alpha]_D^{22}$ 0°, which is hydrolysed to the non-crystalline 6-β-d-*galactosido-α-glucose*, $[\alpha]_D^{18}$ +36·4° in water, probably a mixture of isomerides. The corresponding *phenylosazone* has m. p. about 185° (corr.), $[\alpha]_D^{25}$ −69·6° to −23·9° in 4 hrs. The non-identity of the synthetic sugar with melibiose indicates that the accepted constitution or configuration of the latter substance is untenable. H. Wren.

Pentose of digitonin. H. Kiliani (Ber., 1926, 59, [*B*], 2462—2465).—Hydrolysis of digitonin with aqueous hydrochloric acid leads to the production of *d*-galactose, dextrose, and *l*-xylose, identified as strontium *l*-xylonate. Hydrolysis of glucosides such as digitonin is advantageously effected with alcoholic hydrogen chloride when the main purpose is the isolation of the corresponding genin; the use of alcohol should be avoided if the liberated sugars are to be identified, since ethyl glucosides are formed to a considerable extent. H. Wren.

Cellulose. XXII. Crystalline trimethylcellulose. K. Hess and H. Pichlmayr (Annalen, 1926, 450, 29—40; cf. A., 1925, ii, 782).—Trimethylcellulose, prepared from natural cellulose, " viscose " silk, or " copper " silk, after one precipitation from benzene–light petroleum is readily obtained crystalline from chloroform–alcohol. If separation is too rapid, the product is amorphous, but may be rendered crystalline by moistening with chloroform–alcohol and keeping for a few days. The crystalline form is retained after removal of the solvent. Like crystalline cellulose triacetate, crystalline trimethylcellulose gradually undergoes association in glacial acetic acid solution, the mol. wt. (determined cryoscopically) increasing from about 300 to about 850 in 30 hrs. C. Hollins.

Cellulose. XXIII. Acetolysis of cellulose. II. K. Hess and H. Friese (Annalen, 1926, 450, 40—58; cf. Hess, Weltzien, and Singer, A., 1925, i, 641; Irvine and Robertson, *ibid.*, 1926, 823).—A product representing an intermediate stage in the acetolysis of cellulose to cellobiose and *iso*cellobiose is described. Cellulose is treated below −5° with a mixture of acetic acid and anhydride containing 2·5% of sulphuric acid; the temperature is raised slowly and maintained at 30° for 2·5 days. After filtering and pouring into water, a white precipitate is obtained which, after extraction with hot methyl alcohol, leaves pure *hexa-acetylbiosan*, $C_{24}H_{34}O_{16}$, m. p. 258—259°, $[\alpha]_D^{18}$ −12·61° (in chloroform). This is hydrolysed by methyl-alcoholic sodium hydroxide to *biosan*, decomp. about 270°, which reduces Fehling's solution, and may be re-acetylated to hexa-acetylbiosan by boiling acetic anhydride and pyridine, or acetolysed to cellobiose and *iso*cellobiose. Methylation of biosan with methyl sulphate and alkali gives *hexamethylbiosan*, m. p. 210—215°, $[\alpha]_D^{20}$ −10·18° (in water), which is converted by methyl-alcoholic hydrogen chloride into 2 : 3 : 6-trimethylglucose-αβ-methylglucoside, m. p. 118—120°, $[\alpha]_D^{22}$+62·04° (in methyl alcohol), from which by the action of aqueous hydrochloric acid 2 : 3 : 6-trimethylglucose, identical with that from cellulose or cellobiose, is obtained. It is suggested that biosan is a true dimeride of the fundamental cellulose molecule as opposed to cellulose, which is an agglomerate of such molecules. It is shown that cellobiose formation is independent of the degree of association of cellulose or cellulose acetates. Hexa-acetyl- and hexamethyl-biosans do not exhibit the tendency to association shown by cellulose acetates. C. Hollins.

Cellulose. K. Hess. XXIV. Presence of a foreign substance in cellulose fibres. F. Micheel and W. Reich (Annalen, 1926, 450, 59—65).—Cellulose purified by the usual methods is found to contain a compound which is difficult to separate and shows itself as an insoluble, gelatinous substance when the completely acetolysed cellulose is re-acetylated with pyridine and acetic anhydride. After freeing from ash (35—45%, mainly calcium oxide), the substance has $[\alpha]_D$ about +20°, decomp. 230—240°. It shows no crystal structure under the microscope, but the *X*-ray diagram indicates the presence of crystals and has no relation to that of cellulose or mercerised cellulose. C. Hollins.

[Constitution of cellulose.] G. Schultze and K. Hess (Annalen, 1926, **450**, 65—74; cf. Pringsheim and others, A., 1926, 942).—Repetition fails to confirm the " de-association " of cellulose acetates when heated in boiling naphthalene, and " cellosan " is shown to have no relation to cellulose.

C. Hollins.

Substituted amines. Preparation of substituted acetamides and the corresponding primary amines. J. L. E. Erickson (Ber., 1926, 59, [*B*], 2665—2668).—Acetamide is converted by benzyl bromide at 200° into acetbenzylamide, b. p. 157°/2 mm., m. p. 61° (yield 80%); ammonium bromide and diacetamide are also produced by the action of the liberated hydrogen bromide on a portion of the acetamide. *Acet-β-phenylethylamide*, b. p. 154°/2 mm., m. p. 45°, is prepared similarly in 388% yield. The following substituted acetamides are produced at 200—220°: acetethylamide, b. p. 206°; acet-*n*-propylamide, b. p. 225°; *acet-*n*-butylamide*, b. p. 229°; *acetisoamylamide*, b. p. 232°. The amides are hydrolysed by concentrated hydrochloric acid to the corresponding amines. H. Wren.

Simple synthesis of α-amino-acids. G. Schroeter (Z. angew. Chem., 1926, 39, 1460).—When *p*-tolylsulphonamides are treated with α-halogenocarboxylic acids in aqueous or alcoholic alkali solution *p*-tolylsulphonamido-acids result, which are converted into α-amino-acids by hydrochloric acid, acetyl or chloroacetyl chloride. E. Holmes.

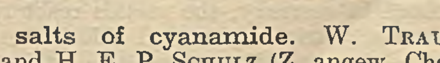
Action of Grignard reagents on amino-acids. Action of mineral acids on β-amino-αα-diphenylethanol. X. Experiments with acylamino-acids and peptides. F. Bettzieche [with R. Menger and K. Wolf] (Z. physiol. Chem., 1926, 160, 263—269; 270—300).—IX. β-Amino-αα-diphenylethanol when heated in a sealed tube with 40% sulphuric acid gives deoxybenzoin (yield 62%), obtained also from diphenylacetaldehyde and 4% sulphuric acid, the amount decreasing the stronger the acid. If the reaction is carried out with concentrated sulphuric acid in ice, however, the yield is 76%. Diphenylacetaldoxime when heated under reflux with 4% sulphuric acid also gives deoxybenzoin. Triphenylacetaldehyde yields triphenylethanone when heated with hydrochloric acid under reflux, the yield being greater with 40% sulphuric acid and being very good with ice-cooled sulphuric acid.

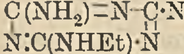
X. The following substances react with the appropriate Grignard reagent: ethyl benzoylphenylalanine, giving β-benzamido-β-benzyl-αα-diethylethanol, m. p. 135°, yield 69%; phenylglycine ester hydrochloride, giving an oil the benzoyl derivative of which has m. p. 136°; ethyl benzoylphenylglycine, giving *β-benzamido-β-phenyl-αα-dimethylethanol*, m. p. 136°; ethyl benzoyl-leucine, giving *β-benzamido-αα-diphenyl-*β-iso*butylethanol*, m. p. 184°, yield 52%; ethyl benzoylalanine, giving *β-benzamido-αα-dibenzylpropanol*, m. p. 122°, synthesised for comparison by benzoylation of the free amino-alcohol, the yield here being 66%; ethyl toluenesulphonylglycine with magnesium phenyl bromide, giving *β-toluenesulphonamido-αα-diphenylethanol*, m. p. 138° (*sodium* salt), yield 50%, identical with a sample obtained from toluenesulphonyl chloride and β-amino-αα-diphenylethanol; ethyl toluenesulphonylglycine, giving *β-toluenesulphonamido-αα-dibenzylethanol*, m. p. 150—151°, yield 35%, identical with a sample obtained from toluenesulphonyl chloride and β-amino-αα-dibenzylethanol; ethyl toluenesulphonalanine, giving *β-toluenesulphonamido-αα-dibenzylpropanol*, m. p. 161—162°, yield 39%, identical with a sample obtained by acylation of the amino-alcohol; ethyl benzenesulphonylglycine, giving *β-benzenesulphonamido-αα-diphenylethanol*, m. p. 139°, yield 51%; ethyl naphthalenesulphonylglycine, giving *β-naphthalenesulphonamido-αα-diphenylethanol*, m. p. 163—164°, yield 43%; ethyl glycylalanine hydrochloride, giving *β-glycylamido-αα-diphenyl-β-methylethanol*, m. p. 186·5—187°; ethyl glycylalanine hydrochloride, giving *β-glycylamido-β-methyl-αα-dibenzylethanol*, m. p. 107·5°; ethyl benzoylglycylalanine, giving *β-benzoylglycylamido-αα-diphenyl-β-methylethanol*, m. p. 187·5—188°, yield 61%; ethyl benzoylglycylalanine, giving *β-benzoylglycylamido-β-methyl-αα-dibenzylethanol*, m. p. 183°; ethyl benzoylglycylphenylaminoacetate, giving *β-benzoylglycylamido-ααβ-triphenylethanol*, m. p. 213·5—214°; ethyl benzoylglycylphenylaminoacetate, giving *β-benzoylglycylamido-β-phenyl-αα-dibenzylethanol*, which first melts at 147—148°, resolidifies at 175°, and then melts at 187·5—188°, the difference being probably due to intramolecular change; ethyl phthalamidoacetate, giving several products, of which the chief was *ethyl* o*-benzoylbenzoylglycine*, m. p. 143°, which on partial hydrolysis gave *o*-benzoylhippuric acid, m. p. 183°, and on more complete hydrolysis, benzoylbenzoic acid, m. p. 126—127°, and glycine ester hydrochloride.

P. W. Clutterbuck.

Action of sodium hypochlorite on acid amides. III. I. J. Rinkes (Rec. trav. chim., 1926, 45, 819—824; cf. A., 1920, i, 322).—The urethanes formed from amides of unsaturated fatty acids are soluble in the aqueous methyl alcohol, and owing to their greater ease of hydrolysis the reaction must be carried out at 0°. Δ^a-Nonenoamide (Harding and Weizmann, J.C.S., 1910, 97, 301) thus treated yields Δ^a-*octenylurethane*, m. p. 28·5°, b. p. 155—160°/10 mm., which on hydrolysis with dilute sulphuric acid yields octaldehyde (*p*-nitrophenylhydrazone, m. p. 75°). The monoamide of maleic acid, m. p. 172—173° (decomp.) (Anschütz, A., 1891, 176, gives 152—153°), yields β-*carboxyvinylurethane*, m. p. 126° (decomp.), whilst *cyclo*hexenecarboxylamide gives *cyclo*hexanone, isolated as its dibenzylidene derivative. Decomposition of the ozonide of *o*-allylphenol with zinc and acetic acid yields *o*-hydroxyphenylacetaldehyde, b. p. about 90°/vacuum (*semicarbazone*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 148°).

J. W. Baker.

Acylation of β-aminocrotonanilide. E. Benary and W. Kerckhoff (Ber., 1926, 59, [*B*], 2548—2551; cf. A., 1923, i, 37, 201).—Acylation of β-aminocrotonanilide differs from that of β-aminocrotonic ester in that there is little tendency towards the production of *N*-derivatives. Benzoyl chloride and β-aminocrotonanilide in pyridine afford *β-amino-α-benzoylcrotonanilide*, $NH_2\cdot CMe{:}CBz\cdot CO\cdot NHPh$, m. p. 173°, converted by boiling dilute sulphuric acid into benzoylacetanilide and by phenylhydrazine into 1 : 5(3)-*diphenyl*-3(5)-*methylpyrazole*-4-*carboxyanilide*, m. p. 167°. β-*Amino*-α-*cinnamoylcrotonanilide*, m. p. 201°, prepared similarly, is hydrolysed to *cinnamoylacetanilide*, m. p. 107°, and converted by phenylhydrazine into 1-*phenyl*-3(5)-*methyl*-5(3)-*cinnamylpyrazole*-4-*carboxyanilide*, m. p. 224°. β-*Amino*-α-*chloroacetylcrotonanilide*, m. p. 155°, is converted by methyl-alcoholic potassium hydroxide into 3-*hydroxy*-5-*methylpyrrole*-4-*carboxyanilide*, m. p. 181°, and by potassium hydrogen sulphide into 3-*hydroxy*-5-*methylthiophen*-4-*carboxyanilide*, m. p. 125°. The latter substance is transformed by nitrous acid into 2-*oximino*-3-*keto*-5-*methyl*-2 : 3-*dihydrothiophen*-4-*carboxyanilide*, decomp. 235° after darkening at 150°, and by isatin and concentrated sulphuric acid into the *compound*  $C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}CO\cdot C\cdot CO\cdot NHPh\\ \| \\ S{-}CMe\end{matrix}$, decomp. above 280°. H. Wren.

Sodium salts of cyanamide. W. Traube, F. Kegel, and H. E. P. Schulz (Z. angew. Chem., 1926, 39, 1465—1469).—When an aqueous solution of disodium cyanamide is kept at 0° for 20 hrs., it deposits 68% of *monosodium cyanamide dihydrate.* Calcium and disodium cyanamides give the stable dialkylcyanamides quite smoothly (Traube and Engelhardt, A., 1911, i, 955), but the monosodium salt gives mono- and dialkyl-derivatives, which are unstable and give polymerisation products. Among these is *guanylmethylcarbamide*, $C_3H_8ON_4$, which gives a *hydrochloride*, $C_3H_8ON_4,HCl,H_2O$, m. p. 155°, and is proved to have two free amino-groups by the production of a *copper* derivative, $Cu(C_3H_7ON_4)_2,4H_2O$, m. p. 208°. Monosodium cyanamide with the ethyl halides gives 19% of diethylcyanamide, b. p. 60—70°/12 mm., 186°/760 mm.; it does not condense in an analogous manner to the methyl compound, but 2 mols. together with 1 mol. of free cyanamide give ring closure with the production of *diethylmelamine*,  $\begin{array}{l}\mathrm{C(NH_2){=}N{-}C{\cdot}NHEt}\\ \mathrm{N{:}C(NHEt){\cdot}N}\end{array}$, b. p. 200°/11 mm., 330°/atm. pressure, m. p. 155—156° (*hydrochloride*, m. p. 265°; *nitrate*, m. p. 169—170°). On heating disodium cyanamide with methyl sulphate, 19% of iso*trimethylmelamine*, m. p. 179°, is obtained with a little guanylmethylcarbamide. E. Holmes.

Nitrosyl derivatives of bivalent sulphur. III. Nitrosyl thiocyanate. H. Lecher and F. Graf (Ber., 1926, 59, [*B*], 2601—2602).—Ethyl nitrite reacts with thiocyanic acid in anhydrous ethereal solution at −78° with formation of nitrosyl thiocyanate (cf. Söderbäck, A., 1920, i, 219), which is too unstable to permit its isolation. H. Wren.

[Thiocyanogen chloride.] H. Lecher and G. Joseph (Ber., 1926, 59, [*B*], 2603—2606; cf. Kaufmann and Liepe, A., 1924, i, 839).—The properties of monothiocyanogen chloride are not in harmony with a unimolecular structure, and determinations of the mol. wt. in boiling benzene or chloroform indicate the composition $(CNClS)_6$. With diethylamine, it gives half the quantity of diethylrhodanamine (cf. A., 1923, i, 661) which is derivable theoretically from the unimolecular compound, but the fate of the remainder of the compound could not be ascertained. With dimethylaniline, it affords *p*-thiocyanodimethylaniline in quantitative yield. The constitution of the substance cannot yet be elucidated, but "unimolecular thiocyanogen chloride" should be deleted from the literature. H. Wren.

Reactions of sodium nitroprusside. N. Tarugi (Annali Chim. Appl., 1926, 16, 407—413).—Sodium nitroprusside and thiocyanate mixed in alkaline solution and acidified give a violet solution from which are obtained blue crystals of a *substance*, probably $Na_2Fe(CN)_5{\cdot}N(OH){\cdot}SCN$, which further loses water to give a green substance. E. W. Wignall.

Rubidium and cæsium alkyls. A. von Grosse (Ber., 1926, 59, [*B*], 2646—2654; cf. A., 1926, 555).—Rubidium and cæsium are conveniently prepared by heating their respective chlorides to dull redness with metallic calcium in a high vacuum. When dissolved in mercury, the metals react readily with a solution of triphenylmethyl chloride in anhydrous ether, giving *rubidium triphenylmethyl* and *cæsium triphenylmethyl* as very reactive, dark red powders giving blood-red solutions in ether. *Lithium triphenylmethyl* is an orange-red powder which yields a stable *etherate.* Rubidium and zinc ethyl give the additive *compound*, $RbEt,ZnEt_2$, m. p. 70—75°; cæsium appears to yield a similar substance. H. Wren.

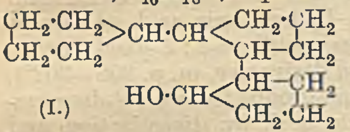
Reducing action of Grignard reagents. J. Stas (Bull. Soc. chim. Belg., 1926, 35, 379—386; cf. A., 1925, i, 1052).—Further attempts to synthesise tri*iso*propylcarbinol (βδ-dimethyl-γ-*iso*propylpentan-β-ol) by the action of magnesium *iso*propyl bromide or chloride on di*iso*propyl ketone at low temperatures were unsuccessful, the tertiary alcohol alone being obtained. A similar result was obtained with the cyanohydrin of the ketone; magnesium ethyl bromide yields exclusively βδ-dimethyl-γ-ethylpentan-β-ol. Examination of the behaviour of di*iso*propyl, dipropyl, ethyl *iso*propyl, methyl *iso*propyl, diethyl, and dimethyl ketones with magnesium alkyl bromides shows that the reducing action of magnesium *iso*propyl bromide increases with the substitution of methyl groups in the ketone. It appears that the nature of the ketone is a more important factor than the nature of the Grignard reagent in determining whether reduction takes place. The following are described: βγδ-*trimethylpentan-γ-ol*, b. p. 156·5°, d_4^{20} 0·8492, n_D^{20} 1·4353; βδ-*dimethyl-γ-ethylpentan-γ-ol*, b. p. 176—177°/755 mm., d_4^{20} 0·8610, n_D^{20} 1·4434; β-*methyl-γ-*iso*propylhexan-γ-ol*, b. p. 73—74°/14 mm., 184°/760 mm. (decomp.), d_4^{20} 0·8537, n_D^{20} 1·4427; δ-ethylheptan-δ-ol, d_4^{20} 0·8337, n_D^{20} 1·4332; δ-iso*propylheptan-δ-ol*, b. p. 79—81°/14 mm., 188—190°/760 mm. (slight decomp.), d_4^{20} 0·8436, n_D^{20} 1·4390; γ-iso*propylhexan-γ-ol*, b. p. 176·5—177·5°/755 mm., d_4^{20} 0·8506, n_D^{20} 1·4398; and βγ-*dimethylhexan-γ-ol*, b. p. 61—62°/18 mm., d_4^{20} 0·8371, n_D^{20} 1·43087. Di*iso*propyl ketone and magnesium phenyl bromide afford γ-*phenyl*-βδ-*dimethylpentan-γ-ol*, b. p. 118—119°/11 mm., d_4^{20} 0·9755, n_D^{20} 1·5239. R. Brightman.

Coupling action of the Grignard reagent. III. Formation of αβγ-triphenylpropane and similar hydrocarbons in coupling reactions of benzyl halides. R. C. Fuson (J. Amer. Chem. Soc., 1926, 48, 2937—2942; cf. A., 1926, 1237).—Späth's supposed αβγ-triphenylpropane (A., 1914, i, 1) obtained in the reaction of Grignard reagents with benzyl halides, has been identified as α-*phenyl*-β-p-*benzylphenylethane*, b. p. 213—216°/5 mm., or 225—230°/10 mm., d_4^{18} 1·0394, n_D^{23} 1·5929, which is obtained by heating benzyl chloride with dibenzyl either alone or in presence of a little zinc dust. As Späth was probably operating with a deficiency of Grignard reagent, this reaction explains the presence of the above hydrocarbon in his reaction product. αβγ-*Triphenylpropane*, b. p. 179—181°/2 mm., or 225—230°/10 mm., d_4^{18} 1·0482, n_D^{23} 1·6042, was prepared by reducing phenyldibenzylcarbinol with hydriodic acid (cf. Klages and Heilmann, A., 1904, i, 487). p-*Benzyl*-n-*propylbenzene*, b. p. 152—155°/10 mm., d_4^{18} 0·9739, n_D^{20} 1·5552, is obtained similarly from *n*-propylbenzene and benzyl chloride, and is identical with Späth's supposed αβ-diphenylbutane. F. G. Willson.

Inactive 1 : 3-dimethyl*cyclo*pentane. G. Chavanne (Bull. Acad. roy. Belg., 1926, [v], **12**, 105—122).—See A., 1926, 1130.

1 : 2-Dimethyl*cyclo*pentane compounds. M. van Rysselberge (Bull. Acad. roy. Belg., 1926, [v], 12, 171—192).—See A., 1926, 1238.

Catalytic dehydrogenation ; polycyclic hydrocarbons. N. D. Zelinski, I. Titz, and L. Fatejev (Ber., 1926, 59, [*B*], 2580—2590; cf. A., 1924, i, 665, 952).—Reduction of *cyclo*pentanone in moist ethereal solution by sodium affords *cyclo*pentanol, an *alcohol*, $C_{10}H_{18}O$, b. p. 107—108°/9 mm., d_4^{20} 0·9862, n_D^{20} 1·4903, and the *substance* (I), m. p. 76—77°. Treatment of the alcohol, $C_{10}H_{18}O$, with hydrogen iodide in glacial acetic acid followed by hydrogenation of the product in the presence of platinised charcoal gives a hydrocarbon, $C_{10}H_{18}$, b. p. 190—191°, d_4^{20} 0·8780, n_D^{20} 1·4711, which is converted by platinised charcoal at 300° into hydrogen and naphthalene. *cyclo*Pentanol is converted by hydrogen bromide into the corresponding bromide, which, with sodium in the presence of ether, affords *cyclo*pentene with smaller amounts of di*cyclo*pentyl, b. p. 188—189°/753 mm., d_4^{20} 0·8604, n_D^{20} 1·4652. The latter hydrocarbon differs in physical properties from the product described above, and like the monocyclic *cyclo*pentane hydrocarbons does not suffer catalytic dehydrogenation. The hydrocarbon derived from *cyclo*pentyl*cyclo*pentanol is in all probability a mixture of *cis*- and *trans*-decahydronaphthalenes, and rearrangement of ring systems appears to occur under the influence of hydrogen iodide.


(I.)

Reduction of 3-methyl*cyclo*pentanone with sodium gives 3-methyl*cyclo*pentanol and a saturated, dicyclic *alcohol*, $C_{12}H_{22}O$, b. p. 124—126°/13 mm., $d_4^{14\cdot5}$ 0·9483, $n_D^{14\cdot5}$ 1·4798. The latter substance is converted by potassium hydrogen sulphate into an unsaturated *hydrocarbon*, $C_{12}H_{20}$, b. p. 215—217°/760 mm., d_4^{17} 0·8676, which is reduced to the saturated *hydrocarbon*, $C_{12}H_{22}$, b. p. 215—216° (corr.), d_4^{20} 0·8451, n_D^{20} 1·4570. Since the latter hydrocarbon does not suffer dehydrogenation at 300° in presence of platinised charcoal, the series of compounds must contain the di*cyclo*pentyl arrangement. When, however, the unsaturated hydrocarbon is treated with zinc dust and hydrobromic acid and then reduced, the *product*, $C_{12}H_{22}$, b. p. 214—215°/750 mm., $d_4^{15\cdot5}$ 0·8548, d_4^{20} 0·8518, is readily dehydrogenated to a dimethylnaphthalene, m. p. 86—87° (picrate, m. p. 139°). Similarly, the saturated alcohol, $C_{12}H_{22}O$ (see above), when cautiously treated with zinc dust and hydriodic acid, gives a saturated hydrocarbon, $C_{12}H_{22}$, b. p. 218—219°, $d_4^{18\cdot5}$ 0·8751, $n_D^{18\cdot5}$ 1·4753, and when more drastically treated with the same reagents a hydrocarbon, $C_{12}H_{22}$, b. p. 217—219°, d_4^{18} 0·8622, n_D^{18} 1·4682; each of these hydrocarbons is dehydrogenated to a dimethylnaphthalene, m. p. 91° and 106·5—107°, respectively (picrates, m. p. 130° and 143°). The alcohol, $C_{12}H_{22}O$, and an excess of zinc dust and fuming aqueous hydriodic acid yield a saturated hydrocarbon, b. p. 217·5—219°/760 mm., d_4^{20} 0·8594, dehydrogenated to a dimethylnaphthalene, m. p. 75—76° (picrate, m. p. 122°). Change in the ring system of the alcohol is therefore caused by hydriodic acid. A similar change is caused by zinc dust and hydrobromic acid, which give a saturated hydrocarbon, b. p. 216—218°/760 mm., d_4^{20} 0·8666, dehydrogenated to a dimethylnaphthalene, m. p. 86—87°. Final proof that 3 : 3′-*dimethyl*cyclo*pentyl* is incapable of catalytic dehydrogenation rests on the behaviour of the hydrocarbon, b. p. 213—215°, d_4^{20} 0·8483, n_D^{20} 1·4582, synthesised from 3-methyl*cyclo*pentyl iodide and sodium.

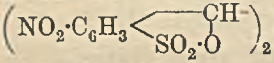
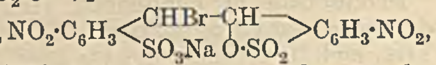
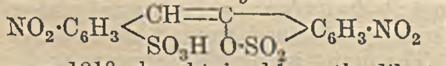
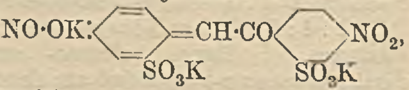
Di*cyclo*hexyl, b. p. 239·5—240°, d_4^{20} 0·8847, n_D^{20} 1·4800, prepared from *cyclo*hexyl bromide and sodium, is readily dehydrogenated to diphenyl. H. Wren.

Production of condensed ring systems by catalytic dehydrogenation. N. D. Zelinski, I. Titz, and M. Gaverdowskaja (Ber., 1926, 59, [*B*], 2590—2593).—Fluorene is readily obtained by the passage of di*cyclo*hexylmethane, b. p. 250—252° (corr.), d_4^{20} 0·8750, n_D^{20} 1·4752, or diphenylmethane over platinised charcoal at 300°. Under similar conditions, dibenzyl gives phenanthrene. Fluorene is likewise obtained from di*cyclo*hexyl ketone or benzophenone. Carbazole is obtained from di*cyclo*hexylamine or diphenylamine. The yellow colour of solutions of carbazole in concentrated sulphuric acid appears peculiar to the compound isolated from anthracene oil. H. Wren.

Preparation and physical constants of γ-phenylpropinene. L. Bert and P. C. Dorier (Bull. Soc. chim., 1926, 39, 1610—1612).—γ-Phenyl-Δ^{α}-propinene is most economically prepared by the action of sodamide on γ-chloroallylbenzene (A., 1925, i, 803, 1373). A 75% yield is obtained after purification through the copper derivative. The substance has b. p. 68—69°/17 mm., d_4^{0} 0·917, $d_4^{13\cdot5}$ 0·910, d_4^{20} 0·899, $n_D^{8\cdot6}$ 1·514, n_D^{20} 1·509 (cf. Bourguel, A., 1923, i, 430; 1925, i, 770). M. Clark.

Kekulé formula for benzene and the existence of isomeric *o*-disubstitution products. H. H. Hodgson (J. Soc. Dyers and Col., 1926, 42, 365—368).—The author claims that 3-*chloro*-1-*bromo*-4 : 6-*dinitrobenzene*, slender parallelograms (from alcohol), m. p. 101°, as prepared from 3-chloro-4 : 6-dinitroaniline by the diazo-reaction is isomeric with the 1-*chloro*-3-*bromo*-4 : 6-*dinitrobenzene*, hexagonal plates, m. p. 101°; similarly obtained from 3-bromo-4 : 6-dinitroaniline. The first "isomeride" appears to be the stable form, and is also obtained by the nitration of 1-chloro-3-bromobenzene. The "1-chloro-" is converted into the "1-bromo-" compound on fusion or repeated crystallisation from alcohol; from benzene, both separate in plates.

3-*Chloro*-4 : 6-*dinitroaniline*, m. p. 174°, and 3-*bromo*-4 : 6-*dinitroaniline*, m. p. 178°, are described. Diazotisation of the latter in the presence of hydrochloric acid and cuprous chlorides affords, according to the conditions, 1 : 6-*dichloro*-3-*bromo*-4-*nitrobenzene*, m. p. 70°, 1 : 4 : 6-*trichloro*-3-*bromobenzene*, m. p. 138°, or mixtures of these. 3-*Bromo*- and 3-*chloro*-4 : 6-*dinitrobenzeneazo*-β-*naphthol* are described. R. Brightman.

Acetylene derivatives. VI. 2 : 2′-Disulphonic acids of the stilbene, tolane, and deoxybenzoin series. P. Ruggli and E. Peyer (Helv. Chim. Acta, 1926, 9, 929—950).—The action of halogens and alkali on several derivatives of stilbene-2 : 2′-disulphonic acid in a manner analogous to that employed in the case of the corresponding dicarboxylic acids (Ruggli and Meyer, A., 1922, i, 343) has been studied. Although the sulphonic acids also show a great tendency to form lactonic compounds, it is not so pronounced as in the earlier case, so that it was possible to isolate derivatives of tolane-2 : 2′-disulphonic acid. Sodium 4 : 4′-dinitrostilbene-2 : 2′-disulphonate treated with bromine yields, instead of the dibromide, the *dilactone* (I),  $\left(NO_2\cdot C_6H_3<\begin{matrix}CH-\\SO_2\cdot O\end{matrix}\right)_2$ decomp. 290°, and the *bromo-monolactone* (II),  $NO_2\cdot C_6H_3<\begin{matrix}CHBr-CH-\\SO_3Na\ \ O\cdot SO_2\end{matrix}>C_6H_3\cdot NO_2$, decomp. 234—237° (which is converted into the dilactone when heated in aqueous solution above 65°), whilst the mother-liquors, on treatment with potassium acetate and methylation of the potassium salt with methyl sulphate, yield the *dibromide* of methyl 4 : 4′-dinitrostilbene-2 : 2′-disulphonate, m. p. 245—250° (decomp.), also obtained by the direct action of bromine on the disulphonate (*dipyridine* additive compound, m. p. 203—214°, which when treated with alkali yields the *potassium* salt of the dibromide). Chlorine similarly yields the dilactone and the *chloromonolactone.* When treated with methyl sulphate, the original disodium salt yields *methyl* 4 : 4′-*dinitrostilbene*-2 : 2′-*disulphonate* (*pyridine* compound, m. p. 259—261°; *phenylhydrazine* additive compound), which with chlorine gives the *dichloride*, decomp. 252° (*pyridine* compound, m. p. 247—250°, which on treatment with alkali behaves in a manner similar to the bromine compound). The bromomonolactone (II) on treatment with pyridine and methyl sulphate yields *methyl* 4 : 4′-*dinitro*-ω-*bromostilbene*-2 : 2′-*disulphonate*, m. p. 204°, and on treatment with alkali and potassium chloride yields the corresponding *dipotassium* salt. On treatment with a large excess of 50% potassium hydroxide solution, it yields *potassium* 4 : 4′-*dinitrotolane*-2 : 2′-*disulphonate*, from which is obtained the free *acid*, $+5H_2O$, which on rapid heating has m. p. 190—195° and is converted into the *lactone* of 4 : 4′-*dinitrodeoxybenzoin*-2 : 2′-*disulphonic acid*,  $NO_2\cdot C_6H_3<\begin{matrix}CH{=}C-\\SO_3H\ \ O\cdot SO_2\end{matrix}>C_6H_3\cdot NO_2$ [*methyl* ester, m. p. 181°, also obtained from the dilactone (see below); *pyridine* compound of the dimethyl ester, m. p. 202—203°]. Methyl sulphate converts the dinitrotolanedisulphonic acid into its *methyl* ester, m. p. 234—235° (*pyridine* compound, m. p. 246—247°; *dibromide*, m. p. 242—253°), whilst treatment with phosphorus pentachloride and phenol yields the *phenyl* ester, m. p. 185—186°. The dilactone (I) on treatment with methyl-alcoholic potassium hydroxide solution yields *tripotassium* 4 : 4′-*dinitrodeoxybenzoin*-2 : 2′-*disulphonate* (*aci*-form)  which on decomposition with concentrated hydrochloric acid yields the corresponding *acid*, $+4H_2O$ (normal form), m. p. 185° (decomp.) (*methyl* ester, m. p. 231°). Pyridine converts the dilactone into an additive *compound*, m. p. 211—212°, which on treatment with methyl sulphate yields the methyl ester of the lactone of dinitrodeoxybenzoindisulphonic acid previously obtained. Reduction of the dinitrotolanedisulphonic acid with stannous chloride yields 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonic acid* (*diacetyl* derivative). Phenyl *trans*-4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid (Green, Marsden, and Scholefield, J.C.S., 1904, 85, 1434) on treatment with chlorine yields a dichlorinated *compound*; the position of the chlorine atoms is not known. On reduction with stannous chloride in acetic–hydrochloric acid solution it yields *phenyl* 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonate*, m. p. 245—250° (*diacetyl* derivative, m. p. 298—302°). Elimination of the amino-groups from 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid by diazotisation and treatment of the product with phosphorus pentachloride and phenol yields *phenyl stilbene*-2 : 2′-*disulphonate*, m. p. 184·5—185°. J. W. Baker.

Electrochemical oxidation of benzene homologues. III. *p*-Xylene. F. Fichter and M. Rinderspacher (Helv. Chim. Acta, 1926, 9, 1097—1101).—The electrochemical oxidation of *p*-xylene in 0·5*N*-sulphuric acid suspension with a lead oxide anode, a lead cathode, and using a diaphragm, yields *p*-tolualdehyde, *p*-toluic acid (in which the side-chain only has been attacked), *p*-xylenol, *p*-xyloquinol, *p*-xyloquinone, and (impure) 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenyl (in which the nucleus is attacked). When no diaphragm is used, the products are αβ-dihydroxy-αβ-di-*p*-tolylethane (*p*-hydrotoluoin, 70%), *iso*-*p*-hydrotoluoin (10%), and some *p*-tolylmethyl alcohol. In a mixture of acetone and 2*N*-sulphuric acid the products are *p*-tolualdehyde, traces of terephthalic acid, and ω′-*acetylstyrene*-p-*carboxylic acid*, m. p. 143—145°, which is produced by condensation of the acetone with the terephthalaldehydic acid produced by the electrochemical oxidation. *p*-Xylenol by electrochemical oxidation in 2*N*-sulphuric acid suspension yields 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenyl and *p*-xyloquinone. J. W. Baker.

Oxidations in the benzene series by gaseous oxygen. II. Alkylbenzenes with two or more carbon atoms in the side-chain. H. N. Stephens (J. Amer. Chem. Soc., 1926, 48, 2920—2922; cf. A., 1926, 1028).—The action of gaseous oxygen at about 100° on aromatic hydrocarbons containing *n*-, *sec.*-, and *tert.*-alkyl groups causes oxidation only at the α-carbon atom of the side-chain. Thus ethylbenzene, *n*-propylbenzene, cumene, and *p*-cymene yielded, respectively, acetophenone, propiophenone, acetophenone, and *p*-tolyl methyl ketone. At least one hydrogen atom must be attached directly to the α-carbon atom for oxidation to take place, *tert.*-butylbenzene, for example, being unattacked after treatment with gaseous oxygen at 102—104° for 25 days. The presence of water inhibits the oxidation when at least two hydrogen atoms are attached to the α-carbon, but favours it when only one hydrogen atom occupies that position. It is suggested that in the latter case the elements of an alcohol are eliminated, *e.g.*, methyl alcohol from an *iso*propyl group, and that water, not being a product of reaction, is, consequently, without retarding effect. F. G. Willson.

Intermediate products in the Friedel and Crafts reactions. S. C. J. Oliver (Rec. trav. chim., 1926, 45, 817—818).—Nitrobenzene forms a crystalline additive compound with aluminium chloride, which dissolves in, but does not itself react with, benzene, whilst the solution when treated with benzyl chloride gives a better yield of diphenylmethane than when aluminium chloride alone is used as the catalyst. This observation supports Böeseken's theory of catalysis (A., 1926, 806) as opposed to the view that the catalyst acts by virtue of the intermediate compounds formed, since neither benzene nor benzyl chloride forms an additive compound with aluminium chloride. J. W. Baker.

Preparation of 2 : 3- and 1 : 4-dinitronaphthalene. R. K. Chudozilov (Chem. Listy, 1926, 20, 509—511).—6-Nitro-7-aminotetrahydronaphthalene is converted by means of the diazo-reaction into 6 : 7-*dinitrotetrahydronaphthalene*, m. p. 98—99°, which affords 2 : 3-*dinitronaphthalene*, m. p. 170·5—171°, and 6-*nitro-7-hydroxytetrahydronaphthalene*, m. p. 83—84°. Similarly, 1-nitro-4-aminotetralin is converted by the diazo-reaction into 5 : 8-*dinitrotetralin*, m. p. 87—88°, affording on dehydrogenation 1 : 4-dinitronaphthalene, m. p. 131—132°. The latter is also obtained from 1-nitro-4-aminonaphthalene by the diazo-reaction (cf. A., 1923, i, 550). R. Brightman.

Manufacture of primary and secondary aromatic amines. E. Merck, Assees. of W. W. Krauss.—See B., 1926, 964.

Derivatives of hydroxyphenylglycine. II. K. Shimo (Bull. Chem. Soc. Japan, 1926, 1, 226—233; cf. A., 1925, i, 1423; Galatis, *ibid.*, 1921, i, 556; 1926, 1243).—The following derivatives of anilinoacetonitrile were prepared :

p-Acetoxy-*N*-acetyl-, m. p. 94—95°; p-*benzoyloxy-*N-*benzoyl-*, m. p. 129—130°; p-*acetoxy-α-methyl-*, m. p. 129—131°; p-*acetoxy-αα-dimethyl-*, m. p. 77—78°; p-*benzoyloxy-α-phenyl-*, m. p. about 200°; p-*acetoxy-α-phenyl-*, m. p. 119—120°; p-*acetoxy-α-phenyl-α-methyl-*, m. p. 142—143°; o-*hydroxy-*N-*acetyl-*, m. p. 167—168°; o-*acetoxy-*N-*acetyl-*, m. p. 105—106°; o-*benzoyloxy-*, m. p. 120—121°; m-*acetoxy-α-phenyl-α-methyl-*, m. p. 123—124°.

Schotten–Baumann benzoylation of the *p*-hydroxy-αα-dimethyl- or *p*-hydroxy-α-phenyl-α-methyl-derivatives gives *p*-benzoyloxybenzanilide.

From *p*-hydroxyphenylglycine the methyl ester, m. p. 97—98°, ethyl ester, m. p. 78—79°, the N-*acetyl* derivative, m. p. 174—175°, and p-*acetoxy-*N-*acetylphenylglycine*, m. p. 203—204°, were obtained. o-*Hydroxy-*N-*acetylphenylglycine*, m. p. 201—202° (decomp.), was also prepared. E. W. Wignall.

Reactions of thiocarbanilide. R. T. C. Loh and W. M. Dehn (J. Amer. Chem. Soc., 1926, 48, 2956—2959).—Thiocarbanilide is oxidised quantitatively in alkaline solution by sodium peroxide to diphenylcarbamide; other alkaline oxidising agents give yields decreasing in the order : potassium permanganate, potassium chromate, potassium persulphate, bleaching powder, potassium hypobromite, and potassium hypoiodite. The conversion of the thion- into the keto-group by alkaline oxidising agents appears to be a general reaction. Treatment of a solution of thiocarbanilide in sulphuric acid (prepared cold) with fuming nitric acid at 75—85° affords *s*-tetranitrodiphenylcarbamide, m. p. 204°, which, when heated with mixed nitric and sulphuric acids, yields *s*-hexanitrodiphenylcarbamide, m. p. 209°. When heated with a freshly-prepared aqueous solution of the calculated quantity of mercurous nitrate, thiocarbanilide affords di-*p*-nitrothiocarbanilide, m. p. 161°. Thiocarbanilide forms an additive *compound*, m. p. 85°, with 1 mol. of mercuric chloride, when the two are mixed in alcoholic solution. Additive *compounds* with the following metallic halides were prepared by mixing the components in methyl ethyl ketone and precipitating with toluene : cupric bromide (0·5 mol.), m. p. 187°; cadmium bromide (0·5 mol.), yellow, m. p. 140°; mercuric iodide (0·5 mol.), m. p. 183°; zinc chloride (0·5 mol.), m. p. 172°; auric chloride (0·5 mol.), m. p. 194°; stannic chloride (0·5 mol.), m. p. 260°; arsenious bromide, (1 mol.), m. p. above 250°; arsenious iodide (1 mol.), yellow, m. p. similar; and mercuric iodide (1 mol.), yellow, m. p. 139°. F. G. Willson.

Catalytic preparation of amines. II. Preparation of the toluidines and *m*-phenylenediamine. E. Briner, A. Ferrero, and B. Paillard (Helv. Chim. Acta, 1926, 9, 956—958; cf. Briner, Ferrero, and Luserna, A., 1924, i, 503).—The yields of *o*-, *m*-, and *p*-toluidines obtained by passing a mixture of the corresponding cresol and ammonia over freshly-prepared aluminium oxide at 420° are 43·1, 40·0, and 42·4%, respectively, which are increased to 55·1, 51·4, and 52·3%, respectively, when a catalyst which has been used once previously is employed. Further use of the catalyst decreases its activity. The corresponding yields of *m*-phenylenediamine obtained from resorcinol are 36·9 and 53·0%, respectively. J. W. Baker.

Free ammonium radicals. VII. The ammonium character of triarylamines. E. Weitz and H. W. Schwechten (Ber., 1926, 59, [*B*], 2307—2314; cf. A., 1924, i, 425).—If it be assumed that an aryl group attached to nitrogen makes more demand on the latter than corresponds with a complete valency, the triarylamines must be regarded as ammonium radicals and hence capable of forming salts, not by addition of acids, but of acid residues. These salts, $[Ar_3N]\cdot X$, designated triarylaminium salts, are described. Triphenylamine is unsuitable, since it is readily converted by oxidising agents into *NN'*-tetraphenylbenzidine or its *meri-* or *holo*-quinonoid salts. *Tri-*p-*tolylaminium picrate* is produced by oxidation of the amine in strongly-cooled benzene and light petroleum with lead dioxide in presence of picric acid. *Tri-*p-*tolylaminium perchlorate*, m. p. 123°, is not formed by the oxidation of the amine in presence of perchloric acid, but is readily produced by the action of chlorine peroxide on the base in ethereal solution. The salts give intensely coloured solutions. They are readily transformed by reducing agents, even by ferrous salts, into tri-*p*-tolylamine. H. Wren.

Action of aminosulphonic acid on aromatic amines. A. Quilico (Gazzetta, 1926, 56, 620—630; cf. Levi and Quilico, Giorn. Chim. Ind. Appl., 1915, 7, 127).—Further evidence is advanced to show the extreme instability of α-naphthylaminesulphonic acid and the identity of Paal and Jänicke's sulphamic acid (A., 1896, i, 235) with α-naphthylamine-2-sulphonic acid. The general character of the reaction by which sulphamic derivatives are formed when amines are heated with aminosulphonic acid is verified, the reaction being extended to the cases of *m*-toluidine and β-naphthylamine. In all instances, this reaction yields first sulphamic derivatives, which at higher temperatures give sulphonic derivatives. The transposition takes place very readily with α-naphthylamine, but less so with β-naphthylamine. With amines of the benzene series, the *para*-position or, if this is occupied, the *ortho*-position is preferred by the migrating sulphonic group. α-Naphthylamine gives the 2-sulphonic, and β-naphthylamine the 6-sulphonic acid. T. H. Pope.

Ring-formation. A. C. Sircar and P. K. De (J. Indian Chem. Soc., 1926, 3, 245—252).—The hypothetical *p*-diphenylene is not produced in the action of copper on 4 : 4′-di-iododiphenyl or *p*-di-iodobenzene (cf. Turner, J.C.S., 1915, **107**, 1495). The formation of the following derivatives is advanced as evidence against the Kaufler type of formula for 4 : 4′-diaminoazobenzene: a *diphthalyl* derivative, m. p. above 300°, using phthalyl chloride, whilst phthalic anhydride does not react; an *oxalyl* derivative, m. p. above 300°; *di-o-hydroxybenzylidene* derivative, m. p. 265°; *di-3 : 4-dihydroxybenzylidene* derivative, darkening at 250°, but not melted at 270°, and 2 : 4 : 2′ : 4′-*tetramethylazoquinoline*, m. p. 193°, produced by the action of acetylacetone. The *di-p-anisylidene* derivative of benzidine, m. p. 246—248°, is also described. G. M. Bennett.

Diphenylyl derivatives of ammonia, *p*-phenylenediamine, and benzidine. *meri*-Quinonic salts. J. Piccard (J. Amer. Chem. Soc., 1926, 48, 2878—2885).—An extension of the known series of *meri*-quinonoid salts derived from *p*-phenylenediamine and benzidine (cf. Piccard, A., 1911, i, 568). The colours of these *meri*-quinonoid salts from the respective bases are as follows: *p*-phenylenediamine, yellow; monomethyl-, orange; dimethyl-, red; phenyl-, violet-red; trimethyl-, violet; tetramethyl-, violet-blue; diphenyl-, blue; didiphenylyl-, bluish-green; tetraphenyl-, green; diphenyldidiphenylyl-, green; and tetradiphenylyl-*p*-phenylenediamine, yellowish-green; benzidine, blue; diethyl-, green; tetramethyl-, greenish-yellow; diphenyl-, yellow; didiphenylyl-, orange-yellow; tetraphenyl-, orange; diphenyldidiphenylyl-, red; and tetradiphenylyl-, violet-red. These series illustrate the regular succession of colours through those of the first order to those of the second. As the colour of the *meri*-quinonoid salt derived from benzidine itself is blue, the colours of the corresponding salts from its above derivatives are chiefly of the second order (cf. Piccard, A., 1926, 1079).

Phenyldiphenylylamine (*diphenylylaniline*), m. p. 112° (*acetyl* derivative, m. p. 110°), is obtained by heating together diphenylylacetamide, iodobenzene, potassium carbonate, nitrobenzene, and a trace of copper powder at 230—250° for 12 hrs., or alternatively from acetanilide and *p*-iododiphenyl by the same method, with subsequent hydrolysis. *Phenyldidiphenylylamine* (*didiphenylylaniline*), m. p. 160°, is prepared analogously from iodobenzene and aminodiphenyl, and from aniline (1 mol.) and iododiphenyl (2 mols.). Tridiphenylylamine, m. p. 257—259°, is obtained in the same way from didiphenylylamine and iododiphenyl. When pure, this substance gives a colourless solution in concentrated sulphuric acid, but the solution turns green rapidly in presence of air (cf. Bülow, A., 1924, i, 1183). Diphenyldiphenylylamine was also synthesised similarly from aminodiphenyl (1 mol.) and iodobenzene (2 mols.). Tetraphenylbenzidine (cf. Wieland, *ibid.*, 1913, i, 1386) was obtained as above from 4 : 4′-di-iododiphenyl and diphenylamine, and from benzidine and iodobenzene. *Didiphenylylbenzidine*, m. p. 300° (diacetyl derivative, m. p. 245—249°), was obtained similarly from diphenylylacetamide (2 mols.) and 4 : 4′-di-iododiphenyl (1 mol.), and from diacetylbenzidine (1 mol.) and iododiphenyl (2 mols.), and analogous methods were applied for the synthesis of diphenyldidiphenylylbenzidine (cf. Piccard, *ibid.*, 1924, i, 208) and *tetradiphenylylbenzidine*, m. p. 254—259°. The latter forms an orange-red additive *compound*, m. p. indefinite, with 2 mols. of nitrobenzene (cf. Ostromisslensky, *ibid.*, 1911, ii, 195), and a yellow additive *compound* with 1 mol. of toluene. Diphenyldidiphenylylbenzidine was also obtained by oxidation of diphenyldiphenylylamine to diphenyldidiphenylyldiphenoquinonedi-immonium acetate and subsequent reduction (cf. Piccard and Abouchy, *ibid.*, 1924, i, 316; Piccard, Helv. Chim. Acta, 1924, 7, 789). F. G. Willson.

Preparation and hydrolysis of isomeric azoxybenzyl bromides. J. B. Shoesmith and W. E. Taylor (J.C.S., 1926, 2832—2834; cf. *ibid.*, 1922, **121**, 1391; A., 1923, i, 908; 1926, 389).—The rates of hydrolysis of the isomeric azoxybenzyl bromides with aqueous propyl alcohol are found to be in the order *o*>*p*>*m*. Since the azoxy-group directs *ortho-para* substitution, the results are in agreement with the rule that in a series of substituted benzyl halides, $R\cdot C_6H_4\cdot CH_2Hal$, the isomerides in which the $\cdot CH_2Hal$ group is attached to the carbon atom of the benzene nucleus which is attacked during substitution of the $R\cdot C_6H_5$ compound are the ones which are most readily hydrolysed.

o-*Azoxybenzyl bromide*, m. p. 105° (violent decomp. at 106°), and m-*azoxybenzyl bromide*, m. p. 119°, are prepared from the corresponding alcohols by the action of hydrogen bromide. A complex by-product is formed with the *ortho*-derivative. p-*Azoxybenzyl bromide*, m. p. 203°, is prepared from p-*azoxybenzyl alcohol*, m. p. 167°, by treatment with phosphorus pentabromide in bromoform solution. H. Burton.

Stability of benzenediazonium chloride solutions. II. Reaction of benzenediazonium chloride with certain organic hydroxy-substances. H. A. H. Pray.—See this vol., 26.

Relationship between quinonehydrazones and *p*-hydroxyazo-compounds. V. *p*-Arylsulphonazophenols. W. Borsche and R. Frank (Annalen, 1926, 450, 75—84; cf. Borsche and Ockinga, A., 1905, i, 719).—Benzenesulphonhydrazide reacts with *p*-benzoquinone below 0° in the presence of dilute hydrochloric acid to give 4-*benzenesulphonazophenol*, $PhSO_2\cdot N_2\cdot C_6H_4\cdot OH$, m. p. 101° [*benzoate*, m. p. 149° (decomp.)], decomposed slowly by water, quickly by acids, into benzenesulphinic acid and a *p*-hydroxybenzenediazonium salt. At ordinary temperatures the azo-compound decomposes as it is formed, and the sulphinic acid produced combines with the quinone to give 2 : 5-dihydroxydiphenylsulphone. This provides a preparative method for *p*-hydroxybenzenediazonium salts. 2 : 4 : 4′-*Trihydroxyazobenzene* melts at 226°. Attempts to reduce *p*-benzenesulphonazophenol with phenylhydrazine gave benzenesulphonphenylhydrazide, m. p. 164·5°. 4-p-*Toluenesulphonazophenol*, m. p. 95° (decomp.; *benzoate*, decomp. 137°; NN′-*di*-p-*toluenesulphonyl*-p-*benzoyloxyphenylhydrazine*, m. p. 174°, from the benzoate and *p*-toluenesulphinic acid), prepared from *p*-benzoquinone and *p*-toluenesulphonhydrazide (m. p. 115°; acetone derivative, m. p. 159—160°), behaves similarly. 2 : 5-Dihydroxyphenyl-*p*-tolylsulphone, m. p. 211° (p-*toluenesulphonate*, m. p. 162°), and p-*toluenesulphonphenylhydrazide*, m. p. 171—172°, are described. *Quinol di*-p-*toluenesulphonate*, m. p. 159°, and p-*hydroxyphenyl* p-*toluenesulphonate*, m. p. 98—99°, are prepared from quinol and *p*-toluenesulphonyl chloride in pyridine. C. Hollins.

Etherification of hydroaromatic alcohols. J. B. Senderens and J. Aboulenc (Compt. rend., 1926, **183**, 830—832).—*cyclo*Hexyl ethers cannot be prepared by the catalytic method (cf. A., 1926, 46) from *cyclo*hexanol or its mixtures with aliphatic alcohols, the *cyclo*hexanol being always dehydrated to *cyclo*hexene and $\Delta^{1:1'}$-di*cyclo*hexene. When, however, a mixture of *cyclo*hexanol and benzyl alcohol with 2% of sulphuric acid trihydrate is refluxed at 130—135°, benzyl ether and cyclo*hexyl benzyl ether*, b. p. 182—183°/50 mm., d_4^{15} 1·008, are obtained. The latter is decomposed on warming with sulphuric acid dihydrate into *cyclo*hexene and resinous matter. The following derivatives were prepared similarly: 3-*methyl*-, b. p. 186·5—187·5° (corr.)/50 mm., d_4^{15} 1·006; 4-*methyl*-, b. p. 190·5—191·5°/50 mm., d_4^{15} 1·004; 3 : 4-*dimethyl*-, b. p. 192—193°/50 mm., d_4^{15} 1·005; and 3-*methyl*-6-iso*propyl*-cyclo*hexyl benzyl ether*, b. p. 198—200°/50 mm., d_4^{15} 1·001. H. E. F. Notton.

Catalytic action of Japanese acid earth. IV. Action on *cyclo*hexanol and its derivatives. H. Inoue (Bull. Chem. Soc. Japan, 1926, 1, 219—226; cf. A., 1926, 1110, 1132).—The dehydrogenation of *cyclo*hexanol in presence of Japanese acid earth yields at 200° mainly *cyclo*hexene, but at 330° mainly methyl*cyclo*pentane, which can also be obtained by using *cyclo*hexene, but not from *cyclo*hexane. Methyl*cyclo*hexanol yields, at 250°, methyl*cyclo*hexenes; at 350°, a dimethyl*cyclo*pentane is formed, with other products. E. W. Wignall.

Bromophenols. XX. Behaviour of pentahalogenophenols towards aluminium chloride in benzene. M. Kohn and G. Dömötör (Monatsh., 1926, 47, 207—240; cf. A., 1926, 832).—When chlorophenols are gently warmed with excess of bromine and a little iron powder, in absence of moisture (cf. *ibid.*, 521), good yields of pentahalogenophenols are obtained. These are oxidised by nitric acid (*d* 1·5) to the corresponding tetrahalogeno-*p*-benzoquinones, whilst, when they are treated with aluminium chloride in presence of benzene, the *o*- and *p*-bromine atoms are replaced by hydrogen, chlorine and *m*-bromine atoms remaining unattacked. In spite of their high mol. wt., many of these phenols can be distilled without decomposition at atmospheric pressure. 2 : 4 : 6-*Trichloro*-3 : 5-*dibromophenol*, m. p. 204° (all m. p. corr.), monoclinic (*methyl ether*, m. p. 127°, b. p. 336—340°/747 mm.; *benzoate*, m. p. 196°), is oxidised to 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, m. p. above 280°. The crystallographic and optical properties of the compounds the crystalline form of which is indicated are fully described. 2 : 4-*Dichloro*-3 : 5 : 6-*tribromophenol*, m. p. 209°, triclinic (*methyl ether*, m. p. 143—144°, b. p. 350—355°/752 mm.; *benzoate*, m. p. 202°), obtained by the general method from 2 : 4-dichlorophenol, is oxidised to *chlorotribromo*-p-*benzoquinone*, m. p. above 275°, which affords, on reduction by Kohn and Grün's method (A., 1925, i, 1265), *chlorotribromoquinol dimethyl ether*, m. p. 185—186°. The dichlorotribromophenol reacts with aluminium chloride in presence of benzene, giving 2 : 4-*dichloro*-3 : 5-*dibromophenol*, m. p. 122°, rhombic pyramidal (*methyl ether*, m. p. 114°, b. p. 329—331°/757 mm.), from which 2 : 4-*dichloro*-3 : 5-*dibromo*-6-*nitrophenol*, m. p. 141° (*methyl ether*, m. p. 86°); 2 : 4-*dichloro*-3 : 5-*dibromo*-6-*iodophenol*, m. p. 187° (*methyl ether*, m. p. 148°), and 2-*chloro*-3 : 5-*dibromo*-6-*iodobenzoquinone*, m. p. above 280°, are obtained. 2 : 6-Dichloro-4-bromophenol, prepared by chlorinating *p*-bromophenol, is successively converted by similar methods into 2 : 6-*dichloro*-3 : 4 : 5-*tribromophenol*, m. p. 223·5°, monoclinic (*methyl ether*, m. p. 145°, b. p. 335—345°/765 mm.; *benzoate*, m. p. 175°); 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, m. p. above 292°; 2 : 6-*dichloro*-3 : 5-*dibromophenol*, m. p. 128°, monoclinic (*methyl ether*, m. p. 109·5°, b. p. 309—311°/740 mm.); 2 : 6-*dichloro*-3 : 5-*dibromo*-4-*nitrophenol*, m. p. 179·5° (*methyl ether*, m. p. 131°); 2 : 6-*dichloro*-3 : 5-*dibromo*-4-*iodophenol*, m. p. 210—212° (*methyl ether*, m. p. 167°). *p*-Chlorophenol is brominated to 4-*chloro*-2 : 3 : 5 : 6-*tetrabromophenol*, m. p. 215°, monoclinic (*methyl ether*, m. p. 161°, b. p. 353—355°/756 mm.; *benzoate*, m. p. 203°), from which tetrabromobenzoquinone; 4-*chloro*-3 : 5-*dibromophenol*, m. p. 121°, b. p. 320—321°/743 mm., monoclinic (*methyl ether*, m. p. 82·5°, b. p. 300°/745 mm.); 4-*chloro*-3 : 5-*dibromo*-2 : 6-*dinitrophenol*, m. p. 149° (*methyl ether*, m. p. 128—129°); 4-*chloro*-3 : 5-*dibromo*-2 : 6-*di-iodophenol*, m. p. 203° (decomp.) (*methyl ether*, m. p. 173°); and 3 : 5-*dibromo*-2 : 6-*di-iodobenzoquinone* are obtained. Similarly, *o*-chlorophenol affords 2-*chloro*-3 : 4 : 5 : 6-*tetrabromophenol*, m. p. 224° (*methyl ether*, m. p. 158·5°, b. p. 346—350°/765 mm.; *benzoate*, m. p. 178°); chlorotribromobenzoquinone; 2-*chloro*-3 : 5-*dibromophenol*, m. p. 68°, b. p. 285—287°/754 mm. (*methyl ether*, m. p. 102·5°, b. p. 291—293°/754 mm.); 2-*chloro*-3 : 5-*dibromo*-4 : 6-*dinitrophenol*, m. p. 155—157° (*methyl ether*, m. p. 125°); 2-*chloro*-3 : 5-*dibromo*-4 : 6-*di-iodophenol*, m. p. 177° (decomp.) (*methyl ether*,

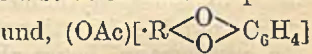
m. p. 172°), and 2-chloro-3 : 5-dibromo-6-iodobenzoquinone. H. E. F. NOTTON.

Bromophenols. XXI. New halogenated phenols from *m*-chlorophenol. M. KOHN and A. ZANDMAN (Monatsh., 1926, **47**, 357—377).—Bromination of *m*-chlorophenol in aqueous solution yields 3-*chloro*-2 : 4 : 6-*tribromophenol*, m. p. 106°, of which the *methyl ether*, m. p. 96°, b. p. 323—325°/766 mm., is converted by nitration into 3-*chloro*-2 : 4 : 6-*tribromo-5-nitroanisole*, m. p. 116°, demethylated to the corresponding phenol, m. p. 146·5°. Fuming nitric acid oxidises the free chlorotribromophenol to 3-*chloro*-2 : 6-*dibromobenzoquinone*, m. p. 165°, reduced by sulphurous acid to 3-*chloro*-2 : 6-*dibromoquinol*, m. p. 144° (*dimethyl ether*, m. p. 90°, b. p. 317—319°/756 mm.; *dibenzoate*, m. p. 165°). The action of iodine on *m*-chlorophenol in alkaline solution yields 3-*chloro*-2 : 4 : 6-*tri-iodophenol*, m. p. 140° (*methyl ether*, m. p. 115·5°), converted by fuming nitric acid into 3-*chloro*-2 : 6-*di-iodobenzoquinone*, m. p. 175°. Bromination of *m*-chlorophenol with bromine and iron powder gives 3-*chloro*-2 : 4 : 5 : 6-*tetrabromophenol*, m. p. 210°, which is debrominated by the action of aluminium chloride and benzene with production of 3-*chloro-5-bromophenol*, m. p. 68—69° (*methyl ether*, m. p. 31·5°, b. p. 238—240°/746 mm.). Nitration of this phenol produces 3-*chloro-5-bromo*-2 : 4 : 6-*trinitrophenol*, m. p. 165·5°, of which the *methyl ether*, m. p. 106—107°, results from the nitration of 3-chloro-5-bromoanisole with nitric and sulphuric acids, whilst nitration with cold fuming nitric acid alone yields 3-*chloro-5-bromo*-2 : 4-*dinitroanisole*, m. p. 165°, demethylated to 3-*chloro-5-bromo*-2 : 4-*dinitrophenol*, m. p. 97°.

The direct iodination of 3-chloro-5-bromophenol furnishes 3-*chloro-5-bromo*-2 : 4 : 6-*tri-iodophenol*, m. p. 207° (*methyl ether*, m. p. 199°), which is oxidised by fuming nitric acid to 3-*chloro-5-bromo*-2 : 6-*di-iodobenzoquinone*, m. p. 253—255°. Chlorination of 3-chloro-5-bromophenol in glacial acetic acid solution yields 2 : 3 : 4 : 6-tetrachloro-5-bromophenol, m. p. 197° (cf. McCombie and Ward, J.C.S., 1913, **103**, 1995) (*methyl ether*, m. p. 115·5°, b. p. 310—313°/745 mm.). In a similar way, 3 : 4 : 5-tribromophenol gives 2 : 6-dichloro-3 : 4 : 5-tribromophenol (cf. preceding abstract) (methyl ether, m. p. 145°). Bromination of 3-chloro-5-bromophenol in glacial acetic acid solution furnishes 3-*chloro*-4 : 5-*dibromophenol*, m. p. 116—117°, of which the *methyl ether*, m. p. 72—75°, b. p. 296—300°/746 mm., yields on nitration 3-*chloro*-4 : 5-*dibromo*-2 : 6-*dinitroanisole*, m. p. 100—101°. 3-Chloro-4 : 5-dibromophenol is converted by chlorine in glacial acetic acid into 2 : 3 : 6-*trichloro*-4 : 5-*dibromophenol*, m. p. 204—205°, from which 2 : 3 : 5-*trichloro-5-bromobenzoquinone*, not melted at 260°, is obtained by oxidation. The same chlorodibromophenol yields by direct iodination 3-*chloro*-4 : 5-*dibromo*-2 : 6-*di-iodophenol*, m. p. 191—192°. G. M. BENNETT.

Benzoquinonethiolimines. E. GEBAUER-FÜLNEGG and E. RIESZ (Monatsh., 1926, **47**, 57—61).—*p*-Aminophenol reacts in ether solution with 4-chloro-2-nitro-1-chlorothiolbenzene to yield 4-*chloro-2-nitrophenylthiol*-p-*hydroxyanilide*, $C_6H_3(NO_2)Cl{\cdot}S{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, red, m. p. 119°, which is oxidised by dichromate in acetic acid solution to *benzoquinone-4-chloro-2-nitrophenylthiolimine*, $C_6H_3(NO_2)Cl{\cdot}S{\cdot}N{:}C_6H_4{:}O$, orange, m. p. 194°. The latter gave neither an oxime nor a phenylhydrazone. Simultaneous acetylation and reduction of either substance with zinc and acetic anhydride yields 4-*chloro*-1-*methylbenzthiazole*, m. p. 68°, through the intermediate formation of the *o*-acetamidothiophenol. G. M. BENNETT.

Constitution of australol. J. C. EARL and M. T. TRIKOJUS (J. Proc. Roy. Soc. N.S.W., 1925, **59**, 301—305).—The essential oil from *Eucalyptus polybractea* (d^{15} 0·970, saponification number 50—51; after acetylation, 121) yielded 10% of phenols, from which the solid, m. p. 60°, was separated which had been given the name "australol" by Smith ("Research on the Eucalypts," 2nd ed., 395) when obtained from a similar source (Robinson and Smith, A., 1915, i, 978). This is now identified as *p*-*iso*propylphenol (*p*-hydroxycumene) (m. p. 60°, benzoate, m. p. 71·5°). G. M. BENNETT.

Co-ordination valency of two hydroxyl groups in the *ortho*-position. III. Polyphenolic complexes of the rare earths. L. FERNANDES (Gazzetta, 1926, **56**, 682—688; cf. A., 1926, 1036).—When pyrocatechol (or pyrogallol) is added to the solution of a salt of a rare-earth metal and the liquid is then rendered alkaline by means of an alkali hydroxide or ammonia, a flocculent or pulverulent precipitate is formed, $[OH{\cdot}R({\cdot}O{\cdot}C_6H_4{\cdot}OH)_2]$ (1). This compound is electrolytically almost neutral and exhibits amphoteric behaviour. In a weak acid such as acetic acid it dissolves to a solution which deposits a white crystalline compound,  $(OAc)[{\cdot}R{<}^{O}_{O}{>}C_6H_4]$ (2), on cooling, but if it is dissolved in alkali hydroxide (or ammonia) solution, the complex radical acts as an acid and the compound $[R({\cdot}O{\cdot}C_6H_4{\cdot}OH)_3]R'_3$ (3) is formed: $R{=}Ce$, La, Pr, Nd; $R'{=}K$, Na, NH_4.

When the complex molecule contains only one phenolic radical, in acid solution, the grouping exerts a basic function, the alkalinity of the metal being only partly neutralised; thus, compounds of type (2) are formed. When, however, two phenol residues enter the complex radical, this becomes neutral and, hence, undissociated; and when three phenolic radicals enter, the compound exhibits acid properties. Compounds of types (2) and (3) are usually moderately stable, whilst the neutral compounds decompose so easily that they explode violently at 90° and oxidise with liberation of heat in the air even at the ordinary temperature.

The compounds of praseodymium, neodymium, and lanthanum are similar in properties, but the cerium compounds are different, the cerium salts, with both pyrocatechol and pyrogallol, being deep violet instead of white. The hydroxide of the pyrocatechol–cerium compound, unlike its analogues, dissolves in concentrated ammonia solution to a deep violet liquid, which, when boiled, deposits a deep violet, crystalline compound, $[Ce(C_6H_4O_2)_3](NH_4)_2H,H_2O$.

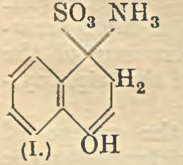
Seventeen of these complex compounds were prepared and analysed. T. H. POPE.

5-Halogenoresorcinols. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1926, 2826—2827).—The three 5-halogenoresorcinols are prepared by converting the

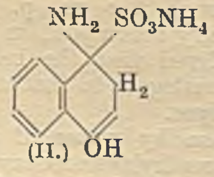
5-halogeno-*m*-anisidines (A., 1926, 1034) into the 5-halogeno-3-hydroxyanisoles and hydrolysing these with aqueous hydriodic acid. 5-*Chloro*-3-*hydroxyanisole*, m. p. 99°; 5-*bromo*-3-*hydroxyanisole*, m. p. 102°; and 5-*iodo*-3-*hydroxyanisole*, m. p. 90°, on bromination are converted into 5-*chloro*-2 : 4 : 6-*tribromo*-3-*hydroxyanisole*, m. p. 110°; 2 : 4 : 5 : 6-*tetrabromo*-3-*hydroxyanisole*, m. p. 120°; and 2 : 4 : 6-*tribromo*-5-*iodo*-3-*hydroxyanisole*, m. p. 125°. 5-*Chlororesorcinol* and 5-*iodoresorcinol* form *monohydrates* having m. p. 67° and m. p. 92·3°, respectively. The anhydrous chloro-compound has m. p. 117°; the iodo-compound could not be dehydrated completely. 5-*Bromoresorcinol*, m. p. 87°, crystallises from water as the *monohydrate*, m. p. about 79°. The halogenoresorcinols on bromination yield 5-*chloro*-2 : 4 : 6-*tribromoresorcinol*, m. p. 143°; 2 : 4 : 5 : 6-tetrabromoresorcinol, m. p. 212° (Claassen, A., 1878, 868, gives m. p. 163°; Benedikt, Monatsh., 1880, **1**, 366, gives m. p. 167°), and 2 : 4 : 6-*tribromo*-5-*iodoresorcinol*, m. p. 214°. H. BURTON.

Derivatives of stilbene. J. N. ASHLEY (J.C.S., 1926, 2804—2807).—2-*Nitro*-4-*amino*-3′ : 4′-*dimethoxystilbene*, m. p. 186—187° (*hydrochloride*, m. p. 223° after darkening at 200°; *acetyl* derivative, m. p. 183—184°), obtained by reduction of the 2 : 4-dinitro-compound with ammonium sulphide, is converted into 4-*chloro*-2-*nitro*-3′ : 4′-*dimethoxystilbene*, m. p. 124—125°, and then into 4-*chloro*-2-*amino*-3′ : 4′-*dimethoxystilbene*, m. p. 147—148° (*acetyl* derivative, m. p. 180°). A suspension of the diazonium sulphate of this chloroamine on treatment with copper powder yielded an amorphous nitrogen compound, with no trace of a phenanthrene derivative. Nitration of 4-chloro-2-nitro-3′ : 4′-dimethoxystilbene in glacial acetic acid yields 4-*chloro*-2 : 6′-*dinitro*-3′ : 4′-*dimethoxystilbene*, m. p. 175°, which on reduction and acetylation gives 4-*chloro*-2 : 6′-*diacetamido*-3′ : 4′-*dimethoxystilbene*, m. p. 275° (decomp.). Phosphoryl chloride does not convert this diacetamido-compound into a 2 : 6-naphthyridine (cf. Gulland and Robinson, A., 1925, i, 1188), but into a *compound*, $C_{20}H_{19}O_3N_2Cl$, m. p. about 230° (decomp.) after darkening at 160°, probably a quinoline derivative. H. BURTON.

Tautomerism of phenols. VII. 1 : 4-Dihydroxynaphthalene and 4-amino-α-naphthol. VIII. 1 : 2-Dihydroxynaphthalene. W. FUCHS and H. PIRAK (Ber., 1926, **59**, [*B*], 2454—2458, 2458—2461; cf. A., 1924, i, 960).—VII. 4-Amino-α-naphthol is prepared by coupling α-naphthol with diazotised aniline and reductive fission of the azo-derivative with tin and hydrochloric acid. Its oxidation to α-naphthaquinone and subsequent reduction affords 1 : 4-dihydroxynaphthalene in poor yield. Treatment of 1 : 4-dihydroxynaphthalene or 4-amino-α-naphthol or its hydrochloride with ammonium sulphite or hydrogen sulphite affords the *substances* (I) and (II), which are readily transformed into 4-amino-α-naphthol. Dihydroxynaphthalene and 4-amino-α-naphthol give additive products, soluble in water, with sodium hydrogen sulphite. The product from dihydroxynaphthalene is converted by ammonia into 4-amino-α-naphthol, whereas that from amino-naphthol yields dihydroxynaphthalene when decomposed by alkali hydroxide; the ratio Na : S in the additive compound is variable and never 1 : 1.



(I.)



(II.)

VIII. 1 : 2-Dihydroxynaphthalene is prepared by coupling β-naphthol with diazotised aniline, reductive fission of the azo-dye to 2-amino-α-naphthol, and oxidation of the latter substance to the corresponding quinone, which is subsequently reduced. 1 : 2-Dihydroxynaphthalene and sodium hydrogen sulphite afford *sodium* 1 : 2-*dihydroxy*-1 : 2-*dihydronaphthalene*-1-*sulphonate*. Ammonium hydrogen sulphite gives *ammonium* 1-*amino*-2-*hydroxy*-1 : 2-*dihydronaphthalene*-1-*sulphonate*. The additive products are converted by alkali hydroxide into 1 : 2-dihydroxynaphthalene and 1-amino-β-naphthol, respectively. With phenylhydrazine, they yield the *compound*, $C_{22}H_{18}N_4$, m. p. 211—212°, regarded as the diphenylhydrazone of β-naphthaquinone. H. WREN.

Distillation of cholesterol with zinc dust. P. FANTL and M. KABOS (Monatsh., 1926, **47**, 251—258).—The mixture of hydrocarbons obtained by distilling cholesterol with zinc dust in a stream of hydrogen at atmospheric pressure (cf. van der Haar, A., 1922, i, 565) is separated by distillation into four fractions, b. p./7 mm., (*a*), 50—60°, (*b*), 95—97° (n_D 1·5060), (*c*), 162—168° (n_D 1·5301), (*d*), 185—187°. These approximate in composition and mol. wt. to the formula $(C_5H_8)_n$, where $n=1, 2, 3$, and 4, respectively. The mol. refractions indicate that both (*b*) and (*c*) are doubly unsaturated, but the double linkings cannot be detected by titration with bromine. When cholesterol is distilled with zinc dust at 10 mm. pressure, the hydrocarbon skeleton is retained unchanged, cholesterilene, m. p. 73°, $[\alpha]_D^{20}$ −53·37° (cf. Tschugaeff and Fomin, A., 1910, i, 734), being formed in 50—60% yield. This substance is not reduced by sodium and boiling amyl alcohol, but catalytic hydrogenation in presence of palladium-black converts it into a mixture of cholestane and ψ-cholestane (cf. Windaus, *ibid.*, 1919, i, 204). When cholesterilene dissolved in benzene is shaken with aqueous acetic and sulphuric acids, a small amount of cholesterol, identified as the digitonide, is regenerated.

H. E. F. NOTTON.

Substitution by halogen of the hydroxyl group of secondary alcohols. P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1926, **70**, 355—364).—By the general method of resolution of Pickard and Kenyon (J.C.S., 1907, **91**, 2058) there were obtained l-*phenylmethylcarbinol*, $[\alpha]_D^{20}$ −54·86°, l-*phenylethylcarbinol*, $[\alpha]_D^{20}$ −55·54°, l-*phenylpropylcarbinol*, $[\alpha]_D^{20}$ −57·21°, d-*phenylisopropylcarbinol*, $[\alpha]_D^{20}$ +47·66°, and d-*phenylbutylcarbinol*, $[\alpha]_D^{20}$ +40·83°. *d*-Phenylmethylcarbinol, $[\alpha]_D^{20}$ +16·36°, when heated with thionyl chloride gives d-α-*phenylethyl chloride*, $[\alpha]_D^{20}$ +11·89°; *l*-phenylethylcarbinol, $[\alpha]_D^{20}$ −54·53° gave similarly l-α-*phenylpropyl chloride*, $[\alpha]_D^{20}$ −50·34°; with hydrogen bromide at 0° *d*-phenylethylcarbinol, $[\alpha]_D^{20}$ +34·83°, gave l-α-*phenylpropyl bromide*, $[\alpha]_D^{20}$ −1·51°. *d*-Phenylpropylcarbinol, $[\alpha]_D^{20}$ +23·39°, with thionyl chloride gives d-α-*phenyl*-n-*butyl chloride*, $[\alpha]_D^{20}$ +26·88°, and with hydrogen bromide d-α-*phenyl*-n-*butyl bromide*, $[\alpha]_D^{20}$ +4·62° *l*-Phenyl*iso*propylcarbinol, $[\alpha]_D^{20}$ —25·19°, with thionyl chloride gives l-α-*phenyl*-β-*methyl*-n-*propyl chloride*, $[\alpha]_D^{20}$ —28·34°; *d*-phenyl*iso*propylcarbinol, $[\alpha]_D^{20}$ +47·03°, with hydrogen bromide gives d-α-*phenyl*-β-*methyl*-n-*propyl bromide*, $[\alpha]_D^{20}$ +27·02°. *l*-Phenyl-*n*-butylcarbinol, $[\alpha]_D^{20}$ —4·01°, with thionyl chloride gives l-α-*phenyl*-n-*amyl chloride*, $[\alpha]_D^{20}$ —13·43°; another sample, $[\alpha]_D^{20}$ —12·83°, gave, with phosphorus pentachloride, a product $[\alpha]_D^{20}$ —5·12°. The absence of Walden inversion in some cases is ascribed to differences in the distortion of the asymmetric carbon atom by the halogenating agent employed. C. R. Harington.

Ability of enolic ethers to undergo catalytic hydrogenation. Constitution of thebaine. H. Wieland and P. Garbsch (Ber., 1926, 59, [*B*], 2490—2493).—α-Ethoxystyrene is readily hydrogenated in alcoholic solution in the presence of palladium-black to α-phenylethyl ethyl ether, b. p. 69°/12 mm. *cyclo*Hexanone dimethylacetal is transformed by benzoyl chloride and quinoline into Δ^1-*methoxy*cyclo*hexene*, b. p. 36°/12 mm., which is smoothly hydrogenated in the absence of moisture to hexahydroanisole, b. p. 130—131°/720 mm. The ready hydrogenation of the substances indicates that the group ·C(OMe)⁚C⁚ is not present in thebaine and renders necessary revision of the formula ascribed to this substance by Knorr and Hörlein (cf. Wieland and Kotake, A., 1925, i, 1448). H. Wren.

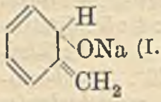
Aryl ethers of triphenyl-, diphenyl-, and naphthyl-carbinols and the corresponding cryptophenols. Tautomerism of toluene. P. Schorigin (Ber., 1926, 59, [*B*], 2502—2509).—*o*-Cresol is converted by the successive action of sodium and triphenylmethyl chloride in boiling ethereal solution into o-*tolyl triphenylmethyl ether*, m. p. 112—113°, which is also prepared from triphenylmethyl chloride and *o*-cresol in anhydrous pyridine. o-βββ-*Triphenylethylphenol*, m. p. 183°, is obtained as by-product (yield 33%) in the first method of preparing the ether described above; it becomes the main product when triphenylmethyl chloride is heated at 120° with a solution of sodium in an excess of *o*-cresol. Its constitution is established by its oxidation to triphenylcarbinol and conversion into triphenylmethane by distillation with zinc dust.

Diphenylmethyl bromide and sodium phenoxide in presence of anhydrous ether yield *phenyl diphenylmethyl ether*, m. p. 54°, b. p. 233—243°/23 mm., and *o*-diphenylmethylphenol, m. p. 125°, b. p. 245—250°/13 mm.; these substances with diphenylketazine are also obtained from diphenyldiazomethane and phenol.

Phenol and α-naphthylmethyl bromide in the presence of alcoholic potassium hydroxide afford *phenyl* α-*naphthylmethyl ether*, m. p. 76—77°, b. p. 238—240°/19 mm.; o-*tolyl* α-*naphthylmethyl ether*, b. p. 230°/11 mm., m. p. 60°, is similarly prepared. Under like conditions, β-naphthylmethyl bromide yields *phenyl* β-*naphthylmethyl ether*, m. p. 115—116°, and o-*tolyl* β-*naphthylmethyl ether*, m. p. 94—95°. With these compounds, the formation of cryptophenols is not observed.

α-Naphthylmethyl bromide has b. p. 167°/10 mm., m. p. 53·5—54·5°.

The unusual phenomenon of the entry of the alkyl group into the side-chain of *o*-cresol is explained by the hypothesis that this substance reacts in its tautomeric form (I). Similarly, substitution in the side-chain of toluene is simply explained by the assumption that it is transformed by addition of energy (action of heat or radiation) into methylenedihydrobenzene. Addition then occurs at the double linking of the methylene group, and is followed by elimination from the adduct in such a manner as to restore the normal arrangement of double linkings in the benzene nucleus. H. Wren.



(I.)

Decomposition of ethers by metallic sodium. P. Schorigin (Ber., 1926, 59, [*B*], 2510—2514; cf. A., 1923, i, 207; 1924, i, 1185, 1188; 1925, i, 1404).—Under the influence of sodium at 100°, *o*-tolyl triphenylmethyl ether undergoes normal fission into triphenylmethane and *o*-cresol and phenolic transformation into *o*-βββ-triphenylethylphenol. Phenyl diphenylmethyl ether is similarly converted into a mixture of diphenylmethane, *s*-tetraphenylethane, phenol, and triphenylcarbinol. Phenyl α-naphthylmethyl ether yields αβ-di-1-naphthylethane, m. p. 162—163°, 1-methylnaphthalene, and phenol; *o*-tolyl 1-naphthylmethyl ether behaves similarly. Phenyl 2-naphthylmethyl ether affords phenol, 2-methylnaphthalene, αβ-di-2-naphthylethane, and phenyl-2-naphthylcarbinol, whereas 2-methylnaphthalene, αβ-di-2-naphthylethane, and (?)*o*-β-2-naphthylethylphenol, m. p. 129—130°, are derived from *o*-tolyl 2-naphthylmethyl ether. H. Wren.

Coloured salts of the di- and tri-phenylmethane series. II. W. Madelung (J. pr. Chem., 1926, **114**, [ii], 1—55).—The theoretical discussion of the various theories of the constitution of coloured salts of the di- and tri-phenylmethane series is continued (cf. A., 1925, i, 1459), experiments being described supporting the view that these salts are best represented by formulæ containing organic complex positive ions.

[With F. Völker.]—When a mixture of aniline, aniline hydrochloride, and *pp*′-diaminobenzophenone is heated, it yields pp′-*diaminobenzophenoneanil*, m. p. 206°. Ammonia converts the orange-yellow *hydrochloride* of this alkyl-free analogue of auramine into pp′-*diaminobenzophenoneimine*, m. p. 170°, which with alkali cyanides yields pp′-*diaminodiphenylaminoacetonitrile*, m. p. 197°, a colourless leuco-cyanide which dissolves in acetic acid to a green solution, and with hydrogen sulphide yields pp′-*diaminothiobenzophenone*, red needles, m. p. 238° (*diacetyl* derivative, green crystals, m. p. 237°). The sulphur content of different samples of the thioketone varied considerably, although the m. p. was constant. Apart from the ready decomposition of some derivatives, it is considered that the behaviour of the auramine series is analogous to that of the triphenylmethane series of dyes.

The decomposition by water of the orange-red methiodide of *p*-dimethylaminobenzylideneaniline is explained by the formulation [CHR·NMePh]I+

$H_2O \rightleftharpoons HI+CHR(OH)\cdot NMePh \longrightarrow RHC{:}NPh+MeOH$. This structure for the methiodide is supported by the fact that *p*-dimethylaminobenzaldehyde yields a *methiodide*, m. p. 148—149°, which reacts with aniline, yielding a colourless *methiodide*, m. p. 172—173°, of *p*-dimethylaminobenzylideneaniline. The aldehyde combines with methylamine, yielding p-*dimethylaminobenzylidenemethylamine*, m. p. 60°, which yields a yellow *hydrochloride* and *methiodide*, both unstable towards water, and a *perchlorate*.

The complex formula demands that just as $R_2C{:}NH \xrightarrow{HX} [R_2C\cdot NH_2]X$, so $R_2C{:}O \xrightarrow{HX} [R_2C\cdot OH]X$, and this suggests that a mono-salt of Michler's ketone should be a dye salt. *pp'*-Tetramethyldiaminobenzophenone (*diperchlorate* described) yields a yellow *perchlorate* having an absorption curve corresponding with that of auramine; this dissolves in acetic anhydride to a deep violet solution, which deposits green crystals of an *acetyl* derivative corresponding with equivalent proportions of acetylated and unacetylated perchlorate. The presence of the hydroxyl group makes possible the indirect preparation of alkyl derivatives. With sodium methoxide, the keto-chloride of Michler's ketone (cf. Staudinger, A., 1909, i, 905) yields the yellow *dimethylacetal*, m. p. 130°, which is the methyl ether of the *O*-methylated carbinol base; but although it gives carmine-coloured solutions with acids, the corresponding dye salt cannot be isolated. With sodium ethoxide, the keto-chloride yields the *diethylacetal*, m. p. 118°, and with sodium cyanide it yields pp'-*tetramethyldiaminodiphenylmalononitrile*, m. p. 191°, a yellow substance of which the acetic acid solution develops an intense green colour by the action of sunlight or heat, suggesting an equilibrium between the leuco-cyanide and the ionised complex cyanide. With sodium ethyl sulphide, the keto-chloride yields the *diethylthiol*, m. p. 122°, which with acetic acid gives a stable, green dye salt (*perchlorate*, green needles).

With sodium ethoxide, *pp'*-tetramethyldiaminothiobenzophenone ethiodide yields pp'-*tetramethyldiaminodiphenyl-α-ethoxy-α-ethylthiolmethane*, m. p. 130°, which with acids gives the carmine colour of the *O*-ethyl dye salt with evolution of mercaptan, showing that the tenacity of the ethylthiol is less than that of the ethoxy-radical. With sodium cyanide, the thioketone yields pp'-*tetramethyldiaminodiphenyl-α-ethylthiolacetonitrile*, m. p. 158°, which with acids gives a green dye salt with evolution of mercaptan. Oxidation of the thioketone with ferric chloride solution yields a violet-coloured *substance* (*perchlorate*, $C_{34}H_{40}O_8N_4S_2Cl_2$, described) :

$$2[R_2C\cdot SH]X \longrightarrow [R_2C\cdot S\cdot S\cdot CR_2]X_2.$$

The reactions of phenolic aldehydes and ketones and the relationship between colour and structure are discussed from the point of view of complex formulæ.

R. W. West.

Halochromy of triphenylmethane derivatives. J. S. P. Blumberger (Chem. Weekblad, 1926, 23, 534—546).—A summary of the literature.

Esters of chaulmoogric acid. P. P. Herrera-Batteke and A. P. West (Philippine J. Sci., 1926, **31**, 161—168).—The following esters are described : *α-methyl*-n-*heptyl*, b. p. 214·6°/0 mm.; *allyl*, b. p. 222·3°/5 mm.; *phenyl*, b. p. 233° (in a vacuum), m. p. 40°; o-*tolyl*, b. p. 218·8°/0 mm.; m-*tolyl*, b. p. 207·4°/0 mm.; p-*tolyl*, b. p. 207·1°/0 mm. J. M. Gulland.

Reactivity and stability of linking of organic radicals. I. Addition of hydrogen sulphide to nitriles, and hydrolysis of esters. K. Kindler (Annalen, 1926, **450**, 1—20; cf. A., 1923, i, 568).—In the conversion of nitriles, R·CN, into thioamides and in the hydrolysis of ethyl esters, $R\cdot CO_2Et$, the rate of reaction is found to be a direct function of the stability of the linking between R and the ·CN or $\cdot CO_2Et$. Substituents which loosen this linking diminish the rate of addition or hydrolysis, whilst "positive" substituents greatly increase it. The rate of reaction of benzonitriles and benzoic esters increases with varying substituent groups in the order: *p*-NO_2, *m*-NO_2, *m*-I, *p*-I, *m*-Br, *p*-Br, *m*-Cl, *p*-Cl, H, *m*-Me, *p*-Me, *p*-MeO, *m*-NH_2, *p*-NH_2. This observation suggests a simpler means for determining the relative stability of linking of radicals than the dissociation, oxazole, and carbinol methods (Walden, "Chemie der freien Radikale," Leipzig, 1924; Skraup and Moser, A., 1922, i, 574; Skraup and Freundlich, *ibid.*, 539). The effect of substituents in a benzene ring on the stability of linking of each of the remaining hydrogen atoms is correlated with Körner's rules. As the dissociation constants of substituted benzoic acids, $X\cdot C_6H_4\cdot CO_2H$, increase with increased negativity of X, so the rate of hydrolysis of esters, $X\cdot C_6H_4\cdot CO_2Et$, and the firmness with which the NH_2 group is held in arylamines, $X\cdot C_6H_4\cdot NH_2$ (measured by their weakness as bases), decreases.

For the determination of thioamides an alcoholic solution is treated with alcoholic silver nitrate, and excess of silver is titrated with $0\cdot 1N$-potassium thiocyanate. Aromatic thioamides are not decomposed by evaporation of their alcoholic solutions at 25—30° under reduced pressure. The m. p. of halogenated thiobenzamides are: p-*chloro*-, 124°; p-*bromo*-, 141·5°; m-*bromo*-, 120°; p-*iodo*-, 153°. Velocity constants are determined for the formation of these thiobenzamides from halogenated benzonitriles by the action of hydrogen sulphide under 1·75 atm. pressure at 60·6° in absolute alcohol in the presence of sodium ethoxide.

Velocity constants are also given for the hydrolysis of the following ethyl esters by a solution of sodium in 87·83% aqueous alcohol: benzoate, *m*- and *p*-chloro-, *m*- and *p*-bromo-, *p*-iodo-, *m*- and *p*-nitrobenzoates, *m*- and *p*-toluates, anisate, and *m*- and *p*-aminobenzoates. C. Hollins.

Alkaline hydrolysis of *d*-lysuric acid [dibenzoyl-lysine]. P. Karrer and M. Ehrenstein (Helv. Chim. Acta, 1926, 9, 1063—1066; cf. A., 1926, 603).—Hydrolysis of *d*-dibenzoyl-lysine with baryta under the given conditions yields in addition to *d*-ε-benzoyl-lysine, m. p. 253°, and not 235° as previously given (*loc. cit.*), which is the main product, a small quantity of (?)α-monobenzoyl-lysine, m. p. 227—228°, isolated after conversion of the ε-compound into α-bromo-ε-benzamidohexoic acid, by the action of nitrosyl bromide, the α-compound being unattacked. The observation of Passoth (Z. physiol. Chem., 1926, **155**, 294) that the alkaline hydrolysis of dibenzoyl-lysine yields α-benzoyl-lysine may be correct under the different experimental conditions employed. α-Benzoylornithine is also unattacked by nitrosyl bromide.

J. W. Baker.

Compounds of titanium halides with oxygenated organic substances. G. Scagliarini and G. Tartarini (Atti R. Accad. Lincei, 1926, [vi], 4, 318—324).—With oxygenated organic compounds which do not contain hydroxyl and cannot pass into enolic modifications, titanium halides form in the cold additive compounds analogous to those formed by stannic halides. The following compounds are described: with benzophenone, $TiCl_4,COPh_2$; with methyl phthalate, $TiCl_4,C_6H_4(CO_2Me)_2$; with piperonal, $TiCl_4,2CHO\cdot C_6H_3\cdot O_2CH_2$.

With hydroxylated compounds such as salicylic acid, it is not possible to obtain at the ordinary temperature true additive compounds with titanium halides, but the following substituted compounds (cf. Dilthey, A., 1904, i, 290) were prepared: with salicylaldehyde, $TiCl_2(O\cdot C_6H_4\cdot CHO)_2,HCl$, a violet-red crystalline powder, slowly decomposing in the air, and $TiBr_2(O\cdot C_6H_4\cdot CHO)_2,HBr$, a brown compound; with salicylic acid, $Ti(O\cdot C_6H_4\cdot CO_2H)_2TiCl_6$, a red powder, turning first orange and then red; with methyl salicylate, $Ti(O\cdot C_6H_4\cdot CO_2Me)_2TiCl_6$, red crystals, altering rapidly in the air; with phenyl salicylate, $Ti(O\cdot C_6H_4\cdot CO_2Ph)_2TiCl_6$, dark red powder, readily alterable.

T. H. Pope.

Synthesis of *dl*-2 : 4-dihydroxyphenylalanine (*dl*-resorcylalanine). K. Hirai (Biochem. Z., 1926, 177, 449—452).—Condensation of resorcylaldehyde with glycine anhydride gave a non-crystalline product, whilst condensation with hydantoin yielded no result. The aldehyde was therefore methylated and then condensed with glycine anhydride by Sasaki's method. *Di-2 : 4-dimethoxybenzylidineglycine anhydride* crystallises from hot acetic acid, m. p. 286—287°, and on treatment with hydrogen iodide and red phosphorus gives dl-2 : 4-*dihydroxyphenylalanine*, m. p. 223–224° (decomp.). It gives a dark greenish-violet colour with ferric chloride.

P. W. Clutterbuck.

Decomposition of organic compounds [alkyl phthalates] by heat. W. Nagel and R. H. Abelsdorff (Wiss. Veröff. Siemens-Konz., 1926, 5, 193—210).—With the exception of dimethyl phthalate all the dialkyl esters of phthalic acid decompose on prolonged boiling, yielding phthalic anhydride and the corresponding alcohol and olefine, thus: $C_6H_4(CO_2\cdot C_nH_{2n+1})_2 = C_6H_4(CO)_2O + C_nH_{2n+1}\cdot OH + C_nH_{2n}$. The mixed esters containing a methyl radical yield methyl alcohol and the olefine derived from the other ester radical. The velocity of the reaction increases with the length of the carbon chain of the alcohol, and is greater with tertiary alcohols than with secondary. The following new esters have been prepared by heating the acid chloride of monomethyl phthalate with the appropriate alcohol: *methyl* n-*propyl phthalate*, b. p. 294—296°; *methyl* iso*propyl phthalate*, a yellow oil decomposed on heating; *methyl* n-*butyl phthalate*, and *methyl* iso*butyl phthalate*, b. p. 303—304°. *Methyl* tert.-*butyl phthalate* is formed by the interaction of the acid chloride of monomethyl phthalate with the reaction product of magnesium ethyl iodide and *tert.*-butyl alcohol; it is a brown oil which cannot be distilled.

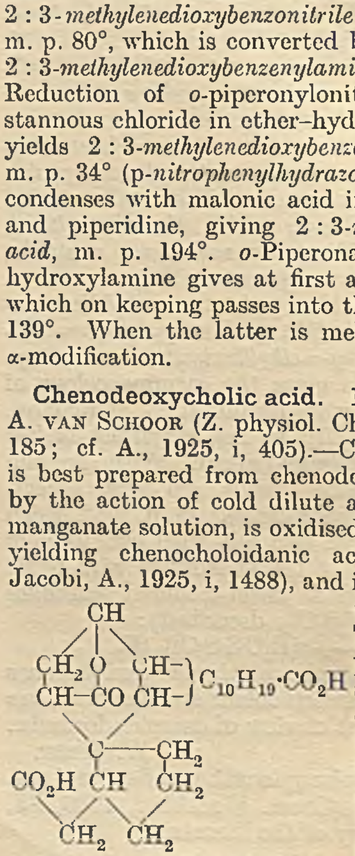
A. R. Powell.

Synthesis of derivatives of methylenedioxybenzene. W. H. Perkin and V. M. Trikojus (J.C.S., 1926, 2925—2932).—Meconinecarboxylic acid on hydrolysis with hydriodic acid gives 3-*hydroxy*-4-*methoxyphthalidecarboxylic acid*, m. p. 203°, and finally 3 : 4-*dihydroxyphthalidecarboxylic acid* (*normeconinecarboxylic acid*), m. p. 215° [*methyl* ester separates from dilute methyl alcohol with $1H_2O$, m. p. 104°; m. p. (anhydrous) 150°]. Attempts to methylenate this acid under various conditions were unsuccessful.

2 : 3-Dihydroxybenzoic acid (*o*-protocatechuic acid), prepared by oxidising *o*-veratraldehyde with potassium permanganate to *o*-veratric acid, followed by demethylation with hydriodic acid, is converted into 2 : 3-*methylenedioxybenzoic acid* (o-*piperonylic acid*), m. p. 227° (*ethyl* ester, m. p. 35·5°), by methylene iodide and aqueous-alcoholic potassium hydroxide. This acid condenses with formaldehyde in presence of acetic–hydrochloric acid, forming 3 : 4-*methylenedioxyphthalide*, m. p. 226°, which could not be converted into the corresponding methylenedioxyphthalaldehydic acid by oxidation. *o*-Piperonylic acid on treatment with thionyl chloride gives 2 : 3-*methylenedioxybenzoyl chloride*, m. p. 116°, which is converted by ammonia into 2 : 3-*methylenedioxybenzamide*, m. p. 176°. Treatment of the amide with thionyl chloride yields 2 : 3-*methylenedioxybenzonitrile* (o-*piperonylonitrile*), m. p. 80°, which is converted by hydroxylamine into 2 : 3-*methylenedioxybenzenylamino-oxime*, m. p. 139°. Reduction of *o*-piperonylonitrile with anhydrous stannous chloride in ether–hydrogen chloride solution yields 2 : 3-*methylenedioxybenzaldehyde* (o-*piperonal*), m. p. 34° (p-*nitrophenylhydrazone*, m. p. 258°), which condenses with malonic acid in presence of pyridine and piperidine, giving 2 : 3-*methylenedioxycinnamic acid*, m. p. 194°. *o*-Piperonal when treated with hydroxylamine gives at first an α-*oxime*, m. p. 127°, which on keeping passes into the β-*oxime*, m. p. 138—139°. When the latter is melted, it reverts to the α-modification.

H. Burton.

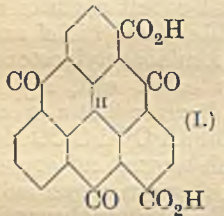
Chenodeoxycholic acid. III. A. Windaus and A. van Schoor (Z. physiol. Chem., 1926, 157, 177—185; cf. A., 1925, i, 405).—Chenodeoxybilianic acid is best prepared from chenodehydrodeoxycholic acid by the action of cold dilute alkaline potassium permanganate solution, is oxidised by fuming nitric acid, yielding chenocholoidanic acid (cf. Wieland and Jacobi, A., 1925, i, 1488), and is readily hydrogenated to deoxybiliobanic acid. This when kept with potassium hydroxide solution yields a *tricarboxylic acid*, $C_{24}H_{38}O_7$, which on heating loses water with regeneration of deoxybiliobanic acid. It follows that deoxybiliobanic acid is a lactone, probably represented by the annexed formula, and that cheno(anthropo)-deoxycholic acid is a 3 : 12-dihydroxycholanic acid.



The tetracarboxylic acid, $C_{23}H_{36}O_8$, obtained by

heating chenocholoidanic acid, is also formed when the keto-dicarboxylic acid, $C_{23}H_{36}O_5$, obtained from hyodeoxycholic acid, is oxidised with fuming nitric acid.
R. W. West.

Triphenylmethane compounds with linked benzene nuclei. II. Triketotrimethylenetriphenylmethanedicarboxylic acids. R. Weiss, A. Spitzer, and J. L. Melzer (Monatsh., 1926, 47, 307—312; cf. A., 1925, i, 560).—Phthalyl chloride condenses with *p*-xylene in presence of aluminium chloride to give 1 : 4-dimethylanthraquinone and *di*-p-*xylylphthalide*, m. p. 180—184°, reduced by sodium amalgam to o-2 : 5 : 2′ : 5′-*tetramethylbenzhydrylbenzoic acid*, m. p. 236°, which is oxidised by alkaline permanganate to *triphenylmethane*-2 : 2′ : 2″ : 5 : 5′-*pentacarboxylic acid*, an amorphous powder (*pentamethyl* ester, m. p. 138—143°, made by means of diazomethane). The action of boiling concentrated sulphuric acid converts this substance into *triketotrimethylenetriphenylmethane*-3 : 3′-*dicarboxylic acid* (I), an insoluble amorphous powder, decomp. above 250° (*trisodium* salt, $+3{\cdot}5H_2O$), soluble in sulphuric acid or alkalis with a blue colour.



(I.)

Di-m-*xylylphthalide*, m. p. 159—162°, prepared in an analogous manner, is converted successively into o-2 : 4 : 2′ : 4′-*tetramethylbenzhydrylbenzoic acid*, m. p. 234—240°, *triphenylmethane*-2 : 2′ : 2″ : 4 : 4′-*pentacarboxylic acid* (*pentamethyl* ester, m. p. 160—162°), and *triketotrimethylenetriphenylmethane*-4 : 4′-*dicarboxylic acid*, decomp. above 250° (*trisodium* salt, $+1{\cdot}5H_2O$, one of the keto-groups being assumed to develop acidic properties).
G. M. Bennett.

2-Mercaptoanthracene-3-carboxylic acid and anthracene-2-thioglycol-3-carboxylic acid. Soc. of Chem. Ind. Basle.—See B., 1926, 942.

Negative catalysis in the oxidation of benzaldehyde. O. M. Reiff (J. Amer. Chem. Soc., 1926, 48, 2893—2899).—The rate of oxidation of benzaldehyde by gaseous oxygen is increased by addition of silica sand or broken glass and by shaking or stirring. Removal of water vapour inhibits the reaction, the chief factor in the promotion of which appears to be the formation of an active surface by the adsorption of a polar water layer on the wall of the reaction vessel, or other surface present. Stirring promotes the diffusion of oxygen to the active surface. The abnormal decrease in the rate of oxidation of benzaldehyde, as the reaction continues, is regarded as due to a poisoning action on the polar water layer by the condensation and oxidation products of benzaldehyde, the reaction being thus auto-inhibited. Negative catalysis caused by the addition of various inhibitors is explained by a similar poisoning action on the active surface by the inhibitor (cf. Taylor, A., 1925, ii, 562).
F. G. Willson.

Chloro- and chloronitro-derivatives of *m*-hydroxybenzaldehyde. Brit. Dyestuffs Corpn., and H. H. Hodgson.—See B., 1926, 973.

Terpenes and related compounds. II. Preparation of piperonal from *iso*safrole using potassium dichromate. N. Hirao (J. Soc. Chem. Ind. Japan, 1926, 29, 504—508).—The optimum temperature for the oxidation of *iso*safrole to piperonal by means of chromic acid is 46—58°. The oxidising solution containing 45·4 g. of potassium dichromate, 60·4 g. of sulphuric acid, and 400 g. of water is added drop by drop to 25 g. of *iso*safrole during 2 hrs. with stirring, and piperonal (m. p. 35°) is obtained in a yield of 54% of theory. By increasing the amount of oxidising agent, the yield was raised to about 61%. The yield is markedly increased by the presence of salts of iron, cobalt, and manganese, the maximum yield being about 72%.
K. Kashima.

Isomerisation of safrole under pressure. S. Nagai (J. Soc. Chem. Ind. Japan, 1926, 29, 364—370; cf. *ibid.*, 1924, 27, 631).—High yields of *iso*safrole, up to 90—95% of theory, are obtained by heating safrole with alcoholic sodium or potassium ethoxide for 5—6 hrs. under 6—8 atm. pressure (cf. Hirao, A., 1926, 1135).
K. Kashima.

Carbon rings. VIII. Constitution of muscone. L. Ruzicka (Helv. Chim. Acta, 1926, 9, 1008—1117; cf. A., 1926, 1143).—Muscone on reduction by Clemmensen's method yields a *methyl*cyclo*pentadecane*, m. p. −19°, b. p. 150°/12 mm., d_4^{17} 0·8626, n_D^{17} 1·4776, which gives no m.-p. depression when mixed with a synthetic methyl*cyclo*pentadecane,* m. p. −19·5°, d_4^{17} 0·8608, n_D^{17} 1·4753 (the syntheses of substances marked with an asterisk are the subject of later communications). By the reduction of the corresponding ketones with sodium and boiling alcohol, 3- and 4-*methyl*cyclo*pentadecanol*, m. p. 55° and 50°, respectively, are prepared, but give no m.-p. depression when mixed with each other or with muscol (*loc. cit.*). Synthetic α-, β-, γ-, and δ-*methyltridecane-αν-dicarboxylic acids* * have m. p. 94°, 76° or 70°, 69° or 63°, and 55°, respectively, whilst β-, γ-, and δ-*methyldodecane-αμ-dicarboxylic acids* * have m. p. 75°, 77°, and 74°, respectively. Repeated crystallisation of the mixture of dibasic acids, $C_{16}H_{30}O_4$, obtained by the oxidation of muscone (*loc. cit.*), however, yields an acid, m. p. 78°, which is higher than that of any of these except α-methyltridecane-αν-dicarboxylic acid. Since a mixture of this acid and the β-methyl isomeride would be obtained from 2-methyl*cyclo*pentadecanone, muscone is probably identical with the latter. In confirmation of this view, muscone forms a *benzylidene* derivative, b. p. 200—220°, which on oxidation with ozone and chromic acid yields an *acid*, m. p. 68—69° (58—60° on remelting), α_D +5°, which is very probably d-β-*methyltridecane-αν-dicarboxylic acid*,* since it gives no depression with a synthetic specimen of this acid, m. p. 70—73° (61—62·5° on remelting) (*anilide*, m. p. 139—140°; anilide of synthetic acid, m. p. 132—133°, mixed m. p. 133°). Heating with 50% potassium hydroxide solution, esterification (*methyl* ester, α_D +4°), and hydrolysis of the ester does not racemise the acid, so that the optical inactivity of the oxidation mixture, $C_{16}H_{30}O_4$, is probably due to compensation of equal *d* and *l* components. Muscone is therefore very probably *l*-2-methyl*cyclo*pentadecanone.
J. W. Baker.

Catalytic reduction of hydroxymethylenehydrindone and its condensation with phenyl-

hydroxylamine. H. Rupe and H. Wieland (Helv. Chim. Acta, 1926, 9, 1001—1008).—Catalytic reduction of hydroxymethylenehydrindone yields *hydrindolylmethyl alcohol*, m. p. 56·5° (*acetate*, m. p. 63°; *benzoate*, m. p. 82°), which can be isolated only if all the operations are carried out at the ordinary temperature, since it readily loses 1 mol. of water to yield *methylenehydrindone*, which shows a great tendency to polymerise, and was obtained either as a gelatinous product or a white powder, decomp. above 360°, which is a polymeride of 12 mols. Hydroxymethylenehydrindone condenses with phenylhydroxylamine to yield *phenylhydroxylaminomethylenehydrindone*, m. p. 185° [*sodium* salt; *oxime*, decomp. 160°; *methyl ether*, m. p. 123° (decomp.)], which, hydrolysed with 5% sodium hydroxide solution, yielded azobenzene. On reduction with zinc dust and acetic acid, it yields *anilinomethylenehydrindone*, m. p. 215—217° (decomp.) (*hydrochloride*; *dibromide*, decomp. 250°; *oxime*, decomp. 170°), which is also obtained by the direct condensation of aniline with hydroxymethylenehydrindone. J. W. Baker.

Synthesis of a higher homologue of curcumone and a ketodimethyltetrahydronaphthalene. H. Rupe and F. Schütz (Helv. Chim. Acta, 1926, 9, 992—1000).—The synthesis of γ-*p*-tolylbutyl methyl ketone has been effected and this ketone shown not to be identical with curcumone, thus confirming the structure already assigned (Rupe and Wiederkehr, A., 1924, i, 1066). Ethyl β-*p*-toluylpropionate is converted by magnesium methyl bromide into γ-*p*-tolyl-Δ^{β}-pentenoic acid, together with 2-p-*tolyl*-2 : 5 : 5-*trimethyltetrahydrofuran*, b. p. 118—120°/10 mm., which is the main product (43% yield) if a large excess of the Grignard reagent is employed. When treated with hydrogen bromide, it yields a *hydrocarbon*, $(C_{14}H_{18})_2$, m. p. 53°. Reduction of the pentenoic acid to γ-*p*-tolylvaleric acid is best effected by hydrogenation with a nickel catalyst (cf. Rupe and Steinbach, *ibid.*, 1911, i, 293) (*ethyl* γ-p-*tolylvalerate* has b. p. 142—143°/9 mm.). Thionyl chloride converts the reduced acid into its *chloride*, b. p. 134—135°/9 mm., which with zinc methyl yields γ-p-*tolylbutylmethyl ketone*, b. p. 141—141·5°/11·5 mm. (*semicarbazone*, m. p. 142°; *oxime*, b. p. 167°/8 mm.; *benzylidene* derivative, m. p. 67°). The acid chloride treated with aluminium chloride yields 4-*keto*-1 : 6-*dimethyltetrahydronaphthalene*, b. p. 146·5—147°/11·5 mm. (*semicarbazone*, m. p. 194—195°; *oxime*, m. p. 78·5°), which with magnesium methyl iodide yields 1 : 4 : 6-*trimethyl*-1 : 2-*dihydronaphthalene*, b. p. 122—123°/12 mm., but under certain experimental conditions (especially low temperature) the intermediate 1 : 4 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthol*, b. p. 138·5—139°/11 mm., can be isolated. Ozonolysis of 1 : 4 : 6-trimethyl-1 : 2-dihydronaphthalene yields β-2-*acetyl*-4-*methylphenylbutyric acid*, m. p. 124° (*semicarbazone*, m. p. 176·5°), together with a small quantity of an *aldehyde*, b. p. 151—153°/9 mm. (*semicarbazone*, m. p. 227—228°), probably possessing the structure:

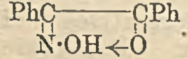
$$\mathrm{MeC_6H_3}\left\langle\begin{array}{l}\mathrm{CHMe}\\ \mathrm{-CMe}\end{array}\right\rangle\mathrm{C{\cdot}CHO}.$$

J. W. Baker.

Stereoisomerism and isomorphism of the phenyl styryl ketones. C. Dufraisse and A. Gillet (Compt. rend., 1926, **183**, 746—748).—Two stereoisomeric forms of phenyl β-methoxystyryl ketone exist, *A*, m. p. 66°, and *B*, obtained in isomorphous forms, m. p. 78° and 81°, respectively. Phenyl α-bromo-β-methoxystyryl ketone exists in isomeric forms, m. p. 72° and 102°, respectively. *Phenyl* β-*ethoxystyryl ketone* exists in two stable isomorphous forms, m. p. 75° and 78°. Dibenzoylmethane has two isomorphous forms, m. p. 71° and 78°, respectively. When insolated, one form of α-phenyl α-bromo-β-methoxystyryl ketone, m. p. 72°, is changed into the other, m. p. 102°, and after further insolation this form is changed back to the first, m. p. 72°. L. F. Hewitt.

Metallic compounds of monoximes and the structure of oximes. T. W. J. Taylor and (Miss) E. K. Ewbank (J.C.S., 1926, 2818—2825; cf. *ibid.*, 1903, 83, 24; A., 1922, i, 661).—The investigation of 11 monoximes of different types, and the possibility of obtaining from them co-ordinated complexes with iron, nickel, cobalt, and copper, gave the following results. (In the following formulæ R=1 mol. of oxime —1H). Oximinoacetone, Me·CO·CH:N·OH, gives with solutions of nickel and cobalt acetates in presence of sodium hydroxide, ill-defined *nickel* and *cobalt* salts, R_2Ni and R_2Co. Oximinoacetylacetone, Me·CO·C(:N·OH)·COMe, yields a *cobalt* salt, R_3Co; with ammoniacal nickel acetate, it gives first a green *compound*, CMe(:NH)·C(CO·Me):N·O·Ni·O·CO·Me, changing rapidly to a reddish-brown *compound*, $\mathrm{[CMe(:NH){\cdot}C(CO{\cdot}Me){:}N{\cdot}O{\cdot}]_2Ni}$. A green *copper* salt, $\mathrm{R{\cdot}Cu{\cdot}O{\cdot}CO{\cdot}Me,H_2O}$, is described. Oximinobenzoylacetone, Ph·CO·C(:N·OH)·COMe, gives a *cobalt* salt, R_3Co, and a *copper* derivative, R·CuOH. Ethyl oximinoacetoacetate, $\mathrm{Me{\cdot}CO{\cdot}C(:N{\cdot}OH){\cdot}CO_2Et}$, gives a *cobalt* salt, R_3Co, a *nickel* complex of the same type as that obtained from oximinoacetylacetone, and a *copper* derivative, $\mathrm{R{\cdot}CuOH,H_2O}$ (anhydrous salt explodes at 100—110°). Oximinoacetophenone forms *iron*, *cobalt*, and *nickel* salts of the formulæ R_2Fe, R_3Co, and R·NiO·CO·Me(?). Oximinomalonanilide, $\mathrm{OH{\cdot}N{:}C(CO{\cdot}NHPh)_2}$, yields iron, *cobalt*, *nickel*, and *copper* derivatives, R_2M (M=1 atom of metal). α-Benzilmonoxime, Ph·CO·CPh:N·OH(α), forms a *copper* derivative, R·CuOH (see also Tschugaev, A., 1907, i, 830).

No complex salts could be prepared from β-benzilmonoxime, ethyl oximinomalonate, ethyl oximinobenzoylacetate, and methyl α-oximinoethyl ketone. The necessary conditions for metallic complex formation appear to be (i) the presence of a reactive carbonyl group in the oxime, (ii) co-ordination between the carbonyl group and the metallic salt, (iii) ring closure through elimination of a hydrogen ion or a molecule of the acid originally united with the metal. These views indicate that α-benzilmonoxime contains a reactive carbonyl group, whereas the β-oxime does not. This is explained by assigning to the β-oxime the co-ordinated structure



$$\begin{array}{ccc}\mathrm{PhC} & \text{———} & \mathrm{CPh}\\ \| & & \| \\ \mathrm{N{\cdot}OH} & \leftarrow & \mathrm{O}\end{array}.$$

The structure of other oximes is discussed in view of the results. H. Burton.

Unsaturated 1 : 4-diketones. I. Synthesis and structure of αβ-di-(2 : 4 : 6-trimethylbenzoyl)-

vinyl alcohol. R. E. Lutz (J. Amer. Chem. Soc., 1926, 48, 2905—2915; cf. A., 1925, i, 681).—Further investigation has shown that the addition of halogens to dibenzoylethylene and its analogues leads generally to two stereoisomeric dihalides, the lower-melting (α-) isomeride being separable from the higher-melting (β-) isomeride by differences in solubility, the latter generally separating directly from the reaction mixture. The following were prepared: *αβ-dibromo-αβ-dibenzoylethane*, m. p. 107—107·5° (α-) and m. p. 179° (decomp.) (β-); *αβ-dichloro-αβ-dibenzoylethane*, m. p. 86° (α-) and m. p. 167° (decomp.) (β-) (*loc. cit.*); *αβ-dibromo-αβ-di*-p-*bromobenzoylethane*, m. p. 138° (α-) and m. p. 208·5° (decomp.) (β-); *αβ-dichloro-αβ-di*-p-*bromobenzoylethane*, m. p. 129—129·5° (α-) and m. p. 215·5° (decomp.) (β-); *αβ-dibromo-αβ-di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethane*, m. p. 161·5° (α-) and m. p. 207° (decomp.) (β-); and *αβ-dichloro-αβ-di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethane*, m. p. 215° (decomp.), only the β-isomeride being obtained in this case. The pairs of isomerides gave the same dibenzoylethanes when reduced with zinc and acetic acid. Conversion of the α- into the β-isomeride was effected to some extent by boiling in alcoholic solution. Treatment of either modification of αβ-dibromo-αβ-di-*p*-bromobenzoylethane with methyl-alcoholic sodium methoxide affords *α-methoxy-αβ-di*-p-*bromobenzoylethylene*, m. p. 155°. *α-Bromo-αβ-di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethylene*, yellow, m. p. 110°, is obtained when αβ-dibromo-αβ-di-(2 : 4 : 6-trimethylbenzoyl)ethane is boiled in alcohol. Treatment of αβ-dibromo-αβ-di-*p*-bromobenzoylethane with alcoholic sodium acetate affords *α-hydroxy-αβ-di*-p-*bromobenzoylethylene*, orange, m. p. 101·5—102·5° (*copper* salt), whilst αβ-dibromo-αβ-di-(2 : 4 : 6-trimethylbenzoyl)ethane affords similarly *di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethanone*, $Me_3C_6H_2{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_2Me_3$, yellow, m. p. 145—145·5°, a small proportion of the *enolic* modification, *α-hydroxy-αβ-di*-(2 : 4 : 6-*trimethylbenzoyl*)*ethylene*, yellow, m. p. 103·5—104·5° (*copper* salt), being formed at the same time. The latter modification was always obtained by the application of excess of alcoholic sodium acetate, either to the original dibromo-derivative or to the ketonic form. Treatment of the above enolic derivative with ethereal diazomethane affords a yellow *isomeride*, m. p. 107·5—108°, of the α-methoxy-αβ-di-(2 : 4 : 6-trimethybenzoyl)-ethylene previously described (*loc. cit.*), the preparation of which, it is now found, leads also to a trace of the yellow modification. Dibenzoylacetylene is obtained by treating αβ-dibromo-αβ-dibenzoylethane with a trace of sodium acetate in acetone-alcohol in presence of sodium carbonate. Treatment of αβ-dibromo-αβ-dibenzoylethane with alcoholic methylamine affords α-methylamino-αβ-dibenzoylethylene, yellow, m. p. 164°, whilst dimethylamine yields similarly a yellow *compound*, $C_{19}H_{22}O_2N_2$, m. p. 96·5°. Trimethylamine affords, in the same way, a *substance*, m. p. above 230°, together with α-bromo-αβ-dibenzoylethylene and dibenzoylacetylene.

F. G. Willson.

Alkylation of hydroxynaphthaquinone. I. Oxygen Ethers. L. F. Fieser (J. Amer. Chem. Soc., 1926, 48, 2922—2937).—The methoxynaphthaquinone obtained by Sachs, Berthold, and Zaar (A., 1907, i, 426) from the silver salt of hydroxynaphthaquinone ("naphthalenic acid") can be separated by fractional crystallisation into two isomerides, *4-methoxy-β-naphthaquinone* (I), orange-yellow, m. p. 190°, and *2-methoxy-α-naphthaquinone* (II), pale yellow, m. p. 183·5°; (I) is readily hydrolysed by dilute aqueous alkali, and is transformed quantitatively into (II) when treated with boiling methyl-alcoholic hydrogen chloride. When treated with boiling aqueous sodium hyposulphite, (I) affords *4-methoxy-1 : 2-naphthaquinol*, decomp. 130° (*diacetate*, m. p. 135°), whilst boiling alcoholic *o*-phenylenediamine affords 6-methoxynaphthaphenazine, m. p. 180° (cf. Kehrmann and Messinger, A., 1891, 1213). (I) yields a *semicarbazone*, m. p. 246° (decomp.) (cf. Sachs, *loc. cit.*), whilst warm aqueous *p*-toluidine affords 4-*p*-toluidino-β-naphthaquinone, m. p. 250° (decomp.) (cf. Elsbach, A., 1882, 853), and toluidinonaphthaquinonetoluidide, m. p. 177° (cf. Fuchs, A., 1876, i, 247). Toluidino-β-naphthaquinone methyl ether has m. p. 147° (cf. Zincke and Brauns, A., 1883, 209). (II) is less readily hydrolysed by acids than (I). It is obtained by esterification of hydroxynaphthaquinone by methyl alcohol and hydrogen chloride, or by the action of diazomethane. On reduction as above, it yields *2-methoxy-1 : 4-naphthaquinol*, decomp. 107° (*diacetate*, m. p. 129—130°). It does not react with aqueous or alcoholic *p*-toluidine, but in acetic acid solution yields *p*-toluidino-α-naphthaquinone, m. p. 200° (cf. Elsbach, *loc. cit.*). Treatment of the silver salt of hydroxynaphthaquinone with ethyl iodide also yields a mixture (m. p. 96—97°; cf. Miller, A., 1911, i, 308; 1916, ii, 19), which can be separated by crystallisation from benzene or by means of aqueous sodium hydrogen sulphite, in which the *p*-quinone derivative is less soluble, into 4-ethoxy-β-naphthaquinone, m. p. 126° (cf. Baltzer, A., 1882, 204) (corresponding *ethoxynaphthaquinol diacetate*, m. p. 108—109°; *6-ethoxynaphthaphenazine*, m. p. 158·5°), and *2-ethoxy-α-naphthaquinone*, m. p. 120° (*quinol diacetate*, m. p. 81·5°). The following alkoxynaphthaquinones were prepared by the action of the appropriate alkyl bromide on the above silver salt: 4-n-*butoxy-β-naphthaquinone*, orange-yellow, m. p. 98°; 2-n-*butoxy-α-naphthaquinone*, brownish-yellow, m. p. 104°, and 4-iso*propoxy-β-naphthaquinone*, orange-yellow, m. p. 126°. Treatment of the silver salt of 2-chloro-3-hydroxy-α-naphthaquinone with ethyl iodide yields *3-chloro-2-ethoxy-α-naphthaquinone*, yellow, m. p. 97—98° (cf. Zincke, A., 1888, 708). It is concluded that, in solution, hydroxynaphthaquinone exists as a mixture of tautomerides, in which the *p*-quinonoid form greatly preponderates. F. G. Willson.

Anthraquinone-2-glycine-3-carboxylic acid. Soc. of Chem. Ind. Basle.—See B., 1926, 942.

Wool dyes. [Sulphonic acids of 1 : 1′-dianthraquinonylamine and their halogen derivatives.] Farbenfabr. vorm. F. Bayer und Co.—See B., 1926, 973.

Phytochemistry. III. Betulin. II. O. Dischendorfer and H. Grillmayer (Monatsh., 1926, 47, 241—249; cf. A., 1924, i, 65).—With the object of definitely establishing the formula of betulin (cf. Schulze and Pieroh, A., 1922, i, 1045), some new derivatives have been prepared. *Betulin dianisate*, m. p. 192—193° (uncorr.), $[\alpha]_D^{17}$ +49·13° (all rotations observed in chloroform), and *di*-m-*nitrobenzoate*, m. p. 267—268°, $[\alpha]_D^{15}$ +38·37°, and allo*betulin* p-*bromobenzoate*, m. p. 276° after sintering, $[\alpha]_D^{16}$ +66·24°; *anisate*, m. p. 295°, $[\alpha]_D^{16·5}$ +77·32°, and m-*nitrobenzoate*, m. p. 277—278°, $[\alpha]_D^{21}$ +69·24°, are described. When *allo*betulone is heated at 150° with benzoyl chloride, enolisation takes place and allo*betulenol dibenzoate*, $C_{30}H_{46}(OBz)_2$, m. p. 228—230°, $[\alpha]_D^{16·5}$ +33·16°, is formed, thus showing the presence of a $\cdot CH_2\cdot CO\cdot$ grouping in *allo*betulone. allo*Betulenol di*-p-*bromobenzoate* has m. p. 225°, $[\alpha]_D^{12}$ +37·18°. The following additional data are recorded: monobromobetulin diacetate, $[\alpha]_D^{14}$ +6·18°; betulin dibenzoate, $[\alpha]_D^{14·5}$ +43·28°; betulin di-*p*-bromobenzoate, $[\alpha]_D^{16}$ +44·19°. Bromination of *allo*betulone in chloroform solution at the ordinary temperature yields *dibromo*allo*betulone*, m. p. 220° (decomp.) after darkening at 218°. Analyses of these compounds, especially the last-named, leave no doubt that the composition of betulin is represented by the formula $C_{30}H_{50}O_2$ or $C_{30}H_{48}O_2$. H. E. F. NOTTON.

Higher terpene compounds. XXIX. L. RUZICKA, R. STEIGER, and H. SCHINZ (Helv. Chim. Acta, 1926, 9, 962—978).—Manila copal is separated into (1) an acid portion, 80%, (2) a neutral, ether-soluble portion, 10%, and (3) a portion insoluble in sodium hydroxide and ether, 10%. The lower-boiling fraction of the neutral portion contains pinene and other terpenes (cf. Brooks, A., 1910, i, 691), whilst from the highest-boiling portion a primary sesquiterpene alcohol, b. p. 120—130°/0·3 mm., was isolated by means of its phthalic ester. The acid portion contains (*a*) soluble in ether 33·3%, (*b*) soluble in acetone 33·3%, (*c*) insoluble in acetone 33·3%. The combined acids in fractions (*a*) and (*b*) were converted into their methyl esters through their silver salts (OMe in mixture, 12·3%) and distilled in a high vacuum. The b. p. of the mixture rises continuously, but the lower fraction, b. p. 120—160°/0·3 mm., corresponds approximately with the ester of a monobasic *acid* $C_{15}H_{24}O_2$ or $C_{16}H_{26}O_2$, and the higher fraction, b. p. 207—208/9·5 mm., with that of a dibasic *acid*, $C_{23}H_{34}O_4$ (cf. Richmond, *ibid.*, 690, who obtained an acid, $C_{22}H_{34}O_4$). On hydrolysis, only amorphous acids could be obtained. The fraction (*c*) consists essentially of a dibasic *acid*, $C_{40}H_{60}O_4$, which decomposes when heated in a high vacuum, yielding a neutral distillate containing a *hydrocarbon*, $C_{38}H_{56}$, b. p. 230—250/0·3 mm. Dry distillation of the whole acid portion (1) at 330° in a vacuum yields acidic (not investigated) and neutral products; the latter on distillation boiled continuously from 100°/12 mm. to 250°/0·3 mm., the low fraction containing a dicyclic *hydrocarbon*, $C_{14}H_{22}$, b. p. 115°/12 mm., d_4^{17} 0·9371, n_D^{17} 1·5201, which on catalytic reduction yields the *hydrocarbon*, $C_{14}H_{26}$, b. p. 115°/12 mm., d_4^{24} 0·9010, n_D^{24} 1·4860, whilst the composition of the high fraction corresponds with the formula $C_{38}H_{56}$. The fraction b. p. 100—150°/12 mm. on dehydrogenation with sulphur yields a methylethylnaphthalene, $C_{13}H_{14}$, b. p. 140°/12 mm., d_4^{18} 1·011, n_D^{18} 1·6082 (*picrate*, m. p. 138°; *styphnate*, m. p. 131°), which on oxidation with alkaline potassium ferricyanide solution yields a new *naphthalenedicarboxylic acid*, m. p. 310° (probably the 1 : 3-, 1 : 5-, 2 : 6-, or 2 : 7-isomeride). Dehydrogenation of the fraction b. p. 130—150°/0·3 mm. yields a small quantity of the dimethylphenanthrene, m. p. 86°, previously obtained from *d*-pimaric acid (Ruzicka and Balas, A., 1923, i, 818). The methyl esters of the acid products obtained by the dry distillation of the acetone-soluble (ether-insoluble) acids (*b*) yielded, on distillation, two fractions, corresponding with the *methyl* esters of the acids $C_{15}H_{24}O_2$ and $C_{19}H_{30}O_2$, d_4^{16} 1·028, n_D^{16} 1·5071, and d_4^{22} 1·010, n_D^{22} 1·5113, respectively, which on dehydrogenation yielded respectively the methylethylnaphthalene and the dimethylphenanthrene. A scheme by which the hydrocarbons are derived is suggested, and the relationships of the results to the preparation of copal varnish are discussed. J. W. BAKER.

Synthesis of *l*-α-pinene from nopinene. G. AUSTERWEIL (Bull. Soc. chim., 1926, 39, 1643—1646; cf. A., 1926, 619).—Pure nopinene, rectified over calcium, is heated with 3 parts of colophony at 160°⟶100°. Rectification of the terpene product gives more than 70% of pure *l*-α-pinene. A similar result is obtained by heating nopinene with commercial stearin at 145°. *l*-α-Pinene shows remarkable stability towards organic acids. Heated at 125—130° with 1 part of benzoic acid, it gives only 3—5% of bornyl benzoate and scarcely a trace of limonene, whilst 90% is unattacked. Nopinene, under similar treatment, gives 14% of bornyl benzoate and the remainder of the nopinene is almost quantitatively converted into *l*-α-pinene. M. CLARK.

Production of *iso*borneol from a mixture of camphene and associated oils. H. GAMMAY.—See B., 1926, 995.

Production of camphor from *iso*borneol. H. GAMMAY.—See B., 1926, 995.

Manufacture of esters of *iso*borneols and borneols. CHEM. FABR. VORM. SCHERING.—See B., 1926, 995.

Ring fission with coumaranone derivatives. K. VON AUWERS and H. LORENZ (Ber., 1926, 59, [*B*], 2628—2635; cf. A., 1919, i, 217).—Introduction of a basic residue in the 2-position of 2-alkylcoumaranones does not increase the stability of the furan ring; since halogen, hydroxyl, or methoxyl also fails to produce a stabilising effect, the remarkable stability of 2 : 2-dialkylcoumaranones remains unexplained.

2-Bromo-2 : 5-dimethylcoumaranone is converted by aniline in benzene into 2-*anilino*-2 : 5-*dimethylcoumaranone*, m. p. 140°, which with semicarbazide slowly yields the *semicarbazone* of *p-hydroxyphenyl α-anilino-α-semicarbazidoethyl ketone*, $OH\cdot C_6H_4\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CMe(NHPh)\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 216°, whereas with *p*-nitrophenylhydrazine it rapidly affords the *p*-nitrophenylosazone of *p*-hydroxyphenyl methyl diketone, m. p. 264°. 2-o-*Toluidino*-2 : 5-*dimethylcoumaranone*, m. p. 126°, similarly gives the *semicarbazone* of p-*hydroxyphenyl* α-o-*toluidino-α-semicarbazidoethyl ketone*, m. p. 219°. 2-α-*Naphthylamino*-2 : 5-*dimethylcoumaranone*, m. p. 103—105°, appears stable to semicarbazide, but with *p*-nitrophenylhydrazine it yields the *p*-nitrophenylosazone of *p*-hydroxyphenyl methyl diketone, decomp. 261°. 2-β-*Naphthylamino*-2 : 5-*dimethylcoumaranone* is unaffected by semicarbazide. 2-Bromo-2 : 5-dimethylcoumaranone is transformed by ethyl sodiomalonate into *ethyl* 2 : 5-*dimethylcoumaranylmalonate*, m. p. 42—45° (corresponding *acid*, m. p. 178°), which, although stable towards semicarbazide, suffers fission with *p*-nitrophenylhydrazine. 2-*Thiocyano*-2 : 5-*dimethylcoumaranone*, m. p. 102°, from 2-bromo-2 : 5-dimethylcoumaranone and potassium thiocyanate in ether, is readily converted by semicarbazide into the disemicarbazone of *p*-hydroxyphenyl methyl diketone.

2-*Bromo*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 51°, is prepared from bromine and the coumaranone in dry carbon disulphide. 2-*Anilino*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 136—137°, is decomposed by *p*-nitrophenylhydrazine, but is stable towards semicarbazide. 2-α-*Naphthylamino*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 167—168°, behaves similarly. 2-*Thiocyano*-2 : 4 : 6-*trimethylcoumaranone*, m. p. 78°, is stable towards semicarbazide. H. WREN.

Unsaturated 1 : 4-diketones. II. Formation of certain derivatives of furan. R. E. LUTZ (J. Amer. Chem. Soc., 1926, 48, 2916—2919; cf. this vol., 58).—When treated with acetic anhydride in presence of a trace of concentrated sulphuric acid, *trans*.-dibenzoylethylene yields 2 : 5-*diphenyl*-3-*acetoxyfuran*, m. p. 95°. 2 : 5-*Di*-p-*tolyl*-3-*acetoxyfuran*, m. p. 100·5°, is obtained analogously, whilst substitution of acetyl chloride for the anhydride yields 3-*chloro*-2 : 5-*diphenylfuran*, m. p. 76°, and 3-*chloro*-2 : 5-*di*-p-*tolylfuran*, m. p. 85°, respectively. The above 3-chloro-2 : 5-di-*p*-tolyl derivative was also prepared by dehydration of the additive product from di-*p*-toluylethylene and hydrogen chloride. Whilst both the isomeric *s*-dichlorodibenzoylethanes are readily converted into furans (cf. Conant and Lutz, A., 1925, i, 681), only the α-isomeride of the corresponding dibromodibenzoylethane could be converted, by the combined action of acetic anhydride, acetyl chloride, and sulphuric acid, into 3 : 4-*dibromo*-2 : 5-*diphenylfuran*, m. p. 88·5—89°. Furans could not be obtained similarly from " β "-α-chloro-αβ-dibenzoylethylene or from dibenzoylacetylene.

F. G. WILLSON.

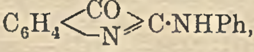
5-Hydroxyfurfuraldehyde. T. REICHSTEIN (Helv. Chim. Acta, 1926, 9, 1066—1068).—Pure 5-hydroxyfurfuraldehyde is an exceedingly hygroscopic, crystalline solid, m. p. 35—35·5°, b. p. 115—120°/0·5 mm. [α-naphthylamide, m. p. 135—135·5°; semicarbazone, m. p. 194—195° (decomp.)]. On oxidation, it gives hydroxymethylpyromucic acid in 84% yield. J. W. BAKER.

Derivatives of furfuraldehyde. III. Transitory coloration of furyl ketones. I. KASIWAGI (Bull. Chem. Soc. Japan, 1926, 1, 233—236).—The red colour produced by the action of alkali on saturated furyl ketones, or by keeping these, is changed irreversibly to yellow on heating or acidifying. The effect is ascribed to the formation of labile polymerides. E. W. WIGNALL.

Grape pigments. IV. Anthocyans of Isabella grapes. R. J. ANDERSON and F. P. NABENHAUER (J. Amer. Chem. Soc., 1926, 48, 2997—3003; cf. A., 1924, i, 1390).—The pigment of the skins of Isabella grapes was isolated as the picrate and converted into the *chloride*, $C_{21}H_{19}O_{10}(OMe)_2Cl,4H_2O$, which, on hydrolysis, yielded dextrose and the anthocyanidin chloride (œnidin), $C_{15}H_9O_5(OMe)_2Cl,1{\cdot}5H_2O$, identical with that previously described (*loc. cit.*). The latter yielded a *tetra-acetate*, which, on oxidation with permanganate in acetone, afforded *acetylsyringic acid*, m. p. 190° after sintering at 187°, a synthesis of which is described. The pigment thus appears to be identical with that of the European grape, *Vitis vinifera* (cf. Willstätter and Zollinger, A., 1915, i, 285).

F. G. WILLSON.

Catalytic reduction of cyanogen compounds. H. RUPE and A. HECKENDORN (Helv. Chim. Acta, 1926, 9, 980—991).—The catalytic reduction using a nickel catalyst at the ordinary temperature and pressure, of various unsaturated cyano-keto-derivatives has been studied. Ethyl benzylidenecyanoacetate yields the *aldehyde* of ethyl benzylmalonate (yield 80%; *semicarbazone*, m. p. 121°), which with phenylhydrazine and *p*-nitrophenylhydrazine yields, respectively, 1-*phenyl*-4-*benzylpyrazolone*, m. p. 143°, and 1-p-*nitrophenyl*-4-*benzylpyrazolone*, m. p. 176°, together with a secondary base isolated as its *oxalate*, m. p. 210°, and to which the constitution $[CH_2Ph{\cdot}CH(CO_2Et){\cdot}CH_2]_2NH$ is assigned. Similar reduction of ethyl benzylcyanoacetate yields the same aldehyde, showing that the double linking is reduced in the former case. In the reduction of ethyl *o*-nitrobenzylidenecyanoacetate, only the nitro-group is reduced, the product being *ethyl* 2-*aminoquinoline*-3-*carboxylate*, m. p. 135° (*hydrochloride*; *picrate*, m. p. 177°; *benzoyl* derivative, m. p. 160°), which on hydrolysis yields the free *acid*, m. p. 290°, purified by means of its *magnesium* salt, $+7H_2O$. The ester does not react with cold nitrous acid, but when warmed with sodium nitrite in hydrochloric acid solution it yields 2-hydroxyquinoline-3-carboxylic acid, which on heating yields carbostyril. The main product of the reduction of ethyl β-phenyl-γ-benzyl-α-cyanobutyrate [*nitrosoamine*, m. p. 148° or 153°, yielding the corresponding *diphenylhexahydronicotinic acid*, m. p. 196° (*silver* salt), on hydrolysis] is ethyl 1 : 3-diphenylpiperidine-4-carboxylate, formed by the reduction of the tetrahydropyridine derivative obtained by the elimination of water from ethyl α-methylamino-γ-benzoyl-β-phenylbutyrate, m. p. 104° (*hydrochloride*; *picrate*, m. p. 185°; *picrolonate*, m. p. 183°), which is also obtained in small yield. On hydrolysis it yields the free *acid*, m. p. 300—301°, isolated as its *hydrochloride*, from which it is obtained by conversion into its *copper* salt, which is decomposed by hydrogen sulphide. J. W. BAKER.

Derivatives of isatin and 4-nitroisatin. H. RUPE and K. APOTHEKER (Helv. Chim. Acta, 1926, 9, 1049—1059).—Reduction of isatinphenylhydroxylamine (Rupe and Stöcklin, A., 1924, i, 764) with zinc dust and acetic acid, or, better, catalytically with a nickel catalyst, yields the lactim form of *isatin-α-anil*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{N}{\geqslant}C{\cdot}NHPh$, m. p. 176°, which on treatment with semicarbazide, hydroxylamine, or phenylhydrazine yields, respectively, isatin-β-semicarbazone, -oxime, or -phenylhydrazone. The constitution of the product is confirmed by its non-identity with the dihydro-compound, β-anilinoindoxyl (isatin leuco-2-anil) (Pummerer and Göttler, A., 1910, i, 511), with which, however, the analytical data more closely agree, and the fact that the previously supposed lactam and lactim forms of isatin-α-anilide (Meyer-Jacobson, "Lehrbuch," II, 3, 274) are both represented by the lactam formula, since they are interconvertible on crystallisation, are both hydrolysed by hydrochloric acid with equal ease, and with semicarbazide, hydroxylamine, and phenylhydrazine both yield, respectively, *isatin-α-semicarbazone*, m. p. 226—228°, phenylhydrazone, and oxime, a mechanism for this reaction being suggested. Catalytic reduction of 4-nitroisatin (Rupe and Kersten, A., 1926, 843) yields *4-aminodioxindole* (isatin itself, under the same conditions being reduced to dioxindole), which with phenylhydrazine yields *4-aminoisatin-β-phenylhydrazone*, m. p. 243—245° (also obtained by the reduction of *4-nitroisatin-β-phenylhydrazone*, m. p. 286°), and with hydroxylamine and semicarbazide yields *4-aminoisatin-β-oxime*, m. p. 258°, and *4-aminoisatin-β-semicarbazone*, decomp. above 300°, respectively. Catalytic reduction of 4-nitroisatinphenylhydroxylamine (Rupe and Stöcklin, *loc. cit.*, there designated as the 6-compound; cf. Rupe and Kersten, *loc. cit.*) yields *4-aminoisatinanil*, $NH_2\cdot C_6H_3<\overset{CO}{\underset{N}{-}}\geqslant C\cdot NHPh$, m. p. 96° (*hydrochloride*), which with semicarbazide and phenylhydrazine yields, respectively, 4-aminoisatin-β-semicarbazone and -β-phenylhydrazone. J. W. BAKER.

[Constitution of the dyes from 2-methylated indolenium salts and phenylhydrazine.] E. ROSENHAUER and A. FEILNER (Ber., 1926, 59, [*B*], 2682; cf. A., 1926, 1257).—A correction. H. WREN.

Thioamides. VI. Some amino-acid derivatives containing sulphur in thioamide combination. E. S. GATEWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1926, 48, 2900—2905).—2 : 5-Dithionpiperazine (cf. Johnson, A., 1912, i, 304) is obtained, together with a light brown *powder*, m. p. not below 280°, by adding aminoacetonitrile sulphate to aqueous-alcoholic ammonia and passing ammonium sulphide through the resulting solution at below 0°. It decomposes rapidly in alkaline solution, and affords hydrogen sulphide and glycine on hydrolysis. Treatment of ethyl hippurate with phosphorus pentasulphide in dry benzene affords *ethyl thionhippurate*, m. p. 38—40°, which, on hydrolysis, yields *thionhippuric acid*, m. p. 148—150°. The action of phosphorus pentasulphide on ethyl acetoaminoacetate (cf. Radenhausen, A., 1896, i, 137) or ethyl phenylaceturate (cf. Klages and Haack, A., 1903, i, 560) did not lead to purifiable products, whilst this reagent was without action on ethyl aminoacetamidoacetate (cf. Fischer and Fourneau, A., 1901, i, 675). F. G. WILLSON.

Action of phenylthiocarbimide and phenylcarbimide on isatic acid. A. REISSERT and H. SCHAAF (Ber., 1926, 59, [*B*], 2494—2502).—Isatin is converted by phenylthiocarbimide and sodium hydroxide in boiling aqueous-alcoholic solution into *4-hydroxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline-4-carboxylic acid*, $C_6H_4<\begin{matrix}C(OH)(CO_2H)\cdot NPh\\ NH\text{———————}CS\end{matrix}$, m. p. 159—160° (decomp.) after becoming red at 140—145°; the *alkali*, *alkaline-earth*, *copper*, and *lead* salts are described. The *ethyl* ester, prepared by means of cold ethyl alcohol and hydrogen chloride, has m. p. 184°, the *methyl* ester, m. p. 166—167°. Treatment of the acid with ethyl sulphate in alkaline solution affords *ethyl 4-ethoxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline-4-carboxylate*, m. p. 192—194°; *methyl 4-methoxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline-4-carboxylate* has m. p. 179—180°. The esters do not dissolve in cold alkali hydroxide, but are transformed by the boiling reagent into the hydroxy-acid. Protracted treatment of the hydroxy-acid with boiling ethyl alcohol leads to loss of carbon dioxide and production of *4-ethoxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 194—196°; *4-methoxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline* has m. p. 190—192°. The reaction appears to be due to initial formation of 2-thio-3-phenyl-2 : 3-dihydroquinazoline, which subsequently adds methyl or ethyl alcohol. In support of this view, it is found that the hydroxy-acid is converted when heated in neutral media of sufficiently high b. p. into *bimolecular 4-hydroxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 215°, converted by boiling glacial acetic acid into *unimolecular 4-hydroxy-2-thio-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 172°, which with the requisite boiling alcohol gives the methoxy- and ethoxy-compounds described above. The hydroquinazoline loses water at 245° and yields *2-thio-3-phenyl-*2 : *3-dihydroquinazoline*, m. p. 252—255°, which with boiling ethyl alcohol affords 4-ethoxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline. The latter substance is converted by boiling 2*N*-hydrochloric acid into *di-4-ethoxy-3-phenyl-*3 : *4-dihydro-2-quinazolyl sulphide*, m. p. above 345°.

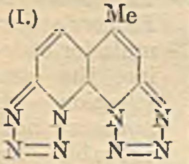
*4-Hydroxy-2-keto-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline-4-carboxylic acid*, m. p. 174° (decomp.), is obtained from the corresponding thio-acid and mercuric oxide, or from sodium isatate and phenylcarbimide in the presence of anhydrous ether; the *hydrochloride* is described. It is converted by boiling ethyl alcohol into *4-ethoxy-2-keto-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 185—186° (corresponding *methoxy*-compound, m. p. 199—201°). *Bimolecular 4-hydroxy-2-keto-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 210—212°, is transformed by glacial acetic acid into the unimolecular *variety*, m. p. 182—184°, which readily becomes polymerised. 2 : *4-Diketo-3-phenyl-*1 : 2 : 3 : *4-tetrahydroquinazoline*, m. p. 272°, is prepared by oxidation of 4-hydroxy-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline-4-carboxylic acid or its sulphur-free analogue with hydrogen peroxide in alkaline solution. H. WREN.

[Quinoxaline.] O. HINSBERG (Ber., 1926, 59, [*B*], 2560).—A question of priority (cf. Körner Memorial notice, *ibid.*, [*A*], 102). H. WREN.

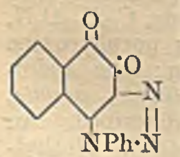
Syntheses of derivatives of 1 : 8-naphthyridine. O. SEIDE (Ber., 1926, 59, [*B*], 2465—2473).—

2 : 6-Diaminopyridine is converted by ethyl acetoacetate at 145—150° into 7-*amino*-2-*hydroxy*-4-*methyl*-1 : 8-*naphthyridine*, decomp. about 405° after darkening at 340° (*hydrochloride*). The base is converted by sodium nitrite in 33% sulphuric acid solution into 2 : 7-*dihydroxy*-4-*methyl*-1 : 8-*naphthyridine*, m. p. 337° (decomp.) (*sodium* salt), which with phosphorus pentachloride affords 2 : 7-*dichloro*-4-*methyl*-1 : 8-*naphthyridine*, m. p. 193°. Hydrazine hydrate at 150° converts the dichloro-compound into 2 : 7-dihydrazino-4-methyl-1 : 8-naphthyridine, isolated as the *dihydrochloride dihydrate* and characterised further as the *dibenzylidene* derivative, m. p. 263°. The constitution of the series of compounds is established by the transformation of the dihydrazino-derivative by nitrous acid into 1 : 2 : 7 : 8-*ditetrazole*-4-*methyl*-1 : 2 : 7 : 8-*tetrahydro*-1 : 8-*naphthyridine* (I), m. p. about 190° (decomp.), and its oxidation by permanganate to tetrazole, identified as the silver salt and in substance. 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine is converted by boiling hydriodic acid (b. p. 127°) into 2 : 7-dihydroxy-4-methyl-1 : 8-naphthyridine and by the acid (*d* 1·96) and red phosphorus at 170—180° into 4-*methyltetrahydronaphthyridine*, m. p. 103° [*picrate*, m. p. 248° (decomp.) after blackening at 235°; *chloroplatinate*, m. p. 215° (decomp.); *acetyl* derivative, m. p. 94°]. H. Wren.

(I.)

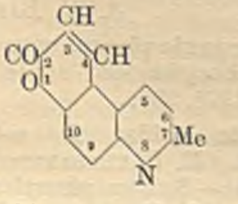


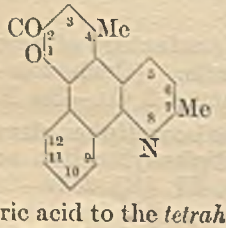
1 - Phenyl - αβ - naphthatriazolequinone. G. Charrier (Atti R. Accad. Lincei, 1926, [vi], 4, 312—315).—Like its 3-phenyl isomeride (A., 1926, 848), 1-phenyl-αβ-naphthatriazole is oxidised by chromic acid in acetic acid solution to 1-*phenyl*-αβ-*naphthatriazolequinone* (annexed formula) (yellow, decomp. about 212°), which forms a phenylhydroxyazo-derivative and a phenazine, to be described later, and gives 3-phenyl-4-*o*-carboxyphenyl-1 : 2 : 3-triazole-5-carboxylic acid when oxidised by alkaline permanganate. T. H. Pope.



Quinolino-6 : 5-α-pyrones. [ψ-1 : 8-*iso*Naphthoxazones.] B. B. Dey, I. Sarkar, and T. R. Seshadri (J. Indian Chem. Soc., 1926, **3**, 187—196; cf. Dey and Goswami, J.C.S., 1919, **115**, 531).—6-Aminocoumarin condenses with paracetaldehyde in presence of hydrochloric acid to yield 2-*methylquinolino*-6 : 5-α-*pyrone* [7-*methyl*-ψ-1 : 8-iso*naphthoxazone*, (I)], m. p. 220° [*hydrochloride*, *mercurichloride*, *mercuri-iodide*, *dichromate* ($3\frac{1}{2}H_2O$), *picrate*, *chloroplatinate*, *methiodide*, m. p. 245° (decomp.), *benzylidene* derivative, m. p. 205° (*hydrochloride*) described], which is reduced by tin and hydrochloric acid to the *tetrahydro*-derivative, m. p. 179° [*hydrochloride*, *picrate*, *chloroplatinate*, *nitroso*-compound, m. p. 161°, *acetyl* derivative, m. p. 139°, methiodide, m. p. 202° (decomp.) described]. In the same way, 6-amino-4-methyl-αβ-naphthapyrone yields 2-*methyl*-7 : 8-*benzoquinolino*-6 : 5-α-4′-*methylpyrone* [4 : 7-*dimethyl*-ψ-*benzo*-1 : 8-iso*naphthoxazone* (II)], m. p. 248° (*hydrochloride*, *picrate*, *dichromate*, *chloroplatinate*, *mercurichloride*, and *mercuri-iodide* described), reduced to the *tetrahydro*-derivative, m. p. 204° [*acetyl* derivative, m. p. 202°, *chloroplatinate*, *nitroso*-derivative, m. p. 168° (decomp.), described]. 6-Aminocoumarin condensed with acetone and paraldehyde gives 2 : 4-*dimethylquinolino*-6 : 5-α-*pyrone* [5 : 7-*dimethyl*-ψ-1 : 8-iso*naphthoxazone*], m. p. 265° (*hydrochloride*, *dichromate*, *chloroplatinate*, *picrate*, *mercurichloride* described), reduced to the *tetrahydro*-derivative, m. p. 121° (*nitroso*-derivative, m. p. 177°, *benzoyl* derivative, m. p. 171°, described). G. M. Bennett.

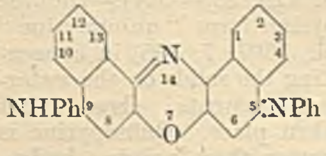
(I.)



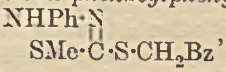


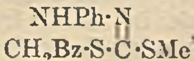
(II.)

Azoxines. III. H. Goldstein and H. Radovanovitch (Helv. Chim. Acta, 1926, 9, 959—961).—Oxidation of 1-amino-4-anilino-β-naphthol yields 9-*anilino*-N-*phenyl*-αα′-*dinaphthoxaz*-5-*ime* (annexed formula), m. p. 259°, a molecule of the quinonedi-imine first formed condensing with an unoxidised molecule. The same substance is obtained by the condensation of anilino-β-naphthaquinone with 1-amino-4-anilino-β-naphthol, and it is the chief product when hydroxy- or amino-β-naphthaquinone is condensed with 1-amino-4-anilino-β-naphthol, traces only of 9-*anilino*-αα′-*dinaphthazox*-5-*one*, m. p. 328—330°, and 9-*anilino*-αα′-*dinaphthoxaz*-5-*ime*, respectively, being formed. J. W. Baker.



Thiodiazines. IV. P. K. Bose (J. Indian Chem. Soc., 1926, **3**, 197—210; cf. A., 1926, 1159).—Condensation of alkyl phenyldithiocarbazinates with phenacyl bromide under various conditions yields their phenacyl derivatives in *cis* and *trans* isomeric forms, which are distinguished by the fact that the *cis*-compound is the more readily converted into the corresponding thiodiazine derivative (cf. Busch, A., 1901, i, 430; 1911, i, 811). The *trans*-compound results when the condensation is carried out by the addition of alkali or calcium carbonate to the mixture of the reagents in alcoholic solution, whilst the *cis*-isomeride is formed when the dithiocarbazinate is previously dissolved in the alkali or the reaction conducted in cold pyridine solution. The following pairs of isomerides were obtained in this way from the requisite esters and phenacyl bromides: *methyl* trans-*phenacylphenyldithiocarbazinate*,


$\substack{NHPh\cdot N \\ \| \\ SMe\cdot C\cdot S\cdot CH_2Bz}$, m. p. 100° (*phenylhydrazone*, m. p. 127°), and the cis-*isomeride*,


$\substack{NHPh\cdot N \\ \| \\ CH_2Bz\cdot S\cdot C\cdot SMe}$, m. p. 93°, both of which were converted by heating at 100° in alcoholic solution into 2-*methylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine*, m. p. 180°; *ethyl* trans-*phenacylphenyldithiocarbazinate*, m. p. 82° (*phenylhydrazone*, m. p. 136°), and the cis-*isomeride*, m. p. 86°, converted into 2-*ethylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-

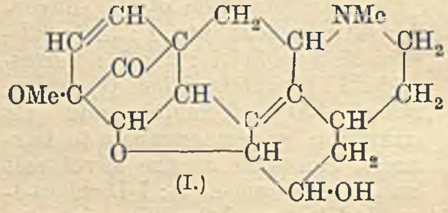
thiodiazine, m. p. 150°, this and the other thiodiazine derivatives being also obtained in the original condensation if the pyridine solution is boiled; n-*propyl* trans-*phenacylphenyldithiocarbazinate*, m. p. 56° (from the n-*propyl phenyldithiocarbazinate*, m. p. 125°), and its cis-*isomeride*, m. p. 61°, converted into 2-n-*propylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine*, m. p. 151°; *methyl* trans-p-*methylphenacylphenyldithiocarbazinate*, m. p. 110° (*phenylhydrazone*, m. p. 124·5°), and its cis-*isomeride*, m. p. 54°, of which the *trans*-compound was converted by heating at 100° in alcoholic solution into 2-*methylthiol*-4-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*, m. p. 187°, whilst the *cis*-compound was converted only into its isomeride; *ethyl* trans-p-*methylphenacylphenyldithiocarbazinate*, m. p. 95°, and its cis-*isomeride*, m. p. 77°, converted at 120—130° in alcoholic solution into 2-*ethylthiol*-4-*phenyl*-5-p-*tolyl*-1 : 3 : 4-*thiodiazine*, m. p. 148°. *Benzyl phenacylphenyldithiocarbazinate*, m. p. 75°, was obtained in only one form. G. M. Bennett.

Additive compounds. C. G. Santesson (Arch. exp. Path. Pharm., 1926, **118**, 313—324).—Quinine hydrochloride and antipyrine form "quinopyrine" (cf. Skand. Arch. Physiol., 1897, **7**, 385) in concentrated solution or on heating the solids on the water-bath. Conductivity measurements show that chemical reaction has taken place. Quinopyrine is much more soluble in water than quinine hydrochloride, gives the antipyrine reaction with ferric chloride, but gives the thalleioquin reaction only on considerable dilution, by which it is decomposed.

Pyramidone and veronal (2 : 1) form "veramone," which is not homogeneous, but react in molecular equivalents to yield a definite substance (Pfeiffer, A., 1925, i, 1318; 1926, 739), which the author considers to be a co-ordinated compound.

Cocaine hydrochloride and phenylurethane form a similar compound ("albromine"). J. M. Gulland.

Constitution of porphyroxine. J. N. Rakshit (Ber., 1926, **59**, [*B*], 2473—2486; cf. J.C.S., 1919, **115**, 456).—Porphyroxine is converted by distillation with zinc dust mainly into phenanthrene with small amounts of ammonia and trimethylamine and traces of other bases. It contains one methoxyl group. As a tertiary base, it is readily converted into the corresponding *methosulphate*, m. p. 205° (decomp.) after softening at about 180°, $[\alpha]^{25}$ −74·6° in methyl alcohol, and *methiodide*, m. p. 150—152°, $[\alpha]^{25}$ −82·5° in methyl alcohol, from which the *methochloride*, m. p. 171° (slight decomp.) after softening at 145°, $[\alpha]^{34}$ −90·4° in water, and *methohydroxide*, m. p. 112—115° (decomp.), $[\alpha]^{34}$ −71·8° in alcohol, are derived. Treatment of porphyroxine with acetic anhydride or acetyl chloride affords the *monoacetate*, $C_{21}H_{25}O_5N$, m. p. 125° after softening at 110°, $[\alpha]^{31}$ −187·2° in alcohol; since the alkaloid is insoluble in alkali hydroxide, the presence of a secondary alcoholic group is established. Porphyroxine acetate yields a *sulphate*, decomp. about 190° after softening at 170°, $[\alpha]^{30}$ −150·2° in water, *hydrochloride*, m. p. 126°, $[\alpha]^{30}$ −123·4° in water, *chloroplatinate*, m. p. 230° (decomp.) after darkening at 225°, *hydrobromide*, m. p. 155° (decomp.) after softening at 150°, $[\alpha]^{35}$ −98·8° in water, and *hydriodide*, m. p. 105—107° (decomp.). The presence of the ketonic group in porphyroxine is established by the isolation of the corresponding *oxime*, $C_{19}H_{24}O_4N_2$, m. p. about 198° (decomp.), *semicarbazone*, incipient decomp. 244°, and *phenylhydrazone*, m. p. 150° (slight decomp.). Insight into the constitution of porphyroxine is mainly afforded by the observation that it is converted by hydrogen peroxide in boiling weakly alkaline solution into codeine and formic acid. Porphyroxine differs from codeine in containing two additional atoms of hydrogen and a carbonyl group, and since these are readily and simultaneously removed (as water and formic acid) in a single reaction, it is very probable that they are attached to the same ring system. On the basis of Pschorr's formula for codeine, the constitution (I) appears most probable for porphyroxine. Attempts to hydrogenate the base were unsuccessful.



(I.)

Methylporphyroxine, m. p. 125—126°, $[\alpha]^{28}$ −131·8° in chloroform, is prepared by the action of sodium methoxide on porphyroxine methiodide, or, preferably, from porphyroxine methosulphate and methyl-alcoholic potassium hydroxide. The *hydrochloride*, *hydrobromide*, *sulphate*, *oxalate*, *hydriodide*, *acetate*, *phosphate*, and *chloroplatinate* have been prepared. The substance does not yield an acetate. It gives an *oxime*, m. p. 185—186°, *semicarbazone*, m. p. 217° (decomp.), and *phenylhydrazone*, m. p. 189° (slight decomp.). *Methyltetrahydroporphyroxine*, $C_{20}H_{29}O_4N$, m. p. 150°, is prepared by reducing porphyroxine methosulphate with sodium amalgam; the *hydrochloride*, *hydrobromide*, *hydriodide*, *nitrate*, *acetate*, *chloroplatinate*, and *chloroaurate* are described. An acetyl derivative could not be prepared. Methyltetrahydroporphyroxine yields an *oxime*, m. p. 234—235°, *semicarbazone*, incipient decomp. 210°, and *phenylhydrazone*, m. p. 126°. H. Wren.

Two new alkaloids from Yohimba bark. P. Karrer and H. Salomon (Helv. Chim. Acta, 1926, **9**, 1059—1062).—Two new alkaloids have been isolated from Yohimba bark. ψ-*Yohombine*, $C_{21}H_{26}O_3N_2$, differing only from yohombine in its crystalline form and its m. p., 264—265°, $[\alpha]_D^{18}$ +26·6° (*hydrochloride*, m. p. 258°), is obtained in only 0·01—0·015% yield. The second alkaloid, *corynanthine*, $C_{20}H_{22}O_2N_2(OMe)_2$, is isolated as its *hydrochloride*, m. p. 205°, $[\alpha]_D$ +12·15°, which, in distinction from the hydrochloride of ψ-yohimbine, is soluble in chloroform. J. W. Baker.

Manufacture of new organic phosphorus compounds. [Carbazole-phosphinous acids.] L. Cassella & Co.—See B., 1926, 996.

Carboxydiphenylarsinic acids. I. *o*-Carboxydiphenylarsinic acid. E. Sakellarios (Ber., 1926, **59**, [*B*], 2552—2554).—Sodium phenylarsinite couples with diazotised anthranilic acid in alkaline solution, yielding *o*-carboxydiphenylarsinic acid, m. p.

166° (decomp.) when rapidly heated (Aeschlimann and McCleland record m. p. above 300°; cf. A., 1924, i, 1358), benzoic acid and azobenzene-*oo'*-dicarboxylic acid, m. p. 237° (decomp.). *o*-Carboxydiphenylarsenious oxide, prepared from the acid and sodium hydrogen sulphite, has m. p. 133°. Attempts to convert these substances into compounds containing arsenic in a heterocyclic ring were unsuccessful.

H. WREN.

Compound of pyrocatechol and arsinoacetic acid. B. ENGLAND (Ber., 1926, 59, [*B*], 2669—2671).—The *compound*, $CO_2H{\cdot}CH_2{\cdot}As(C_6H_4O_2)_2,AcOH$, m. p. 146°, crystallises from solutions of arsinoacetic acid and pyrocatechol in glacial acetic acid; an analogous *compound*, m. p. 137°, is formed when the components are heated together. The *methyl* ester, $CO_2Me{\cdot}CH_2{\cdot}As(C_6H_4O_2)_2$, m. p. 117°, is described.

H. WREN.

Azo-dyes containing antimony. F. DUNNING and E. E. REID (J. Amer. Chem. Soc., 1926, 48, 2959—2963).—*p*-Aminophenylstibinic acid is obtainable (yield 35—60%) by diazotising *p*-aminoacetanilide, dissolved with the calculated amount of antimony trioxide in just sufficient 15% hydrochloric acid, filtering off the precipitated double salt (cf. May, J.C.S., 1912, 101, 1037), suspending this in water, and adding gradually aqueous 10% sodium hydroxide at 3—5°, neutralising, precipitating impurities with carbon dioxide, and finally adding dilute acetic acid (cf. Schmidt, A., 1920, i, 900), the acetyl group then being removed by Schmidt's method (*ibid.*, 1922, i, 1203). The following dyes, mostly of brown shades, were prepared from the above stibinic acid: 4-*hydroxyazobenzene*-4'-*stibinic acid* (impure); 4-*hydroxy*-2-*chloro*-, 4-*hydroxy*-3-*nitro*-, 4-*hydroxy*-3-*amino*-, 4-*hydroxy*-3-*methyl*-, and 4-*hydroxy*-3-*carboxy-azobenzene*-4'-*stibinic acid*. Diazotised *p*-aminophenylstibinic acid and pyrocatechol gave a *product* other than the expected dye. *Disodium* salts of the above are described. They are stable in aqueous solution.

F. G. WILLSON.

Halogenated proteins. VI. Chlorocasein. A. J. J. VANDEVELDE (Rec. trav. chim., 1926, 45, 825—829).—The action of a saturated solution of chlorine in carbon tetrachloride on casein yields a *chlorocasein* (N, 10·5; Cl, 32%) soluble in potassium hydroxide solution, the amounts of chlorine in this compound and of bromine in the corresponding bromocasein (A., 1925, i, 1477) not being proportional to the mass of the two atoms. The action of water at 18° and 61°, potassium hydroxide and acetic acid, alcohol and ether on this chlorocasein has been investigated in detail, in each case a product containing a smaller percentage of chlorine being obtained. In all the compounds examined, correct results for the determination of chlorine could be obtained only by the method of ter Meulen and Heslinga (*ibid.*, 1924, ii, 55).

J. W. BAKER.

Chemical nature of hæmochromogen and its carbon monoxide compound. R. HILL (Proc. Roy. Soc., 1926, B, 100, 419—430; cf. A., 1925, i, 994).—The spectra of nickel and copper hæmatoporphyrins are not appreciably altered by the addition of denatured globin or excess of pyridine or ammonia—a behaviour similar to that of free hæmatoporphyrin. Artificial iron hæmatoporphyrin, however, gives hæmochromogen, behaving exactly as hæmin prepared from blood, and on reduction does not show the hæmochromogen spectrum of other metallic hæmatoporphyrins except in presence of a nitrogeneous substance. Hence the hæmochromogen is the ferrous compound of the porphyrin. The iron atom alone confers on the reduced pigment the property of forming additive compounds.

Quantitative experiments on the combination of pyridine with reduced hæmatin show that in carbon monoxide-hæmochromogen one nitrogenous mol. is replaced by carbon monoxide. On addition of pyridine to carbon monoxide-reduced hæmatin, 1 mol. of the former is taken up, whilst an excess displaces carbon monoxide, and hæmochromogen results. These changes have been observed spectroscopically and occur with any nitrogenous compound, including denatured globin. The author proposes general formulæ in which the nitrogen and the carbon monoxide are co-ordinated with the iron, which has a co-ordination number of 6, and represents a carbon monoxide-hæmochromogen as $\mathrm{Hph}\vdots\mathrm{Fe}{<}^{\mathrm{CO}}_{\mathrm{N}\vdots}$, a hæmochromogen as $\mathrm{Hph}\vdots\mathrm{Fe}{<}^{\mathrm{N}\vdots}_{\mathrm{N}\vdots}$, and the carbon monoxide compound of reduced hæmatin as $\mathrm{Hph}\vdots\mathrm{Fe}{<}^{\mathrm{CO}}_{\mathrm{X}}$, where Hph is a porphyrin and X another molecule of the complex or a molecule of water.

J. M. GULLAND.

Constitution of sponges. I. The common bath sponge, *Hippospongia equina*. V. J. CLANCEY (Biochem. J., 1926, 20, 1186—1189).—Spongin yields on hydrolysis mainly glutamic acid and glycine, with smaller quantities of leucine, aspartic acid, arginine, proline, lysine, tryptophan, and iodogorgonic acid.

S. S. ZILVA.

Denaturation of egg-albumin by weak acids in the presence of salts. H. MASTIN and S. B. SCHRYVER (Biochem. J., 1926, 20, 1177—1185).—A well-defined acidic denaturated product of albumin can be obtained by the action of acid on or by electrolysis of egg-white in the presence of ammonium sulphate and other salts. The formation of this compound is characterised by an increase in the number of free acid groups without a corresponding increase in the amino-groups and by the appearance of free thiol groups.

These changes are probably due to hydrolysis of the protein at a thiodepside ($C{\cdot}CO{\cdot}S{\cdot}C{\cdot}$) grouping in the molecule.

S. S. ZILVA.

Preparation and physico-chemical properties of sericin. K. KODAMA (Biochem. J., 1926, 20, 1208—1222).—Some physico-chemical properties of sericin and sericin-peptone dissolved in hydrochloric acid and sodium hydroxide solutions are given. The isoelectric points of sericin and sericin-peptone exist near p_H 3·9 and 4·4, respectively. The sericin in this investigation was prepared by a modification of Bondi's method (A., 1902, i, 579). The extraction of sericin in the autoclave deprives the protein of its precipitability by dilute acids. The glyoxylic acid reaction for tryptophan also disappears after this treatment. S. S. Zilva.

Micro-determination of the Hausmann numbers of proteins. K. V. Thimann (Biochem. J., 1926, 20, 1190—1195).—The method requires only 3—6 mg. of total nitrogen in each determination. The various sources of error of the macro-method are avoided. S. S. Zilva.

[Rapid, dry method for the determination of carbon and hydrogen.] E. Berl and H. Burkhardt (Ber., 1926, 59, [*B*], 2682; cf. A., 1926, 749). —A method is described whereby the total content of the combustion tube can be heated to dull redness in a simple manner. H. Wren.

Sources of error in organic elementary analysis. I. Lead peroxide. J. Lindner (Ber., 1926, 59, [*B*], 2561—2573).—The adsorption of carbon dioxide by lead peroxide is appreciable at temperatures at which elementary analyses are performed. The carbon dioxide is removed more rapidly by a moist than by a dry current of air. The effect on the analytical values for carbon falls generally within the limits of normal variation, but in certain circumstances may contribute to the production of error. Large charges of finely-divided lead peroxide and low temperatures (about 150°) should be avoided as far as possible. Protracted heating at 200° does not cause any disturbance. Reception of carbon dioxide by peroxide which has been heated at a higher temperature appears to depend on the formation of carbonate; the carbon dioxide is completely evolved from the peroxide at normal, lower temperatures, whereas this is not the case with lead oxide containing lead carbonate. The action of nitric oxide causes absorption of carbon dioxide and the peroxide suffers protracted damage. The carbon dioxide is as loosely retained by such charges as by superheated peroxide. H. Wren.

Determination of phosphorus or arsenic in organic substances. R. Poggi and A. Polverini (Atti R. Accad. Lincei, 1926, [vi], 4, 315—318).—A solution of the material (0·35 g. of cacodylic acid or 0·2 g. of triphenylphosphine) in sulphuric acid (10 c.c.) is mixed with 5 g. of powdered potassium persulphate, and heated gently during about an hour, with further additions of persulphate (about 6 g. in all) until the liquid is colourless. The arsenic is then determined as magnesium ammonium arsenate or the phosphorus as ammonium phosphomolybdate. T. H. Pope.

Detection of methyl alcohol by use of potassium guaiacolsulphonate. R. Bauer (Pharm. Ztg., 1926, 71, 1543).—In applying the test, the oxidation with permanganate and dilute sulphuric acid must be very cautiously effected, as traces of formaldehyde are readily destroyed. S. I. Levy.

Detection of methyl alcohol; replacement of guaiacol by potassium guaiacolsulphonate to avoid errors. H. Matthes (Pharm. Ztg., 1926, 71, 1508—1509).—Since acetaldehyde reacts readily with guaiacol in presence of sulphuric acid with development of a red coloration, it is preferable to use potassium guaiacolsulphonate, which does not so react, but gives the formaldehyde reaction equally readily. If much methyl alcohol is present, the colour obtained is a strong violet-red. S. I. Levy.

Identification of amines. III. Toluene-ω-sulphonamides. C. S. Marvel and H. B. Gillespie (J. Amer. Chem. Soc., 1926, 48, 2943—2944).—Toluene-ω-sulphonyl chloride (1 mol.) and an amine (2 mols.) react in benzene solution to give a precipitate of the amine hydrochloride, and the corresponding toluene-ω-sulphonamide, which is recovered by evaporation, and is readily purified by recrystallisation from dilute alcohol. The following substituted sulphonamides are described: *allyl-*, m. p. 79°; *diethyl-*, oil; *piperidyl-*, m. p. 131·5°; n-*heptyl-*, m. p. 76°; *di*-n-*butyl-*, oil; o-*tolyl-*, m. p. 83°; m-*tolyl-*, m. p. 75°; o-*chlorophenyl-*, m. p. 91°; p-*chlorophenyl-*, m. p. 110°; m-*bromophenyl-*, m. p. 99·5°; p-*bromophenyl-*, m. p. 133·5°; *phenylmethyl-*, m. p. 101°; *phenylethyl-*, m. p. 118·5°; *phenyl*-n-*propyl-*, m. p. 135°; *phenyl*-n-*butyl-*, m. p. 108°; o-*anisyl-*, m. p. 72°; p-*anisyl-*, m. p. 103°; and *toluene-ω-sulphon*-p-*phenetidide*, m. p. 117·5°. Toluene-ω-sulphon-*o*-phenetidide has m. p. 74°, and not 85° as given by Fromm and Palma (A., 1906, i, 819). *Ditoluene-ω-sulphonanilide* has m. p. 71·5°, and *ditoluene-ω-sulphon*-p-*toluidide*, m. p. 74·5°. F. G. Willson.

Crystallographic constants. G. Gilta (Bull. Soc. chim. Belg., 1926, 35, 365—371).—Crystallographic methods are of value in determining the degree of purity of organic compounds and in detecting the formation of hydrates. For example, acetylsalicylic acid is monoclinic, $a:b:c=1{\cdot}7075:1:0{\cdot}8528$ $\beta=95°\,24'$. When the pure substance is recrystallised, leaflets flattened parallel to {100} are obtained, but in presence of acetic or salicylic acid needles elongated along the *c*-axis separate (cf. A., 1919, i, 124; 1920, i, 841). Sodium *m*-xylene-4-sulphonate crystallises from water $(+1H_2O)$ at the ordinary temperature in monoclinic plates, $a:b:c=1{\cdot}7739:1:0{\cdot}8558$, $\beta=99°\,30'$, but below about 8° orthorhombic leaflets $(+4 \text{ or } 5H_2O)$ are produced. H. E. F. Notton.

Biochemistry.

Aërobic and anaërobic metabolism of the common cockroach (*Periplaneta orientalis*). I. J. G. Davis and W. K. Slater (Biochem. J., 1926, 20, 1167—1172).—The cockroach while living in nitrogen goes into debt for oxygen, and when it is returned to air it consumes oxygen in excess of the normal uptake until the debt has been discharged. The rate of metabolism of the insect is influenced by its weight. The respiratory quotient, as in the case of higher animals, is depressed by starvation. S. S. Zilva.

Regulation of respiration. III. Continuous method of recording changes in acidity applied

to the circulating blood and other body fluids. IV. Tissue acidity, blood acidity, and pulmonary ventilation. Effects of semipermeability of membranes and the buffering action of tissues. R. Gesell and A. B. Hertzman (Amer. J. Physiol., 1926, 78, 206—223, 610—629).—III. A manganese dioxide electrode is placed directly in the blood-stream of a dog, the *E.M.F.* balanced at a potentiometer, and a continuous record made graphically. Whereas electrodes did not give reproducible results in different fluids, they were found to give faithful records of the acid–base changes in any one fluid. Results were controlled by periodical determinations of blood samples by the hydrogen and quinhydrone electrodes. The effects of anoxæmia, asphyxia, and hæmorrhage and of the administration of carbon dioxide, carbonate, lactic acid, and ammonium chloride were studied. When large doses of sodium cyanide were given, the manganese dioxide electrode was at fault. Precautions against the appearance of reducing substances in the blood are emphasised.

IV. Synchronous records were taken of the changes in acidity of the arterial and venous bloods, the tissues, and the cerebrospinal fluid of dogs by means of manganese dioxide electrodes placed in the blood, fluid, and muscles. The increased acidity following administration of carbon dioxide and the increased alkalinity following sodium carbonate were found to be greater and to be more rapidly attained in the arterial than in the venous blood. In both cases, the tissues acted as buffers. Injection of sodium hydrogen carbonate increased the alkalinity of the blood, whilst the cerebrospinal fluid and the muscles became more acid. The buffering due to the tissues appeared to be minimal. These results suggest an impermeability of cell membranes for base and confirm the conclusion that it is the hydrogen-ion concentration of the respiratory centre itself which controls respiration. R. K. Cannan.

Preparation and properties of the globin of oxyhæmoglobin. R. Hill and H. F. Holden (Biochem. J., 1926, 20, 1326—1339).—Oxyhæmoglobin is decomposed with a minimum amount of hydrochloric acid at a low temperature, and after the addition of ether and kieselguhr is filtered. The globin is precipitated from the filtrate with ammonia. It is soluble in presence or absence of salts over the range p_H 5—10. On treatment with hæmin dissolved in alkali carbonate, it yields methæmoglobin, from which typical hæmoglobin and oxyhæmoglobin are obtained. The equilibrium of the reaction between globin and hæmatin with which it reacts over the range p_H 5—10 has been investigated. Globin yields compounds with certain porphyrins and their metallic derivatives. Oxyhæmoglobins have been prepared from the iron compounds of hæmatoporphyrin and mesoporphyrin.

Protoporphyrin was prepared by inoculating fresh defibrinated sheep's blood with *Bacillus coli*, precipitating the reduced blood with concentrated hydrochloric acid, and extracting the hydrochloride of the porphyrin with 97% alcohol. S. S. Zilva.

Use of light filters in colorimetry. Determination of hæmoglobin. R. P. Kennedy (Amer. J. Physiol., 1926, 78, 56—63).—In the eye-piece of the colorimeter is fitted a colour filter transmitting light of a wave-length which is prominent in the absorption spectrum of the substance to be determined. A standard neutral grey Wratten filter replaces the usual colour standard, and the depth of the solution is then adjusted so that the transmission matches that through the standard filter. The method is illustrated by determinations of hæmoglobin as carboxyhæmoglobin, the results being controlled by the oxygen capacity of the hæmoglobin and by a spectrophotometric method. Certain theoretical principles of colorimetry are discussed. R. K. Cannan.

Ammonia in blood. P. B. Rehberg (Physiol. Papers dedicated to August Krogh, 1926, 248—267).—For the determination of ammonia in blood, vacuum aëration is followed by micro-titration; the content, which increases 2—3 hrs. after a meal, varies from 0·03 to 0·22 mg. per 100 c.c. Chemical Abstracts.

Photo-oxidation by means of fluorescent pigments. H. Gaffron (Biochem. Z., 1926, 179, 157—185).—Blood-serum, in presence of small amounts of various porphyrins, of chlorophyll, and of certain dyes, absorbs large amounts of oxygen, with simultaneous evolution of carbon dioxide and formation of ammonia; the $CO_2:O_2$ ratio is 1:4 and the $NH_3:O_2$ ratio 1:7; the greater part of the carbon dioxide is liberated from the hydrogen carbonate of the serum by acids set free during the oxidation. Results of a similar type were obtained with solutions of caseinogen.

Hæmin and the heavy metal derivatives of hæmatoporphyrin have no activating effect, but the zinc derivative is as active as hæmatoporphyrin itself. That the photo-oxidation is concerned exclusively with the colloidal constituents of serum is shown by the absence of the phenomenon from the ultrafiltrate of the latter. The rate of photo-oxidation is accelerated considerably by the presence of bile salts and by increase in the partial pressure of oxygen, and to a slight extent by rise in temperature. Photo-oxidation of tyrosine and of phenol takes place readily in presence of 1 equivalent of sodium hydroxide; in the former case, the uptake of oxygen is more than 4·5 mols., and the $CO_2:O_2$ ratio is 1 : 3. In the photo-oxidation of uric acid, 1 mol. of oxygen is absorbed, an equivalent amount of carbon dioxide being evolved. C. R. Harington.

Plasma calcium-ion concentration. E. J. Warburg (Biochem. Z., 1926, 178, 208—223).—The formulæ for the calculation of the calcium-ion concentration of the plasma are brought into accord with Bjerrum's ionic activity theory (cf. Marrack and Thacker, A., 1926, 855). In the expression $Ca^{\cdot\cdot}=K[H^{\cdot}]/[HCO_3']$ for plasma, K^{18} is 515 and K^{38} 275. It is uncertain whether or not plasma is normally saturated with calcium ions, but it is improbable that it is supersaturated. J. Pryde.

Calcium–phosphate compounds of the serum. H. Dolhaine (Biochem. Z., 1926, 178, 233—242).—From experiments on the isolated frog heart it is concluded that the removal from solution of ionic calcium by phosphate in the presence of fresh serum is not immediate, but commences some 2—24 hrs. later. This behaviour is in strong contrast to that shown in circulating blood. J. Pryde.

Determination of phosphorus in blood. J. H. Gaddum (Biochem. J., 1926, **20**, 1204—1207).—The "inorganic phosphate" in 0·5 c.c. of blood is determined by dissolving the precipitate of phosphomolybdate in 0·1N-sodium hydroxide and titrating the excess of the alkali with 0·1N-hydrochloric acid by means of a micrometer syringe (cf. Trevan, A., 1926, 211). The maximum deviation in four determinations in normal horse-serum was 0·0004 mg. S. S. Zilva.

Degradation of dextrose by the blood corpuscle of the rabbit. II. J. T. Irving (Biochem. J., 1926, **20**, 1320—1325).—The addition of dextrose to a suspension of blood-corpuscles does not lead to the formation of an organic phosphorus compound, nor does the initial concentration of free phosphorus have any appreciable influence on the rate of glycolysis. Potassium hexosediphosphate is only very slowly attacked by the action of the corpuscles. The optimum $p_{\rm H}$ for glycolysis by blood-corpuscles lies between 8 and 9. Very small quantities of acid inhibit the reaction very markedly. Fluorides and oxalates have also an inhibiting effect. Dextrose, lævulose, and mannose are degraded equally fast by the corpuscles of the adult rabbit, but galactose is much more slowly attacked. In the infant rabbit, on the other hand, galactose is degraded as fast as dextrose. S. S. Zilva.

Distribution of reducing sugar and mode of glycolysis in human blood. J. H. Dowds (Biochem. J., 1926, **20**, 1173—1176).—In human blood, the red corpuscles contain a considerable amount of reducing sugar. In capillary blood, there is generally more sugar in the plasma than in the corpuscles; the reverse is the case in venous blood. In separated plasma, glycolysis is very slight compared with that in the whole blood. In the latter case, the decrease in the sugar is mainly in the plasma. Glycolysis is therefore almost entirely due to the activity of the leucocytes. S. S. Zilva.

Blood-coagulation. XV. Relation of glycolysis to coagulation of blood. B. Stuber and K. Lang (Biochem. Z., 1926, **179**, 70—85).—The disappearance of sugar from shed blood and the simultaneous increase of lactic acid are inhibited by those substances which prevent the coagulation of blood; no change in the glycogen content was observed to be associated with coagulation, but the presence of anti-coagulants inhibited the uptake of oxygen by plasma. The respiratory quotients observed with normal plasma indicated formic acid as the probable oxidation product of the lactic acid derived from the dextrose, and this was confirmed by observation of an increase of the formic acid of the blood during coagulation. It is concluded that the anti-coagulants act by interfering with the oxidative phase of the degradation of dextrose; coagulation is regarded as being brought about by a change in physical conditions due to the formation of acids from the dextrose, rather than by a specific coagulation enzyme. C. R. Harington.

Preparation and properties of prothrombin. E. B. Cekada (Amer. J. Physiol., 1926, **78**, 512—532).—Howell's acetone method is preferred. Prothrombin may be activated by ethyl alcohol, chloroform, and carbon tetrachloride, by calcium ions, spontaneously, on keeping for 36 hrs. at the ordinary temperature. A precipitate is formed, and both this and the residual solution are active. These soluble and insoluble forms of thrombin differ in that the insoluble form leads only to a temporary clotting of fibrin, followed by solution of the clot. Insoluble thrombin contains phosphorus, soluble thrombin does not. Precipitation of prothrombin by ammonium sulphate begins at a salt concentration of 35% and is complete at 50%. It is suggested that prothrombin is an aggregate of two thrombin groups. Activation consists in the precipitation of one in a modified form and the liberation of the other in the solution. R. K. Cannan.

Regulation of the blood-sugar. H. C. Hagedorn (Physiol. Papers dedicated to August Krogh, 1926, 80—100).—A comparison, before and after ingestion of carbohydrate, of blood from the ear and from the median cubital vein shows that the ingestion of carbohydrate causes a much higher hyperglycæmia in the arterial blood than in that of the median cubital vein. Dextrose is stored in the peripheral tissues during alimentary hyperglycæmia. During the hyperglycæmia following the administration of adrenaline, no difference between arterial blood and that from the median cubital vein was observed. Experiments were also performed in which the administration of adrenaline was followed by that of dextrose, and *vice versa*. Chemical Abstracts.

Hepatic amylase and its probable rôle in the regulation of blood-sugar. H. A. Davenport (J. Biol. Chem., 1926, **70**, 625—638).—Neither the course of hydrolysis of starch by hepatic amylase nor the optimum $p_{\rm H}$ for the reaction was affected by addition of adrenaline or of insulin. The amylase was activated to about the same extent by addition of 0·1N-sodium chloride as by addition of the mixture of chlorides employed by Cammidge and Howard (J. Metabol. Res., 1924, **5**, 95). This type of experiment did not therefore throw any light on the possible part played by hepatic amylase in controlling the concentration of sugar in the blood. C. R. Harington.

Inverse change between the concentration of dextrose and chloride in the blood. T. G. Ni (Amer. J. Physiol., 1926, **78**, 158—167).—Histamine, sham feeding, and partial obstruction of the intestine cause a fall in blood chlorides often accompanied by a rise in blood-sugar. The inverse effects are probably related only through a reflex stimulation of the adrenals. Hyperglycæmia following depancreatisation is accompanied by a fall in blood chlorides. Insulin reduces the blood-sugar and raises the chlorides. There is evidence that there is here a direct attempt at osmotic or other compensation. R. K. Cannan.

Micro-determination of blood-sugar. K. Salomon (Biochem. Z., 1926, **178**, 228—232).—Contrary to Dresel and Rothmann (A., 1925, i, 714), blood samples dried on the paper and kept for some days show a decrease in reducing power. Blood-sugar determinations carried out on such samples are therefore not trustworthy. Blood samples may be kept in zinc hydroxide solution for periods of 3 days or more without diminution in their reducing power.

J. Pryde.

Colorimetric determination of sugar. L. Fábián (Biochem. Z., 1926, **179**, 59—61).—A reagent prepared by mixing a solution of potassium carbonate, hydrogen carbonate, and thiocyanate with one of copper sulphate is heated with the sugar-containing solution; the reduction in intensity of colour as compared with that of the original reagent gives the amount of sugar. Within physiological limits of blood-sugar concentration, the error of the method is ±5%. C. R. Harington.

Determination of sugar. M. Somogyi (J. Biol. Chem., 1926, **70**, 599—612).—The apparent concentration of dextrose as determined by the method of Shaffer and Hartmann (A., 1921, ii, 417) varies with the p_H of the solution during the process of reduction; a modification of the original alkaline copper solution, described by these authors, is therefore recommended, by the use of which a more constant degree of alkalinity is obtained; with the improvement in the reagent, the method becomes applicable to the determination of sugar in 0·2 c.c. of blood. C. R. Harington.

Determination of p_H of blood with the aid of the Duboscq colorimeter. J. F. McClendon, S. Russell, and E. Tracy (J. Biol. Chem., 1926, **70**, 705—711).—By the use of an indicator such as "orthochrome-T" or *p*-nitrophenol, which shows only change in intensity of colour, and not a mixture of colours, with change in the reaction, it is possible to determine the p_H of blood plasma directly in a colorimeter of the Duboscq type.

C. R. Harington.

Detection of enzymic processes conditioned by immunisation. V. E. Kupelwieser. **VI.** E. Kupelwieser and E. Navratil. **VII. Modification of Van Slyke's apparatus for the determination of primary aliphatic amino-nitrogen.** E. Kupelwieser and K. Singer. **VIII.** K. Singer (Biochem. Z., 1926, **178**, 298—318, 319—323, 324—331, 332—341).—V and VI. Further attempts (cf. A., 1926, 86) with sera, obtained during the anti-anaphylactic condition, from guinea-pigs which had received preliminary treatment with horse-serum, to detect proteolytic action on the antigen were again negative.

VII. A modification of Van Slyke's apparatus for the determination of primary aliphatic nitrogen is described which allows of both micro- and macro-determination in the same apparatus with the same accuracy.

VIII. The modified Van Slyke apparatus (VII) is used to detect proteolytic action in the above sera (V and VI). Of 12 experiments, 11 were nil, 1 was positive in the case of anti-anaphylactic serum, and of 8 experiments with anaphylactic serum, 6 were nil, 1 was positive, and 1 negative. The evidence is therefore still against the presence of such proteolytic action. P. W. Clutterbuck.

Application of Löwe-Zeiss interferometer to investigation of blood. J. W. Amschler (Biochem. Z., 1926, **179**, 199—209).—A detailed description of technique. C. R. Harington.

Collagen. II. R. O. Herzog and W. Jancke (Ber., 1926, **59**, [*B*], 2487—2489; cf. A., 1925, i, 1488).—Röntgen spectrographic investigation of stretched fibres confirms the identity of the collagen from various sources (*loc. cit.*). H. Wren.

Chemistry of corpus luteum. VI. Lipins of ether extract. VII. Kephalin fraction. M. C. Hart and F. W. Heyl (J. Biol. Chem., 1926, **70**, 663—674, 675—682; cf. A., 1926, 424).—VI. An ethereal extract of corpus luteum was precipitated with acetone; the kephalin fraction so obtained varied in composition with different samples and was contaminated with small amounts of a substance of the nature of protagon. From the mother-liquor were prepared samples of lecithin free from kephalin which, on hydrolysis, yielded palmitic, arachidonic, and oleic acids; a small amount of a hexabromoarachidic acid was also obtained, but stearic, linoleic, and linolenic acids could not be detected.

VII. The kephalin fraction (see above) was of similar composition to the corresponding fractions obtained by previous workers from the lipins of heart, liver, and brain. C. R. Harington.

Basic proteins. I. Nitrogen distribution and percentages of amino-acids in the protamine of the sardine, *Sardinia cærulea*. M. S. Dunn (J. Biol. Chem., 1926, **70**, 697—703).—By extraction of the ripe testes of the sardine with 1% sulphuric acid and subsequent precipitation of the extract with alcohol, there was obtained 0·5% of a protamine sulphate, having 18·35% of total nitrogen; figures are given for the distribution of nitrogen determined by the method of Van Slyke. The substance contained arginine, 15·8%; cystine, 0·95%; histidine, 15·7%; lysine, 5·22%; tyrosine, 1·09%; tryptophan, 0·87%. The fact that the free amino-nitrogen of the protamine is greater than half the lysine-nitrogen suggests the presence of free amino-groups other than those accounted for by this amino-acid. C. R. Harington.

Muscle hæmoglobin as a source of bile pigment. G. H. Whipple and F. S. Robscheit-Robbins (Amer. J. Physiol., 1926, **78**, 675—682).—Injection of muscle hæmoglobin into the blood, peritoneum, or muscles of dogs was followed by excretion of bile pigment in the urine.

R. K. Cannan.

Colorimetric determination of phosphoric acid in muscle extracts. K. Lohmann and L. Jendrassik (Biochem. Z., 1926, **178**, 419—426).—The colorimetric method of Fiske and Subbarow (A., 1926, 443) for the determination of phosphorus, with slight modification, is quite satisfactory for the determination of phosphoric esters of muscle extracts, taking quantities of 0·05—0·5 mg. of phosphoric oxide per determination. P. W. Clutterbuck.

Distribution of chlorides and proteins between blood plasma and synovial fluid. F. Fremont-

SMITH and M. E. DAILEY (J. Biol. Chem., 1926, 70, 779—784).—The ionic equilibrium between blood plasma and synovial fluid is similar to that observed previously (cf. Loeb and others, J. Gen. Physiol., 1921—1922, 4, 591) to exist between blood plasma and ascitic and pleural fluids. C. R. HARINGTON.

Caseinogen. H. MEYER (Biochem. Z., 1926, **178**, 82—104).—Human milk from different individuals varies greatly in the ease with which it may be flocculated. The variations are ascribed to differences in the heat coagulation points, *i.e.*, the temperature below which flocculation does not occur even at the isoelectric point, which may differ by as much as 10°. The flocculation point of the milk of any one individual is characteristic and does not vary, at least during one lactation period. The purified caseinogen obtained from different human milks exhibits the same behaviour, and the variations encountered in whole milk are therefore ascribed to the caseinogen. Cow's milk and caseinogen prepared from it give similar results. On this basis, it is suggested that not only does the individuality of caseinogen vary from species to species, but also with each individual within the species.

J. PRYDE.

Hydrogen-ion concentration of calcium chloride serum from normal and pathological cow's milk. W. FREI and H. LIENHARD (Biochem. Z., 1926, **178**, 1—27).—A detailed study of the variations in degree of acidity, p_H, and refractive index of the serum from calcified cow's milk. Various normal and pathological milks were examined, and in general the hydrogen-ion concentration, but not always the acidity, are diminished in pathological cases. J. PRYDE.

Colorimetric determination of p_H of milk, whey, and cream. P. F. SHARP and T. J. McINERNEY (J. Biol. Chem., 1926, **70**, 729—758).—Dilution of whole milk to twenty times its original volume with distilled water gives a fluid which is sufficiently translucent for the colorimetric determination of its p_H; the change in p_H of milk and of whey induced by such dilution has been determined, so that the application of a specified correction to the observed p_H of the diluted fluid gives the p_H of the original milk. The p_H of cream is determined indirectly, on the assumption that it is the same as that of the corresponding skimmed milk. The error of the method is ±0·1 p_H unit. C. R. HARINGTON.

Employment of liquid paraffin in colloidal and physiological chemistry. H. BOHN (Biochem. Z., 1926, **179**, 220—226).—The carbon dioxide content, ammonia content, and p_H of urine remained constant over long periods when the fluid was kept in sterile vessels under liquid paraffin. A layer of the latter, therefore, constitutes a useful protective cover for such unstable solutions. C. R. HARINGTON.

Colloid chemistry of urine. I. Dependence of surface tension of urine on its specific gravity. II. Relationship of surface tension to the amount, colour, rotation, and urea content of urine. III. Surface tension of urine and the rate of sinking of blood-corpuscles. IV. Relationship of the colloid content of normal urine to its surface tension and viscosity. V. Are surface-active substances excreted in the urine in regular daily amounts ? VI. Relationship of the viscosity of normal urine to its specific gravity, volume, and rotation. F. V. VON HAHN (Biochem. Z., 1926, **178**, 245—253, 254—261, 262—264, 265—269, 277—281, 282—285).—I. The view of Donnan that the surface activity of urine depends on its density is confirmed, the equation $Gh=690(d-1{\cdot}004)$, in which Gh=surface activity (%), being found to apply for 1182 out of 1224 urines examined.

II. The surface activity does not vary absolutely sharply with the volume, but the activity of the urine of females increases with decreasing volume, whilst that of males has a mean value when the volume is maximal. Surface activity and intensity of colour of urine do not vary directly together, but mean values indicate that the more highly pigmented the greater is the activity. A definite relationship between optical rotation and surface activity was not obtained, but mean values indicate that the more highly active the more lævorotatory is the urine. The dependence of surface activity on carbamide content, assumed by Donnan, could not be confirmed.

III. In normal urine, the dependence of the rate of sinking of blood-corpuscles on the surface activity could not be confirmed.

IV. The view that substances which decrease surface activity increase the viscosity does not hold in respect to the constituents of urine.

V. A large number of curves show that the excretion of surface-active substances in the urine varies from person to person and in the same person from day to day.

VI. Increase of viscosity with specific gravity is related by the formula $V_c=2200(d-1{\cdot}001)$, where V_c=increase in viscosity. Of 162 urines, 80% gave values within the limits ±2·5%. Generally, the smaller the urinary volume the greater the viscosity and the more strongly is the urine lævorotatory.

P. W. CLUTTERBUCK.

Volumetric determination of urea in urine. Constitution of mercury urea nitrates and the reactions between urea, mercuric nitrate, and water. B. GLASSMANN and S. SKUNDINA (Z. physiol. Chem., 1926, **160**, 77—90).—A new method for the titration of urinary urea by means of mercuric nitrate is described and the theory of the reactions discussed. P. W. CLUTTERBUCK.

Terwen's method for the determination of urobilin in urine and fæces. E. GREPPI (Fol. Clin. Chim. Micro., 1926, **1**, 61—67).—A full description and discussion of this method (A., 1925, i, 1351).

T. H. POPE.

Reversible interchange between secondary alcohols and ketones of their degree of oxidation. H. W. KNIPPING and W. PONNDORF (Z. physiol. Chem., 1926, **160**, 25—60; cf. A., 1926, 520).—New methods for the determination of acetone and *iso*propyl alcohol in the breath and urine of animals are devised and used to investigate quantitatively the interchange of these substances in the body.

P. W. CLUTTERBUCK.

Alcaptonuria in a rabbit. J. H. Lewis (J. Biol. Chem., 1926, **70**, 659—661).—A case of typical alcaptonuria, occurring in a rabbit, is recorded.

C. R. Harington.

Blood-gases in adrenal insufficiency. O. P. Estrada and V. Deulofeu (Rev. Soc. Argent. Biol., 1926, 2, 359—366).—In adrenalectomised dogs, a diminution in the oxygen saturation of the venous blood is observed; this is due partly to the decreased and disturbed circulation. In some cases, there is an increase in the total oxygen capacity of the blood, consequent on an increased concentration of the blood, an effect which depends on the previous state of hydration of the tissues. Diminution in the content of carbon dioxide is more marked in the arterial blood, probably as a consequence of hyperpnœa. The oxygen saturation of arterial blood is unaffected. G. W. Robinson.

Adrenal insufficiency in dogs. II. J. M. Rogoff and G. N. Stewart (Amer. J. Physiol., 1926, **78**, 711—730).—A study is reported of the composition of the blood of adrenalectomised dogs. There is an increase in non-protein nitrogen due, chiefly, to a rise in urea. Changes in blood-sugar, uric acid, creatinine, calcium, and chlorides are also reported. R. K. Cannan.

Avian diabetes and glycosuria. T. Koppanyi, S. C. Ivy, A. L. Tatum, and F. T. Jung (Amer. J. Physiol., 1926, **78**, 666—674).—The normal blood-sugar of the chicken varies from 0·15 to 0·45%. Injection of dextrose or adrenaline produces hyperglycæmia and glycosuria. Total removal of the pancreas leads to a temporary diabetic condition. After 8 days, hyperglycæmia and glycosuria disappear and the liver stores glycogen. R. K. Cannan.

Bülow acetone reaction. R. Loetze (Pharm. Ztg., 1926, **71**, 1490; cf. A., 1925, ii, 1210).—A stronger solution of 2 : 4-dinitrophenylhydrazine (5 g. in 250 c.c. of boiling 90% alcohol with 25 c.c. of hydrochloric acid) is used. The acetone solution or diabetic urine is treated with a little concentrated hydrochloric acid, and then one tenth of the volume of the warmed hydrazine reagent. The milky, yellow precipitate separates quickly. An approximate value for the acetone content of urine can quickly be obtained by comparing the speed and extent of precipitation from 10 c.c. of urine, 1 c.c. of hydrochloric acid, and the reagent with those from 0·5%, 0·1%, and 0·05% solutions of acetone and later with intermediate strengths. A. Wormall.

Urea concentration test. H. W. Jones and A. Cantarow (Arch. Int. Med., 1926, **38**, 581—589).—The urea concentration test of MacLean and de Wesselow (Brit. J. Exp. Path., 1920, **1**, 53) is modified by comparing urea concentration of the urine after ingestion of 15 g. of urea in 150 c.c. of water (" urea response level ") with that after 150 c.c. of water alone (" resting level "). The percentage variation between the two levels is much lower in the case of nephritic patients, and it is claimed that this value is more significant than the urine-urea concentration alone. The results of 93 normal and 30 nephritic cases are given and divided into 5 groups, according to the " resting level " urea concentration. A. Wormall.

Glutathione content of normal animals. J. W. Thompson and C. Voegtlin. **Glutathione content of tumour animals.** C. Voegtlin and J. W. Thompson (J. Biol. Chem., 1926, **70**, 793—800, 801—806).—The utility of the method of Tunnicliffe (A., 1925, i, 752) for the determination of glutathione is confirmed. The tissues of the normal rat contain glutathione almost entirely in the reduced form; the total concentration of glutathione declines progressively from the early fœtal stage to adult life; glutathione is present in the blood-corpuscles, but not in the serum.

Actively-growing cancerous tissue contains a concentration of glutathione of the same order as that found in normal liver, which is the richest of the organs in this substance. As the tumour increases in size, the glutathione content of the rest of the body becomes progressively less; it is suggested that this may help to account for the general malnutrition associated with extensive cancer.

C. R. Harington.

Possible source of energy in anaërobic metabolism with notes on the properties of sorbitol. J. G. Davis, W. K. Slater, and V. Smith (Biochem. J., 1926, **20**, 1155—1166).—The heats of combustion in dilute solution of dextrose, gluconic acid, and *d*-sorbitol are 676·08, 618·59, and 732·44 kg.-cal. per g.-mol., respectively. The small amount of heat produced by the autoxidation and reduction of dextrose to gluconic acid and sorbitol is therefore negligible as a source of anaërobic energy. The chemical and physical properties of sorbitol and conditions for the reduction of dextrose to sorbitol by metallic reducing agents have been investigated.

S. S. Zilva.

Regulation of the hydrogen-ion concentration and its relation to metabolism and respiration in the starfish. L. Irving (J. Gen. Physiol., 1926, **10**, 345—358).—In two starfish, *Patiria miniata* and *Asterias ochraceus*, the cæcium and the cœlomic fluid are maintained at p_H 6·7 and 7·6, respectively, apparently by the carbon dioxide produced during metabolism. W. O. Kermack.

Physico-chemical properties of dissociated sponge cells. P. S. Galtsoff and V. Pertzoff (J. Gen. Physiol., 1926, **10**, 239—255).—The effect of variations of hydrogen-ion concentration on cells of two species of sponges, *Microciona prolifera* and *Cliona celata*, in a medium of known composition has been studied with particular reference to the acid-combining power and to their vitality.

W. O. Kermack.

Human metabolism with enemata of alcohol, dextrose, and lævulose. T. M. Carpenter (Carnegie Inst. Wash. Pub., 1925, 369, 1—197).—After rectal administration of 5, 7·5, and 10% alcohol solutions, less than 2% was unabsorbed; the urine contained 0—0·40, 0—0·56, and 0·10—0·33 mg. per c.c., respectively, representing 0—0·9, 0—1·2, and 0·4—0·7% of the dose. After oral administration, the urine values were 0·19—0·32 mg. per c.c., representing 0·5—1·1% of the alcohol administered. When 60 g. of dextrose were administered in 1 litre of 0·6% sodium chloride solution, 34·6 g. were absorbed in 5 hrs. 25 min. The amount of lævulose absorbed was 16·2—21·8 g. for a 25 g. dose, 24·8—48·0 g. for a 50 g. dose. Rectal administration of alcohol, dextrose, or lævulose decreased the urinary elimination of nitrogen and sodium chloride.

Chemical Abstracts.

Rôle of phosphates in carbohydrate metabolism in skeletal muscle. II. Comparison of the muscles of normal, fatigued, and depancreatised animals. F. Beattie and T. H. Milroy (J. Physiol., 1926, **62**, 174—191).—In the normal muscle of the cat, the lactacidogen phosphoric acid is not less than 0·18%, the glycogen not less than 0·5%, and the lactic acid concentration between 0·08 and 0·2%. After hydrolysis, the total phosphate averages 0·48% and the lactic acid 0·5—0·8%. In the presence of fluoride, a synthesis of lactacidogen occurs to the extent of 75% of the total phosphate, and when phosphate and glycogen are added in the correct proportions for the formation of hexosediphosphate, 90% of the added phosphate is converted into lactacidogen with the loss of all the glycogen. In severe pancreatic diabetes, the original lactic acid content of the muscles may be 0·03—0·06%, the lactacidogen less than 0·17%, and the lactic acid maximum after hydrolysis less than 0·4%. There is diminished capacity for synthesis of lactacidogen and for decomposition of glycogen in the presence of fluoride. R. K. Cannan.

Brain metabolism. III. Carbohydrate metabolism; relationship of glycogen and lactic acid. E. G. Holmes and B. E. Holmes (Biochem. J., 1926, **20**, 1196—1203).—The lactic acid content of rabbits' brains shows no appreciable rise, nor does the glycogen content show any significant fall when the chopped tissue is kept at the ordinary temperature, or incubated under anaërobic conditions at alkaline p_H. Under aërobic conditions, lactic acid rapidly disappears from chopped brain, but glycogen suffers no significant change. The glycogen content of rabbits' brains is small and very variable.

S. S. Zilva.

Chemical changes in the blood during fasting in the human subject. W. G. Lennox, M. O'Connor, and M. Bellinger (Arch. Int. Med., 1926, **38**, 553—565).—A study of thirty fasting periods varying from 3 to 21 days, the water intake being unlimited. Non-protein nitrogen and urea-nitrogen gave varying values with only transient increases, the amino-nitrogen remained constant, but the uric acid nitrogen increased considerably. After the fast, the amino-nitrogen still remained constant, but the other nitrogen values became subnormal. During the first week of the fast, the sugar and plasma hydrogen carbonate values fell considerably, but a gradual rise in each case nearly to the pre-fasting level followed. Inorganic phosphorus and total calcium remained constant, whilst cholesterol and fibrin gave conflicting results. In a fast of 3 days without water, the results suggested unusually rapid destruction of body proteins. A. Wormall.

Metabolism of hydantoins and carbamido-acids. O. H. Gaebler and A. K. Keltch (J. Biol. Chem., 1926, **70**, 763—777).—After administration of hydantoin to dogs the compound is largely excreted unchanged and no increase occurs in the excretion of oxalic acid; methylhydantoin and methylcarbamidoacetic acid, however, under similar conditions, are excreted unchanged to a small extent only, and their administration is followed by a marked increase in the output of oxalic acid; this increase was greater after methylhydantoin than after methylhydantoic acid, and is thought to be due to the direct oxidation of the former substance to methylparabanic acid.

C. R. Harington.

Synthesis of amino-acids in the animal body. IV. Synthesis of histidine. B. Harrow and C. P. Sherwin (J. Biol. Chem., 1926, **70**, 683—695).—Histidine may be replaced, in the diet of young rats, with good results, by glyoxaline-4(or 5)-lactic acid; glyoxaline-4(or 5)-pyruvic acid was a less efficient substitute, and glyoxaline-4(or 5)-acrylic acid was still less useful; glyoxaline itself was of no use in this respect (cf. Cox and Rose, A., 1926, 973).

C. R. Harington.

Growth and reproduction on synthetic diets. I. G. A. Hartwell (Biochem. J., 1926, **20**, 1273—1278).—A description of various synthetic diets which produce good but not maximal growth. Some diets were found suitable for growth but not for reproduction; one functioned in the reverse way.

S. S. Zilva.

Yeast extract as a supplement to gelatin. G. A. Hartwell (Biochem. J., 1926, **20**, 1279—1281). Yeast extract supplements gelatin in a synthetic diet. S. S. Zilva.

Sodium deficiency in a maize ration. H. G. Miller (J. Biol. Chem., 1926, **70**, 759—762).—A diet containing 80% of maize and no other source of sodium was not sufficient for normal growth in rats; this amount of maize contained sufficient chlorine for normal growth and reproductive cycle.

C. R. Harington.

Influence of inorganic and organic alkali salts on the urinary C : N ratio. T. Taslakowa (Biochem. Z., 1926, **178**, 270—276).—Addition to a diet of carrots, with rabbits, of tap-water did not materially affect the urinary C : N ratio, of distilled water increased it, and of solutions of sodium citrate and tartrate either increased it or had no effect.

P. W. Clutterbuck.

Influence of feeding sodium chloride, bromide, and iodide on the urinary C : N ratio in rabbits. M. Watanabe and T. Taslakowa (Biochem. Z., 1926, **178**, 286—297).—Peroral doses of 0·3—0·75 g. of sodium chloride per kg. do not affect the urinary C : N ratio in rabbits. With sodium bromide (5 experiments), in one the ratio was unchanged, in two it was increased, and in two diminished. With sodium iodide the ratio always decreases, the absolute amount of carbon decreasing, the nitrogen being either increased, unchanged, or very little decreased.

P. W. Clutterbuck.

Penetration of basic dye into *Nitella* and *Valonia* in the presence of certain acids, buffer mixtures, and salts. M. Irwin (J. Gen. Physiol., 1926, **10**, 271—287).—When cells of *Nitella* are exposed to sodium acetate–acetic acid or phosphate buffer mixtures and then transferred to a solution of brilliant-cresyl-blue, the rate of entrance of the dye into the cell is less than when the cells are transferred directly into the dye from tap water. Phosphate buffer mixtures are less active than acetate mixtures in producing this decrease in the rate of entry of the dye, and the action would seem to be due to ions other than hydrogen ions. In the case of cells of *Valonia*, increase of the p_H by ammonia or decrease by acetic acid results in a decrease in the rate of entrance of the dye. W. O. Kermack.

Derivatives of phenylarsinic acid in the treatment of trypanosomiasis. II. Relation between the therapeutic action of aromatic arsinic acids and their constitution. E. Fourneau, [M.] Tréfouel, [Mme.] Tréfouel, and [Mme.] de Lestrange-Trévise (Ann. Inst. Pasteur, 1926, **40**, 933—951; cf. A., 1923, i, 983).—The authors have prepared three new hydroxyphenylarsinic acids (no details), so that the ten possible isomerides are now known and have been compared as to their action on trypanosomiasis in mice. The best results are obtained with substituents in the *ortho* and *para* positions. The effect of the introduction of a methyl group into phenylarsinic acid derivatives is in general to decrease the chemotherapeutic index (tolerated dose/curative dose). Similarly, the effect of the introduction of a chlorine atom is in general to decrease the index except in the cases of 6-chloro-3-aminophenylarsinic acid and 4-acetamidoamino-2-chlorophenylarsinic acid. Many derivatives have been prepared with the view of determining the effect of the acylation of an amino-group, but the results are not uniform. W. O. Kermack.

Hyperglycæmia and glycosuria in the dog under ether anæsthesia. I. Fujii and K. Takai (J. Biophysics, 1924, **1**, xxxviii).—Dogs under ether anæsthesia present hyperglycæmia and glycosuria, which may be considerably reduced by keeping the temperature at the ambient level. The adrenaline content of the adrenals is reduced.

Chemical Abstracts.

Experimental liver intoxication with a by-product of chloranil. I. Attempted isolation of the toxic substance. H. Staub (Biochem. Z., 1926, **178**, 167—180).—A commercial preparation of chloranil, tetrachloroquinone, $C_6O_2Cl_4$ (Höchst, 1922), was found to contain a highly toxic impurity with a marked action on the liver of rabbits. The toxic substance was soluble in benzene, ether, alcohol, acetone, sulphuric acid, and dilute alkali, and was volatile in steam. The most active fraction was obtained by distillation in superheated steam, the lethal dose being 0·25 g. per kg. body-weight. About 1% of the toxic substance was present in the chloranil, but it has not yet been isolated. J. Pryde.

Influence of hydrazine and its derivatives on metabolism. I. Effect of substitution in the hydrazine molecule on the hypoglycæmic action of hydrazine. S. Izume and H. B. Lewis (J. Pharm. Exp. Ther., 1926, **30**, 87—93).—When administered to a rabbit, equimolecular amounts of hydrazine hydrate, hydrazine sulphate, and hydrazine acetate have equal effects in lowering the blood-sugar and also equal toxicities. Hypoglycæmia is also caused by benzoylhydrazine, hippurylhydrazine, *s*-acetylbenzoylhydrazine, *s*-di*iso*propylidenehydrazine, *iso*propylideneacetylhydrazine, and *iso*propylidenebenzoylhydrazine. Although the introduction of the benzoyl radical increased the hypoglycæmic activity, *o*-, *m*-, and *p*-hydroxybenzoyl decreased this activity and also the toxicity, except in the case of *o*-hydroxybenzoyl, in which the toxicity was increased. Thiocarbaminylhydrazine and dithioformylhydrazine possess great toxicity but no hypoglycæmic, but rather a hyperglycæmic, action.

W. O. Kermack.

Cyanamide poisoning. II. Action of cyanamide on cysteine and cystine *in vitro*. S. Glaubach (Arch. exp. Path. Pharm., 1926, **117**, 257—265; cf. A., 1926, 1274).—Solutions of cysteine containing cyanamide rapidly lose the power of combining with iodine, particularly at p_H approximately 7·0. Evidence is adduced to indicate that the effect is due to a change in the internal constitution of the cysteine molecule, and not to an alteration of cystine–cysteine equilibrium. It is considered that these observations on solutions of cysteine are analogous to the effects observed in cyanamide poisoning, where the power of the tissues to combine with iodine is lessened. W. O. Kermack.

Pharmacology of the cholesterol and sitosterol series. H. Seel (Arch. exp. Path. Pharm., 1926, **117**, 282—305).—Cholesterol, cholesterol oxide, cholestantriol, cholestandionol, cholestendione, cholestandione, sitosterol, and sitostantriol tend to increase the tonus of the heart and of smooth muscle, but the various compounds differ in the intensity of their effects. They all show remarkable power in antagonising many toxic substances. On the other hand, certain acid derivatives of cholesterol are highly toxic. W. O. Kermack.

Influence of arsenious acid on respiration and fermentation. K. Dresel (Biochem. Z., 1926, **178**, 70—74).—Arsenious acid markedly inhibits the respiration of Jensen's rat sarcoma, but does not affect the fermentative action of the tumour on dextrose to the same extent. On the contrary, both the respiratory and fermentative processes of yeast are inhibited by arsenious acid, but the action of the latter varies with the concentration of the sugar in the substrate.

J. Pryde.

Mercury poisoning. II. Parenteral mercury poisoning. E. Hesse (Arch. exp. Path. Pharm., 1926, **117**, 266—278).—Certain compounds containing sulphur, particularly strontium thioacetate, act as antidotes in poisoning by mercury and bismuth compounds. W. O. Kermack.

Effect of snake venom on the diffusion of potassium, phosphorus, and hæmoglobin, and on the formation of lactic acid in different organs. B. A. Houssay and P. Mazzocco (Rev. Soc. Argent. Biol., 1926, **2**, 383—391).—As a consequence of the action of cobra venom, the red blood-corpuscles of dogs lose hæmoglobin and potassium at an approximately parallel rate. The elimination of phosphates is less regular. Elimination of potassium, and to a less degree of phosphorus, occurs in different isolated organs. There is also a certain liberation of lactic acid. The diffusion of potassium is the best index of cytolysis. G. W. Robinson.

Action of snake venom *in vivo* on the gases and salts of the blood. B. A. Houssay, A. D. Marenzi, and P. Mazzocco (Rev. Soc. Argent. Biol., 1926, 2, 392—405).—Intravenous injection of the venom of *Lachesis alternatus*, *L. neuwiedii*, and *Naja tripudians* produces diminution in red corpuscles, hæmoglobin, and oxygen in the blood of dogs. There is also, as a result of hæmolysis, a marked increase in the inorganic potassium and phosphorus of the plasma. A small, fugitive increase in the alkaline reserve occurs during the primary shock after injection of *Lachesis* venom. G. W. Robinson.

Inorganic salt balance. VI. Influence of radium emanation on salt balance of the rabbit. E. Stransky (Biochem. Z., 1926, **179**, 19—45).—The negative salt balance observed in rabbits on a diet of oats and ordinary tap water is changed to a positive balance by the presence of radium emanation in the water; substitution of Carlsbad mineral water for tap water also brings about a positive salt balance, which is further increased by radium emanation. The effect of the emanation is to increase the storage of calcium and still more that of phosphate, so that the increased storage is chiefly observed in the anions. C. R. Harington.

Photoactivity. VII. Effect of unsaturated fatty acids on blood sugar. S. Lee (Biochem. Z., 1926, **179**, 210—214).—Subcutaneous injection of 1—2 c.c. of oleic, linoleic, or ricinoleic acids into rabbits causes a definite hyperglycæmia; the result was not constantly affected by preliminary irradiation of the acids. This observation confirms the hypothesis that part at least of the hyperglycæmic action of vegetable oils is due to their content of unsaturated acids. C. R. Harington.

Existence of "disaggregating" enzymes. C. Oppenheimer (Biochem. Z., 1926, **179**, 261—262).—In view of the results of Waldschmidt-Leitz (Naturwiss., 1926, H. 8), it is no longer necessary to assume the existence of enzymes with the specific function of introducing water of hydration (cf. the author's "Die Fermente und ihre Wirkungen"). C. R. Harington.

Enzyme purification by adsorption: pancreatic amylase. H. C. Sherman, M. L. Caldwell, and M. Adams (J. Amer. Chem. Soc., 1926, **48**, 2947—2956).—The procedure of Willstätter, Waldschmidt-Leitz, and Hesse (A., 1923, i, 507; 1925, i, 736) for the purification of pancreatic amylase was critically studied, special attention being directed to establishing the most favourable conditions for each step in the process. It was found possible in this way to increase the amylase activity per mg. of nitrogen of the original extract three- to four-fold, but this activity is only about half that previously obtained by Sherman and Schlesinger (A., 1911, i, 827; 1912, i, 815; 1923, i, 621). These results indicate that pancreatic amylase either is protein or contains protein as an essential constituent. It appears to be amphoteric and to have an isoelectric zone in the region of p_H 7, which coincides with its zone of optimum activity (cf. Sherman, Thomas, and Caldwell, A., 1924, i, 1142). F. G. Willson.

Formation of lactic acid from methylglyoxal by the action of enzymes. Keto-aldehyde mutases. I. R. Kuhn and R. Heckscher (Z. physiol. Chem., 1926, **160**, 116—153).—The average yield of methylglyoxal, using the method of Fischer and Taube (A., 1924, i, 1167), is 40% (not 100%). A 0·4% solution may be stabilised by adding a few drops of dilute sulphuric acid and covering with a layer of toluene, the loss then amounting to 3—4% in a month and to 9—10% in 2—3 months. In mixtures of methylglyoxal and lactic acid, the amount of the former is obtained by an iodometric method, and of the latter is calculated from the result of oxidation with permanganate in acid solution, knowing that, under similar conditions, lactic acid gives 95% and methylglyoxal 8% of acetaldehyde. A 95% yield of lactic acid is obtained when methylglyoxal is treated with $2N$-sodium hydroxide. In phosphate-buffered solution, whereas at p_H 4·5—7 the transformation is negligible, at p_H 8, 2% is converted in 5 hrs. at 30° and 11% in 25 hrs., and at p_H 9 the change becomes very considerable. At p_H 7·5, however, which is optimal for enzymic transformations, the conversion due to buffer may be neglected, providing the time of the experiment is not too long. In the enzymic conversion, activity is optimal at p_H 7·5, decreasing slowly on the alkaline side and quickly on the acid, at p_H 5·5 being only half that of the optimal. Enzyme solutions prepared from the livers of freshly-killed animals differ greatly in activity and in stability, the stability in dialysed solution being considerably increased by addition of a little acetic acid. The corresponding conversion of phenylglyoxal into mandelic acid is followed polarimetrically. The optimal p_H is 8·2 (7·5—9), but at p_H 5·5, whereas methylglyoxalase retained half of its activity, phenylglyoxalase is inactive. The stability of phenylglyoxalase is very small, the activity of solutions decreasing to one half on keeping at the ordinary temperature for 15 hrs. P. W. Clutterbuck.

Insulin and co-zymase in their relation to glyoxalase; separation of antiglyoxalase and trypsin. Keto-aldehyde mutases. II. R. Kuhn and R. Heckscher (Z. physiol. Chem., 1926, **160**, 154—168).—The dismutation of ketoaldehydes by liver glyoxalase is followed, with and without addition of insulin, by three methods, first, by iodometric titration with methylglyoxal as substrate, secondly, by polarimetric determination of the active mandelic acid formed from phenylglyoxal, and thirdly, by analysis of the total mandelic acid (active+racemic) formed. All methods showed that insulin, if sufficiently purified, is without effect on the reaction velocity. Many commercial preparations of insulin contain an impurity which inhibits both lactic acid and mandelic acid formation (possibly the antiglyoxalase of Dakin and Dudley). By heating such preparations in aqueous solution for ¼ hr. on the water-bath, the inhibiting action is completely lost. English insulin is practically free from, but German insulin contains considerable amounts of, this inhibiting substance. Differing from Meyerhof, the authors find that glyoxalase is not activated, using methylglyoxal or phenylglyoxal as substrate, by co-zymase solutions prepared from dried and fresh yeasts and from muscle of calf, pig, or pigeon. Antiglyoxalase can be obtained free from insulin and is present in tryptic preparations which are without insulin action. Antiglyoxalase may be separated from trypsin by Willstätter's adsorption method.

P. W. Clutterbuck.

Enzymic formation of lactic acid in muscle extracts. I. and II. Hydrolysis of polysaccharides and hexosediphosphoric acid. O. Meyerhof (Biochem. Z., 1926, **178**, 395—418, 462—490).—I. The methods for separation of the lactic acid-forming enzyme from muscle and for the measurement of glycolysis in aqueous solution are described. The enzyme solution (almost carbohydrate-free) forms lactic acid from added starch or glycogen for several hours with a velocity which, referred to the weight of muscle, corresponds with the rate of spontaneous formation of lactic acid in muscle pulp. The stability of the enzyme is small. Further data are given for the separation of the co-enzyme, for the determination of the effect of dilution and of the addition of phosphate on the rate of enzyme action. By the precipitation of the enzyme solution with acetone and drying, a powder is obtained which possesses 40% of the activity of the extract.

II. Glycogen, starch, amylopectin, amylose, and di- and tri-hexosan are converted into lactic acid by the above muscle-enzyme solutions at the same concentrations with almost the same velocity, thus differing from the fermentable hexoses, which, under ordinary conditions, are either not at all or only faintly glycolysed by muscle extracts. Hexosediphosphoric acid is converted into lactic acid, on the average, more slowly than polysaccharides by fresh muscle extracts, the reverse being true of old extracts. The ester-hydrolysing enzyme is much more stable than the glycolytic enzyme. Complete separation of the enzymes responsible for hydrolysis of the ester and of the polysaccharides can be attained (*a*) by keeping the extracts 24 hrs. on ice, (*b*) by heating the extracts at 37° for 15 min., (*c*) by separation of the co-enzyme either by dialysis or by washing the tissue before preparation of the enzyme solution. During hydrolysis of the polysaccharides, phosphoric ester accumulates at first quickly, then more slowly, and can be completely decomposed into lactic acid and phosphate by warming at 37°. By hydrolysis of fermentation hexosediphosphoric acid, equimolecular amounts of lactic and phosphoric acids are formed. If hydrolysis of hexosediphosphoric acid by an active extract has come to a standstill, addition of polysaccharide causes the formation of further amounts of lactic acid, in which considerable amounts remain as phosphoric ester. The increase of hexosediphosphoric acid in muscle preparations on addition of sodium fluoride and oxalate (Embden) depends on the inhibition of the decomposition of phosphoric ester and not on increased synthesis. Calcium does not appear to be necessary to the glycolytic enzyme complex.

P. W. Clutterbuck.

Dissociation constants of hexosediphosphoric acid and glycerophosphoric acid. O. Meyerhof and J. Suranyi (Biochem. Z., 1926, **178**, 427—443).—The electrotitration curves of orthophosphoric acid and of two samples of hexosediphosphoric acid are given, pK'_1, pK'_2 for the former being 1·99, 6·81, and for the latter 1·48, 6·29, respectively. Dilution of the phosphoric acid from $M/25$ to $M/270$ causes a shift of the second dissociation constant from 6·82 to 7·15 and of hexosediphosphoric acid from 6·37 to 6·73. The effect of addition of anions on the second dissociation constant is greater for hexosediphosphoric acid than for phosphoric acid, pK'_2 for phosphoric acid in presence of $0{\cdot}1M$-solutions of water, potassium chloride, potassium iodide, sodium fluoride, potassium sulphate, sodium oxalate, and sodium tartrate being 6·89, 6·77, 6·75, 6·74, 6·75, 6·78, 6·76, and for hexosediphosphoric acid 6·25, 6·01, 5·99, 6·02, 5·92, 6·01, 5·99, respectively. The electrotitration curve for glycerophosphoric acid is also given, pK'_1, pK'_2 being 1·40, 6·326, respectively. The effect of addition of salts on the value of pK'_2 is similar to but rather less than that of hexosediphosphoric acid. Finally, the shift of p_H of muscle extracts during esterification of inorganic phosphate and during breakdown of phosphoric esters is examined and discussed in the light of the dissociation constants found.

P. W. Clutterbuck.

Hydrolysis of glycogen by the diastatic enzyme of muscle. K. Lohmann (Biochem. Z. 1926, **178**, 444—461).—By the use of a not too permeable membrane, the greater part of the dialysable, non-fermentable carbohydrate formed by the diastatic decomposition of glycogen consists of a saccharide which is shown by the following determinations both in the free condition and as the acetyl derivative to be closely similar to the amylotriose obtained by Pringsheim from glycogen and amylopectin by decomposition with hydrochloric acid: for the free saccharide, mol. wt., 480, $[\alpha]_D^{17}$ +137·5°, reducing power, 18·1%, comparable with, for amylotriose, mol. wt. 504, $[\alpha]_D^{20}$ +124°, reducing power 22%; for the acetyl derivative, mol. wt. 1010, $[\alpha]_D^{17}$ +127°, acetyl groups 46·2%, reducing power 45·2%, comparable with, for acetylamylotriose, mol. wt. 1020, $[\alpha]_D^{17}$ +125°, acetyl groups, 48·97%, and for reducing power 45·2%. Elementary analyses agreed fairly closely, but the amount of the material was too small for complete identity to be shown.

P. W. Clutterbuck.

Hydrolysis of corn [maize] starch by commercial pancreatin. J. H. Walton and H. R. Dittmar (J. Biol. Chem., 1926, 70, 713—728).—The rate of hydrolysis of maize starch by commercial pancreatin is slower than that of potato starch, owing to the presence in the former of a resistant hemicellulose; the hydrolysis ceased when the maltose had reached 85% of the original starch. The rate of hydrolysis of the starch was not accelerated by treatment by the method of Lintner (A., 1886, 386), by autoclaving in presence or absence of water, by freezing, or by extraction with ether. As activating salts, potassium or ammonium chloride could be substituted for the sodium chloride, and sodium citrate, sodium succinate, or sodium ammonium hydrogen phosphate for the sodium dihydrogen phosphate usually employed for this purpose.

C. R. Harington.

Elutriation of various peptidase systems and the activation of elutriates. A. Fodor and R. Schoenfeld (Z. physiol. Chem., 1926, **160**, 169—188).—Further experiments on the elutriation of kaolin adsorbates with amino-acid solutions yielding active filtrates (cf. A., 1925, i, 1214, 1215). Glycine and still more so *dl*-leucine activate fresh, strongly active yeast macerates, but do not activate if the macerate is old and less active. The action of leucine is optimal at p_H 8. *dl*-Leucine and, much more so, *l*-tyrosine inhibit the activity of glycine elutriate.

P. W. Clutterbuck.

Effect of enzyme purity on the kinetics of tryptic hydrolysis. H. B. Merrill (J. Gen. Physiol., 1926, **10**, 217—225).—When keratose, obtained from keratin by partial hydrolysis by alkali, is treated with trypsin at p_H 8·0 the rate of hydrolysis is more nearly unimolecular the weaker the enzyme preparation used. It is suggested that in the weak enzyme solutions trypsin is absorbed by inactive material and is gradually liberated as the free trypsin is destroyed, so that the effective trypsin concentration remains constant throughout the reaction. In the case of the stronger trypsin preparations, destruction of the enzyme occurs, so that the rate of reaction decreases more rapidly than would that of a purely unimolecular reaction.

W. O. Kermack.

Nephelometric determination of trypsin. P. Rona and H. Kleinmann (Biochem. Z., 1926, **177**, 107—108).—In the method already described (A., 1926, 543), it is recommended that in place of 5 c.c. of a slightly alkaline or neutral solution of quinidine hydrochloride, 7·5 c.c. of a slightly acid solution should be used.

J. Pryde.

Optimal p_H for the determination of trypsin by Gross' method. J. A. Smorodinzev and A. N. Adowa (Z. physiol. Chem., 1926, **160**, 189—195).—The p_H optima for the digestion of caseinogen by trypsin, using distilled water for dilution, are 6·83—7·95, using 0·85% saline 6·68—7·4, and using sodium hydroxide 7·71—8·7.

P. W. Clutterbuck.

Distribution of xanthine oxydase. I. E. J. Morgan (Biochem. J., 1926, **20**, 1282—1291).—The organs of the sheep, goat, rabbit, cat, hedgehog, domestic pigeon, and fowl and the tissues of the lobster, oyster, and the caterpillar and pupæ of *Pieris brassicæ* have been investigated for the presence of xanthine oxydase. The evidence obtained favours the assumption that xanthine oxydase and Schardinger's enzyme are identical.

S. S. Zilva.

Action of oxydo-reductase on glyceraldehyde, dihydroxyacetone, and methylglyoxal. A. Lebedev (Z. physiol. Chem., 1926, **160**, 97—115).—The intensity of the reduction of methylene-blue by glyceraldehyde in presence of the Schardinger enzyme of milk depends on the concentrations of both aldehyde and enzyme, the optimal concentration of the former being about 2%. An acid, probably glyceric acid, is produced, but the formation of glycerol was not detected. The reduction of methylene-blue by acetaldehyde in presence of oxydo-reductase is not influenced by the presence of sodium sulphite, ferrous chloride or sulphate, nor are these substances oxidised during the reduction. Glyceraldehyde in buffered solution in presence of methylene-blue is dehydrogenated almost twice as quickly as dihydroxyacetone, the process being accelerated by the presence of oxydo-reductase. It is considered that dihydroxyacetone in aqueous and in buffered solution passes to an equilibrium mixture of dihydroxyacetone and glyceraldehyde. Methylglyoxal, which is present in solution probably as the hydrate, is dehydrogenated under similar conditions at only 1/30 the rate of glyceraldehyde, a circumstance favouring the author's view that glyceraldehyde and not methylglyoxal is the intermediate in fermentation processes. The action of the enzyme on crotonaldehyde under similar conditions also depends on the concentrations of both enzyme and aldehyde. P. W. Clutterbuck.

Rôle of hydrogen peroxide in biological oxidations. A. von Szent-Györgyi (Biochem. Z., 1926, **178**, 75—76).—Hydrogen peroxide oxidises reduced glutathione, the reaction being unaffected by the presence of cyanides. It proceeds more rapidly at higher than at lower p_H, is not accelerated by peroxydases, and has a temperature coefficient of 2—3 for 10°. It is therefore necessary to consider glutathione in relation to the decomposition of hydrogen peroxide in biological oxidations.

J. Pryde.

Significance of cyanic acid in the carbamide–urease system. W. R. Fearon (J. Biol. Chem., 1926, **70**, 785—792).—An answer to the criticisms of Sumner (A., 1926, 758) regarding the author's previous conclusions (*ibid.*, 1924, i, 351) as to the rôle of cyanic acid in the enzymic hydrolysis of carbamide.

C. R. Harington.

Phytochemical reduction of quinones. H. Lüers and J. Mengele (Biochem. Z., 1926, **179**, 238—247).—By addition of an aqueous solution or suspension of the substance to actively fermenting yeast, the following quinones were reduced to the corresponding dihydroxy-compounds in yields of 9—65%; benzoquinone, thymoquinone, bromoanil, tetrabromo-*o*-benzoquinone, α-naphthaquinone, α-juglone, αβ-naphthaquinone, and phenanthraquinone. Anthraquinone could not be reduced; *p*-nitrosophenol and benzoquinonedioxime gave *p*-aminophenol and *p*-phenylenediamine, respectively.

C. R. Harington.

Relationship between the total exchange of carbohydrate and its enzymic combination with phosphoric acid. H. von Euler and E. Brunius (Z. physiol. Chem., 1926, **160**, 242—255).—The combination with phosphoric acid and the rate of fermentation of various sugars with dry bottom yeast are studied at p_H 6·3 and at 30° in presence and absence of phenol. The two processes are inhibited by the same concentration of phenol (0·07*N*). With smaller concentrations, the reaction has a latent period, the delay being greater the greater is the concentration of phenol. No difference could be detected in the velocities of combination with phosphoric acid of α- and of β-dextrose. Combination with phosphoric acid occurs at the same rate with sucrose and lævulose, but more slowly with dextrose.

It is concluded that of the invert-sugar, lævulose is first attacked, and that this sugar more readily passes into the labile (γ) form than does dextrose. Both the rate of fermentation and that of combination with phosphoric acid are slightly greater for maltose than for dextrose. In presence of phenol, however, maltose ferments more slowly than dextrose and in neither is combination with phosphate detectable. It is concluded that an enzyme takes part in the fermentation of maltose which is unnecessary for dextrose fermentation and is partly inactivated by phenol. P. W. Clutterbuck.

Co-zymase and co-reductase. H. von Euler and R. Nilsson (Z. physiol. Chem., 1926, **160**, 234—241).—No support could be obtained for the view that co-zymase acts as a co-isomerase of dextrose. The stability of apo-zymase, co-zymase, and total zymase and the mechanism of the action of co-reductase are discussed. P. W. Clutterbuck.

Enzymic metabolism of bacteria. III. H. W. Nicolai (Biochem. Z., 1926, **179**, 86—103; cf. A., 1926, 868).—The method of Rona and Lasnitzki (A., 1925, i, 471) has been applied to the determination of lipase in bacteria. The rate of respiration of *Bacillus coli* is proportional to the logarithm of the tension of oxygen in the gas to which the culture is exposed; it is independent of the p_H between the limits 4·63 and 7·37; the isoelectric point of the organisms is about p_H 4·5. In presence of varying amounts of dextrose and of inorganic salts, the respiration reaches a maximum when the total osmotic concentration is 1·5 times that of blood-serum. Comparison of the respiratory quotients observed with different substrates indicates that the latter can be divided into two groups, in one of which the quotient is independent of the number of organisms and in the other of which it shows variations. C. R. Harington.

Preparation of bacterial proteolytic enzymes from liquid cultures by precipitation with mastic. M. Schierge (Biochem. Z., 1926, **179**, 248—251).—The culture medium is treated with an aqueous emulsion of mastic and acidified with acetic acid; the precipitate after keeping for 24 hrs. is filtered off and the mastic removed by extraction with alcohol and ether. The residual precipitate shows strong proteolytic activity. The method is not applicable to the separation of proteolytic enzymes from blood-serum. C. R. Harington.

Bacterial nutrition. III. Phosphates and the growth of *Streptococci*. H. R. Whitehead (Biochem. J., 1926, **20**, 1147—1154).—A tryptic digest of caseinogen was rendered first 66% and then 86% alcoholic. Three fractions were thus obtained, the two precipitates, A and B (both water-soluble) and the residual liquid, C. All the inorganic phosphate of the medium was found in fraction A, whilst fractions B and C contained some phosphorus in organic combination. None of the fractions singly showed any growth. A combination of the three fractions behaved like the original broth, that of A and C was almost as good, whilst the combination BC showed a lag period before growth occurred. In the presence of disodium hydrogen phosphate, fractions AC showed no significant growth after 48 hrs.; fractions BC, on the other hand, showed growth as good as the control. No inhibition was observed in this case even if the concentration of phosphate was made double that present in AC. A combination of A and B gave slight growth in presence or absence of added phosphate.

The deterioration and darkening of caseinogen medium which occur on steaming are probably due to the presence of phosphate, a growth factor present among the simpler protein derivatives being inactivated. S. S. Zilva.

Soluble specific substance of *Pneumococcus*. IV. Nature of specific polysaccharide of type III *Pneumococcus*. M. Heidelberger and W. F. Goebel (J. Biol. Chem., 1926, **70**, 613—624; cf. A., 1926, 545).—The yield of the specific polysaccharide from type III *Pneumococcus* has been increased to a little above 0·01% of the broth by addition of 0·3% of dextrose to the medium. Hydrolysis of the polysaccharide with sulphuric acid in the cold yielded, exclusively, acidic products with equivalent weight about 340, which showed no specific properties towards anti-pneumococcus serum. More intensive hydrolysis gave dextrose, together with an *acid*, $C_{12}H_{20}O_{12}$, $[\alpha]_D$ +10·0° in water (*morphine* salt, m. p. 153—156°, $[\alpha]_D$ −47·9°, mutarotating to −54·0° in water). The acid had one half the reducing power of dextrose and gave a positive reaction with naphthoresorcinol; oxidation with hypoiodite indicated an aldehyde group; on oxidation with nitric acid, saccharic acid was obtained, and, after prolonged acid hydrolysis, a small amount of dextrose was detected. It is thought, therefore, that this acid is a disaccharide of dextrose with an acid of the type of glycuronic acid, and that the specific substance itself is a polymeride of this compound.

C. R. Harington.

Determination of the digestibility of foodstuffs containing cellulose with the help of stomach bacteria. C. Brahm (Biochem. Z., 1926, **178**, 28—35).—Measurements have been made of the amounts of carbon dioxide evolved during the digestion of cellulose-containing and other animal foodstuffs by stomach and other gastro-intestinal bacteria from horses, rabbits, oxen, and goats. It is found that when the straws etc. are soaked, or imbibition is induced by alkali treatment, the extent of digestion is markedly increased. The amount of carbon dioxide obtained from straws previously treated with alkali is increased when salts of simple aliphatic, lactic, or hippuric acids are present. Of individual straw components, xylan and xylose are readily digested, lignin only with great difficulty. J. Pryde.

Experiments with insulin *in vitro*. E. Glaser and G. Halpern (Biochem. Z., 1926, **179**, 144—156).—In presence of certain catalysts, especially ferric chloride and nickel chloride, the action of insulin on dextrose *in vitro* causes a decrease in the fermentable sugar with no simultaneous change in the reducing power of the solution. It is suggested that this observation may have some bearing on the fact that the non-fermentable anhydro-sugars are metabolised in the diabetic organism. The presence of acetone does not affect the course of the reaction, and in no case were the results sufficiently constant for the quantitative determination of insulin. It is shown that the reaction proposed by Wyss (A., 1925, i, 1220) for the determination of insulin is given, with even greater intensity, after the insulin has been inactivated by heat; further, preparations of insulin accelerate the oxidation of dextrose by permanganate, but the effect is due, not to the active insulin, but to the proteins and the higher degradation products of protein which accompany it. C. R. Harington.

Changes in the physiological action of insulin induced by exposure to ultra-violet light. M. M. Ellis and E. B. Newton (Amer. J. Physiol., 1925, **73**, 530—538).—When insulin solutions are exposed, in an atmosphere of nitrogen, in silica vessels, to ultra-violet light, the hypoglycæmic activity is lost, and a hyperglycæmic activity is substituted. These results were not observed when "pyrex" glass vessels were used. With ozone and free oxygen in daylight, the former, but not the latter, effect is observed. A. A. Eldridge.

Effect of insulin on the respiratory exchange of decerebrate and decapitate cats. A. C. Taylor and J. M. D. Olmsted (Amer. J. Physiol., 1926, **78**, 17—27).—The oxygen consumption remained fairly constant, but the respiratory quotient rose. The total metabolism in calories did not change notably, but the proportion due to carbohydrate rose from a low value until it accounted for nearly the whole of the metabolism. Similar results were obtained on injection of insulin into curarised animals. Secondary changes are recorded in oxygen consumption, respiratory exchange, and total metabolism accompanying hypersensitivity and convulsions.
R. K. Cannan.

Respiratory exchange in frogs during muscular exercise and after injection of insulin. J. M. D. Olmsted and J. M. Harvey (Amer. J. Physiol., 1926, **78**, 28—33).—Insulin did not raise the metabolic rate of winter frogs kept at the ordinary temperature, but changed the incidence of metabolism from fat to carbohydrate. The frogs did not retrieve an oxygen debt by increased oxygen consumption, but by a reduction in the normal metabolism.
R. K. Cannan.

Influence of the pancreatic hormone on the fate of infused dextrose. T. Kurokawa (J. Biophysics, 1925, **1**, lxviii).—Infusion of large quantities of dextrose was not followed by increased glycogen storage in the liver of the normal rabbit if a strongly hypoglycæmic pancreatic extract was given at the same time. When sugar was injected for therapeutic purposes the extract caused a more rapid reduction of blood sugar, whilst glycosuria was not affected. Chemical Abstracts.

Effect of injections of dextrose and of insulin and dextrose on blood-sugar. W. Thalhimer, F. Raine, M. C. Perry, and J. Buttles (J. Amer. Med. Assoc., 1926, **87**, 391—392).—The intravenous injection of 10% dextrose at a slow rate into normal persons induces a more rapid removal of sugar from the blood, so that during the latter part of the injection the blood-sugar level, instead of continuing to rise, actually falls. Insulin mixed with the dextrose solution and given intravenously causes a more rapid and greater removal of sugar from the blood than when the insulin is given subcutaneously.
Chemical Abstracts.

Insulin and co-zymase. II. A. I. Virtanen (Z. physiol. Chem., 1926, **160**, 308—312).—Polemical.
P. W. Clutterbuck.

Sexual hormone (feminin) of human placenta. E. Glimm and F. Wadehn (Biochem. Z., 1926, **179**, 1—18).—The occurrence of hypertrophy of the uterus of the virgin rabbit after treatment with ovarian or placental extract is a useful qualitative indication of activity in the latter, positive results being obtained with doses of 5—10 mouse units; no evidence was obtained of any difference between the substance causing this hypertrophy and that which brings about the œstrus cycle in ovariectomised rats and mice (cf. Doisy and others, A., 1924, i, 1387). A method is described for the preparation, from human placenta, of extracts with a maximum activity of 1 mouse unit per 0·1 mg., the total yield being 500—1000 mouse units per kg. of fresh placenta. The extract may be administered subcutaneously, or, in larger doses, orally; administration of large doses to young male animals causes atrophy of the generative organs. Extracts of corpus luteum, but of no other tissues investigated, showed similar physiological properties. C. R. Harington.

Nature of Fearon's colour reaction and its non-specificity for vitamin-*A*. O. Rosenheim and T. A. Webster (Biochem. J., 1926, **20**, 1342—1345).—Fearon's reaction (A., 1926, 207) has no relation to vitamin-*A*, since the unsaponifiable fraction of cod-liver oil does not give it, and the substance responsible for the reaction can be recovered from the soaps. From biological experiments, it is also found that this colour reaction is not specific for vitamin-*A* activity. S. S. Zilva.

Effects of various agents on colour tests for vitamin-*A*. S. G. Willimott, T. Moore, and F. Wokes (Biochem. J., 1926, **20**, 1292—1298).—From experiments on cod-liver oil in which vitamin-*A* was destroyed by concentrated sulphuric acid, phosphorus pentoxide, or ultra-violet light, it is concluded that Fearon's "pyrogallol" test (A., 1926, 207) for the vitamin is non-specific (cf. Rosenheim and Webster, *ibid.*, 1181). In following the destruction by ultra-violet light of vitamin-*A* with the aid of the arsenic trichloride (*ibid.*, 1925, i, 1515) and antimony trichloride tests (*ibid.*, 1926, 870), parallel results were obtained. S. S. Zilva.

Physiological rôle of vitamin-*B*. Relation of vitamin-*B* to tissue oxidations. J. C. Drummond and G. F. Marrian (Biochem. J., 1926, **20**, 1229—1255).—The oxidative activity of the muscle and liver-tissue of rats and pigeons is not reduced as a result of the animals being deprived of vitamin-*B*. Muscle from pigeons poisoned by potassium cyanide to simulate polyneuritis behaves similarly. The resting oxygen consumption of rats deprived of vitamin-*B* falls from the normal only during the final phase of the condition of malnutrition induced by the vitamin deficiency when the body-weight, rectal temperature, and food consumption also fall. Starving rats

receiving a supply of vitamin-*B* behave in an analogous way. Animals exhibiting a fall of body temperature and oxygen consumption in the premortal stage will return to the normal consumption of oxygen after their temperature has been artificially raised to normal. In rats suffering from inanition and vitamin-*B* deficiency, a state of hyperglycæmia associated with a hypertrophy of the adrenal glands develops, and this is followed by a hypoglycæmic stage, which coincides with the period characterised by the fall of body temperature and oxygen consumption. Deprivation of vitamin-*B* does not therefore interfere with the oxidative mechanisms of the tissues.
S. S. Zilva.

Relation between vitamin-*B* and protein in the diet of growing rats. Physiological rôle of vitamin-*B*. II. V. Reader and J. C. Drummond (Biochem. J., 1926, 20, 1256—1263).—The inadequate growth of rats on a diet consisting largely of protein (caseinogen) may be made good by raising the vitamin-*B* content of the diet. This confirms Hartwell's (A., 1924, i, 1372) and Tscherkes' (Biochem. Z., 1926, **167**, 203) observations. The hypertrophy of the kidneys of rats on a high protein diet previously observed by the authors (J. Physiol., 1925, 59, 472) is present only when the animal does not grow at a normal rate. S. S. Zilva.

Effect of p_H on rate of destruction of vitamin-*B* by heat. H. C. Sherman and G. W. Burton (J. Biol. Chem., 1926, **70**, 639—645).—The vitamin-*B* of tomato juice is destroyed to the extent of 20% in 4 hrs. on heating at 100° at the natural acidity of the juice (p_H 4·28). As the reaction is made more alkaline, the rate of destruction by heat becomes progressively greater, the loss of activity being complete after 1 hr. at p_H 10·9. C. R. Harington.

Vitamins and other constituents of grapefruit rind. S. G. Willimott and F. Wokes (Biochem. J., 1926, 20, 1299—1305).—Grape-fruit rind contains considerable amounts of vitamin-*B*, but practically no vitamin-*A*. The content of oxidising enzymes as compared with the vitamin-*A* content in the orange, lemon, and grape-fruit is tabulated. Naringin, the specific glucoside of the grape-fruit, is present in the rind and can be extracted from it with alcohol. S. S. Zilva.

Effect of administration of cod-liver oil to thyreoparathyroidectomised dogs. J. H. Jones (J. Biol. Chem., 1926, **70**, 647—657).—Administration of cod-liver oil to dogs for some time previous to removal of the parathyroid glands prevented the occurrence of tetany; no such effect was obtained by treatment with cod-liver oil after the operation. Similar, but less definite, results were obtained by pre-operative irradiation of the dogs with ultraviolet light. In those animals in which tetany was prevented, the usual fall in the concentration of calcium in the blood took place nevertheless; the tetany cannot therefore be entirely ascribed to the reduction of the blood calcium. C. R. Harington.

Antirachitic vitamin of cod-liver oil. S. G. Willimott and F. Wokes (Pharm. J., 1926, **117**, 473—476, 495—497, 521—524).—The differentiation of vitamins-*A* and -*D* is reviewed. A modification of Fearon's test for vitamin-*A* is advocated in which resorcinol replaces pyrogallol (see, however, A., 1926, 1181). The methods of assay of vitamin-*D* by means of bone changes are discussed. An alcohol–acetone extract of spinach may be used as a standard source of vitamin-*A* free from -*D*. The evidence for an intestinal factor in rickets is considered and preliminary experiments on the relation of the p_H of the fæces to rickets and the calcium balance are described. R. K. Cannan.

Antirachitic action of irradiated sawdust. O. Rosenheim and T. A. Webster (Biochem. J., 1926, 20, 1340—1341).—The chloroform extract of sawdust when irradiated acquires antirachitic activity. The growth effect observed by Hume and Smith (A., 1923, i, 728; 1925, i, 211) is therefore most probably due to the ingestion by the rats of sawdust, the sterols of which had become antirachitic by irradiation. There is no association between antirachitic activity and the chemical action on a photographic plate.
S. S. Zilva.

Influence of the cow's diet on the fat-soluble vitamins of winter milk. J. Golding, K. M. Soames, and S. S. Zilva (Biochem. J., 1926, 20, 1306—1319).—The inclusion of kale in the winter ration of the cow raises the vitamin-*A*, but not the vitamin-*D* content of the milk. The inclusion of cod-liver oil in the winter ration of the cow raises the vitamin-*A* and the vitamin-*D* content of milk. The administration of high doses of cod-liver oil to cows reduces the percentage of fat in their milk (cf. B., 1923, 623A; 1925, 23). S. S. Zilva.

Test for vitamin-*D*. H. Jephcott and A. L. Bacharach (Biochem. J., 1926, 20, 1351—1355).—The alkalinity of the fæces which albino rats develop on high calcium–low phosphorus diets can be brought to the acid side of neutrality by administering cod-liver oil or irradiated cholesterol and by direct irradiation of the animal. The latter treatment prevents the production of alkalinity in the fæces of rats on the rachitic diet. S. S. Zilva.

Ionic activation of plant enzymes in relation to nutrition. II. Invertase of sugar beets poor in potassium. G. Doby and R. P. Hibbard (Biochem. Z., 1926, **178**, 139—151).—Nitrate up to concentration of 0·1*N* activates the invertase of beet, whilst higher concentrations and chlorides inhibit its action. The inversion constant is diminished in the presence of salts. Plants poor in potassium contain more invertase than normal plants, but in the latter the amount of the enzyme increases more rapidly with development than in the former plants. In beets deprived of potassium and in the presence of nitrate, invertase is liberated by autolytic processes, but subsequently undergoes a rapid destruction, presumably by a substance which is itself activated by nitrates and is absent from normally grown beets. Importance is attached to electrolytes in regulating the action of plant enzymes. J. Pryde.

Assimilation of iron by plants. M. I. Sidorin (Nauch. Agron. Zhur., 1925, 2, 47—63).—When furnished with iron to which sulphur was added, only young rootlets of maize exhibited partial penetration; older plantlets showed normal development of colour.

Sulphur appeared to act in much the same partial manner as iron when given separately.

CHEMICAL ABSTRACTS.

Sucrose formation in potatoes during drying. II. C. J. DE WOLFF (Biochem. Z., 1926, **178**, 36—59).—The formation of sucrose from starch when intact potatoes or potato slices are dried (cf. A., 1926, 1183) is regarded as a different process from the reverse formation of starch from sucrose. Within limits, an equilibrium of the type: starch+water $\rightleftharpoons$ sucrose, holds, and after slight drying leading to increased sucrose formation; restoration of water leads to an increase of starch at the expense of the previously formed sucrose. The starch-forming enzyme (or process) is more liable to destruction than is the other when water is removed, whereas the latter condition promotes the activity of the sucrose-forming enzyme, but if drying is carried too far the original state cannot be regained. Addition of water to a potato which has not been previously dried lowers the sucrose content, but the decrease in sucrose per percentage increase in water content is less than the corresponding increase per percentage diminution of water during drying, since in the latter instance the starch-forming enzyme is partly destroyed. During the formation of sucrose from starch by drying, the reducing sugars of the potato do not increase. The difficulties of reconciling such a reversible sucrose formation with the accepted constitution of starch are discussed. J. PRYDE.

Lecture experiment on the chemistry of chlorophyll. A. VON LINGELSHEIM (Ber. deut. bot. Ges., 1926, **44**, 502—504).—Fresh leaves of *Phaseolus coccineus*, viewed by transmitted light, show the colour changes produced by the action of 25% hydrochloric acid on the chlorophyll of the leaf.

W. ROBSON.

Incrustive substances of plants. VII. Determination of hexoses by fermentation. E. SCHMIDT, F. TREFZ, and H. SCHNEGG (Ber., 1926, **59**, [*B*], 2635—2646; cf. A., 1925, i, 1370). The total hexoses (dextrose, lævulose, mannose, and galactose) in the products of the hydrolysis of hemicelluloses are determined by fermentation with Löwenbräu yeast at p_H 5·5 (phosphate buffer) within 24 hrs.; autofermentation of the yeast is avoided by previous exposure to the air for 24 hrs. Zymohexoses are determined by fermentation with *Schizosaccharomyces Pombe* at p_H 3·7 (acetate buffer). The difference between the data thus obtained is a measure of the galactose present. The latter sugar is not involved in the structure of the hemicelluloses of *Linum usitatissimum* or *Picea excelsa*. H. WREN.

Mucilaginous extracts of seaweeds. P. HAAS and B. RUSSELL-WELLS (Yearbook Brit. Pharm. Conference, 1923, 644—645).—The mucilaginous extract obtained from Irish moss, which has been designated as an ethereal sulphate in which an organic complex is combined with calcium sulphate, is a colloidal electrolyte. Similar extracts have been obtained from *Ceramium rubrum*, *Delesseria sanguinea*, *D. alata*, *Polysiphonia fastigiata*, *Plumaria elegans*, and *Ascophyllum modosum*.

CHEMICAL ABSTRACTS.

Free iodine in *Faulkenbergia Doublettii*, Sauv. E. CHEMIN and R. LEGENDRE (Compt. rend., 1926, **183**, 904—906).—Contrary to the statement of Sauvageau (*ibid.*, 1925, **181**, 293), free iodine is not present in *Faulkenbergia Doubletii*, Sauv., but it is liberated when any part of the plant, excepting the young growing cells, is treated with an acid, even carbonic acid. The iodine cannot be present as iodide, but must be in loose organic combination.

H. E. F. NOTTON.

Non-protein cysteine in plants. Attempted isolation of glutathione from the pea (*Pisum sativum*). A. KOZLOWSKI (Biochem. J., 1926, **20**, 1346—1350).—The pea contains non-protein cysteine in the ovules, young and ripe seeds, and in the green shells of the unripe fruit. Cystine is present in the leaves. Histochemical tests suggest that cysteine is probably widespread in the higher plants, not only in the meristem, but also in the "reserve" tissues and in latex. S. S. ZILVA.

Acetyl groups in pectin. E. K. NELSON (J. Amer. Chem. Soc., 1926, **48**, 2945—2946).—The acetyl group is not an essential constituent of lemon, apple, or tomato pectin (cf. Ehrlich and von Sommerfeld, A., 1926, 441). F. G. WILLSON.

Presence of amines in distillate from Kjeldahl nitrogen determinations. R. A. GORTNER and W. F. HOFFMAN (J. Biol. Chem., 1926, **70**, 457—459).—At the end of a normal Kjeldahl digestion, about 7% of the nitrogen is present in the form of volatile amines; these may amount to as much as 20% of the nitrogen if the digestion has been carried out in the presence of a salt of a dibasic metal, *e.g.*, magnesium sulphate. C. R. HARINGTON.

Duplicate determinations as a measure of accuracy in quantitative analysis. A. FLEISCH Biochem. Z., 1926, **177**, 375—388).—A method for the calculation of mean errors of biochemical determinations is described. P. W. CLUTTERBUCK.

Dialysis of readily oxidisable colloid-disperse systems. A. GUTBIER and B. OTTENSTEIN (Biochem. Z., 1926, **177**, 249—252).—An apparatus is described for dialysis out of contact with air, provision being made for taking samples of both inner and outer solutions. P. W. CLUTTERBUCK.

Determination of carbon in dilute organic solutions: application to urine and other biological fluids. O. KAUFFMANN-COSLA (Bull. Soc. chim., 1926, [iv], **39**, 1485—1492).—The standard combustion method for determining carbon is modified to deal with the difficulties arising from the evaporation of the solution and condensation of the water. R. BRIGHTMAN.