BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1928.

General, Physical, and Inorganic Chemistry.

Construction of wave-length scales for spectrograms. G. Barr (Trans. Opt. Soc., 1928, **29**, 22—27).—A method is described by which an approximate scale of wave-lengths may be projected geometrically on to a spectrogram from a uniformly divided scale when a number of easily recognisable lines have been identified. C. W. Gibby.

Use of single thermo-junctions and of echlette gratings in the far infra-red. R. M. Budger (J. Opt. Soc. Amer., 1927, **15**, 370—373).—Methods of focussing radiation of the order of 100 μ on to single thermo-junctions are described whereby the diffuse images due to aberrations in reflexion are avoided. The construction of a simple echlette grating from plane parallel glass strips is also described. R. W. Lunt.

Evolution of the theory of spectra. T. Negresco (J. Chim. phys., 1928, **25**, 142—153).—Historical. H. F. Gillbe.

Relativistic interpretation of the theory of fine structure of spectral lines of the hydrogen atom. S. Mohorovičić (Arh. Hemiju, 1928, **2**, 6—14).—The use of the special relativity theory is not permissible and the extended general theory is not capable of accurately defining the orbits of the electron around the proton. The introduction of the special theory into physics is regarded as wholly unnecessary. R. A. Morton.

Intensity distribution in Fraunhofer lines. M. Minnaert (Z. Physik, 1927, **45**, 610—619).—The distribution of intensity in the Fraunhofer lines H_a and Ca*K* has been determined. The results are discussed with reference to those of von Klüber (A., 1927, 909). R. W. Lunt.

Nebulium spectrum. J. C. McLennan and R. Ruedy (Nature, 1928, **121**, 319).—Following a discussion of observations on nebulæ, it is stated that the energy to excite the nebulium lines would be very small if the material (oxygen) were already ionised, and that the lines are essentially emission lines, having as yet no importance in absorption spectra. It is concluded that the oxygen which is responsible for the nebular lines is present as a molecule or molecular ion. A. A. Eldridge.

Origin of the nebulium spectrum. M. Saha (Nature, 1928, **121**, 418).—A discussion of the nature of the transitions, usually prohibited, from which the "nebulium" lines of ionised oxygen and nitrogen arise (Bowen, A., 1927, 997). A. A. Eldridge.

"Nebulium" spectrum in new stars. C. T. Elvey (Nature, 1928, **121**, 453).—The discrepancy between the conclusions of Pike (this vol., 210) and those of the author are ascribed to the inapplicability of the theory of thermal ionisation. A. A. Eldridge.

Nebulium and hydrogen in new stars. B. P. Gerasimovič (Nature, 1928, **121**, 422).—A modified method of calculation leads to a density of 6×10^{-16} as permitting the co-existence of hydrogen and ionised oxygen lines in the spectra of new stars. A. A. Eldridge.

Life of atomic states and the intensity of spectral lines. I. S. Bowen (Proc. Nat. Acad. Sci., 1928, **14**, 30—32; cf. A., 1927, 997).—From the previously published explanation of the strong nebular lines as due to electron jumps from metastable states in oxygen and nitrogen and the known highly rarefied state of the gases in nebulæ, it is concluded that metastable states are not absolutely metastable, but are states with mean lives of the order of a second or so. W. E. Downey.

Spark potentials in nitrogen. B. Frey (Ann. Physik, 1928, [iv], **85**, 381—424).—The influence of water vapour on the potential of the spark discharge in nitrogen has been studied. No change in the discharge potential is produced by the passage of a secondary spark when the gas is dried by liquid air. As the amount of moisture present increases, however, the sparking potential diminishes to a minimum and then increases. Since the same phenomenon is observed when hydrogen is introduced into the nitrogen, and since, also, the effect of moisture is nullified by the presence of a heated tungsten wire in the tube, it is concluded that the behaviour of water vapour is due to dissociation into its constituent gases. The potential lowering caused by very small quantities of hydrogen is probably due to the high activity of the proton in ionisation by collision. With increasing quantities of hydrogen larger ions are formed, ionisation diminishes, and the sparking potential increases. If sparking potental is plotted against the product of pressure and length of spark-gap, for different mixtures of nitrogen and hydrogen, the minimum sparking potential is lower than the minimum for the pure constituents. This appears to indicate that the hydrogen proton can ionise nitrogen better than the positive nitrogen ion, and can also ionise nitrogen better than it can ionise hydrogen. The influence of the electrode materials has been examined. In a state of moderate dryness the sparking potential for magnesium electrodes is some volts lower than for silver, but the reverse is the case in well-dried gas. This behaviour is explained by the formation of a layer of magnesium nitride by the discharge in the dried gas. In the presence of a little moisture, however, this is destroyed.

M. S. Burr.

Regularities in the spectrum of ionised neon. P. K. Kichlu (Proc. Physical Soc., 1928, 40, 41—45).—Hund's theory is applied in tracing doublet terms and intercombinations between doublets and quadruplets. Almost all the lines between 2500 and 3800 Å. have been accounted for with few discrepancies. C. J. Smithells.

Spark spectrum of neon. H. N. Russell, K. T. Compton, and J. C. Boyce (Nature, 1928, **121**, 357).—Fifteen new lines between 462·38 and 353·01 have been observed; 203 lines have now been classified in 59 multiplets. The ionisation potential of the neon ion is 40·9±0·05 volts. A. A. Eldridge.

Spark spectrum of sodium. S. Frish [with (Frl.) A. Ferchmin] (Naturwiss., 1927, **15**, 507; Chem. Zentr., 1927, ii, 784).—Alkali halide is placed in the capillary of a silica Geissler tube, and the tube filled with hydrogen or helium under low pressure. The capillary is heated while a discharge is passed and the tube placed in a magnetic field; the intensity of the arc spectrum of the alkali metal is reduced, and new lines, belonging to the spark spectrum of the metal and the arc spectrum of the halogen, appear, the intensity increasing with that of the magnetic field. The effects are more marked with a Paschen concave cathode. A. A. Eldridge.

Spectrum of ionised sodium. K. Majumdar (Nature, 1928, **121**, 423).—A preliminary statement of the result of an analysis of the spectrum of ionised sodium. The lines $5L_2(M_1\longrightarrow M_2)$ have been completely, and the lines $5L_2(M_2\longrightarrow M_3)$ partly, identified. The ionisation potential is about 47 volts, and the radiation potential 32·8 volts. A. A. Eldridge.

Polarisation of the sodium rumpf (core). H. Bartels (Naturwiss., 1927, **15**, 487—488; Chem. Zentr., 1927, ii, 784).—The polarisability of the sodium rumpf remains unchanged up to the eleventh member of the first sodium subordinate series. Negative polarisability certainly does not occur up to the 17*d* term. A. A Eldridge.

Intensity of the lines in the principal series of potassium. F. Rasetti (Atti R. Accad. Lincei, 1927, [vi], 6, 503—505).—By means of the anomalous dispersion method described in a previous paper (A., 1927, 1118) the number of electrons per atom responsible for the dispersion (n) has been determined in the potassium series 4^2S-m^2P for the lines corresponding with $m=4$, 5, 6, 7, and 8. The corresponding values of n are 1·0, $9{\cdot}0\times10^{-3}$, $7{\cdot}8\times10^{-4}$, 2×10^{-4}, and $1{\cdot}3\times10^{-4}$ within 5%. O. J. Walker.

Structure of the cobalt I spectrum. II. M. A. Catalán (Anal. Fís. Quím., 1927, **25**, 518—548, and Z. Physik, 1928, **47**, 89—113; cf. A., 1925, ii, 611).—The discovery of new terms has led to the classification of more than 700 lines, so that about 1200 lines in the arc spectrum have now been classified. The low terms result from two different outer electron configurations, viz., d^7s^2 and d^8s^1. They are in agreement with the theory of Hund. J. S. Carter.

Spectra of krypton and xenon in the extreme ultra-violet. J. H. Abbink and H. B. Dorgelo (Z. Physik, 1928, **47**, 221—232).—Vacuum grating spectra of krypton and xenon under various conditions of excitation have been tabulated for the region 1500—500 Å. Certain lines ascribed by Taylor (A., 1927, 178) to krypton appear to belong to xenon. The following ionisation potentials are deduced: krypton 13·9, xenon 12·0 volts. R. A. Morton.

Spark spectrum of silver. K. Majumdar (Indian J. Phys., 1928, **2**, 257—266).—The known lines in the spark spectrum of silver have been analysed and classified with a view to a comparison with the spark spectra of copper and gold. New lines determined with the vacuum grating have also been given in the region from 3372·65 to 1932·76 Å.

M. S. Burr.

Intensity distribution in Wood's resonance spectrum of iodine. O. Oldenberg (Z. Physik, 1927, **45**, 451—454).—By using plates sensitised with neocyanine the terms 27—37 (7687—8823 Å.) of the molecular spectrum of iodine, excited by the mercury green line, have been observed; the intensities of these newly-observed terms have been determined.

R. W. Lunt.

Recombination spectra of atomic ions and electrons. F. L. Mohler (Physical Rev., 1928, [ii], **31**, 187—194).—With cæsium, continuous bands extending to the violet from the limit $2P_1$ of the subordinate series, from the limit of the F series, and faintly beyond the P series, were observed. Potassium shows a strong band beyond the subordinate series. Intensity measurements were made. Intensity distribution in the line spectrum indicates a relatively high probability of recombination into levels of high quantum number, and relatively improbable recombination into the normal level.

A. A. Eldridge.

Influence of vapour pressure on the intensity and broadening of mercury resonance lines. W. Orthmann and P. Pringsheim (Z. Physik, 1927, **46**, 160—167).—The diminution of intensity and the broadening of the resonance lines in mercury vapour have been determined in the mercury vapour pressure range 0·01—7·3 mm. The effect produced by the addition of a neon–helium mixture of 250 mm. partial pressure is the same as that due to the increase in mercury vapour pressure in the above range. The results are thought to afford evidence of abnormally large values of the effective radius of mercury atoms of the order of 10^{-7} cm. R. W. Lunt.

Hyperfine structure and polarisation of $1^1S_0-2^3P_1$ of mercury in resonance radiation. A. Ellett and W. A. MacNair (Physical Rev., 1928, [ii], **31**, 180—186; cf. MacNair and Ellett, A., 1927, 911).—The incomplete polarisation is due to either or both of the outer hyperfine structure lines.

A. A. Eldridge.

Density of a luminous gas and the emission of light by atoms in metastable states. B. Venkatesachar (Nature, 1928, **121**, 356).—The fact that the intensity of the forbidden line 2270 Å. in the arc spectrum of mercury increases as the density of the vapour in a mercury arc is diminished is evidence in support of Bowen's view that the low density in nebulæ is favourable to the emission of light by atoms in metastable states (A., 1927, 997).

A. A. Eldridge.

Sputtering of metals by disruptive discharge in a magnetic field. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, 3, 643—645).—Previous experiments on sputtering produced by passing a heavy current through metals in loose contact (cf. this vol., 97) were continued in a magnetic field of 30 kilogauss. The paths followed by the luminous particles ejected from different metals are described and photographed. Particles of titanium, chromium, and manganese follow straight paths until near the end of luminosity, when they fork, owing to separation into several parts. Aluminium particles follow curved paths at the end, when the luminous intensity becomes greatest. Tungsten and molybdenum follow straight paths and show sudden increases in luminosity. These effects are ascribed to the oxidation of the particles. The magnetic properties of the metals are not important, since the temperature is above that at which ferromagnetism ceases.

C. J. Smithells.

Filtration of spark lines by disruptive discharge in magnetic field. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, 3, 647—649).—The spectra of the disruptive discharge (preceding abstract) in the absence of a magnetic field show both arc and spark lines of the metal. When a magnetic field is applied the spark lines are confined mainly to the neighbourhood of the poles, and fade towards the middle, whilst the arc lines show little difference in intensity across the gap. Lines which show reversal in the absence of a magnetic field appear strongly marked when the field is applied.

C. J. Smithells.

Discrepancies in Moseley's law. V. Dolejšek (Z. Physik, 1927, 46, 132—141).—It is shown that for the homologous elements of atomic number 36, 54, and 86, the value of $\sqrt{\nu}/R$ is given by the empirical expression $a+bN+cN^2+dN^3$, where N is the atomic number and a, b, c, d are constants. The difference between the experimental value of $\sqrt{\nu}/R$ and that calculated from the above empirical expression is shown to be a periodic function of the atomic number.

R. W. Lunt.

γ-Ray spectrography by crystalline diffraction. Frilley (Compt. rend., 1928, 186, 425—427).—The wave-lengths and the corresponding quantum energies of the rays measured have been determined by the author's apparatus for γ-rays from various sources, the maximum error being 3%. The γ-radiation obeys the Einstein photo-electric law, the upper energy limit investigated being 617 kilovolts (for the ray 20×10^{-11} cm.). The K-rays of radium-C and radium-C' result from the disintegration of radium-B and radium-C, respectively.

J. Grant.

Structure of the $K\alpha$-lines of the metals between calcium and copper. N. Seljakov, A. Krasnikov, and T. Steoozky (Z. Physik, 1927, 45, 548—556).—An examination of the $K\alpha$-lines of the metals calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper by an improved form of Siegbahn spectrograph has revealed the existence of irregularities on one side of the maximum which are associated with the $K\beta$-line.

R. W. Lunt.

Polarisation of the iron $K\alpha$-radiation. H. Haas (Ann. Physik, 1928, [iv], 85, 470—482).—Within the limits of experimental error, in an apparatus described in detail, no polarisation of the iron $K\alpha$-lines has been found for a voltage interval of 7·4—12·6 kilovolts (excitation limit 7·1 kilovolts). This is not in accordance with the observation of Bishop on the molybdenum $K\alpha$-lines (A., 1926, 1187).

M. S. Burr.

Spectrographic researches in the intermediate region. J. Thibaud and A. Soltan (J. Phys. Radium, 1927, [vi], 8, 484—494; cf. A., 1927, 1000).—The following new rays (in Å.) have been detected by the Thibaud vacuum spectrograph (A., 1927, 803), in which a ray of fluorescent oil covering the plates has been found unnecessary: K-rays of nitrogen 31·8, and of boron 68·0; N-rays of tantalum 58·3 and 61·4, of tungsten 56·0 and 59·1, of platinum 48·0 and 51·0, and of gold 46·8 and 49·4; O-rays of thorium 64·5 and 68·1. The N-rays of the heavy elements constitute a regular doublet due to the transition O—N IV—V, the most intense components having the longest wave-lengths. The quantum of the L II—III level of the light elements has been calculated from the energies measured for the K-rays and from the ionisation potentials, and a rise in Moseley's curve for this level, relative to these elements, is shown to exist. The deviations from the results of Dauvillier for the absolute wave-lengths of the K-rays of carbon and boron increase rapidly with the wave-length and are explained by the variation of the refractive index at the high wave-lengths. This variation, which follows the Drude–Lorentz rule, must be allowed for in the determination of high wave-lengths (above 20 Å.) from Bragg's formula.

J. Grant.

Polarisation of spectral X-rays. E. Wagner and P. Ott (Ann. Physik, 1928, [iv], 85, 425—469).—The polarisation in a wave-length range of $\Delta\lambda=0·055$ Å., at about 2 Å., has been examined by reflexion from a sodium chloride crystal at a glancing angle of 45°. The degree of polarisation is defined as the ratio of the reflexion intensity perpendicular to the cathode rays, to the reflexion intensity parallel to the cathode rays. The degree of polarisation increases with diminishing potential, the rate increasing as the minimum potential is approached. The degree of polarisation is not influenced to any great extent by the material of the anticathode. Lead, silver, copper, and iron, which were investigated, gave the same value, $1·4\pm0·2$, for 10·88 kilovolts. A change in the degree of polarisation, due to the simultaneous appearance of approximately equally hard rays characteristic of the anticathode material, was not observed.

M. S. Burr.

Scattering of X-rays from gases. C. S. Barrett (Proc. Nat. Acad. Sci., 1928, 14, 20—23).—Monochromatic radiation from an X-ray tube with a molybdenum target was obtained by means of filters of strontium oxide and zirconium oxide. When such radiation was passed through carbon dioxide, the scattered rays showed interference; no interference, however, was shown by the rays scattered from hydrogen. W. E. Downey.

Soft X-ray emission and absorption spectra with tangential grating. J. Thibaud (Nature, 1928, **121**, 321—322).—By using an intense electronic current and elements of high at. wt. as anticathode, the author has demonstrated the emission of a continuous spectrum from solid bodies between 15 and 250 Å. The continuous background is divided by a succession of fine bands with abrupt edges on the short wave-length sides. A sensitive method for revealing minute quantities of gaseous matter is thus available. The wave-lengths of the K-edges of carbon, nitrogen, and oxygen, respectively, are 43·5, 31·1, and 23·5 Å. A. A. Eldridge.

Absorption of X-rays in various elements. E. Jönsson (Nature, 1928, **121**, 283).—A question of notation. A. A. Eldridge.

Polarisation factor in X-ray reflexion. R. W. James (Nature, 1928, **121**, 422—423).—James and Firth's determinations of the atomic scattering factor (this vol., 225) do not appear to be affected by errors arising from the degree of polarisation of the incident beam. A. A. Eldridge.

Fine-structure and Zeeman effect for the mercury resonance line. M. Schein (Ann. Physik, 1928, [iv], **85**, 257—312).—The intensity of the secondary resonance radiation of mercury vapour shows a sharp decrease in magnetic fields varying from 0 to 1300 gauss (corresponding with 0—$5·8\times10^{-3}$ Å.). The curve obtained by plotting intensity against magnetic fields over the range 0—13,000 gauss (0—$5·8\times10^{-2}$ Å.) shows 5 maxima, corresponding with five equally spaced components approximately 0·01 Å. apart. A similar curve of the absorption of the resonance line shows minima in exactly the same positions as the maxima in emission. The resonance curve for absorption shows no further minima above 13,000 gauss, and it is concluded that the effective breadth of the resonance line under the given experimental conditions cannot exceed 0·076 Å. Each of the five components of the absorption line is resolved in a magnetic field into a triplet.

If the resonance line consists of five equidistant, equally intense, lines, the maxima in the resonance curve should be in the ratios 10 : 8 : 6 : 4 : 2, whereas the observed ratios are 10 : 6·5 : 5·4 : 3·6 : 2·3. Qualitatively, Wood's scheme of resolution is satisfactorily confirmed, but the minima of energy emission in the magnetic field show uniformly higher intensities than would be expected from Wood's scheme, assuming the Döppler effect as the sole line-broadening agency. The maximal absorption coefficient for a layer of vapour 1·1 cm. long at 0·0013 mm. pressure is 3·77. R. A. Morton.

Nuclear moment and Zeeman effect for bismuth. E. Back and S. Goudsmit (Z. Physik, 1928, **47**, 174—183).—A study of the Zeeman effect on bismuth lines with a strong field confirms the authors' view (A., 1927, 706) that the hyperfine structures are due to very narrow multiplet combinations brought about by a nuclear moment. The magnitude of the mechanical nuclear impulse moment is determined from the Zeeman effect to be 4·5 $h/2\pi$. For the first time, Landé's theory of fine structure in the Paschen–Back effect receives experimental confirmation. R. A. Morton.

Zeeman effect in band spectra. R. de L. Kronig (Physical Rev., 1928, [ii], **31**, 195—198).—Anomalies observed by Kemble, Mulliken, and Crawford (A., 1927, 1119) in the intensities of the Zeeman components in the Ångström carbon monoxide bands are explained. A. A. Eldridge.

Stark effect for the spectra of silver, copper, and gold. Y. Fujioka and S. Nakamura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 263—276).—See this vol., 2.

Ionisation potential of helium according to Schrödinger's theory. H. G. Grimm (Naturwiss., 1927, **15**, 561; Chem. Zentr., 1927, ii, 1123).—Schrödinger's theory gives term values 76·994, 77·316, 77·345, and 77·840, corresponding with values of 22·904, 23·226, 23·255, and 23·750 for the difference, in volts, between the energy value of the normal state ($1S$) and the ionisation potential of singly-ionised helium. The experimental term value is 78·564. A. A. Eldridge.

Constitution of the solar atmosphere. S. B. Nicholson and N. G. Perrakis (Compt. rend., 1928, **186**, 492—495).—The solar atmosphere, so far as is known at present, contains neither the extremely stable nor the extremely unstable elements (*e.g.*, rare gases and radioactive elements, respectively). A comparison of the ionisation potentials of the elements from hydrogen to xenon with their atomic numbers shows that the absence of the elements concerned is reproduced periodically, and that they are grouped at the extremities of periods usually occupied by elements of high ionisation potentials. The exceptions (helium and boron) are apparent only, but the almost complete absence of heavy elements is difficult to explain. J. Grant.

[Constitution of the solar atmosphere.] H. Deslandres (Compt. rend., 1928, **186**, 495; cf. preceding abstract).—The high ionisation potential and the exceptional nature of helium recorded by the authors are explainable by the ejection of radioactive substances from solar volcanoes, accompanied by doubly-ionised helium atoms in the form of α-particles. These combine with electrons with great force, with the emission of an intense spectrum. J. Grant.

Photo-electric and thermionic work functions of outgassed platinum. L. A. DuBridge (Physical Rev., 1928, [ii], **31**, 236—243).—With monochromatic light the final value of the photo-electric threshold is 1962 Å. (6·30 volts), and that of the thermionic work function 6·35 volts. A. A. Eldridge.

Optical determination of the thickness of photo-electrically active rubidium films. H. E. Ives and A. L. Johnsrud (J. Opt. Soc. Amer., 1927, **15**, 374—381).—The thickness of photo-electrically active films of sodium and of rubidium deposited on glass and on platinum surfaces has been determined from changes in the azimuth or phase of plane polarised light incident at 45° on the film. The results indicate that complete photo-electric emission is obtained from an approximately unimolecular film of rubidium.

R. W. LUNT.

Critical primary velocities in the secondary electron emission of tungsten. H. E. KREFFT (Physical Rev., 1928, [ii], **31**, 199—214).—The curve showing the number (*n*) of secondary electrons produced by one primary electron as a function of the primary velocity, obtained with tungsten at 1250—1450° Abs. and velocities of 10—700 volts, shows a maximum at 15·3 volts, a minimum at 20 volts, 18 breaks between 25 and 600 volts, and a maximum at 630 volts. The effect of adsorption of gas is investigated.

A. A. ELDRIDGE.

Restored electron theory of metals and thermionic formulæ. R. H. FOWLER (Proc. Roy. Soc., 1928, **A**, **117**, 549—552).—The electron theory of metallic conduction, as re-instated by Sommerfeld (Naturwiss., 1927, **15**, 825), is applied to the calculation of the density of evaporated electrons in equilibrium with the heated metal. A consideration of the equilibrium state of an assembly consisting of a heated metal and an atmosphere of free electrons shows that the vapour pressure has twice the value commonly accepted, owing to the fact that each electron has two orientations. This result is applied to the theory of thermionic emission, and gives values in good agreement with the best determinations for the metals tungsten, molybdenum, tantalum, and platinum in a very pure state.

L. L. BIRCUMSHAW.

Extraction of electrons from cold conductors in intense electric fields. O. W. RICHARDSON (Proc. Roy. Soc., 1928, **A**, **117**, 719—730).—The experimental results of Gossling and of Millikan and Eyring (cf. A., 1926, 448, 219) are discussed, and a theory is developed to account for the phenomenon of an electron current which is independent of the temperature of the emitting substance, but is a continuous function of the field intensity. The sharpness of the photo-electric effect at a metallic surface is explained, and, by treating the attraction of an electron by its mirror image in a conductor as a Schrödinger wave problem, a formula is derived for the field currents from cold conductors which agrees with the experimental data. The theory indicates that in the neighbourhood of a nucleus, electrons are discontinuously coming into space, and are generated at a rate proportional to $(\psi\psi)^{3/2}$. The experimental evidence does not support the view that the localisation of the discharge in restricted areas is due to these areas being sharp protuberances. It is considered that the localisation must be attributed to the possession by different parts of the surface of a different constitution.

L. L. BIRCUMSHAW.

Affinity of oxygen for electrons. M. A. DA SILVA (Compt. rend., 1928, **186**, 583—584).—The author's determinations of the ionisation of pure argon (A., 1927, 809) have been extended to the case of a thin layer of gas on the surface of a plate of the measuring condenser, the other plate, 5 cm. away, being connected to a quadrant electrometer. The current passing through the gas depends on the sense of the applied field, and the tension required to produce saturation is six times as great when it is carried by the positive as by the negative ions. A concentration of oxygen of 3×10^{-4}, or more, produced a deformation in the current–voltage curve in the latter, but not in the former case, indicating that oxygen molecules have a strong affinity for electrons, but not for the positive ions of argon. The latter may probably remove an electron from the neutral molecules of oxygen they meet. A comparison of the deformed curve with that obtained for positive ions indicates that the mean mobility of the negative ion is a function of the applied field. At low tensions they are similar, but as the tension increases the deformed curve approaches saturation more rapidly. The deformation decreases with the (atmospheric) pressure. These results are in agreement with J. J. Thomson's probability theory of ionisation.

J. GRANT.

Existence of sub-electronic charges. F. EHRENHAFT (Z. Physik, 1927, **45**, 577—560).—A review of recent work which indicates the existence of sub-electronic charges on small metallic particles and on oil droplets.

R. W. LUNT.

Errors in Ehrenhaft's technique for the detection of sub-electronic charges. E. WASSER (Z. Physik, 1927, **45**, 561—587).—The probable errors in Ehrenhaft's technique are analysed at length.

R. W. LUNT.

Magnetic moments of the cupric ion. (MLLE.) P. COLLET and F. BIRCH (Compt. rend., 1928, **186**, 499—501).—The work of Cabrera (A., 1926, 7) has shown that a study of the thermal variation of the coefficient of magnetisation is necessary for the determination of the Curie constant. The magnetic moments of the cupric ion in solids and in their solutions have thus been determined for temperature intervals for which the relation is linear. A dominant moment of 10 magnetons was found, and also values of 9 and 9·6 magnetons, but the last may be due to a mixture of carriers of moments of 9 and 10, produced, *e.g.*, by the formation of complex ions in solutions of cuprous chloride at various temperatures.

J. GRANT.

Activation of hydrogen by electric discharge. R. W. LUNT (Nature, 1928, **121**, 357).—A criticism of Glockler's hypothesis (this vol., 140) concerning Elliott's observations (A., 1927, 187).

A. A. ELDRIDGE.

Active nitrogen. E. J. B. WILLEY (Nature, 1928, **121**, 355).—In part, polemical against Lewis (this vol., 258). Between 1 mm. and 10 mm. pressure the process of decay of the after-glow is very complex, although bimolecular with respect to the active nitrogen. Probably the luminosity and the chemical activity are steps in an involved deactivation process, the first stage consisting of a ternary collision between two atoms and a molecule. Objection is raised to Lewis' theory of the formation of ammonia from atomic nitrogen and atomic hydrogen.

A. A. ELDRIDGE.

New effect in the electric discharge. T. R. MERTON (Proc. Roy. Soc., 1928, **A**, **117**, 542—549).—

A peculiar type of striated discharge has been observed in vacuum tubes containing helium. The discharge tubes were provided with tubes of 2 cm. bore, 20—40 cm. long, in place of the usual capillary. Carbon electrodes were used, and the phenomena were best observed at a pressure of 30—40 mm. A state is reached at which the helium tube, when excited by the uncondensed discharge from a high-tension transformer fed with alternating current at 50 cycles, shows an almost uniform green glow. By introducing a condenser and spark-gap into the circuit, it is possible to start a disturbance which gives rise to a new type of disc discharge, which is described in detail. The spectrum of the discs differs from that of the green glow in that the helium lines, which are feeble in the green glow, and the comet bands are very bright in the discs, whilst the Swan bands can be seen only in the green glow, being absent from the discs. On examination of the discs by means of a beam of sunlight it was found that the sunlight is strongly scattered in the neighbourhood of the discs. The scattering is probably due to very small particles of carbon, and the discs seem to be surrounded by an envelope of these scattering particles. An examination of the discharge made by two stroboscopic methods showed that, besides the stationary discs, there are rapidly moving striations throughout the tube (cf. Aston, *ibid.*, 1921, **A**, **98**, 50). The disc discharge is entirely unaffected by weak magnetic fields, unlike Langmuir's streamer discharge (Science, 1924, **60**, 392), which in some respects it resembles. Investigations with unidirectional discharges are described, and the mechanism of the disc discharge is discussed in the light of the results obtained. It is probably closely related to the migration of carbon compounds. A similar type of discharge has also been observed, although much less clearly, in a neon tube provided with carbon electrodes, but experiments with a large number of mixtures of gases gave negative results. It is suggested that the phenomenon of "ball lightning" may be an example of a single disc descending from a charged cloud to earth.

L. .L. Bircumshaw.

High-frequency discharges in gases. S. P. McCallum (Nature, 1928, **121**, 353).

Electrical discharges in gases at low pressures. I. Langmuir (Z. Physik, 1927, **46**, 271—299).—An analysis is advanced of the motion of ions and electrons in gases at pressures such that the mean free path is of the order of 1 cm. with particular reference to discharges between a straight wire emitting electrons surrounded by a coaxial cylindrical anode. Methods of determining the velocity distribution of the ions and electrons are described, and it has been shown that in mercury vapour the Maxwellian distribution obtains. The "electron temperature" corresponding with the observed velocity distribution is not a function of the current, and it is therefore concluded that the ions and electrons are not in thermal equilibrium with the gas molecules, the temperature of which in such discharges is but little higher than that of the walls of the containing vessel. "Electron temperatures" up to 80,000° have been observed in discharges in mercury vapour; somewhat lower values are obtained in argon and in hydrogen.

R. W. Lunt.

Diffusion coefficients of flame gas ions in relation to temperature. H. Bückert (Ann. Physik, 1928, [iv], **85**, 63—80).—The diffusion coefficient D has been measured for positive and negative ions from hydrogen, coal gas, and carbon monoxide flames over the temperature range 20—120°, and in electrical fields ranging from 0 to 16 volts, and also for ions varying in age from 3 to 6·6 sec. For hydrogen D is almost constant at 0·00315 for the positive ion and 0·0037 for the negative ion from 20° to 50°; the values thereafter show a steady increase to 0·0068 and 0·0079, respectively, at or about 120°. Both carbon monoxide and coal gas exhibit similar curves, except that in the former the diffusion coefficients of positive and negative ions are almost identical. The mean value of D for coal gas at 100° is more than twice that for hydrogen and thrice that for carbon monoxide. Determinations of D in an electric field show that the values at 16 volts for both hydrogen and coal gas are about half those at zero voltage, the negative ions showing consistently higher values than the positive ions; in carbon monoxide the two ions behave alike and the effect of the field is less marked.

The ageing of ions from 3 to 6 sec. brings about reductions in D to 80, 60, and 40% of the original values for hydrogen, coal gas, and carbon monoxide, respectively. The values of D indicate large ion complexes and the discontinuity at 50° shows that they are then split up into smaller aggregates. The complex ions in carbon monoxide resist disruption, showing that since no water is formed in the combustion, carbon dioxide must be more strongly attached than water to ions. Lauster's data (Z. Physik, 1920, **3**, 396) are in agreement with these views.

R. A. Morton.

Scattering of canal rays in hydrogen. G. P. Thomson (Z. Physik, 1927, **46**, 93—105).—The scattering of hydrogen canal rays in hydrogen has been determined by a thermopile method; the results agree with those obtained by the photographic method, which is thus established. R. W. Lunt.

Magnetic analysis of a luminous canal-ray beam in hydrogen. C. J. Brasefield (Physical Rev., 1928, [ii], **31**, 215—219).—A luminous canal-ray beam in hydrogen is separated by means of a transverse magnetic field into four component parts: neutral particles, and the charged ions H_2^+, H^+, and H_{2-1}^{+} (ions which passed through the electric field as H_2^+, but dissociated into H^+ before reaching the magnetic field). Measurements of the variation of the intensity of the H_2^+ and H_{2-1}^{+} beams with the pressure lead to a value for the free path for dissociation of a 1000-volt H_2^+ ion into H_{2-1}^{+} of 0·37 cm. at 0·01 mm., about 0·25 of the value, calculated from the kinetic theory, for the neutral molecule.

A. A. Eldridge.

Theory of the Faraday effect in gases. R. de L. Kronig (Z. Physik, 1927, **45**, 508—511).—The author's theory of the Kerr effect in gases has been extended to an analysis of the Faraday effect.

R. W. Lunt.

Theory of the Kerr effect in gases. R. DE L. KRONIG (Z. Physik, 1927, **45**, 458—470).—Mathematical. R. W. LUNT.

Density, compressibility, and at. wt. of neon. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1928, **14**, 50—57; cf. A., 1927, 194).—Crude neon was subjected to exhaustive chemical purification followed by fractional adsorption. The normal density of neon is found to be 0·89990 and the at. wt. calculated therefrom 20·182. W. E. DOWNEY.

Density, compressibility, and at. wt. of argon. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1928, **14**, 57—63; cf. preceding abstract). —The normal density of argon is found to be 1·78364 and the at. wt. 39·943. The conventional method of calculating the deviation from Boyle's law makes the assumption that the value of PV for one atmosphere is correct. A more rational method is to find the best straight line to represent the observed values of some simple function of the density plotted against the pressure and then to extrapolate to zero pressure. This method of distributing the errors produces small differences between the calculated and observed values of the densities at different pressures. The effect on the calculated at. wt. is always less than 0·001 unit, although fortuitously the third decimal place is affected in the case of neon and argon. The values calculated by this method are: oxygen 16·000, nitrogen 14·008, neon 20·183, argon 39·944. The value of the limiting density of oxygen is 1·42764, which yields as the limiting value of molal volume 22·4146 litres (g=980·616). W. E. DOWNEY.

At. wt. of titanium. III. Analysis of titanium tetrabromide. G. P. BAXTER and A. Q. BUTLER (J. Amer. Chem. Soc., 1928, **50**, 408—415).—The above analysis gives 47·90 (Ag=107·88) as the at. wt. of titanium, in agreement with previous results (cf. A., 1927, 86). S. K. TWEEDY.

At. wt. of copper. R. RUER (Z. anorg. Chem., 1928, **169**, 251—256).—The amount of air taken up by copper under the conditions under which it was weighed in the determination of the at. wt. (A., 1926, 1075) has been found by the method previously described (A., 1927, 1134) to be 0·00102 g./100 g. Taking this into account, the at. wt. becomes 63·544±0·003. R. CUTHILL.

Rare earths. XXVI. Purification and at. wt. of erbium. A. E. BOSS with B. S. HOPKINS (J. Amer. Chem. Soc., 1928, **50**, 298—300).—The at. wt. of erbium as determined by the ratio of erbium chloride to silver (107·88) is 167·64 (cf. Hofmann, A., 1910, ii, 1073). Erbium material yielding a constant at. wt. for the element may be obtained from the erbium–yttrium material from gadolinite by fractionation by the nitrate fusion method or by fractional precipitation with sodium nitrite. S. K. TWEEDY.

The Bohr magneton and radioactivity. D. ENSKOG (Z. Physik, 1927, **45**, 852—868).—By adopting the view that magnetic forces are responsible for the attraction between an α-particle and the nucleus immediately previously to the emission of an α-particle, a theory is developed whereby values of the kinetic energy of the emitted α-particle may be calculated from the magnetic moments of the nucleus and of the α-particle and from the nuclear charge. Values calculated in this way are in fairly good quantitative agreement with experiment for a large number of radioactive changes. R. W. LUNT.

Protoactinium as a radioactive and chemical element. O. HAHN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 275—283).—New determinations of the period of protoactinium have been carried out by Walling by measuring the rate of growth of the element in uranium originally carefully freed from it (cf. von Grosse, this vol., 259). A quantitative examination of the amount formed has been made by using its isotope, uranium-*Z*, as a radioactive indicator. The period found is 20,000 years with a possible error of ±10%. The different views as to the origin and at. wt. of protoactinium are discussed. Protoactinium in a suitable quantity in a pure state would form a valuable source of actinium. It would also afford a means of studying the special chemical properties of the elements of atomic number 91 in relation to those of the lower members of the same group, niobium and tantalum, and of the neighbouring elements, uranium and thorium. Protoactinium is also interesting from the fact that elements of odd atomic number, especially in the last horizontal series of the periodic table, are comparatively rare. M. S. BURR.

Charge of α-particles emitted per sec. by 1 g. of radium. H. JEDRZEJOVSKI (Ann. Physique, 1928, [x], **9**, 128—185).—A more detailed account of work already published (A., 1927, 710).

Recoil β-particles from thorium-*B*. K. DONAT and K. PHILIPP (Z. Physik, 1927, **45**, 512—521).—Using a modification of the technique of Barton, the recoil β-particles from thorium-*B* have been investigated. The results are in agreement with those of Barton on radium-*B*. R. W. LUNT.

Retardation of β-rays by matter. J. D'ESPINE (J. Phys. Radium, 1927, [vi], **8**, 502—507).—The values of the retardation of β-rays by aluminium, copper, silver, or gold, as determined with an accuracy of 10% from the magnetic spectra of some of the principal groups of β-rays from thorium-*B* and radium-*B*, have been compared with the results of other workers. Bohr's formula for the expression of this retardation gives a curve having the same shape as that derived from the experimental results, although the individual retardations are higher. Some previous results (A., 1926, 332) are revised. J. GRANT.

Study of atomic particles with the point-counter. W. BOTHE and H. FRÄNZ (Naturwiss., 1927, **15**, 445; Chem. Zentr., 1927, ii, 780).—By using a very pure polonium preparation as source of α-rays, atomic particles can be detected not only with the Geiger point-counter, but also by the absorption curve. Of the elements examined—boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, calcium, and copper—only boron, nitrogen, magnesium, and aluminium clearly gave particles, the range in air being >20, 16,

13, and 16 cm. in air at 15°, respectively. Paraffin gave hydrogen particles of range 15 cm.
A. A. Eldridge.

Validity of Geiger's counter for β-particles and the β-particle emission from radium-*E* and radium-*D*. N. Riehl (Z. Physik, 1928, **46**, 478—505).—The validity of Geiger's counter for β-particles has been examined and it has been shown that for particles of velocities 0·70—0·94*c* a counter chamber pressure of 2·5 atm. should be used for quantitative work; the true number of particles is not obtained at pressures less than 1150 mm. The absorption in argon, as with α-particles, is less than that in air at the same pressure. β-Particles from radium-*D*, 0·34—0·4*c*, are completely absorbed in air at 7 mm. The ratio of the number of β-particles emitted by radium-*E* to the number of atoms disintegrated has been shown to be not less than 1·2. Inconclusive results have been obtained with radium-*D*. R. W. Lunt.

Thermo-dissociation of atom-nuclei. S. Suzuki (Proc. Imp. Acad. Tokyo, 1927, **3**, 650—654).—On the assumption that radium exists in thermal equilibrium with its disintegration products, the heat of reaction calculated from the kinetic energy of an α-particle being $-1\cdot1\times10^{11}$ g.-cal., $\log x^2/(1-x^2).p=2\cdot41\times10^{10}/T+2\cdot5\log T+0\cdot387$. The temperature T_c at which the maximum degree of dissociation should occur is given by $d(2\cdot4\times10^{10}/T+2\cdot5\log T)/dT=0$, whence $T_c=10^{10}$ degrees. The amount of radium should therefore decrease up to 10^{10} degrees, but decompose into radon at higher temperatures. Unless $x^2/(1-x^2).p>10^{27\cdot8}$ atm. no equilibrium can exist, and no observable change in the degree of dissociation would be expected at the b. p. of radium under a few thousand atmospheres pressure. Since the heat of reaction is of the same order for all the heavy elements, it is assumed that their disintegration into hydrogen, helium, and protons would take place at about 10^{10} degrees.
C. J. Smithells.

Internuclear reactions. B. Cabrera (Compt. rend., 1928, **186**, 501—503).—The theory (this vol., 216) that the Aston packing fraction is a measure of the internal energy of the system and gives an indication of the evolution of atomic nuclei, is developed, and extended to internuclear reactions. The theory requires an emission of energy equivalent to $15\cdot2\times10^{-27}$ g. during the disintegration of nitrogen by bombardment with α-particles with the formation of a proton and an isotope of oxygen (O^{17}). This probably takes the form of a radiation hitherto unnoticed. The theory is also applied to the evolution of elements in the cosmos. J. Grant.

Relative masses of a proton and an electron. J. C. Ghosh (Naturwiss., 1927, **15**, 445; Chem. Zentr., 1927, ii, 779).—The observed relations are derived on the supposition that if two light quanta of frequency ν impinge, a part *E* of the energy is converted into matter in the form of a proton and an electron, whilst the remainder is converted into heat-motion. Each photon is transformed into a hohlraum. A. A. Eldridge.

Structure of the hydrogen atom. H. Ghosh (Naturwiss., 1927, **15**, 506—507; Chem. Zentr., 1927, ii, 1121).—The mass 1·008 of the hydrogen atom is regarded as that of the nucleus (1) plus that of 16 electrons (0·008), the latter mass being distributed in a spherical shell as radiation energy.
A. A. Eldridge.

Scheme [for the prediction of the atomic masses] of isotopes. G. Beck (Z. Physik, 1928, **47**, 407—416).—Theoretical. Aston's results on isotopes are arranged in a tabular scheme and used to predict, by the regularities observed, other as yet unobserved isotopes. It is further concluded that there are arrest points in the building up of the various atomic nuclei. W. E. Downey.

Quantum theory of the electron. P. A. M. Dirac (Proc. Roy. Soc., 1928, **A**, **117**, 610—624).—The assignment to each electron of a spin and a magnetic moment, in order to make the quantum theory, when applied to the problem of the structure of the atom, agree with observation, is shown to be unnecessary. Agreement with experiment can be obtained without arbitrary assumptions by the correct relativistic application of quantum mechanics to the point-charge electron. The Hamiltonian function on which the present theory is based is linear in energy and momentum, and leads to an explanation of all duplexity phenomena without further assumption. The spinning electron model is, however, justifiable for many purposes, at least as a first approximation. Its most important failure seems to be that the magnitude of the resultant orbital angular momentum of an electron moving in an orbit in a central field of force is not a constant, as the model leads one to expect. L. L. Bircumshaw.

Quantum theory of homopolar valencies. F. London (Z. Physik, 1928, **46**, 455—477).—It is shown that homopolar valencies calculated from the symmetry characteristics of Schrödinger's characteristic function are in agreement with the periodic classification, and it is thought that they may be interpreted as quantum mechanical resonance effects.
R. W. Lunt.

Explanation of some properties of spectra from the quantum mechanics of the spinning electron. J. von Neumann and E. Wigner (Z. Physik, 1928, **47**, 203—220).—The kinematic properties of any system of spinning electrons (without further assumptions) have been deduced with the aid of the Dirac–Jordan transformation theory. R. A. Morton.

Infra-red spectra of hydrogen halides according to Schrödinger's theory. M. Czerny (Z. Physik, 1927, **45**, 476—483).—An analysis of the available data for the infra-red spectra of hydrogen halides by Schrödinger's theory leads to values of the molecular constant somewhat different from those derived from the quantum theory. R. W. Lunt.

Refraction quotient of the De Broglie waves of electrons. O. Klemperer (Z. Physik, 1928, **47**, 417—421).—It is shown that there is a limiting angle for the total reflexion of cathode rays on the theory of wave mechanics. W. E. Downey.

Theory of collision processes in hydrogen. W. Elsasser (Z. Physik, 1927, **45**, 522—538).—Mathematical. R. W. Lunt.

Theory of the collisions between atoms and slow electrons. (FRL.) L. MENSING (Z. Physik, 1927, **45**, 603—609).—The collision process between atoms or slow electrons has been analysed by wave mechanics; comparisons of the predictions of theory with experiment show that an atom cannot be regarded as a charged shell. R. W. LUNT.

Minimum proper time and its applications (1) to the number of the chemical elements, (2) to some uncertainty relations. H. T. FLINT and O. W. RICHARDSON (Proc. Roy. Soc., 1928, **A**, **117**, 637—649).—It has been shown that the proper time of a particle has a minimum value h/m_0c^2, where m is the rest mass. This conclusion is now reached by a method which is independent of the assumptions as to the metrics of space and time, made previously. An upper limit $[n/(n+1)]^{\frac{1}{2}}C$ is placed on the velocity of an electron in an atom in an orbit of total quantum number n. This involves an upper limit 97 for the atomic number of any chemical element, and also an upper limit for the quantum number of an intranuclear orbit. The limit is a function of the atomic number of the nucelus. L. L. BIRCUMSHAW.

[Use of Winther's gauze in] spectrophotometry. G. LANDSBERG (Z. Physik, 1927, **46**, 106—108).—The use of a blackened gauze as a constant extinction filter (Winther, A., 1923, ii, 519) has been examined in the visible region and up to 2026 Å. The extinction of such gauzes is constant within 1% in the range examined. R. W. LUNT.

Graphic representation of colours. S. RÖSCH (Physikal. Z., 1928, **29**, 83—91).—Every colour can be defined by means of its "relative brightness," the relative width of its spectrum, and the mean wavelength. An apparatus is described whereby any colour may be compared by synthesis in terms of these three co-ordinates. W. E. DOWNEY.

Characteristic of the hydrogen molecule in the normal state. Y. SUGIURA (Z. Physik, 1927, **45**, 484—492).—Mathematical. R. W. LUNT.

Quantum levels and resulting constants of the hydrogen molecule. R. T. BIRGE (Proc. Nat. Acad, Sci., 1928, **14**, 12—19).—Theoretical. It is contended that the discrepancy between the observed value of the ionisation potential of hydrogen and the theoretical value as calculated from Richardson's analysis of the band spectrum (A., 1927, 916) is only apparent. W. E. DOWNEY.

Hydrogen molecule. O. W. RICHARDSON (Nature, 1928, **121**, 320).—A discussion (cf. Birge, this vol., 216). It now appears that the suspected coincidence of the author's 2^3P level with Dieke and Hopfield's C level is accidental; the case for the coincidence of the author's 2^1S level with their B level is much more convincing. An examination of Werner's plates shows that the 2^1S states are formed, and that they pass with difficulty into the 1^1S state; apparently the excitation energy is discharged by dissociation of the hydrogen molecules on collision. A. A. ELDRIDGE.

Residual effect in the actinic absorption of chlorine. W. TAYLOR and A. ELLIOTT (Proc. Durham Phil. Soc., 1926—1927, **7**, 172—181).—See A., 1927, 216.

Measurement of residual rays in the visible region of the spectrum. G. JOOS (Physikal. Z., 1928, **29**, 117—118).—The absorption spectra of potassium chromium selenate crystals, and of other chromium double salts of the alum type, disclose the existence of sequences of lines separated by about 43 cm.$^{-1}$ and containing as many as 11 terms. The frequency difference corresponds with 232 μ, a wavelength in the range of residual rays. R. A. MORTON.

Absorption spectra of potassium ferro- and ferri-cyanides. F. H. GETMAN (J. Physical Chem., 1928, **32**, 187—191; A., 1921, ii, 287).—A further, more refined, spectroscopic examination of 0·0005M-solutions of potassium ferro- and ferri-cyanides has been made. The absorption spectra differ markedly from each other. The molecular extinction coefficients of the compounds designated by Briggs (J.C.S., 1911, **99**, 1019) as the α- and β-ferrocyanides of potassium are identical, supporting the view of Bennett (A., 1917, i, 449) that these salts are not isomeric. The corresponding coefficients for the α- and β-ferricyanides are different from each other, however, confirming the previous finding of the author (*loc. cit.*) and the view of Locke and Edwards (A., 1899, i, 407). An apparatus for producing sparks under water between tungsten electrodes to detect narrow or weak absorption bands is described. L. S. THEOBALD.

Spectrochemical researches on some porphyrins and some compounds of hæmatoporphyrin with iron. E. BOIS (Can. Chem. Met., 1927, **11**, 261—264).—The absorption spectra are considered to provide a new basis for the explanation of molecular structure by spectra. The fluorescence spectrum is the most sensitive reaction for the detection of porphyrin and blood-spots. Synthetic hæmatin shows a stage in the transformation of foods into blood. CHEMICAL ABSTRACTS.

Spectrographic study of complex cyanogen compounds of iron. I, II. L. CAMBI and L. SZEGÖ (Gazzetta, 1928, **58**, 64—71, 71—76).—See A., 1927, 809, 916.

Optically excited iodine bands with alternate missing lines. R. W. WOOD and F. W. LOOMIS (Nature, 1928, **121**, 283).—A study of the fluorescence bands which develop around the "fundamental" doublets when iodine is excited, in presence of helium, by the green mercury line, shows that only those alternate lines occur in the spectrum of the fluorescence for which m' is even. Thus the rotational quantum number of the excited iodine molecules can change only by even numbers during these collisions of the second kind. The result, although incomprehensible on the classical Bohr–Lenz theory, affords direct evidence in support of the theories of Hund and Dennison. A. A. ELDRIDGE.

Band fluorescence of mercury vapour. P. PRINGSHEIM and A. TERENIN (Z. Physik, 1928, **47**, 330—343).—Mercury vapour fluoresces under the influence of an uncooled mercury lamp or of an aluminium spark. The intensity of the fluorescence excited by a mercury lamp is not a quadratic function of the intensity of the incident light. It increases, at first, very strongly with increasing thickness of mercury vapour and then slowly. At small thicknesses the effect of indifferent gases is very marked. Hydrogen and oxygen weaken the effect. From the effect of hydrogen it is concluded that the duration of light emission has an upper limit of 10^{-3} sec. Parallel with the visible fluorescence there occurs an emission of the line at 2537 Å. W. E. Downey.

Absorption of ultra-violet light by dextrose, lævulose, and lactose. L. Kwieciński and L. Marchlewski (Bull. Acad. Polonaise, 1927, **A**, 379—394).—Contrary to the statements of Purvis (J.C.S., 1923, **123**, 2515) and Niederhoff (A., 1927, 396), pure preparations of dextrose and lactose show no selective absorption in the ultra-violet. Even after several crystallisations *d*-lævulose shows a band at about 2800 Å. It is not certain, however, that all traces of impurity are removed by crystallisation and this particular result is not at present regarded as conclusive. J. S. Carter.

Colour and colour equilibria of phenolphthalein and its derivatives. E. Vogt (Z. physikal. Chem., 1928, **132**, 101—130).—The quinone-phenoxide theory of Acree is regarded as the most satisfactory explanation of the colour changes experienced by phenolphthalein, the phthalein esters and sulphonephthaleins, and other triphenylmethane dyes.

Comparative measurements of the absorption of the various halogen derivatives of phenolphthalein indicate not a quinonoid ring, but the central carbon atom, as the chromophore. The extinction curves are substantially in agreement with Ostwald's theory of indicators, having regard to the dibasic nature of the phthaleins. The two dissociation constants of phenoltetrachlorophthalein are $7 \cdot 9 \times 10^{-9}$ and $3 \cdot 73 \times 10^{-9}$, respectively. For substances of which the two dissociation constants are widely different the simple theory applicable to monobasic acids is valid.

H. F. Gillbe.

Intensity ratio of the *D*-lines. W. Lochte-Holtgreven (Z. Physik, 1928, **47**, 362—378).—The appearance of one *D*-line under fluorescence excitation by the other *D*-line has been quantitatively studied for both lines. In the presence of rare gases, the intensity ratio between the two lines is in accord with that required by theory. The extinction of secondary resonance by gases was established and a separation effected between collisions which force the atom back into the unexcited state without emission and those which transform it into the adjacent 2*p*-state. Collisions between excited sodium atoms and sodium or potassium atoms are some two hundred times more effective for the second transition mentioned than are collisions with rare-gas atoms. W. E. Downey.

Duration of fluorescence of solid uranyl salts and of their solutions. F. Perrin and R. Delorme (Compt. rend., 1928, **186**, 428—430; cf. A., 1926, 223, 558).—The duration of emission of fluorescence of uranyl salts has been measured by means of the phosphorometer, an adaptation of Becquerel's phosphoroscope in which the rate of rotation of the vanes under the influence of the radiation is measured by means of an optical rotating-wheel device. For simple fluorescence the exponential decrease in luminescence after instantaneous illumination was confirmed. The mean lives (in 10^4 sec.) of crystalline uranyl sulphate and nitrate were 2·5 and 6·1, respectively. Solutions of the former in pure sulphuric acid gave times and fluorescing powers of the same order as the solid salt but slightly lower, and decreasing when the concentration or temperature was raised, or when water was added. J. Grant.

Fluorescence of mercury–inert gas bands. O. Oldenberg (Z. Physik, 1928, **47**, 184—202).—The question whether atoms can be excited by the joint action of collisions and irradiation, can be tested indirectly by considering the reverse process, viz., the distribution of energy of excitation between kinetic energy and emission. Investigation of the fluorescence spectrum of mercury vapour in the presence of helium or neon at atmospheric pressure discloses a range of continuous emission on both sides of the resonance line, extending from 2519 to 2570 Å. for helium. On the other hand, the spectra obtained with argon and krypton as the added gases exhibited banded structure, whilst with nitrogen the results resembled those obtained with helium and neon. Hydrogen and oxygen, as added gases, did not cause the appearance of either the continuous or banded spectrum. It appears that excited mercury atoms in the 2^3P_1 state can form " molecules " on colliding with an atom of argon or krypton, the attraction originating from a polarisation of the rare gas atom in the field of the excited mercury atom. The continuous spectra obtained with helium and neon may be unresolved band (molecular) spectra. If, however, they are not of this type, the continuous spectra must illustrate the joint action referred to. It is shown that the banded spectra also appear in absorption. R. A. Morton.

Excitation of fluorescence by *X*-rays of different wave-lengths. R. Glocker, E. Kaupp, and H. Widmann (Ann. Physik, 1928, [iv], **85**, 313—332).—The relation between ionisation and fluorescent light intensity has been investigated for two zinc silicate screens of different thicknesses, using radiations ranging from 0·12 to 1·54 Å. At 0·19 Å. the brightness of the screen varies approximately with the thickness of fluorescent material, whereas at 0·71 Å. the linear relation no longer holds, because the absorption does not increase linearly with the thickness. From calculations of the fraction of incident *X*-ray energy which represents electron energy, it is shown that fluorescence largely originates from the electron energy, and not from the absorbed energy provided the screen consists of a very thin layer. An ionisation chamber responds much more readily to changes in wave-length than does the fluorescent screen. A method is given for evaluating losses in light intensity due to absorption and diffuse reflexion in the screen. The light emission from the zinc silicate screen consists of a broad band extending from 505 to 573 $\mu\mu$ (maximum 520—530 $\mu\mu$). The relative intensities of the short-wave and long-wave sides have been determined under different conditions of excitation, and no differences have been detected which could be traced to changes in the wave-length of the exciting *X*-rays. R. A. Morton.

Photoluminescence of solutions of æsculin at low temperatures. J. Starkiewicz (Bull. Acad. Polonaise, 1927, **A**, 459—471).—The fluorescence band of solutions of æsculin in glycerol moves gradually towards the violet as the temperature is depressed from +20° to −80°. A faint green phosphorescence, more intense when a solution of sucrose is used as solvent, is observed at −80°. A more intense and more permanent phosphorescence is observed with glycerol solutions at −180°, the spectrum showing intensity maxima at the wave-lengths 480, 495, 515, 540, and 560 $m\mu$. Phosphorescence and fluorescence are not correlated phenomena. J. S. Carter.

Light emission of gases excited by α-rays. H. Greinacher (Z. Physik, 1928, **47**, 344—356).—The emission of light by air, carbon dioxide, oxygen, and hydrogen under the influence of α-particles has been studied. The intensity of the emitted light was examined photographically and was found to be independent of the recombination of the ions. The ratios of the light intensities for the gases examined were found to be different from those of Walter (Ann. Physik, 1906, [iv], **20**, 327). The light from hydrogen was found to be as strong as that from air, whereas Walter found it was only one tenth. This is explained as due to the use of a quartz filter by Walter which cut off the ultra-violet band spectrum. The energy and collision ratios are discussed in this light and are found to be in agreement. W. E. Downey.

Influence of temperature on the absorption bands of alkali halide phosphors. H. Lorenz (Z. Physik, 1927, **46**, 558—567).—The extinction coefficients of the following phosphors have been determined in the range 1800—3000 Å. and at temperatures from −180° to 600°: potassium chloride+thallium, potassium bromide+thallium, potassium chloride+lead. Reduction of the temperature diminishes the width of the bands; the long wave-length band shifts 30—40 Å. to the red and the short wave-length band 10—20 Å. in the temperature range investigated. R. W. Lunt.

Residual rays of mixed crystals. F. Krüger, O. Reinkober, and E. Koch-Holm (Ann. Physik, 1928, [iv], **85**, 110—128).—Residual ray spectra in the far infra-red have been obtained for mixed crystal series of sodium, rubidium, and thallium chlorides with potassium chloride. Wave-lengths characteristic of the components do not occur, but each mixed crystal shows a wave-length of its own, intermediate between those of the components. The frequency varies approximately linearly with the concentration change. The decomposition of a mixed crystal coincides with the disappearance of its own wave-length and the appearance of those of the components. R. A. Morton.

Refraction and absorption of electrical waves by electrolytes. I. K. Zakrzewski (Bull. Acad. Polonaise, 1927, **A**, 489—503).—The absorption indices κ at temperatures of the order of 19° of water and solutions of sodium chloride, the concentrations of which ranged up to 6%, have been determined for waves of wave-length 23 cm. Calculations based on the data of Pfannenberg (Z. Physik, 1926, **37**, 767) indicate values for the refractive indices n of the more concentrated salt solutions which are considerably smaller than the value for pure water. Even after making allowance for the absorptive effect of the solvent, the experimental numbers are not in agreement with the Maxwell relation $n\kappa=\sigma\tau$ (σ=conductivity). J. S Carter.

Distribution of energy in molecules. L. S. Kassel (Proc. Nat. Acad Sci., 1928, **14**, 23—30).—Theoretical. Given a number of oscillators and a value for the total energy of these oscillators, the chance that a specified one of the oscillators shall have energy in excess of some given value is calculated for a number of types of oscillators. W. E. Downey.

Dielectric constant of liquid bromine. (Miss) A. I. Anderson (Proc. Physical Soc., 1928, **40**, 62—70).—The dielectric constant of liquid bromine was found to be 3·12 at 15°, and at a frequency of 187,000 per sec. The temperature coefficient referred to 0° is −0·00191. The value $0{\cdot}40\times10^{-18}$ is deduced for the electric moment of the bromine molecule Br_2. The electrical conductivity was found to be $9{\cdot}6\times10^{-10}$ ohm^{-1} cm.$^{-1}$ at 0°, and the temperature coefficient −0·0188 per degree. C. J. Smithells.

Variation of dielectric constant of some gases with temperature at different pressures. (Frl.) M. Forró (Z. Physik, 1928, **47**, 430—445).—The measurements were carried out in a similar apparatus to that of Herweg (Verh. Physikal. Ges., 1919, **21**, 572). The gases examined were hydrogen, nitrogen, air, carbon monoxide, and carbon dioxide between 0° and 300° and between 0 and 6 atm. For hydrogen, nitrogen, and air, the constants a and b in Debye's equation $(\epsilon-1)T/(\epsilon+2)d=aT+b$ are not found to vary with pressure; a is constant and b is zero. For carbon monoxide, the variation of b can be expressed either by a linear or by a quadratic relationship. For carbon dioxide, the variation of b follows a quadratic relationship with pressure. W. E. Downey.

Influence of electrostatic fields on dielectric constants. F. Kautzsch (Physikal. Z., 1928, **29**, 105—117).—The variation of the dielectric constant with varying electrostatic fields has been studied for ethyl ether, chloroform, and chlorobenzene. Saturation phenomena are found for ether and chloroform. Using the Debye kinetic theory of dielectrics, and extrapolating to zero voltage, the dipolar moments of ethyl ether, chloroform, and chlorobenzene are 12·02, 10·07, and $8{\cdot}50\times10^{-19}$, respectively. Herweg's data (Z. Physik, 1921, **8**, 1) lead to values 12·07, 10·26, and $6{\cdot}45\times10^{-19}$. The variation of the dielectric constant of carbon disulphide in different fields has been studied. R. A. Morton.

Refractive indices of some molten salts. O. H. Wagner (Z. physikal. Chem., 1928, **131**, 409—441).—Heck's method for the measurement of the refractive index of molten salts has been improved, and results are given at 800° for lithium, sodium, potassium, rubidium, cæsium, silver, and thallium nitrates, silver chloride, sodium chlorate, and sodium tungstate. The refractive indices show a linear decrease as the temperature rises. The negative temperature coefficients of the first eight salts are approximately equal to the decrease of refractive index produced by the decrease of density, whilst those of the remaining two salts are much greater than the density effects. The absorption of the first group lies in the ultra-violet, and of the second group in the infra-red. Increase of temperature causes the absorption in both cases to shift towards the longer wave-length region, producing in one case a decrease, and in the other an increase, of the negative temperature coefficient. Sodium tungstate possesses an infra-red absorption band at 1·777 μ. Approximate values of the atomic refractions of the cations have been determined. H. F. Gillbe.

Refractive indices and rotatory power of sodium rubidium tartrate. S. Kozik (Bull. Acad. Polonaise, 1927, **A**, 229—236).—The geometric properties of sodium rubidium tartrate (d^{16} 2·025) closely resemble those of other dialkali tartrates; $a:b:c=0·8332:1:0·4319$. Values of the refractive indices and of the angle of the optic axes at 9 wave-lengths between 670 and 405 μμ are tabulated (n_α^{17} 1·4909, n_β^{17} 1·4948, n_γ^{17} 1·4975, V_γ^{17} 50° 23′ [Na]). The crystals are feebly optically negative, with the optic axial plane b (010). Both the crystals and the solution are dextrorotatory. Values of the specific and molecular rotatory powers of the crystals and solution at 8 wave-lengths between 670 and 436 μμ are tabulated ($M[\alpha]_D$: crystals, 24,830°; solution, 6374°). The rotatory power of the crystals is the same along both optic axes. J. S Carter.

Refraction in gases. J. Tausz and G. Hornung (Z. techn. Physik, 1927, **8**, 338—355; Chem. Zentr., 1927, ii, 2040).—The constants of refraction for sulphur dioxide, methane, ethylene, acetylene, propylene, and carbon dioxide were measured for four wave-lengths (656·4, 587·6, 546·1, 435·8). From Nanton's equation, $a\Delta=[(3\pi e^2)/(e/m)]eM$, the number of dispersion electrons in the gases is computed to be 4·72, 4·46, 5·07, 4·56, 7·22, and 5·28, respectively. A. A. Eldridge.

Visible and ultra-violet dispersion of organic substances. K. Feussner (Z. Physik, 1927, **45**, 689—716).—The refractive indices of acetophenone, aniline, benzaldehyde, quinoline, nitrobenzene, and carbon disulphide have been determined to six significant figures in the range 2500—6680 Å. The method of perpendicular incidence was used in the visible region and that of crossed prisms in the ultra-violet region. For benzaldehyde and carbon disulphide the optical constants have been calculated from the experimental curves. R. W. Lunt.

Anomalous dispersion of alkali halide phosphors. M. A. Bredig (Z. Physik, 1927, **46**, 73—79).—The variation of the refractive index of phosphors of potassium bromide containing 0·003—0·03% of lead has been determined by an interferometer method in the neighbourhood of the absorption maximum at 3020 Å. The density of electrons responsible for the observed dispersion has been calculated from Voigt's formula and is found to be approximately 1/600 of the calculated density of lead atoms. R. W. Lunt.

Ultra-violet dispersion of alkali halides. Z. Gyulai (Z. Physik, 1927, **46**, 80—87).—The refractive indices of potassium chloride, bromide, and iodide, sodium bromide, rubidium chloride, and lithium fluoride have been determined in the range 1935—6150 Å. with an accuracy of 0·05%. The values for potassium chloride agree well with those of Martens for natural sylvine. Lithium fluoride is shown to be a suitable material for lenses and prisms in the ultra-violet. R. W. Lunt.

Paramagnetic rotation of the plane of polarisation. R. Ladenbourg (Z. Physik, 1927, **46**, 168—176).—A review of recent experiments in the light of the author's theory. R. W. Lunt.

Optical and electrical properties of liquids. C. V. Raman and K. S. Krishman (Proc. Roy. Soc., 1928, **A**, **117**, 589—599; cf. A., 1927, 93, 397).—Theoretical. A review of the existing theories of the optical and electrical behaviour of liquids shows that they are inadequate to explain the changes of refractivity and dielectric behaviour with density and temperature. A new theory is developed, based on the assumption that the molecules of a liquid are optically and electrically anisotropic, and that the polarisation field acting on a molecule is a function of its orientation. The formulæ deduced are used to show why with increase of density the Lorentz refraction constant usually diminishes. The changes in refractivity and dielectric constant are closely related to a change in the effective optical or electrical anisotropy of the molecule produced by the influence of its neighbours. The anisotropic constants appearing in the formulæ can be evaluated with the aid of the theory of light-scattering in liquids previously developed (*loc. cit.*). L. L. Bircumshaw.

Light-scattering in liquids at high temperatures. S. R. Rao (Indian J. Phys., 1928, **2**, 179—193).—In continuation of previous work (A., 1927, 1127), the variations with temperature of the intensity and depolarisation factor of transversely scattered light have been investigated for the liquids octane, carbon tetrachloride, ethyl acetate, benzene, chlorobenzene, and toluene. The depolarisation factor diminishes with rise of temperature, at first slowly and later more rapidly, the fall again becoming less rapid as the critical temperature is approached. The molecular anisotropy at different temperatures has also been calculated for all the liquids. Graphs obtained by plotting anisotropy against temperature, when combined with the results of previous work (*loc. cit.*) and those of other investigators, have certain peculiarities. The curves for the paraffin hydrocarbons show a remarkable and progressive change in shape with increasing length of molecule. The curves for the esters are similar to one another in form, but the anisotropy of methyl acetate is greater at all temperatures than that of ethyl acetate, and, similarly, that of ethyl formate is greater than that of ethyl acetate. The toluene curve resembles that of benzene, but the chlorobenzene curve differs from both, and, whilst it has a higher anisotropy than toluene at the ordinary temperature, it has a lower one at 54°. In all cases the anisotropy of the liquid increases with temperature and tends to attain the value for the vapour. M. S. Burr.

Valency. VIII. Extinction coefficients and molecular conductivities of Vernon's isomeric α- and β-dimethyltelluronium salts. Molecular structure of quadrivalent tellurium compounds. T. M. Lowry, (Mrs.) R. R. Goldstein, and F. L. Gilbert (J.C.S., 1928, 307—321; cf. A., 1924, i, 1212; 1905, ii, 298).—Precautions were taken during the measurement of the extinction coefficients of the α- and β-dihalides (between 2600 and 5000 Å.) to prevent hydrolysis. In spite of marked differences in colour and absorptive power between α- and β-dihalides there is a fundamental similarity of type in the absorption spectra of isomeric α- and β-compounds. The α- and β-di-iodides give twin maxima; this was also observed for iodoform and potassium tri-iodide. The two maxima given by the α-tetraiodide, $TeMe_2I_4$, agree well in wave-length and intensity with those predicted for a mixture of one molecule of α-di-iodide and one equivalent of tri-iodide ion. The molecular conductivities of the dihalides were determined to ascertain whether these compounds behave as binary or ternary electrolytes; the results show that the dihalides lose one halogen atom more or less completely by hydrolysis and the other atom forms a halogen ion, *e.g.*, $[\overset{+}{\mathrm{Te}}\mathrm{Me_2Cl}]\overset{-}{\mathrm{Cl}}+H_2O\rightleftharpoons[\overset{+}{\mathrm{Te}}\mathrm{Me_2OH}]\overset{-}{\mathrm{Cl}}+\overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}}$. The hydroxy-halides produced are strong electrolytes which are not hydrolysed to any large extent even when the equivalent of acid shown in the equation is removed. The free bases are, however, weak electrolytes like ammonia. A discussion of the structural formulæ of these compounds is given, but the authors consider the evidence insufficient to decide between alternatives. H. Ingleson.

Symmetry of electrons [in atoms]. P. Vinassa (Atti R. Accad. Lincei, 1927, [vi], 6, 454—458).—The classification of the elements is discussed and presented in tabular form according to a system which differs from the Mendeléev or Moseley systems in being based, not on the positive nuclei of the atoms, but on the number of peripheral electrons. In this system the entity is not the atom but the atom plus or minus the number of electrons equal to its valency, according as the latter is negative or positive. An element may therefore appear more than once. This leads to certain conclusions regarding a symmetrical arrangement of the electrons in the atom and explains the almost exclusive occurrence of compounds with an even molecular number (*i.e.*, with the sum of the atomic numbers of the atoms in the molecule even). O. J. Walker.

"Dative" chemical linking. A. W. C. Menzies (Nature, 1928, **121**, 457).—The term "dative" is suggested to describe that linking involved when one atom contributes both of the shared electrons. A. A. Eldridge.

Precision measurements in the *L*-series of the new element rhenium. (Frl.) I. Wennerlöf (Z. Physik, 1928, **47**, 422—425).—Three *L*-lines of rhenium have been measured with the following results: $L\alpha_1$ 1429·88, $L\beta_1$ 1236·04, and $L\beta_2$ 1204·1. W. E. Downey.

Rare earths. XXV. Examination of certain rare-earth materials for element 72 [hafnium]. W. B. Holton and B. S. Hopkins (J. Amer. Chem. Soc., 1928, **50**, 255—258).—*X*-Ray analysis of the most soluble (thorium and zirconium) fractions of two different crystallisation series from the yttrium group failed to indicate the presence of hafnium. Arc spectrum analysis showed that thorium is present and zirconium absent in Norwegian gadolinite, in the most soluble fractions from the cerium and yttrium groups, and in the accumulated soluble potassium sulphate residues from various yttrium group series. Hafnium was probably present in the latter. S. K. Tweedy.

Radiograph of a crystal having the body-centred cubic lattice. M. Majima and S. Togino (Sci. Pap. Inst. Phys. Chem. Res., 1927, **7**, 259—261).—Fifty-five Laue photographs of the *X*-ray diffraction patterns produced by α-iron are reproduced. W. E. Downey.

Determination of the crystal lattice of powdered micro-crystalline substances by means of radiograms. G. Allard (Compt. rend., 1928, **186**, 638—640).—Hull's method (A., 1922, ii, 624) may be made general for all crystalline systems by the application of Mauguin's conception of polar lattices (Bull. Soc. franç. Min., 1926, **49**, 5). Then the intervals between successive nodes of the same range of polar lattices are directly proportional to the sines of the angles of diffraction obtained directly from the radiograms. The planes of greatest reticular density give the most intense rays and the smallest angles of diffraction. The position and characteristics of all the rays of the radiogram can then be determined. The application of the method of least squares to the goniometric measurements increases the precision of the method. J. Grant.

***X*-Ray examination of passivity.** F. Krüger and E. Nähring (Ann. Physik, 1927, [iv], **84**, 939—948).—By using the Debye–Scherrer method on finely-powdered specimens of iron, nickel, and chromium in the passive state evidence has been obtained in support of the view that passivity is associated with the formation of a layer of oxide on the metal. R. W. Lunt.

Crystal structure of graphite. H. Ott (Ann. Physik, 1928, [iv], **85**, 81—109).—The graphite lattice has been investigated by methods applied earlier to carborundum (A., 1926, 339, 562). Specimens of graphite embedded in calcite proved specially suitable. A lattice identical with that of Hassel and Mark (A., 1924, ii, 721) and Bernal (A., 1925, ii, 17) was deduced. The *X*-ray study indicates that the carbon atoms in graphite are tervalent and it is argued that Steiger's (A., 1920, ii, 355) calculations on the energy of linking likewise show tervalency to obtain in the aromatic linking. R. A. Morton.

Crystal structure of carbonates. C. Schaefer, F. Matossi, and (Frl.) F. Dane (Z. Physik, 1927, **45**, 493—500).—The crystal structure of magnesite, siderite, dolomite, strontianite, and aragonite has been investigated from observations of the transmissibility of the crystal in the range 6·2—7·5 μ. The results interpreted according to Brester's theory are in agreement with the view that the oxygen atoms are placed at three of the corners of a regular tetrahedron with the carbon atom at the centre. It is thought that the data of Schaefer and Schubert on nitrates (A., 1918, ii, 282) indicate that the nitrate group consists of a pyramidal structure in which the nitrogen atom is situated at one apex and the oxygen atoms are situated at the three basal corners.

R. W. LUNT.

Constitution of the silicates. W. WAHL (Z. Krist., 1927, 66, 33—72).—Structural formulæ are derived for complex alkali aluminosilicates having an equal number of aluminium and alkali metal atoms on the assumption of a complex univalent anion of which the central aluminium atom is quadrivalent. More complex anions are formed by the union of SiO_3 or Si_2O_5 groups. In those compounds having a fewer number of aluminium than alkali atoms certain of the former are regarded as sexavalent, the complex anions being then tervalent. Similar types of formulæ are proposed for the alkaline-earth aluminosilicates. Compounds containing hydrogen are in many cases regarded as acid salts, and their formulæ are derived on this principle and on those given above.

H. F. GILLBE.

Constitution of the silicates. W. WAHL (Z. Krist, 1927, 66, 173—190).—The structure of the additive compounds formed between aluminosilicates and inorganic salts is discussed. Natural non-aluminiferous silicates are regarded as salts of complex anions containing sexavalent silicon; more complex types of anions are produced by the linking of silicon dioxide groups by oxygen chains. Minerals of the pyroxene, amphibole, and mellilite groups are formulated on the hypothesis of bridge formation by SiO_3 groups and oxygen atoms. The structure and mode of polymerisation of the complex silicates are surveyed in the light of their infra-red absorption spectra.

H. F. GILLBE.

Constitution of aluminosilicates, conditions of their formation, and transformation in soil. W. WAHL (Finska Kemistsamfundets Medd., 1927, 36, 22—61; Chem. Zentr., 1927, ii, 1682—1684; cf. preceding abstracts).—In those silicates which are formed at high temperatures, aluminium has a co-ordination number 4, whilst for those formed at low temperatures it tends to be 6. Formulæ with two aluminium atoms are improbable; in the crystalline state the aluminosilicates are highly polymerised. The reactions leading to the formation of minerals in the magma consist of (*a*) dehydration processes and (*b*) additive reactions; the effect of these processes is traced in the formation of hornblende and muscovite. The formation of biotite is summarised as follows:

$$\text{(i)}\ 6K[Al^{IV}O(SiO_3)]+12H_2O= K_6H_{12}[Al_6{}^{VI}O_6(OH)_{12}(SiO_3)_6],$$

$$\text{(ii)}\ 6Mg_2SiO_4+12H_2O=6MgSiO_2(OH)_2+6Mg(OH)_2,$$

$$\text{(iii)}\ K_6H_{12}[Al_6{}^{VI}O_6(OH)_{12}(SiO_3)_6]+6MgSiO_2(OH)_2= K_6H_{12}[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+12H_2O,$$

$$\text{(iv)}\ (K,H)_6H_{12}[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+6Mg(OH)_2= (K,H)_6Mg_6[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+12H_2O.$$

A. A. ELDRIDGE.

Space-group of helvite. C. GOTTFRIED (Z, Krist., 1927, 65, 425—427; Chem. Zentr., 1927, ii, 1537).—The edge of the elementary cell of helvite. $(Mn,Fe)_3Be_3(SiO_4)_3,MnS$, is 8·52$_5$ Å.; space-group T_d^4. There are 2 molecules in the elementary cell.

A. A. ELDRIDGE.

Structure of zinc hydroxide. C. GOTTFRIED and H. MARK (Z. Krist., 1927, 65, 416—424; Chem. Zentr., 1927, ii, 1537).—In the elementary cell of edges 6·73, 7·33, 8·47 Å. there are 8 molecules; the space-group is V_h^{16}.

A. A. ELDRIDGE.

Crystal structure of the system cadmium-mercury. R. F. MEHL (J. Amer. Chem. Soc., 1928, 50, 381—390).—The crystal structure of annealed cadmium amalgams was deduced from *X*-ray powder photographs. The spectra for all compositions in the mercury-rich ω-field are identical in type and dimensions and correspond with either a face-centred tetragonal lattice having $c:a=0{\cdot}520$, or with a body-centred tetragonal lattice having $c:a=0{\cdot}740$. The crystal structure of pure mercury at the m. p. is probably the same as that for ω-solid solutions. Solid solutions in the α-range (cadmium rich) have a triangular close-packed lattice with $c:a=1{\cdot}89$. Both α- and ω-solid solutions contain hexagonal lattices of very similar dimensions, and in each case simple substitution occurs. There are no intermetallic compounds at the ordinary temperature.

S. K. TWEEDY.

Structure of antimonite. C. GOTTFRIED (Z. Krist, 1927, 65, 428—434; Chem. Zentr., 1927, ii, 1537).—The edges of the rhombic cell are 11·39, 11·48, 3·89 Å.; $a:b:c=0{\cdot}992:1:0{\cdot}338$. The cell contains 4 molecules of Sb_2S_3. The most probable space-group is V_h^1.

A. A. ELDRIDGE.

Isomorphism of tervalent molybdenum and iron. G. CAROBBI (Gazzetta, 1928, 58, 35—45).—The isomorphism of compounds of the type R_2MoCl_5,H_2O and R_2FeCl_5,H_2O, where $R=NH_4$ or K, has been investigated. The ammonium compounds are rhombic and isomorphous, the crystallographic constants and molecular volumes of the two salts being practically equal. Isomorphous mixtures of the two salts have been obtained containing up to 10% of the molybdenum compound. The potassium salts are also rhombic and isomorphous and form mixed crystals containing up to 17% of the molybdenum salt. The *compound* $(NH_4)_4MoCl_7,H_2O$ has been prepared and a new case of anomalous mixed crystal formation is described, viz., that between ammonium chloride and molybdenum trichloride.

O. J. WALKER.

Structure of tetraphenylsilicanē, $SiPh_4$. H. MARK and H. MEHNER (Z. Krist., 1927, 65, 455—460; Chem. Zentr., 1927, ii, 1538).—The edges of the unit cell of tetragonal tetraphenylsilicane, which contains 2 molecules, are 11·50 and 6·97 Å. The space-group is V_d^4 or D_{4h}^9.

A. A. ELDRIDGE.

Structure of some methane derivatives. H. MARK and W. NOETHLING (Z. Krist., 1927. 65, 435—454; Chem. Zentr., 1927, ii, 1537—1538).—The elementary cell of the cubic modification of tetranitromethane has an edge of 9·2 Å. and contains 4 molecules. The molecule has trigonal symmetry, indicating the formula $(NO_2)_3C{\cdot}O{\cdot}NO$. The elementary cell of tetramethylmethane has an edge of 12·48 Å., and contains 8 molecules; this molecule also has trigonal symmetry. The molecular constitution cannot be determined crystallographically. For trigonal triphenylcarbinol the axes are *a* 17·9, *c* 12·5 Å.; edge of unit cell containing 3 mols., 11·1 Å. Corresponding values for triphenylbromomethane are 14·05, 22·0, 10·8 Å., respectively. The probable space-groups are discussed. A. A. ELDRIDGE.

Structure and dimensions of the ethane molecule. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 37—41).—Theoretical. A model of the ethane molecule is described. W. E. DOWNEY.

Lattice structure of ethane. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 40—45; cf. preceding abstract).—The *X*-ray diffraction effects as calculated from the model of the ethane molecule are in good agreement with those determined experimentally. W. E. DOWNEY.

Crystal structure of iodoform. J. F. WOOD (Proc. Durham Phil. Soc., 1927, **7**, 168—171).—Laue and rotation photographs show the iodoform molecule to be a tetrahedron in shape. The carbon atom is inside and the hydrogen and iodine atoms are at the corners. The line joining the hydrogen and carbon atoms is the trigonal axis of the molecule. The unit cell contains 2 molecules. W. E. DOWNEY.

Structure of pentaerythritol. H. MARK and K. WEISSENBERG (Z. Krist., 1927, **65**, 499—500; Chem. Zentr., 1927, ii, 1537).—The enantiomorphism demonstrated by Westenbrink and van Melle (*ibid.*, **64**, 548) is not at variance with the pyramidal configuration of the crystal molecule demonstrated by the authors. A. A. ELDRIDGE.

Pyro- and piezo-electricity in pentaerythritol. H. MARK and K. WEISSENBERG (Z. Physik, 1928, **47**, 301).—The fact that pyro-electricity has been detected in pentaerythritol is of importance in determining the crystal structure (cf. preceding abstract). R. A. MORTON.

Polarity and piezo-electric excitation. A. HETTICH and A. SCHEEDE (Z. Physik, 1927, **46**, 147—148).—Arguments are advanced claiming to invalidate the suggestion of Mark and Weissenberg (Z. Krist., 1927, **65**, 435) that the piezo-electric excitation of pentaerythritol affords evidence of polarity in the direction of the principal axis. R. W. LUNT.

Symmetry of crystals of pentaerythritol. H. SEIFERT (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 289—293).—As a result of crystallographic investigation pentaerythritol has been shown to belong to the symmetry class S_4. Only the old tetrahedral model of the pentaerythritol molecule can be reconciled with this class, and not Weissenberg's pyramidal model (A., 1926, 934). On the basis of the results of *X*-ray analysis the origin of the optical anomalies of pentaerythritol is discussed. This compound is apparently the first chemically pure substance with such anomalies which has been crystallographically described. M. S. BURR.

Crystal structure of *p*-nitrotoluene. B. N. SREENIVASAIAH (Indian J. Phys., 1928, **2**, 151—166).—The crystal structure of *p*-nitrotoluene has been examined by the Hull powder method and also by the Laue method. The unit cell appears to be made up of 8 asymmetric molecules and the edges of the cell have the following dimensions: $a=10{\cdot}1$, $b=11{\cdot}18$, and $c=12{\cdot}3$ Å. The crystal structure is the simple orthorhombic lattice Γ_0 in the holohedral class and belongs to the space-group Q_h^1 $(2Di-1)$. Solid *p*-nitrotoluene has *d* 1·305. M. S. BURR.

Preparation of large single crystals. H. C. RAMSPERGER and E. H. MELVIN (J. Opt. Soc. Amer., 1927, **15**, 359—363).—The preparation of large single crystals of substances of m. p. up to 1500° is described. The essential conditions are: (1) a containing vessel sufficiently thin to yield under the strains produced by the cooling crystal (pure platinum foil 0·025 mm. thick is satisfactory); (2) the formation of an initial crystal at the base of the dish; (3) the temperature isotherms should be nearly horizontal to prevent convection currents; (4) the cooling must be sufficiently slow to remove all strains in the crystals. A furnace suitable for such operations is described together with a method of controlling the temperature. Single crystals of about 1 cm. edge of lithium fluoride, sodium chloride, sodium nitrate, and mercuric bromide have been produced in this way. The optical properties of these crystals are under examination. R. W. LUNT.

Magnetic properties of single crystals of zinc and cadmium. J. C. MCLENNAN, R. RUEDY, and (MISS) E. COHEN (Nature, 1928, **121**, 351).—Crystals of zinc and cadmium were obtained by Bridgman's method, and the magnetic susceptibility was determined for every 15° on rotation, correction being applied for the iron content. For zinc, the specific susceptibility in a direction parallel or perpendicular to the principal axis of the crystal is $-0{\cdot}183\times10^{-6}$ or $-0{\cdot}147\times10^{-6}$, respectively,; for cadmium, the corresponding values are $-0{\cdot}276\times10^{-6}$ and $-0{\cdot}169\times10^{-6}$. A. A. ELDRIDGE.

Relation of specific heat to ferromagnetism. J. R. ASHWORTH (Nature, 1928, **121**, 323).—The temperature coefficient of resistance and the thermoelectric power of ferromagnetic substances are abnormal below the critical temperature; the true specific heat rises to a high value (C_θ) at the critical temperature, and immediately above this temperature there is an abrupt change (ΔC) to a lower value. If m and n are the numbers of atoms of at. wt. A in the molecule below and above the critical temperature, respectively, $maC_\theta=5na\Delta C$. Further, $n\Delta CJ\rho=278R'I_0^2$, where I_0 is the maximum intensity of magnetisation, R' the reciprocal of Curie's constant, J Joule's equivalent, and ρ the density of the material. Heusler's alloy, like iron, cobalt, nickel, and magnetite, satisfies these and other energy relations. A. A. ELDRIDGE.

Grating theory of electrolytic conduction in crystals. A. SMEKAL (Z. Physik, 1927, **45**, 869—877).—Braunbek's theory of the mechanism of electrolytic conduction in crystals (A., 1927, 1016) is held to be unsound and the agreement with experiment in the case of potassium chloride consequently spurious. R. W. LUNT.

Temperature variation of the electrical conductivity of crystals. N. Ussataja and B. Hochberg (Z. Physik, 1927, 46, 88—92).—The electrical conductivities of fluorspar, sodium nitrate, sodium chloride, and mica have been determined in the following temperature ranges, respectively: 200—500°, 20—300°, 200—740°, −100—500°. The conductivity, α, is related to the absolute temperature, T, according to the equation $\log \sigma = A/T + B$ for the first two substances, and for sodium chloride below 600°; in accordance with other work on heteropolar crystals A is approximately constant $(1{\cdot}1 \pm 0{\cdot}1)\times 10^4$. The data obtained are discussed with reference to the phenomena of dielectric absorption. R. W. Lunt.

Constitution of solid electrolytes. II. Cuprous bromide. J. N. Frers [with F. Leopold] (Ber., 1928, 61, [*B*], 377—392; cf. A., 1927, 521).—Cuprous bromide, tested as described for cuprous chloride (*loc. cit.*), is found to be a true, mixed conductor in which ionic and electronic conduction are due solely to the copper ion. A complete, continuous transition from exclusively electronic to exclusively ionic conduction is caused by rise of temperature within the range, about 200—330°. Increase in the electrolytic component of the conductivity is caused by surface action, prolongation of the duration of electrolysis, and, to a remarkable extent, by the discharge of silver or lead ions at the cuprous bromide. The observations are readily explained by the supposition of a functional differentiation of the ions in the lattice.

H. Wren.

Contact potential between the solid and liquid phases of bismuth. P. H. Dowling (Physical Rev., 1928, [ii], 31, 244—250).—Solid bismuth has a contact potential with respect to the melted metal of −0·02 volt. The effect of surface charges on melting conditions is discussed.

A. A. Eldridge.

Reflexion, dispersion, and absorption of calcite in the neighbourhood of 7 μ. F. Matossi and (Frl.) F. Dane (Z. Physik, 1927, 45, 501—507).—The reflexion, dispersion, and absorption of calcite have been investigated for various orientations of the crystal to the incident radiation in the range 6·40—7·10 μ. R. W. Lunt.

Deformations and changes in optical properties of quartz under the influence of the electric field. N. T. Ze (J. Phys. Radium, 1928, [vi], 9, 13—37).—The piezo-electric deformations in a direction normal to the optical and electrical axes of a rectangular parallelepiped of quartz, placed in an electric field in the direction of its binary axis, follow Curie's rule up to 3000 volts and then tend towards a limit at about 160,000 volts. They are equal and opposite to those found in the direction of the optical axis. The dielectric deformations are made up of a contraction and an extension in the directions of, and normal to, the lines of force, respectively, and are proportional to the electrical energy per unit volume of the condenser. The variations in birefringence are linear. They change in sign with the sense of the electrical field and are therefore an electro-optical phenomenon, distinct from the Kerr effect.

J. Grant.

Internal strain in *X*-ray photographs. K. Becker (Z. Physik, 1928, 47, 454—456).—Polemical against von Göler and Sachs (A., 1927, 1130).

W. E. Downey.

Change in structure and electrical resistance during cold working of metals. G. Tammann and M. Straumanis (Z. anorg. Chem., 1928, 169, 365—380).—The fall in resistance of hard-drawn copper wire may be considerable even when very little recrystallisation has occurred, whereas the changes in tensile strength and extensibility run approximately parallel with the change in structure. Heating the wire at above 600° causes the resistance to increase again, apparently owing to a change in the structure of the matrix in which the crystallites are embedded. At 800°, the crystallites are so soft that their corners become rounded, with consequent formation of lacunæ, which cause a further increase in the resistance. In copper, there is a definite direction of slip, but this is not so marked in aluminium, which probably accounts for the fact that the resistance of pure aluminium is not affected by cold drawing. R. Cuthill.

Atom deformation in cold wrought tungsten. W. Geiss and J. A. M. van Liempt (Z. Physik, 1927, 45, 631—634).—From measurements of the electrical conductivity of tungsten it has been shown that atom deformation exists in cold wrought specimens.

R. W. Lunt.

Effect of compression and tension on brass crystals. G. Sachs and H. Shoji (Z. Physik, 1927, 45, 776—796).—The mechanical deformation of single crystals of brass in the form of rods has been examined for compressions and for tensions up to 200 kg./mm.² For forces of the order of 4 kg./mm.² such crystals exhibit mechanical hysteresis. R. W. Lunt.

Shrinkage in metals and alloys. F. Sauerwald, E. Nowak, and H. Juretzek (Z. Physik, 1927, 45, 650—662).—Measurements have been made of the shrinkage on solidification of copper, lead, tin, aluminium, zinc, brass, copper–tin (30%), copper–tin (20%), and cast iron. From observations in an inert atmosphere of hydrogen or nitrogen reproducible values were obtained which were independent of the nature of the containing vessel. The values were in agreement with the accepted values for thermal expansivities. Except in the cases of cast iron and bronze no expansion was recorded at the commencement of solidification. R. W. Lunt.

Electrification produced by friction between gases and solid surfaces. I. M. A. Schirmann (Z. Physik, 1927, 46, 209—236).—Two types of electrification by friction have been identified during the operation of mercury vapour diffusion pumps: the first, which takes place at low rates of vapour flow, is due to friction between mercury droplets and glass surfaces; the second takes place at flow rates of the order of 10^4 cm./sec. and is due to friction between the vapour and glass surfaces. Confirmatory experiments have been carried out by releasing compressed nitrogen from a highly insulated metal bomb in which the bomb attains a potential of several hundred volts. R. W. Lunt.

Relation between conductivity and thermo-electric power in magnetic fields. V. GIAMBALVO (Nuovo Cim., 1927, 4, 176—189; Chem. Zentr., 1927, ii, 1444).—The thermo-electric power of antimony-copper alloys in a magnetic field decreases with increase of strength of the field; the changes were measured for weak fields. The results accord with theoretical predictions. A. A. ELDRIDGE.

Schtschukarev's magneto-chemical effect. S. GORBATSCHEV (Trans. Sci. Chem.-Pharm. Inst. [Moscow], 1925, 12, 31—38; Chem. Zentr., 1927, iii, 1797).

Electrical conductivity of palladium in a vacuum and in different gases. A. PUODŽIUKYNAS (Z. Physik, 1927, 46, 253—270).—The conductivity of untreated palladium wire increases by about 15% when the gas contained in the metal is removed by ionic bombardment in a vacuum; the increase in conductivity was proportional to the amount of gas removed, and the total amount of gas evolved was approximately 300 times the volume of the wire. After treatment for 50 min. at bright red heat in pure hydrogen the conductivity fell by 50% and 1486 volumes of gas were absorbed. When the wire was maintained in hydrogen at 1 atm. its conductivity rose slowly, and more rapidly if the wire was in a vacuum until about 900 volumes of gas had been evolved; this indicates that after glowing in hydrogen the metal is supersaturated with hydrogen. When the gas is removed by heating in a vacuum the wire absorbs hydrogen slowly and nitrogen not at all; if, however, the gas is removed in the cold the wire becomes activated and absorbs approximately the same amount of nitrogen or hydrogen.

R. W. LUNT.

Variation of the resistivity of thin layers of platinum as a function of their thickness, and the influence of oxygenated substances. A. FÉRY (J. Phys. Radium, 1928, [vi], 9, 38—48).—The optical density, D, measured by the Fabry microphotometer, is proportional to the thickness (a, in mμ) of a layer of platinum deposited on a sheet of mica by cathodic disintegration, and the relation $a=63{\cdot}4D$ may be used for the determination of the latter. By the elimination of water vapour, deposits 4·4—243 mμ thick, and having resistivities (ρ in ohms-cm.) stable for more than a year, were obtained, for which the relation $\log 10^5\rho=5{\cdot}7-0{\cdot}0156a$ was established. The adsorption of vapour of water or of its electrical analogues (sulphur dioxide, methyl alcohol) increased the resistance considerably, to extents which increased with the specific inductive capacities of the vapours at the temperature concerned. These deposits probably have an internal structure which differs from that of the compact metal, but, as the nature of the results indicates, is homogeneous. J. GRANT.

Electrical conductivity of borax. S. OKA (J. Soc. Chem. Ind. Japan, 1927, 30, 625—632).—The change of electrical conductivity of borax from the molten state to the vitreous state was investigated. The specific conductivity, κ, of the molten borax was found to be much less than that of most of the other molten salts, *e.g.*, $\kappa\times10^3$ is 155 at 800°, 71 at 700°, 17·5 at 600°, and 1·76 at 500°. No break point was found in the conductance-temperature curve at the temperature that corresponds with the m. p. Borax at lower temperatures was in a vitreous state. In the diagram of $\log\kappa$ against $1/T$ a straight line of the type $\log\kappa=-A/T+B$ was found connecting the points found between 660° and 480° from the melted to the vitreous state; the points for the lower temperatures were on another similar straight line. The two intersected at about 480°, but the significance of this point is not known. N. KAMEYAMA.

Conductivity of, and electric absorption in, insulators [amber, sulphur, and paraffin wax], and the effect on them of *X*- and γ-rays. H. NEUMANN (Z. Physik, 1927, 45, 717—748).—The following values of the resistivities of amber, sulphur, and paraffin wax have been assigned from elaborate measurements in a vacuum: $10^{20}-10^{18}$ ohms, $2\times10^{18}-2\times10^{19}$ ohms, and 3×10^{18} ohms, respectively. The dielectric absorption and subsequent slow release of charge have also been examined in these substances.

R. W. LUNT.

Relation of diamagnetic susceptibility in the liquid and vapour states. V. I. VAIDYANATHAN (Indian J. Phys., 1928, 2, 135—150).—Measurements have been attempted of the magnetic susceptibilities of the vapours of the following liquids: carbon disulphide, benzene, *n*-pentane, *n*-hexane, carbon tetrachloride, methyl acetate, ethyl and methyl formate, ether, chloroform, acetone, and heptane. The method employed is based on the fact that a dia- or para-magnetic rod tends to orient itself across or along the field when suspended in a suitable heterogeneous field, and this orienting force is different when the rod is surrounded by different media (cf. Glaser, A., 1925, ii, 82; Hammar, A., 1926, 1197). The results are compared with those obtained by the author by a method described elsewhere. For carbon disulphide, benzene, pentane, and hexane vapours both methods yield a value 20—35% higher than for the corresponding liquids. This is larger than can be accounted for by the experimental errors. In the other cases the differences are smaller. The question of the influence of the proximity of neighbouring atoms or molecules on the diamagnetic properties of the atom is discussed. M. S. BURR.

Allotropic transition point of aluminium. W. GUERTLER and L. ANASTASIADIS (Z. physikal. Chem., 1928, 132, 149—156).—Aluminium undergoes no transition at 560°; the observed thermal and electrical phenomena are due to the presence of silicon.

H. F. GILLBE.

Method of measuring the radiant heat emitted during gaseous explosions. C. H. JOHNSON (Phil. Mag., 1928, [vii], 5, 301—322).—A method is described enabling discrimination to be made between the emission of radiant energy from the wave-front and that from the hot products of combustion from a gaseous explosion. The experiments were made in a long, narrow explosion vessel in which the rapid cooling of the burnt gases behind the explosion wave reduced to practically negligible proportions the amount of radiation from that source. A method of calibrating a linear thermopile, placed at some distance from the bomb, is described which has allowed of a quantitative extension of the previous work of Garner and Johnson (A., 1927, 184). Water vapour and other catalysts have been shown to have a marked effect on the infra-red emission from the wave-front in explosions of carbon monoxide–oxygen mixtures. In a dry gas mixture 7% more of the total heat of combustion was radiated from the wave-front than in a mixture containing 1·9% of water vapour. The importance of this radiation factor in connexion with the effects of water vapour and other catalysts on the spreading of flame in explosions is stressed.

A. E. Mitchell.

Thermal data of tin. J. N. Brönsted (Z. physikal. Chem., 1928, **131**, 366—370).—Polemical.

H. F. Gillbe.

Molecular aggregation. Theory of liquefaction. Y. Rocard (J. Phys. Radium, 1927, [vi], 8, 495—501).—The hypothesis of molecular aggregation independent of all molecular force, postulated by Duclaux and opposed by the author (A., 1925, ii, 1045), is shown mathematically to be incompatible with the variations with temperature of the viscosity of a gas. The assumption of intermolecular forces, with a dipole for each molecule, means that each double molecule has a double dipole. Such double molecules will thus tend to aggregate more readily than single molecules. A possible explanation of the mechanism of liquefaction is thus afforded, from which the vapour-pressure curve of a gas at low temperatures may be derived.

J. Grant.

Conception of polarity derived from physical measurements and its relations to the electronic configuration of aromatic organic compounds. J. F. T. Berliner (J. Physical Chem., 1928, **32**, 293—306; cf. A., 1927, 506).—Theoretical. The entropies of vaporisation of the nitroanilines and toluidines are greater than 13·8 g.-cal./degree, the value considered by Hildebrand (A., 1918, ii, 61) to be the normal for the conditions specified, and this is considered to indicate association of these liquids. The mononitrotoluenes similarly considered are practically non-associated. Using Crocker's conception of the electronic structure of benzene (A., 1922, i, 924), a relationship between electronic configuration and association derived from vapour-pressure measurements is shown to exist and is applied to interpret the variations in the entropies of vaporisation of the compounds in question.

L. S. Theobald.

Metal crystals. VI. Temperature variation of the thermal resistivity of normal metals. E. Grüneisen (Z. Physik, 1927, **46**, 151—159).—The author's earlier theory of the additivity of the "metallic" and "non-metallic" portions of thermal conductivity of crystalline metals (A., 1927, 1017) has been extended by showing that the temperature variation of each of these portions can be expressed in terms of the Debye atomic heat function for the metal concerned. The specific thermal conductivity, w, of a pure metal can on this basis be expressed in the form $w=(1+k\theta/T)f(\theta/T)/Z$, where k is the ratio of the "non-metallic" term w_i to the "metallic" term w_m ($w=w_i+w_m$), T is the temperature Abs., Z a universal constant, $2{\cdot}2\times10^{-8}$ watts degrees^{-2}, and $f(\theta/T)$ the Debye atomic heat function. For pure annealed aluminium, copper, and gold the experimental values of w at 21·2°, 83·2°, 273°, and 373° Abs. are in close agreement with those calculated by the above expression. In impure samples of metals the thermal conductivity does not become zero at 0° Abs., but passes through a minimum in the neighbourhood of 30° Abs.; for such substances the thermal conductivity is given by $w'=w+\alpha/ZT$, where w refers to the pure metal and α is a parameter depending on the purity of the metal and its mechanical treatment.

R. W. Lunt.

Change of properties of substances on drying. H. B. Baker (J. pr. Chem., 1928, [ii], **118**, 96).—A reply to Balarev (A., 1927, 613). The presence of phosphorus in Balarev's dried liquids is probably due to phosphorus trioxide in the pentoxide used.

C. Hollins.

Determination of vapour pressures of sodium and potassium chlorides. S. Horiba and H. Baba (Bull. Chem. Soc. Japan, 1928, 3, 11—17).—Measurements were made by a static method, using a quartz spring manometer sensitive down to a pressure of a few mm., on sodium and potassium chlorides over the ranges 800—1240° and 900—1250°, respectively. The heats of vaporisation, Q, calculated by the Clausius–Clapeyron equation were found to be 39·6 and 36·6 kg.-cal., respectively. Combining these data with those of other workers for the latent heat of fusion, M, and the heat of dissociation of the solid into gaseous ions, U, by means of the relationship $U=M+Q+D$, the heats of dissociation, D, of the gaseous chlorides into gaseous ions were found to be 18 and 42 kg.-cal., respectively. The dissociation constant of gaseous sodium chloride was calculated to be of the order of 10^{-39}.

S. J. Gregg.

Efflorescence of sodium sulphite. D. N. Tarassenkov (Z. anorg. Chem., 1928, **169**, 407—412).—The vapour pressure of the system $Na_2SO_3,7H_2O \rightleftharpoons Na_2SO_3+7H_2O$ between 0° and 70° has been measured. At 15° the pressure is 9·3 mm.

R. Cuthill.

Evaporation of tungsten under various pressures of argon. G. R. Fonda (Physical Rev., 1928, [ii], **31**, 260—266).—The rate of evaporation of tungsten filaments at 2870° Abs. in a mixture of argon (86%) and nitrogen (14%) varies from 2×10^{-9} to 230×10^{-9} g./cm.^{2} sec. as the pressure is reduced from 1650 to 0 mm. The author's view that the evaporating atoms diffuse through a surrounding film of stationary gas is supported by the fact that $m\propto P\log b/a$, where m is the rate of evaporation, P the pressure, and a and b are the diameters of the filament and gas film (calculated from Langmuir's equation for heat loss), respectively, is constant for gas pressures above 100 mm.

A. A. Eldridge.

Vitreous state and dilatation of glasses. M. Samsoen (Ann. Physique, 1928, [x], 9, 35—127).—The linear and cubic dilatations of a number of soda, silica, silicoborate, and industrial glasses have been determined by the Chevenard and ordinary industrial methods, respectively, at temperatures between −200° and 1500°. Boron and phosphorus enamels, resins, pitch, sucrose, "orca" (polymerised acraldehyde), glycerol, and sodium thiosulphate were also examined. The anomalous linear dilatation (A., 1926, 567, 568, 570; B., 1926, 709) previously considered to be a property of silica dissolved in complex glasses is shown to be common to all the substances examined, when in the amorphous state. In the case of cubic dilatation, the anomaly takes the form of a change in the dilatation coefficient. Experiments on the influence of temperature on the rate of crystallisation of glycerol led to the conclusion that the molecules of a solid in the amorphous state are stationary with respect to one another, and that all crystallisation is impossible in the true amorphous state below the transformation temperature. This is in accord with the perfect isotropy of fluids and with the mechanical properties of solids. The transformation temperature, which exists for all amorphous substances, depends only on the viscosity. With thiosulphate and sodium silicates rich in sodium, glasses were obtained by rapid cooling of the substance below the transformation temperature. With boric anhydride and glycerol, the transformation temperatures were also determined from the change in specific heat accompanying them, but a value 25° lower than that given by the dilatation method was always obtained. This is unexplained. The curves expressing the variations of the transformation temperature as a function of chemical composition showed maxima at compositions corresponding with what are usually considered to be definite compounds, in particular with the compounds $2SiO_2,Na_2O$, $2B_2O_3,PbO$, and $2B_2O_3,Na_2O$. Grenet's law of additivity is not acceptable in its entirety, except perhaps in cases where the crystalline system does not correspond with a definite compound or a eutectic. The m. p. of glycerol was found to be 18·07°. J. GRANT.

Chemical affinity, cohesion, compressibility, and atomic volume. Effects of internal pressures. T. W. RICHARDS (J. Chim. phys., 1928, 25, 83—119).—A summary of numerous previous papers. H. F. GILLBE.

Reciprocal attraction and repulsion of gas molecules and their bearing on the theory of internal friction. L. SCHAMES (Physikal. Z., 1928, 29, 91—94).—Mathematical. It is shown that the potential energy, Φ, between two molecules when represented by the expression $-A/r^m+B/r^n$ for the attractive and repulsive forces, respectively, leads to the values $m=8$, $n=8$ for helium. W. E. DOWNEY.

Surface tensions and parachors of fused organic substances. S. S. BHATNAGAR and B. SINGH (J. Chim. phys., 1928, 25, 21—27).—The surface tensions of fused naphthalene, α-nitronaphthalene, phenanthrene, phenol, *o*- and *p*-nitrophenol, and *p*-nitrotoluene have been determined by the use of a modified form of Bircumshaw's apparatus (A., 1926, 895). The parachors of the nuclei of naphthalene and phenanthrene and of the hydroxyl group have been calculated and used in the determination of the theoretical parachors of the above substances, which agree well with those observed. L. F. GILBERT.

Deviation of gaseous mixtures from Dalton's law of partial pressures due to chemical causes. III. Hydrogen chloride and methyl alcohol. J. SHIDEI (Bull. Chem. Soc. Japan, 1928, 3, 25—42; see this vol., 229).—The apparatus was arranged so that the gases came in contact only with mercury and glass, special care being taken to remove all traces of adventitious air. The gaseous pressure of methyl alcohol at several different concentrations was measured at a number of temperatures between 70° and 130°, and the relationship between the pressure and the density of the gas was found to be rectilinear. The pressures of gaseous hydrogen chloride over the range 50—130° show good agreement with van der Waals' equation if the temperature variation of the constants *a* and *b* be corrected for by van Laar's equations. Measurements on the mixture show a diminution in pressure on mixing the gases, which is discussed in the light of the reactions $MeOH+HCl \rightleftharpoons MeOH,HCl$; $MeOH,HCl \rightleftharpoons MeCl+H_2O$. The observed diminutions are too small, however, to permit the accurate determination of the extent of the reactions. S. J. GREGG.

Dielectric constants of binary mixtures. Electric moments of certain nitro-derivatives of benzene and toluene. J. W. WILLIAMS and C. H. SCHWINGEL (J. Amer. Chem. Soc., 1928, 50, 362—368).—Dielectric constant and density data for 25° are recorded for benzene solutions of nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzene, *s*-trinitrobenzene, and *o*-, *m*-, and *p*-nitrotoluene. The changes produced in the electric moments of the solute molecules by substituent nitro-groups are closely parallel to the effects produced by hydroxy- and chloro-groups (Smyth and Morgan, A., 1927, 611). The results, which are critically discussed, are in agreement with previously published work. S. K. TWEEDY.

Internal friction of solutions and mixtures. W. HERZ and G. SCHELIGA (Z. anorg. Chem., 1928, 169, 161—172).—The viscosity at 20°, 40°, and 60° of solutions of iodine, phenanthrene, and naphthalene in benzene, toluene, carbon tetrachloride, carbon disulphide, and acetone increases with increasing concentration, the effect becoming less pronounced, however, with rise in temperature, and being usually greatest with phenanthrene, and least with iodine. With solutions containing both naphthalene and phenanthrene, the viscosity usually differs only slightly from the value calculated additively from the viscosities of the corresponding solutions with only one solute. The viscosity of mixtures of carbon disulphide with benzene or toluene exhibits negative deviations from the mixture rule. Equal amounts of maleic and succinic acids increase the viscosity of alcohol by nearly the same amount, but fumaric acid has a greater effect. The viscosities of aqueous solutions of *d*-tartaric acid and racemic acid of the same concentration are usually unequal, but the difference varies both in sense and magnitude with change in the temperature and concentration. With *l*-malic acid and *dl*-malic acid, however, the difference is always negligible. The viscosity at 20° of aqueous solutions of sodium chloride can be represented fairly satisfactorily by an equation of the type $1/x=ky^n$, where y is the viscosity, x is the concentration in g.-mol. of water/g.-mol. of salt, and k and n are constants. With solutions of magnesium chloride, however, no such equation can be employed, and the viscosities are considerably greater than those of sodium chloride solutions of equivalent concentrations.

R. CUTHILL.

Volume changes attendant on mixing pairs of liquids. J. B. PEEL, W. M. MADGIN, and H. V. A. BRISCOE (J. Physical Chem., 1928, **32**, 285—292; cf. A., 1927, 521; this vol., 21).—For 28 pairs of non-aqueous liquids the volume changes have been calculated from the densities at 25±0·1° of the pure liquids and of various mixtures. The absence of any relation between the volume and temperature changes accords with the values obtained for the heat of mixing and the external work associated with the change in volume, the latter being only an insignificant fraction of the energy change involved. The thermal effect must be attributed to changes in the internal work, and in many cases is due to chemical change.

L. S. THEOBALD.

New kinds of mixed crystals. II. Formation of mixed crystals by barium sulphate and potassium permanganate. H. G. GRIMM and G. WAGNER (Z. physikal. Chem., 1928, **132**, 131—148; cf. A., 1927, 721).—Barium sulphate and potassium permanganate form a series of mixed crystals which at 50° can be studied up to a molar percentage of 60% of potassium permanganate. The content of potassium permanganate in the crystals is approximately proportional to the concentration in the solution with which the crystals are in contact. Mixed crystals containing more than 40% of potassium permanganate are metastable, and are rapidly decomposed by acetone. Crystals stable to acetone are partly broken up by water; the residue, which contains about 8% of potassium permanganate, is very stable towards reducing agents. Barium selenate and chromate, strontium selenate and sulphate, and potassium fluoborate also form mixed crystals with potassium permanganate.

H. F. GILLBE.

New kinds of mixed crystals. VIII. D. BALAREV (Z. anorg. Chem., 1928, **169**, 257—263; cf. this vol., 223).—If barium sulphate is precipitated by the free diffusion of barium chloride and potassium sulphate into a potassium chloride solution, the amounts of water and potassium sulphate included in the precipitate pass through a minimum with increase in the potassium chloride concentration, but are never zero. When the anisotropic crystals of $BaSO_4(K_2SO_4,H_2O)$ are rendered isotropic by warming, they are much more rapidly penetrated by a potassium permanganate solution, probably owing to the capillaries of the small regular crystals constituting the larger crystals becoming connected up in a more regular manner. Similarly, a pure solution of barium chloride diffuses very slowly through a semi-permeable membrane of barium sulphate, but in presence of sugar or potassium permanganate the rate is much increased, because these substances make the barium sulphate crystals isotropic, and so increase their capillaries. The amount of a foreign salt included in precipitated barium sulphate does not appear to depend in any fundamental manner on structural considerations. When a barium sulphate crystal starts to grow in a solution containing a foreign salt, such as permanganate, the thickness of the layer of permanganate solution adsorbed on the surface increases as the crystal grows, and thus the layer becomes less and less readily penetrated by the barium sulphate molecules. When, however, the crystal has reached a certain size, any further increase occurs in the form of deformed growths on its surface, some of the adsorbed layer and a little mother-liquor thereby being mechanically included. With increase in the concentration of foreign salt, the maximum possible size of regular sulphate crystal diminishes.

R. CUTHILL.

Diffusion of thorium through tungsten. P. CLAUSING (Physica, 1927, **7**, 193—198).—Experiments with thoriated tungsten wires, coated with a layer of tungsten, show that at 2150—2800° Abs. thorium moves outwards along the tungsten crystal interfaces, whilst diffusion through the intact tungsten lattice takes place to a negligible extent.

CHEMICAL ABSTRACTS.

Heterogeneity of iron–manganese alloys. C. R. WOHRMAN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1927, No. 14, 32 pp.).—Photomicrographic study of iron–manganese alloys containing 30, 8, and 3% Mn leads to the view that the Widmanstättian and martensitic patterns structures result from the breaking up of a solid phase into two. The latter structure is finer, less well defined, and less regular than the former. On thorough annealing there is formed an aggregate consisting of a ferritic constituent, probably a solid solution of a little manganese in α-iron, and a cementitic constituent, an intermetallic compound rich in manganese. A eutectoid of the two (6% Mn) is also believed to exist, at first martensitic and then pearlitic. The valuable properties of steels are considered to be vested in the solid solutions which iron tends to form, the influence of carbon having been over-emphasised.

CHEMICAL ABSTRACTS.

Incomplete miscibility phenomena in aqueous solutions of ammonia and an inorganic salt. E. JÄNECKE (Z. Elektrochem., 1927, **33**, 518—526).—When concentrated aqueous solutions of potassium carbonate and ammonia are mixed, two liquid layers are formed, the upper being richer in ammonia and the lower in potassium carbonate (cf. Newth, J.C.S., 1900, 77, 775). Raising the temperature leads to the disappearance of one of the layers and for a system of given composition there is a definite "clearing temperature." For a fixed temperature there is a critical ratio of ammonia to potassium carbonate such that on dilution with water the compositions of the two layers eventually become identical: with a higher ratio, dilution leads to homogeneity through disappearance of the lower layer; with a lower ratio, through disappearance of the upper layer. Similar phenomena are exhibited by using tripotassium phosphate, rubidium carbonate, or potassium vanadate instead of potassium carbonate. Equilibria in the systems K_2CO_3–NH_3–H_2O and K_3PO_4–NH_3–H_2O have been investigated in detail and the results exhibited by curves. The conditions for the separation of the solid phases $K_2CO_3,2H_2O$ and $K_3PO_4,8H_2O$ are also indicated. A four-dimensional equilibrium diagram of the system K_2O–CO_2–NH_3–H_2O is given in perspective, together with a projection of this on the triangular base representing the co-ordinates of K_2O, CO_2, and NH_3 (cf. A., 1927, 731).

H. J. T. ELLINGHAM.

Miscibility-gap in molten iron–copper alloys. A. MÜLLER (Z. anorg. Chem., 1928, **169**, 272).—Polemical against Ruer (A., 1927, 928). R. CUTHILL.

Determination of vapour pressure of saturated aqueous solutions. F. POHLE (Mitt. Kali-Forschungs-Anst., 1927, 33—43; Chem. Zentr., 1927, ii, 2047).—Determinations were made of the saturation pressure of saturated solutions of magnesium, sodium, and potassium chlorides and sulphates, and of various mixtures of the salts. The b. p. were also determined. A. A. ELDRIDGE.

Relation between water and salts in crystalline hydrates and in solutions. J. N. RAKSHIT (Z. Elektrochem., 1927, **33**, 578—581; cf. A., 1926, 788).—The molecular contraction observed when a salt forms a crystalline hydrate or a solution with water has been determined for various salts. The values obtained for solutions are generally greater than those for the crystalline hydrates and increase notably with dilution, but for concentrated (including supersaturated) solutions of sodium acetate the molecular contraction is less than for the trihydrate, and for manganous sulphate solutions it is almost negligible compared with the values for the crystalline hydrates. For solutions of sodium sulphate and of sodium carbonate at various concentrations, the molecular contraction has been measured at various temperatures between 15° and 90°, but no indication of transition points corresponding with dissociation of definite hydrates is obtained. It is inferred that the relation between the salt and water in solutions is different from that in the crystalline hydrate.

H. J. T. ELLINGHAM.

Solubility equilibria. F. FLÖTTMANN (Z. anal. Chem., 1928, **73**, 1—39).—The solubility in water and the values of d and n_D for saturated and for 1% solutions of 22 common salts have been determined at 15°, 20°, and 25°, and the results are compared with those obtained by previous investigators.

A. R. POWELL.

Adsorption of strong electrolytes by pure carbon free from ash. I. M. KOLTHOFF (Z. Elektrochem., 1927, **33**, 497—501).—Purified sucrose was carbonised and the finely-powdered product activated by heating for 24 hrs. at 900—960°. The amounts of various inorganic acids adsorbed from $0{\cdot}1N$-solutions by this charcoal decrease in the sequence thiocyanic, hydriodic, nitric, iodic, hydrochloric, hydrobromic, sulphuric, phosphoric; the value for sulphuric acid is very low and that for phosphoric acid is zero. This sequence corresponds with that for the activity of the acids in lowering the surface tension of water. Not only do neutral salts of a strong acid increase the adsorption of that acid by charcoal, but addition of a second inorganic acid has a similar effect. Whereas phenol or amyl alcohol practically prevents the adsorption of the strong acids, the strong acids will partly displace acetic acid from a charcoal surface. It is inferred that the strong acids are adsorbed in the undissociated form. Zero or negative adsorption in the case of strong inorganic bases is confirmed, but a small positive adsorption was obtained with ammonia. Aliphatic primary amines are relatively well adsorbed and the secondary amines much more so: aromatic primary amines are strongly adsorbed. Notable adsorption is found with the strong aromatic and heterocyclic bases, but, whereas alkaloids of low mol. wt. are slightly adsorbed, zero or perhaps negative adsorption is exhibited by alkaloids of high mol. wt., although these substances have a very marked lowering effect on the surface tension of water. Salts of inorganic acids and bases are only adsorbed "hydrolytically" by pure charcoal, the acid being adsorbed and the base remaining in solution. For salts of a given base, the sequence for the extent of this hydrolytic adsorption is the same as that for the adsorption of the corresponding acids. The salts of surface-active organic acids with inorganic bases or of surface-active organic bases with inorganic acids are adsorbed partly hydrolytically but mainly molecularly. Salts of surface-active organic acids and bases are almost entirely adsorbed molecularly. The results obtained for salts of various types are discussed. The polar character of surface-active organic acids and bases is regarded as the essential factor in giving rise to molecular adsorption.

H. J. T. ELLINGHAM.

Comparative adsorption by active charcoal. II. Isoelectric point of charcoal. O. SPENGLER and E. LANDT (Z. ver. deut. Zucker-Ind., 1928, 81—98).—The charcoal is added to a series of buffer solutions at various p_H values, and the isoelectric point of the charcoal is taken to be the p_H value of the buffer solution which is not changed by the addition of the charcoal. The isoelectric points so obtained fell between p_H 5·7 and 8·7.

W. O. KERMACK.

Adsorption of ferric chloride by crystalline barium sulphate. (MLLE.) L. DE BROUCKÈRE (Bull. Acad. roy. Belg., 1927, [v], **13**, 827—836).—The adsorption of ferric chloride by crystalline barium sulphate at 25°, and the influence of varying concentration of hydrochloric acid ($0{\cdot}1$—$0{\cdot}001N$) on the adsorption, have been investigated. In acid-free solutions a larger value for the quantity of iron adsorbed is found when the washed barium sulphate is fused with crystalline sodium carbonate than when it is digested with pure water; it thus appears that a portion of the electrolyte is irreversibly adsorbed, the digestion method removing only the active portion of the micelle. Moreover, the amount of adsorbed iron, as determined by the former method, is much more than equivalent to the adsorbed chlorine ($\frac{1}{3}$Fe : Cl varies from 4 to 10) and hence adsorption of the micelle, which has the composition $[Fe_2(OH)_6]_m,Fe_2Cl_6$, is also postulated. This is also the case with low concentrations of added hydrochloric acid, but the ratio $\frac{1}{3}$Fe : Cl decreases towards a minimum value of 0·6 (corresponding with $H_4Fe_2Cl_{10}$) as the concentration of the acid is increased. It is assumed that the addition of acid breaks down the micelle, adsorption of which is the main factor. Other conditions being the same, the adsorption of iron is 20—100 times as great as that of uni- and bi-valent cations. J. W. BAKER.

Adsorption at crystal faces. I. Growth and dissolution of single copper sulphate crystals in presence of gelatin and dyes. T. S. Eckert and W. G. France (J. Amer. Ceram. Soc., 1927, **10**, 579—591).—Kinematographic observations, at a magnification of 1000, on the growth of crystals from saturated copper sulphate solutions are recorded. Gelatin is very effective in retarding the rate of crystal growth. It is probable that the gelatin is adsorbed to different degrees at different crystal faces, thus changing the crystal habit. The ash of gelatin, *per se*, is without effect in modifying the crystal habit. Quinoline-yellow, Bismarck-brown, and methylene-blue greatly change the crystal habit and decrease the rate of growth of copper sulphate crystals, but naphthol-yellow, ponceau-2R, and methyl-violet do not show such effects. The theory of adsorption in relation to the influence of gelatin and dyes is discussed. It is shown that specific adsorption is largely responsible for changes in crystal form. Viscosity and convection currents affect the rate of dissolution. A. T. Green.

Molecule ion absorption. S. Gorbatschev (Trans. Sci. Chem.-Farm. Inst. [Moscow], 1925, **12**, 7—30; Chem. Zentr., 1927, ii, 1801).—" Sorption " of ions by neutral molecules is postulated; such sorption accompanies dissociation in electrolytes. If the solution contains foreign neutral molecules, one of the ions is " sorbed," and the degree of dissociation and conductivity of the solution are increased.

A. A. Eldridge.

Adsorption and chemical nature of some organic compounds. N. A. Schilov and B. V. Nekrassov (J. Russ. Phys. Chem. Soc., 1928, **60**, 103—112).—See A., 1927, 1135.

Retrograde adsorption of colloidal ferric hydroxide. W. Stollenwerk and M. von Wrangell (Z. Elektrochem., 1927, **33**, 501—503).—Ferric hydroxide " gels " prepared either (*a*) from ferric chloride solution as a dark brown precipitate or (*b*) by oxidation of ferrous hydroxide with hydrogen peroxide, giving a yellow product, were shaken with solutions of mono-, di-, or tri-sodium phosphate of various concentrations, and the amounts of the phosphate radical adsorbed were measured at intervals over a period of 4 days. In the more concentrated solutions of the disodium phosphate, the preparation (*a*) adsorbs rapidly increasing amounts of phosphate, but after about 12 hrs. a maximum is reached and part of the adsorbed phosphate is gradually given up again, whereas the preparation (*b*) adsorbs smaller but continuously increasing amounts, so that eventually the amounts adsorbed by the two preparations tend to approach one another. In more dilute solutions the amounts of phosphate adsorbed in the first 12 hrs. by the two gels are less divergent, and the subsequent retrograde adsorption by the gel (*a*) is less marked. The retrograde adsorption is strongly marked with the gel (*a*) in concentrated solutions of trisodium phosphate and is exhibited to a slight extent by the preparation (*b*) in such solutions, but it is not shown by either preparation in solutions of monosodium phosphate. The interpretation of these results is discussed. H. J. T. Ellingham.

Molecular orientation at surfaces of solids. I. Measurement of contact angle and the work of adhesion of organic substances for water. A. H. Nietz (J. Physical Chem., 1928, **32**, 255—269).—The contact angle for water, the effect on the surface tension of water, the spreading, and the work of adhesion of 70 organic solids have been investigated with results which are in accord with the work of Harkins (A., 1921, ii, 242) and of Langmuir (A., 1917, ii, 525). The Ablett cylinder method and the plate method for measuring the contact angle have been compared in favour of the latter, the former giving inconsistent results which are as yet unexplained. Substances which spread considerably do not always greatly affect surface tension. The effect of humidity during crystallisation or solidification of the solid is marked, increased humidity causing a large increase in the work of adhesion. L. S. Theobald.

Comparison of thickness of oxide films determined by interference colours and by weighing. G. Tammann and K. Bochov (Z. anorg. Chem., 1928, **169**, 42—50).—Calculation of the thickness of an oxide film on the surface of nickel from its colour gives a value about 98 $\mu\mu$ less than that determined by direct weighing. This must be ascribed to the presence on the surface both of the bright and the oxidised metal of a film, which, from its loss in weight on reduction, appears to consist of hydrated nickel oxide and absorbed air and water vapour. On iron, the film has a thickness of 85 $\mu\mu$, and on copper 91 $\mu\mu$ (cf. Vernon, A., 1926, 1108). R. Cuthill.

Surface tension of solutions. W. Herz and E. Knaebel (Z. physikal. Chem., 1928, **131**, 389—404).—The surface tension of an ammonium hydrogen sulphate solution is identical with that of a mixture of equimolar solutions of sulphuric acid and ammonium sulphate of the same equivalent concentration. The formation of an acid salt is indicated in general by an increase of the surface tension of the mixed solution over the arithmetic mean of the surface tensions of the separate solutions. The influence of the alkali and alkaline-earth chlorides and nitrates on the surface tension of water is the same at 20° as at 40°; for each group of cations the increase of surface tension decreases with rise of atomic weight. The surface tension of acetone–water mixtures is lowered by sodium, potassium, and barium salts to an extent which is independent of the salt concentration; this effect is probably due to the insolubility of the salts in acetone, since the solution will then have a lower active water content, *i.e.*, the acetone percentage will increase and the surface tension of the water will thereby be lowered. The chlorides and nitrates of the other alkali and alkaline-earth metals produce at first an increase of the surface tension, and then, at higher concentrations, a decrease. At low concentrations, complexes are formed between the salt and acetone, and the concentration of the latter is lowered; as the salt concentration increases the active water content diminishes, and the reverse effect is observed. A number of measurements have been made of the surface tension of solutions of iodine, naphthalene, and phenanthrene in various organic solvents. In all cases iodine produces a decrease, and the other substances an increase of the surface tension of the solvent. H. F. Gillbe.

Permeability of thin dry collodion membranes. J. H. Northrop (J. Gen. Physiol., 1928, **11**, 233—237).—Dry thin collodion membranes, having a thickness of 2—3 μ and having permeabilities similar to those of the membrane of the sea-urchin egg, have been prepared. The membrane is permeable to water, ammonia, weak acids of low mol. wt., gaseous hydrogen chloride, oxygen, carbon dioxide, and hydrogen sulphide, but impermeable to strong electrolytes and substances of high mol. wt. The rate of effusion of gases through the membrane shows no connexion with the density of the gas and thus the membrane cannot be regarded as a sieve. The results as a whole indicate that the rate of passage of a substance through the membrane is determined by the solubility of the substance in collodion and its diffusion coefficient in collodion, the former probably being the more important factor. A. Wormall.

Function of carbon membranes in osmosis. F. E. Bartell and H. J. Osterhof (Fourth Colloid Symposium Monogr., 1926, 234—245).—Experiments with silica or carbon membranes show that the flow is from water to organic liquid with the former, and eventually the reverse with the latter. Two liquids were separated by a silica or carbon membrane, and the pressure resulting from the osmotic flow was measured. The results indicate that in a strictly semi-permeable membrane one component is adsorbed to the practical exclusion of the other. When the membrane has greater permeability the initial osmotic force and direction of flow are mainly determined by the relative adsorption of the liquids; the membrane may or may not play an active part.

Chemical Abstracts.

Hydrolysis of sugars by membranes in presence of electrolytes. J. Loiseleur (Compt. rend. Soc. Biol., 1927, **96**, 1273—1275; Chem. Zentr., 1927, ii, 678).—Fall in p_{H} of an electrolyte solution in presence of a colloid is observed when sucrose or other hydrolysable sugar is hydrolysed.

A. A. Eldridge.

Chemical method of preparing carbon hydrosol. E. Chirnoaga (J.C.S., 1928, 298—301).—By stirring small amounts of carbon in aqueous solutions of sodium hypochlorite a very stable sol is obtained which may be evaporated without suffering irreversible coagulation. The size of the particles is estimated at 60 μμ. The negative charge carried by the sol is ascribed to the adsorption of chlorine or hydroxyl ions. A theory of the process is advanced and mention is made of the possible industrial application of the sol as a resistant carbon ink.

H. Ingleson.

Preparation of silver hydrosols free from protective colloids and with particles of a uniform size. II. J. Voigt and J. Heumann (Z. anorg. Chem., 1928, **169**, 140—150; cf. A., 1927, 932).—If silver hydrosols with particles of a uniform size are employed as nuclei in the reduction of a silver oxide solution with hydrazine sulphate and sodium carbonate, the silver submicrons grow in an irregular manner, and there is no relation between the number of particles resulting and the number of nuclei. This is due to the formation of colloidal particles by the sodium carbonate itself, these acting as false nuclei. If, however, the presence of sodium carbonate is avoided by using hydrazine hydrate for the reduction, sols are obtained having particles the size of which is uniform and determined by the number of nuclei. Gold nuclei prepared with the aid of phosphorus also yield satisfactory results, and sols have also been prepared with saturated solutions of silver oxide.

R. Cuthill.

Colloid syntheses with the aid of titanium trichloride. VI. Colloidal palladium. A. Gutbier and H. Weithase (Z. anorg. Chem., 1928, **169**, 264—266; cf. A., 1927, 933).—If a solution of titanium trichloride is nearly neutralised with sodium acetate, then boiled, and after cooling added to a 1% solution of palladium dichloride, colloidal palladium is formed by the reaction $Pd^{\cdot\cdot}+2Ti^{\cdot\cdot\cdot}=2Ti^{\cdot\cdot\cdot\cdot}+Pd$. The product is relatively insensitive towards acids, owing to the presence of titanium dioxide as protective colloid, and on dialysis passes into a gel, which can be peptised with water only after being treated with concentrated hydrochloric acid. Undialysed preparations of palladium titanium purple are thixotropic.

R. Cuthill.

Preparation and stabilisation of colloidal mercury. A. Chistoni (Boll. soc. biol. sperim., 1926, **1**, 408—410; Chem. Zentr., 1927, ii, 905).—Mercuric chloride (0·5 g.), sodium hydroxide (2 g.), and fresh egg-albumin (100 g.) form a gel which when warmed with water is converted into a black sol, stable towards boiling and towards heating at 110° in an autoclave. It is coagulated by an equal volume of 10% barium chloride, but not by sodium chloride solution. The electric charge is negative. The sol is not precipitated by hydrogen sulphide or ammonium sulphide; drying at the ordinary temperature and pulverising yields a substance which is again soluble. The disperse phase consists of a sulphide of mercury, produced by hydrogen sulphide from the albumin.

A. A. Eldridge.

Presence of arsenious oxide in arsenic trisulphide hydrosol. V. Gazzi (Zymologica, 1927, **2**, 1—10; Chem. Zentr., 1927, ii, 26—27).—The quantity of arsenious oxide, even in a highly purified sol, is always much greater than that which can be obtained by complete hydrolysis of soluble arsenic trisulphide. The solubility of precipitated arsenic trisulphide is $2 \cdot 10 \times 10^{-6}$ mol./litre, yielding 0·4135 mg. per litre of the trioxide, whereas 1·5—3·0 mg. are found. The value is not connected so much with the solubility of the trioxide as with the loss of hydrogen sulphide. It is impossible to separate the ultramicellar liquid by ultrafiltration without changing its composition. A. A. Eldridge.

Interpretation of the analysis of arsenic trisulphide hydrosol. V. Gazzi (Zymologica, 1927, **2**, 10—12; Chem. Zentr., 1927, ii, 27).—The results obtained by Murphy and Mathews (A., 1923, ii, 156) are considered to be due to the presence of a mixture of arsenious oxide and sulphide. A. A. Eldridge.

[Catalysts for hydrogenation in the cold.] M. Bourguel (Bull. Soc. chim., 1928, [iv], **43**, 231;

cf. this vol., 28).—A printer's omission is corrected and the directions given in the paper for the preparation of colloidal palladium are amplified.
H. Ingleson.

Aluminium hydroxide gels. D. G. R. Bonnell (Z. anorg. Chem., 1928, **169**, 345—355; cf. A., 1927, 1025).—Aluminium hydroxides *B* and *C* form lakes with gold hydrosols, the colour with the *C* gel depending on the relative amounts of gold and alumina. With hydrochloric acid, gels *B* and *C* are not peptised, but pass into crystalloidal solution. Gel *A* is attacked only slightly with hydrochloric acid if an excess of acid is used, but if heated with a small amount of concentrated acid and then diluted it readily yields hydrosols, with particles which are the smaller the greater the quantity of acid used. These sols can be concentrated considerably without the occurrence of gelatinisation, and when evaporated in a vacuum or subjected to ultrafiltration leave a residue again which passes into colloidal solution in water. R. Cuthill.

Theory of the preparation of silica gel by means of water-soluble metal salts. P. N. Grigorjev (J. pr. Chem., 1928, [ii], **118**, 91—95).—Silica gels are obtainable from water-glass ($Na_2O,3SiO_2$) by the action, not only of heavy metal salts (Holmes and Anderson, A., 1925, ii, 518), but also of alkali and light metal salts. Salts of calcium, magnesium, strontium, and barium give silica gels of low activity. The gel formation depends on the hydrolysis of the metal silicates formed by double decomposition. Ferric salts behave exceptionally (cf. Jordis, A., 1907, ii, 876; 1908, ii, 291; 1910, ii, 416).
C. Hollins.

Size-distribution of colloidal particles. N. Rashevsky (Physical Rev., 1928, [ii], **31**, 115—118). —Theoretical. A. A. Eldridge.

State of polarisation of the Tyndall beam of colloids. B. Lange (Z. physikal. Chem., 1928, **132**, 1—26).—Gans' formula for the depolarisation coefficient θ_0 of individual colloidal particles has been verified by measurements with arsenious sulphide, ferric and aluminium hydroxide, cerium dioxide, and vanadium pentoxide sols. For small spherical particles θ_0 becomes zero, *i.e.*, the Tyndall beam is completely polarised; these conditions hold for caoutchouc, mastic, arsenious sulphide, and cerium dioxide sols. Colloidal particles of ferric and aluminium hydroxides and of vanadium pentoxide deviate considerably from the spherical form, and in the case of the latter the deviation increases on ageing. Thixotropic gelatinisation of a cerium dioxide sol results in a reversible increase of θ_0, indicative of aggregation of the particles. H. F. Gillbe.

Depolarisation and light absorption of solutions of colloidal gold. B. Lange (Z. physikal. Chem., 1928, **132**, 27—46).—A series of gold sols having particle sizes from 6 to 150 $\mu\mu$ have been prepared and the absorption coefficients measured. The latter are in close agreement with Mie's theoretical values when calculated on the assumption of spherical particles. The mean particle size calculated thus from the absorption differs widely from the values obtained by ultramicroscopical measurements; this is attributed to the relatively large influence exerted by a small proportion of very small particles. Values obtained from the rate of sedimentation agree closely with those calculated from the absorption. Mie's theory requires the absorption coefficient to be independent of the particle size, but this is shown experimentally not to be the case. The depolarisation coefficient θ_0 for small gold particles deviates from zero, since a certain fraction of the particles is non-spherical. The colour change which accompanies coagulation is associated also with a decrease of θ_0, and is therefore not due to a greater deviation of the particles from the spherical form, but to an increase of size. The sols contain chiefly metallic gold, with but little aurous hydroxide; the percentage of the latter in one case was 1·26. H. F. Gillbe.

Stability of colloidal solutions towards electrolytes. A. Boutaric (Bull. Soc. chim., 1928, [iv], **43**, 146—155).—Measurements are described in which a spectrophotometer is employed to determine the time *t* required by a colloidal solution to reach its maximum opacity in the presence of an electrolyte of concentration *c*. By successively reducing the concentration of electrolyte the equation $t=f(c)$ can be evaluated and the highest value of *c* at which no coagulation occurs can be calculated, thus providing a measure of the stability. When electrolytes with multivalent ions are employed, *e.g.*, ferric chloride, the curve $t=f(c)$ with certain sols reveals the existence of two zones of flocculation. Gelatin, albumin, and gum, when added to colloidal solutions of arsenic sulphide, ferric hydroxide, or gamboge in small amounts up to a certain limit, reduce the resistance of the colloid to coagulation by an electrolyte, but subsequent additions exert a protective action. When a sol is treated with an amount of electrolyte insufficient to coagulate it, the sol is able to withstand the action of an amount of electrolyte which would have been sufficient to precipitate the untreated sol. Contrary to many published statements, the nature of the visible light by which a sol is illuminated has no effect on the time required for coagulation, illumination by intense red and intense blue light giving the same values as those found in the dark. H. Ingleson.

Protection of colloidal solutions. A. Boutaric (J. Chim. phys., 1928, 25, 120—141).—An experimental investigation of the influences exerted on colloidal solutions by small quantities of added substances. H. F. Gillbe.

Kinetics of coagulation of colloids. K. Jabłczyński and M. Soroczyński (Bull. Soc. chim., 1928, [iv], **43**, 159—163; see A., 1925, ii, 34, 35, 665, 666; 1926, 1203).—The equation previously established (using a spectrophotometer), $(\log\tan\alpha-\log\tan\alpha_0)/t=K$, is shown to be a particular case of the more general equation $\log[(\log\tan\alpha_\infty-\log\tan\alpha_0)/(\log\tan\alpha_\infty-\log\tan\alpha)]=K_1t$, where α_0, α, and α_∞ are the angles of rotation of the Nicol at zero time, time *t*, and infinite time respectively. The general equation expresses the fact that the rate of increase of opacity at a given time is proportional to the difference of the opacity in the final state and at the given time. Values of K_1 obtained experimentally with ferric hydroxide sols are in good agreement.
H. Ingleson.

Coagulation of colloids by electrolytes. II. Conductometric study of the coagulation of arsenic trisulphide sols. A. J. Rabinovitsch and W. A. Dorfmann (Z. physikal. Chem., 1928, **131**, 313—337).—Addition of a solution of an electrolyte to an arsenious sulphide sol causes at first a rapid increase of conductivity, which gradually slows down and finally becomes linear. The initial rapid increase is ascribed to the displacement of the rapidly moving hydrogen ions by the cations of the electrolyte, a process which ceases as the conductivity curve becomes linear. The degree of acidity calculated from the form of the conductivity curve is not in agreement with the value obtained from potentiometric measurements with the quinhydrone electrode. When salts of ter- and quadri-valent ions are employed the degree of acidity cannot be calculated on account of hydrolysis. The point at which the linear portion of the conductivity curve sets in varies directly with the concentration of the sol and inversely as the concentration of the electrolyte, whilst the difference between the coagulative powers of cations of different valencies diminishes with increasing sol concentration. The Hardy–Schulze law is applicable only to the coagulation and not to the completion of the displacement of the hydrogen ions by the adsorbed cations; the two processes are essentially different. In order to produce coagulation a cation must either partly or completely displace the hydrogen ions which are attached to the colloidal particles; a certain excess of the cation is also necessary, which is the greater the lower the valency of the ion. The adsorption of cations of different valencies by the colloidal particles reaches a maximum at approximately the same equivalent concentration, but the quantities adsorbed vary. The influence of the dilution of the sol on the coagulative power of various cations forms an argument against the theory that coagulation is due to the solubility product of the added and stabilising ions being exceeded. H. F. Gillbe.

Coagulation of colloids with electrolytes. A. Rabinovitsch and R. Burstein (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 35—53; Chem. Zentr., 1927, ii, 1007).—An investigation of mastic emulsions, prepared (*a*) by addition of water to an alcoholic mastic solution and filtering, (*b*) by pouring alcoholic mastic solution into water and filtering; in this case the residue is greater. Conductometric titration of the latter sols is impossible for lack of a minimum; that of the former gives definite results. Both sols are feebly acidic. The particles of the (*b*) sols are greater than those of the (*a*) sols. On coagulation of the sols with neutral salts, no development of acidity takes place, as with arsenious sulphide sols; a corresponding amount of the coagulating cation is retained in the precipitate. A. A. Eldridge.

Influence of temperature on rate of coagulation of colloids. K. Jabłczyński and M. Knaster (Bull. Soc. chim., 1928, [iv], **43**, 156—159).—From spectrophotometric measurements of the rate of coagulation of a ferric hydroxide sol by potassium chloride solution at intervals of 10° between 0° and 45° the average temperature coefficient of the rate was found to be 2·19 per 10°. The conclusion is reached that the rate of coagulation cannot be determined simply by the rate of diffusion of the particles, since a rise in temperature of 10° increases the rate of diffusion by only 30% in this range of temperature. H. Ingleson.

Kinetics of coagulation. B. N. Desai (Trans. Faraday Soc., 1928, **24**, 181—195).—The coagulation of thorium oxide sols by electrolytes has been studied by an accurate optical method, which eliminates those sources of error which probably have prevented other workers from observing the period of slow coagulation. The rates of coagulation agree with Smoluchowski's theory (A., 1917, ii, 129) only up to a certain concentration of coagulator. Evidence for the autocatalytic nature of the coagulation process is adduced. A formula for the velocity coefficient of the process has been derived. Freundlich's theory of coagulation is supported and extended. L. F. Gilbert.

Action of ultra-violet light on some colloidal dispersions of gold. J. J. Beaver and R. H. Muller (J. Amer. Chem. Soc., 1928, **50**, 304—321).—The photochemical properties of gold sols depend on the nature and conditions of preparation. Sols prepared with hydrazine, phosphorus, formaldehyde, and acetylene as reducing agents, and also Bredig's gold sol, are quite stable towards ultra-violet light; other sols turn blue after 2 days' exposure and are finally peptised to stable red sols. The change is accompanied by an increase and a subsequent decrease in refractive index, and also in conductivity. The colour, rate of formation, and photochemical properties of chemical gold sols vary continuously with the hydrogen-ion concentration of the reducing solution. The absorption spectra of some gold sols are recorded. The photosensitive sols absorb radiation below 2150 Å.; the radiant energy from this region decreases rapidly with ageing of the lamp. The results are explained on the basis of Wilson's theory of the structure of colloidal gold particles (A., 1916, ii, 604), it being assumed that radiation influences the already unequal distribution of ions between the particle surface and the bulk of the solution. The rate of precipitation of Bredig sols is not affected by radiation. S. K. Tweedy.

Coagulation of colloidal clay. R. Bradfield (J. Physical Chem., 1928, 32, 202—208; cf. Oakley, this vol., 16).—The coagulation of a colloidal clay, separated from a silt loam by centrifuging, by potassium and calcium hydroxides and chlorides has been investigated by the method previously used (A., 1923, ii, 470). A portion of the clay was freed from exchangeable bases and electrolytes by electrodialysis, and its behaviour compared with the natural clay. The coagulation values for calcium hydroxide in both cases were linear functions of the concentration of the clay, but the much greater values obtained with the electrodialysed material showed that base exchange must play an important rôle in coagulation phenomena. With potassium hydroxide as coagulant the effect of electrodialysis is even more pronounced, and with the chlorides of potassium and calcium as coagulants the concentration of clay is without effect on the coagulation value. Coagulation values are very sensitive to hydrogen-ion concentration, and this is very pronounced with the electrodialysed clay. L. S. Theobald.

Colloid researches on discharge phenomena and adsorption with quartz suspensions. E. Ramann and collaborators (Kolloidchem. Beih., 1927, **25**, 279—427).—**Coagulation experiments and microscopical observations on quartz suspensions.** [With J. A. Hanley.]—Methods are given for the preparation and preservation of quartz suspensions containing particles of nearly uniform size, graded according to the rate of fall under gravity. In the sedimentation of suspensions containing the finer particles the production of layers was observed. The layers are very sensitive to light and heat, strong sunshine soon destroying them. The bounding surfaces are usually concave, showing that the walls of the vessel hinder the fall of the particles. Experiments were made both macroscopically and under the microscope on the flocculation of quartz suspensions on addition of lime-water. Microscopical observation showed the coagulation to take place in a series of steps, and the first clustering of the particles did not coincide with the threshold concentration of electrolyte necessary to produce macroscopic coagulation, but the agreement was better the smaller were the particles.

Preparation of chemically indifferent quartz of definite particle size and surface. [With G. Krauss.]—A detailed account is given of the purification of finely-ground quartz both from the products with which it is naturally contaminated and from those which are picked up in the grinding process. Directions are given for the preparation and sterilisation of suspensions of the quartz powder. The suspensions were separated into fractions of uniform particle size by means of elutriation. The size of the particles was determined by taking numerous photomicrographs of the suspensions. The difficulty inherent in the pronounced irregularity of the particles was overcome by constructing on the photomicrograph a circle equal in area to the particle, and taking the diameter of the circle as the mean diameter of the particle. A method is deduced from theoretical considerations for estimating the surface of the particles.

Slipping phenomena in sedimentation on inclined surfaces. [With G. Krauss and R. Rüger.]—When non-spherical particles of quartz of uniform size settle from a suspension in distilled water on to a glass surface inclined at an angle to the horizontal, the particles readily slide down the plane and accumulate at the bottom of the vessel. On the other hand, when an electrolyte is present in the suspension, either the slipping does not occur or the angle which the surface makes with the horizontal has to be increased. It is shown that there is a quite definite "sliding-angle," which increases rapidly with increasing concentration of the electrolyte, and that this angle is a measure of the discharging effect. Particles of diameter 0·01—0·02 mm. were most favourable for the experiments, and the electrolytes used were hydrochloric acid, potassium chloride, calcium chloride, calcium hydrogen carbonate, aluminium chloride, and the hydroxides of calcium, potassium, and ammonium. In these cases, Schulze's valency law was found to be valid for the discharging effect of the electrolytes.

Influence of dilute solutions of electrolytes on the movement of suspended quartz particles in a filter of quartz sand. [With M. Storz.]—A filtering apparatus was constructed by filling a lamp glass, the bottom of which was closed by a mesh, with quartz sand, and experiments were carried out on the efficiency of such a filter towards increasing volumes of a fine suspension of quartz. It was found that the weight of retained quartz particles increases with increasing volume of the suspension, at first linearly, and later tends to a constant value, showing that the filter has a saturation capacity. In presence of increasing amounts of electrolyte (hydrochloric acid), however, the curve approaches more and more to a straight line, and with 0·0015*N*-hydrochloric acid in the suspension the quartz sand acts as a nearly perfect filter. Experiments of a similar kind were conducted on the amount of quartz suspension appearing in the filtrate in presence of various quantities of hydrochloric acid, in some cases finely-divided silica being distributed in the filter before the experiment. Experiments in which the filter was divided into vertical sections, each of which could be weighed separately so as to ascertain the amount of quartz retained, showed that the weight of quartz retained diminishes with the depth of the filter, the gradient being greater in presence of increasing concentrations of hydrochloric acid. The capillary rise of quartz suspensions into this type of filter was also investigated. The amount of quartz passing up into the filter increases with the concentration of the suspension, but decreases rapidly with increasing concentration of added hydrochloric acid. The amount of quartz thus transported in presence of *N*-hydrochloric acid is practically nil. A study of the sedimentation of quartz suspensions in presence of electrolytes has led to the construction of a filter of glass balls by means of which the electrolyte in the region of its critical concentration produces rapidly a visible effect on a suspension.

Effect of small concentrations of electrolytes on sedimentation of quartz suspensions. [With H. Sallinger.]—Evidence is adduced to show that concentrations of electrolytes smaller than the critical value required to produce complete flocculation have some effect on suspensions. The effect of various concentrations of the following electrolytes on a quartz suspension was investigated: the chlorides of aluminium, calcium, potassium, and sodium, and calcium hydroxide, sodium carbonate, and hydrochloric acid. It is shown that the curve connecting the velocity of sedimentation with the concentration of electrolyte consists of three parts. For low concentrations of electrolytes the sedimentation velocity is slightly accelerated, then at a certain critical concentration the velocity rises very greatly, and is followed by a third region in which increase of concentration of electrolyte causes only a small increase in sedimentation velocity. It appears that the critical concentration of the electrolyte rises with increasing concentration of the suspension in the case of strongly adsorbable ions such as aluminium and calcium, and the reverse is the case with weakly adsorbable ions.

Adsorption measurements on quartz. [With H. Sallinger.]—Suspensions of quartz were left in contact with solutions of the hydroxides of calcium, strontium, barium, lithium, sodium, potassium, and ammonium, and the carbonates of lithium, sodium, and potassium, respectively. The amount of the electrolyte adsorbed by the quartz was measured directly by titration with hydrochloric acid. Measurements were also made of the total surface of the quartz, and the results point to the formation of a unimolecular adsorption layer. The quartz was never left in the alkali solution for more than an hour, for if left for a longer interval, chemical interaction takes place. The exponent n of the adsorption isotherm for the hydroxides of calcium, strontium, and barium is proportional to the reciprocal squares of the radii of the respective unhydrated cations.

Cause of formation of layers in suspensions. [With G. Krauss.]—The production of layers in suspensions of quartz is considered to be due to the operation of a uniform velocity of fall of the particles. This will operate when the diameter of the particles is below a certain value (the velocity of fall increases with the third power of the diameter), and when the mean distance between the particles is such that a mutual attraction can be exerted. The presence of electrolytes, by partly discharging the particles, should also exert an effect. It is shown that these deductions are in agreement with experiment. Actually, layers were observed only when the diameter of the particles was less than 1 μ, and when the suspension fell between certain limiting concentrations. Layers are not produced in presence of electrolytes.

Theoretical conclusions from measurement of "sliding-angle." [With H. Sallinger.]—A mathematical treatment of the sliding of charged particles of quartz down an inclined plane during sedimentation (see p. 362). From the measurements, an expression is derived for the absolute value of potential at the quartz–water interface, and, taken in conjunction with adsorption measurements, the thickness of the electrical double layer.

Theory of adsorption in dilute solutions. [With H. Sallinger.]—The values obtained in experiments on the adsorption of alkali and alkaline-earth hydroxides on quartz (see above) are compared with some adsorption equations, and conclusions are reached concerning the hydration of the cations.

Dependence of the amount of adsorbed material on the amount of the adsorbent. [With H. Sallinger.]—The expression $x=Km\,.\log d/d_0$ is deduced, where x is the amount of adsorbed material, m the amount of adsorbent, K a constant, and d_0 the thickness of the adsorption layer. The value of d is given by $v/m\,.\,O_1$, where v is the volume of solution, and O_1 the surface of 1 g. of adsorbent. Since d_0 has been determined, it is possible to calculate the specific surface O_1 of the adsorbent from the formula $O_1=v/m\,.\,d_0\,.\,10^{x/Km}$.

Calculation of the hydrolysis constant of dissolved sodium carbonate from adsorption measurements of sodium carbonate and sodium hydroxide on quartz. [With H. Sallinger.]—Since the adsorption of neutral salts by quartz is scarcely measurable, the adsorption of sodium carbonate is due chiefly to the sodium hydroxide produced by hydrolysis. Therefore, in the adsorption equilibrium, an amount x of adsorbed sodium hydroxide must indicate a definite amount c' of dissolved sodium hydroxide. The hydrolysis constant K_h is given by the expression $K_h=2c'(c+x)\,.\,10^{-2}/(c-x-2c')$, where c is the total alkali titre of the solution after the adsorption. The values of c and x are obtained from adsorption measurements of sodium carbonate on quartz, and c' can be determined, knowing x, from the adsorption isotherm for sodium hydroxide on quartz. The value $3{\cdot}4\times10^{-4}$ is given for the hydrolysis constant of sodium carbonate.

Calculation of the electrolytic dissociation constant of ammonia from adsorption data (quartz/ammonia and quartz/potassium hydroxide). [With H. Sallinger.]—The formula $k=(c')^2/v(c-c')$ is derived, where k is the dissociation constant, v the volume of solution, c the total amount of ammonia after the adsorption, and c' the effective amount of ammonium hydroxide. Evaluating the expression from adsorption data, the values $k=1{\cdot}65\times10^{-5}$ and $2{\cdot}5\times10^{-5}$ are obtained for two different concentrations of ammonia. Comparison of c and c' shows that in 0·00238M-ammonia only 8%, and in 0·00442M-ammonia only 7·2% of the total ammonia is present in the form of ammonium hydroxide.

E. S. Hedges.

Ferric acetates. A. Krause (Rocz. Chem., 1927, 7, 402—435, Bull. Acad. Polonaise, 1927, **A**, 237—272, and Z. anorg. Chem., 1928, **169**, 273—292).—The action of acetic acid on ferric hydroxide hydrogel is a typical Zsigmondy's inhibited chemical reaction. As the concentration of acetic acid in the sol rises, three types of sorption take place, *i.e.*, chemisorption, adsorption, and absorption, then peptisation, and finally chemical reaction. The sorption has a periodic character, the minimum value lying at 0·069N-acetic acid (p_H 3·05). Peptisation coincides with absorption, being strongest in 0·035—0·153N-acetic acid (p_H 3·2—2·8), and is complete in 0·79N-acid, above which value and up to 1·58N-acid there supervenes the ionising effect of the addition of acetic acid, as is shown by coagulation, change of colour, and augmentation of surface tension of the sol. An examination of the dry residue from the above sols indicated a minimum acetic acid content from sols the acid concentration of which was 0·069N; above this, the ratio [AcO]/[Fe] of the residues increases with concentration of acid. Thus with 1·58N-acetic acid the monoacetate is formed, with 11·56N-acid the diacetate, and with 14·45N-acid the triacetate. The monoacetate is probably the only chemical compound present in the system ferric hydroxide hydrogel–acetic acid. The above ferric acetates, obtained as dry residues, are unstable, losing acetic acid on exposure to the atmosphere, with the exception of that originating from the sol of p_H 3·05, *i.e.*, at the isoelectric point of ferric acetate, the dissociation constant of which is estimated to be 10^{-13}.

R. Truszkowski.

Action of neutral salts on the artificial caking of collagen. J. Nageotte (Compt. rend. Soc. Biol., 1927, **96**, 828—830; Chem. Zentr., 1927, ii, 29).—The recoagulation of collagen is affected by the process, the acidity, and the quantity and nature of the electrolytes. A. A. Eldridge.

Colloid-chemical model of the double-ring phenomenon. R. Doerr and E. Berger (Klin. Woch., 1927, **6**, 1562—1563; Chem. Zentr., 1927, ii, 1717).—A double ring of precipitate, such as is obtained when 0·1 c.c. of normal horse serum is covered with 1 c.c. of 0·1% thorium sulphate solution, is also obtained when the serum is replaced by 1 c.c. of a 2% solution of sodium carbonate in 5 c.c. of sodium chloride solution. A. A. Eldridge.

Cataphoretic protein mobility. H. A. Abramson (J. Amer. Chem. Soc., 1928, **50**, 390—393).—Quartz particles suspended in dilute protein solutions under certain conditions move cataphoretically as if the surfaces of the particles were pure protein. Using the previously described apparatus based on this principle (Freundlich and Abramson, A., 1927, 931), the migration data for egg-albumin at various hydrogen-ion concentrations recorded by Svedberg and Tiselius (A., 1926, 1104) are confirmed. S. K. Tweedy.

Viscosity and cataphoretic potential of casein sols. B. J. Holwerda (Rec. trav. chim., 1928, **47**, 248—263).—Viscosity measurements and kinetic potential determinations on alkaline casein sols were made to elucidate the condition of hydration of casein in various circumstances. The method of preparing the casein is detailed. The protein content of casein being known, sols of a known casein content could be prepared. Measurements of the relative viscosity of alkaline sodium caseinate and calcium caseinate sols at 25° showed agreement with Poiseuille's law. The casein sols are liable to alteration of viscosity with time and temperature of storage, and with exposure to carbon dioxide. From observations on the influence of hydroxyl ions on the viscosity of sodium and calcium caseinate sols it was found that the viscosity (25°) reaches a maximum at p_H 11·6 and 11·4, respectively. In the case of calcium caseinate, the p_H of the maximum is independent of the concentration of casein in the sols. The influence of neutral salts in small concentrations on the maximum viscosity of sodium and calcium caseinate sols was measured, using equivalent concentrations of the chlorides of sodium and calcium, and of hexamminecobaltic chloride. In all cases, viscosity and p_H value decrease with increasing concentration of the added neutral salt.

A study of the cataphoretic potential showed that the maximum of the viscosity does not correspond with the maximum of the electrokinetic potential. The results suggest a variation in the hydration of the sol particles with a variation of p_H. R. A. Pratt.

Geometrical molecular specificity. R. Ferrier (Compt. rend., 1928, **186**, 577—578).—The adsorption phenomena of certain colloidal substances (*e.g.*, proteins) which precipitate one another from solution in a specific fashion may be explained by the assumption that the molecules of the different substances are oriented in polygons, and that substances which precipitate one another contain geometrically equal polygons oriented in an inverse sense. J. Grant.

Binding of acids and bases by proteins. J. Weber (Z. physiol. Chem., 1928, **172**, 1—37).—When fibrin is allowed to swell in 0·1*N*-hydrochloric acid, the binding of chlorine ions corresponds with that of hydrogen ions and thus no electrolytic decomposition of the protein hydrochloride occurs. The binding of hydrogen ions by fibrin reaches a well-defined maximum and further addition of acid causes no increase. The acid-binding curve for fibrin is not an adsorption curve, and the titration curves of fibrin with hydrochloric acid, sulphuric acid, oxalic acid, and phosphoric acid and with sodium hydroxide are similar to those for soluble proteins. Washed fibrin, heated fibrin, and dried fibrin usually bind different amounts of hydrogen ions, but in some cases washing and drying of the fibrin has no influence on the binding capacity. The isoelectric point of fibrin is p_H 4·7—4·8. During the digestion of fibrin (or other protein) by pepsin, the increase in acid-binding power shows no connexion with the dissolution or digestion of the fibrin, or with changes in optical activity, viscosity (gelatin), surface tension (egg-albumin), or electrical conductivity (egg-albumin, caseinogen, or fibrin). In addition, no relationship exists between the increase in free amino-groups as digestion proceeds and the increase in bound acid, but the latter appears to run parallel with the increase in free carboxyl groups. The results support the view that chemical union occurs between acids and proteins and that acid-binding constituents other than the amino-groups are present. A. Wormall.

Physico-chemical changes in egg-albumin hydrosols caused by latex. I—III. S. Visco (Arch. sci. biol., 1926, **9**, 41—73, 74—77; Chem. Zentr., 1927, ii, 906).—On addition of papain from *Carica* latex the viscosity and gelatinising power of gelatin are reduced. In regard to gelatinising power, the optimal temperature is 70°, and the longer the time of reaction the greater is the effect; the action is independent of p_H. For viscosity, the optimal temperature is 70°, and the effect is more noticeably remote from the isoelectric point. The latex of *Ficus carica* is very effective; its action on the p_H is more marked than that of papain. The density of gelatin solutions is increased by the latex. The results are considered theoretically. A. A. Eldridge.

Swelling of rubber. P. Stamberger (Rec. trav. chim., 1928, **47**, 316—320).—The swelling of raw rubber, of over-rolled rubber, and of over-rolled rubber containing varying amounts of carbon black has been studied. Determinations were carried out in a liquid medium and in its vapour, the lowering of vapour pressure being followed. At the point of maximum swelling in benzene vapour, over-rolled rubber gave a viscous liquid, whilst raw rubber under similar conditions appeared to be stable. With increasing quantities of carbon black, the hardness of these jellies was found to increase. Observations were also made with benzene containing 10% of triolein. The variations in the amount of swelling of raw and of over-rolled rubber, whether swollen in vapour or in liquid, were very marked, being 1880% by volume and 120% by volume, respectively. The results could not be brought into line with any known interpretation of swelling phenomena. R. A. PRATT.

New form of Raoult's laws. I. N. LONGINESCU (J. Chim. phys., 1928, 95, 70—82).—Raoult's f.-p. and b.-p. formulæ are given a form in which the "constants" are much less variable than is usually the case. A modified form of Raoult's equation for the lowering of vapour pressure, which is frequently met, viz., $(P_0-P)/P_0=x/d$, where d is the density of the solvent, is incompatible with Clapeyron's equation. L. F. GILBERT.

Theory of the Soret effect. E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 283—291).—The equations (cf. A., 1926, 797) for the equilibrium states resulting from reversible Soret effects are transformed into $s_A=dF_A/dT=-S_A$, where s_A is a Soret coefficient, F_A the free energy change, and S_A the entropy change, of the surroundings when one mole of constituent A is transferred. The coefficient s_A is proportional to the ordinary coefficient, $d\log_e N_A/dT$, when the solution is sufficiently dilute. The heats of transfer which determine reversible Soret effects in electrolyte solutions are due to changes in the outer of three spheres surrounding the moving ions; the two inner spheres (the "ion-cavity" and the strongly attracted and oriented molecules) move with the ion, whilst the outer changes with the environment of the ion. Values of s are calculated for some electrolytes in water on the basis of this hypothesis; the results agree fairly well with the direct determinations, but are higher than those of Chipman (A., 1926, 1206). Indirect determinations are probably capable of greater accuracy than the direct. The theory requires that the Soret coefficients are additive, individual values being assignable to all ions at infinite dilution (cf. A., 1927, 419). In infinitely dilute solution s is zero for the solvent but not for the solute; the theory indicates a maximum value of s at higher electrolyte concentrations, with the possibility of a minimum as well. Strong electrolytes in dilute aqueous solutions have negative coefficients. In series of chemically similar ions the Soret effects are of the same order. The Soret coefficient in non-electrolyte solutions, and the irreversible Soret effect in all liquid solutions, are small. S. K. TWEEDY.

Theory of hydrates. E. N. GAPON (J. Chim. phys., 1928, 25, 154—156).—The relationship $T\sqrt{m}/d\sqrt{n}=c_1$, in which T is the m. p. in degrees Abs., m the number of ions composing the molecule, d the density, n the number of atoms in the molecule, and c_1 a constant, approximately 58, has been verified for a number of hydrated salts. If MX_n be a salt which forms a hydrate, MX_n,mH_2O, of density d, the molecular volume has the value given by $V_m=MX_n/d+mH_2O/d$; writing this as $V_m=A+B$, the quantity $AB/(A+B)$ has for a large number of salts an approximately constant value of about 0·45. H. F. GILLBE.

Hydrogen-ion concentration of aqueous iodine solutions. H. M. DAWSON (J.C.S., 1928, 259—263).—The practical difficulties of making direct measurements of the concentration are referred to and an indirect method of calculation depending on a knowledge of the equilibria: $I_2+H_2O=\overset{+}{H}+\overset{-}{I}+HIO$; $H_2O=\overset{+}{H}+\overset{-}{OH}$; $I_2+\overset{-}{I}=\overset{-}{I}_3$, is described. The values obtained are applicable only to the freshly prepared solutions. The results indicate that for a fixed concentration of iodine, the hydrogen-ion concentrations fall with increase in the amount of iodide, whilst for solutions with a fixed ratio $[KI]/[I_2]$ they increase with the dilution. H. INGLESON.

Equilibrium between methoxyl and hydroxyl ions in mixtures of methyl alcohol and water. II. Electrometric hydrogen-ion measurements. A. UNMACK (Z. physikal. Chem., 1928, **131**, 371—388).—The hydrogen-ion activity in alkaline mixtures of water and methyl alcohol has been determined at 18° by electrometric measurements, and the partition coefficients of basic ions between water and water–methyl alcohol mixtures have been calculated. The partition exponent at infinite dilution between water and methyl alcohol is about 1·8. On the assumption that the partition coefficient of the hydroxyl ion is equal to that of the hydrated hydrogen ion, the equilibrium constant of the reaction $OH'+MeOH \rightleftharpoons OMe'+H_2O$, calculated on the basis of the Bjerrum–Larsson theory, is about 0·47. H. F. GILLBE.

Micelles and the activity coefficient in alkali silicate solutions. M. RANDALL and (MISS) J. Y. CANN (J. Amer. Chem. Soc., 1928, **50**, 347—358).—If the negative ion of a uni-univalent strong electrolyte, AB, is replaced by an ionic micelle of the form $(B_n)^{n-}$, then, neglecting hydrolysis, the mean molality is $m_+/n^{1/(n+1)}$. When n is infinite the whole of the solute may be regarded as a single particle possessing the entire negative charge of the solution, and surrounded by univalent positive ions. As n increases the micelle becomes progressively a weaker electrolyte, and in the limit probably behaves as a non-electrolyte. The activity coefficients of various sodium silicate solutions are calculated from f.-p., b.-p., dew-point, and vapour-pressure observations. Metasilicate solutions behave as typical uni-bivalent electrolytes; the value of ν in the Lewis and Randall f.-p. equation is taken as 3 instead of 4. The acid silicates have very low activity coefficients, which are explained by the formation of ionic micelles, and are not largely hydrolysed; the formula $NaHSiO_3$ is preferred and $\nu=2$. The fraction of silicate existing as micelles, and the number and size of the micelles, increase with the ratio of silica to sodium oxide. The influence of the micelles on the activity coefficient of the sodium ion is discussed. S. K. TWEEDY.

Production of glycerol by fermentation. IV. Dissociation of acetaldehyde–sodium hydrogen sulphite complex in alkaline solution. Y. TOMODA (J. Soc. Chem. Ind. Japan, 1927, 30, 747—759).—The dissociation equilibrium is represented by $\alpha/(1-\alpha)=K+(K_1/K)[H^{\cdot}]+KK_2/[H^{\cdot}]$, where α is the degree of dissociation, K the dissociation constant of the complex$=2{\cdot}84\times10^{-6}$, K_1 and K_2 the constants for the first and second stage dissociation of the acid.

The above equation for α shows that at p_H 6—8 the dissociation of the complex is not appreciable, but reaches 50% at p_H 10·5. The variation of p_H value during the titration of the complex by alkali was examined, and the p_H of the solution, containing equimolecular alkali and the complex, found to be 12—13, which suggests that the sulphite–aldehyde complex is almost completely dissociated. In the production of glycerol, the p_H value of the fermenting medium scarcely exceeds 8·3, so that the dissociation of the complex must be relatively small (less than 5%). The relation between the degree of dissociation of the complex and the p_H value of the medium was confirmed by measuring the distribution of the free aldehyde between water and benzene at various p_H values. When a solution of acetaldehyde containing an excess of sodium hydrogen sulphite was titrated with 0·1*N*-iodine solution at about p_H 8, the total sulphite was titrated, whereas when the titration was conducted at p_H 1—2, the free sulphite was titrated. The difference represents the amount of the combined sulphite and therefore the acetaldehyde. When a solution of sodium hydrogen carbonate and the complex was distilled, the whole of the acetaldehyde was evolved. S. OKA.

Graphical representation of the law of mass action. K. I. SKÄRBLOM (Tekn. Tidskr., Kemi, 1927, **57**, 87—90; Chem. Zentr., 1927, ii, 2033).—A triangular diagram is employed; a curve is obtained whereby the composition of a mixture can be read. A. A. ELDRIDGE.

Combination and space. N. S. KURNAKOV (Z. anorg. Chem., 1928, **169**, 113—139).—The relation of the physico-chemical changes of matter to the geometrical transformations of space is considered, and topology applied to the development of an analogy between a property–composition surface and a contour map. R. CUTHILL.

Graphical methods and empirical formulæ for the study of electrolytic dissociation. E. DENINA (Notiz. chim.-ind., 1927, **2**, 491—497).—A graphical method of representing the ideal dissociation formula is developed, and diagrams showing variations in the dissociation coefficient are discussed. CHEMICAL ABSTRACTS.

Influence of buffering capacity on the solubility of uric acid. A. JUNG and F. LEUTHARDT (Deutsch. Med. Woch., 1926, **52**, 1985—1988; Chem. Zentr., 1927, i, 3053).—For two different buffer mixtures the solubility of uric acid fell from 0·67 to 0·14 on dilution from 1 : 15 to 1 : 1920, with a corresponding increase of acidity. A. A. ELDRIDGE.

Lead–tin system of alloys re-examined by an electrical resistance method. F. H. JEFFERY (Trans. Faraday Soc., 1928, **24**, 209—211).—The continuous method of recording change of electrical resistance as a function of temperature previously described (A., 1927, 1030) has been applied to the lead–tin system. The equilibrium diagram has been determined down to 75° and is of the Roozeboom type 5, without any complication. The line of eutectic points is at 183°, the phases forming the eutectic mixture containing 16·5 and 97% of tin, respectively. The composition of the eutectic mixture is 66% Sn. L. F. GILBERT.

Transformation of austenite into martensite by liquid air. K. SCHROETER (Z. anorg. Chem., 1928, **169**, 157—160).—The conversion of austenite into martensite by liquid air is shown by the action of the steel on a magnet to occur during the cooling, and not during the subsequent restoration to the ordinary temperature. Measurement of the magnetic saturation before and after cooling indicates a greater relative transformation in a steel hardened in oil than in the same steel hardened in water, the strain due to the increase in volume accompanying the γ—α change being less in the former steel than in the latter owing to its lower austenite content. R. CUTHILL.

Equilibrium pressure over co-existing salt hydrates at temperatures below 0°. J. B. AUSTIN (J. Amer. Chem. Soc., 1928, **50**, 333—386).—The aqueous vapour pressure over a pair of co-existing salt hydrates is less than that over ice or water, and it follows that the heat of hydration of salts per mol. of water is always less than the molar heat of fusion of ice, thus affording a criterion of the accuracy of data on salt hydration. The data for the ten salts which apparently do not obey this rule are open to suspicion. S. K. TWEEDY.

Dissociation of sodium sulphate decahydrate. E. P. PERMAN and W. D. URRY (Trans. Faraday Soc., advance proof, Feb., 1928).—The dissociation pressure of sodium sulphate decahydrate has been measured, using the method of Downes and Perman (A., 1927, 194). The results have been applied in the calculation of (i) the free energy change associated with the hydration of anhydrous sodium sulphate to decahydrate by ice, and (ii) the heat of hydration of sodium sulphate by liquid water. The heat of hydration of sodium sulphate has been measured at four temperatures between 20° and 30°, employing the method of Harrison and Perman (A., 1927, 207). The results are in good agreement with the heats calculated from the free energy changes by means of Nernst's heat theorem. The chemical constant of water is calculated, giving a mean value of 3·63. W. A. RICHARDSON.

Thermodynamic studies on zinc iodide and mercurous iodide. F. ISHIKAWA and E. SHIBATA (Sci. Rep. Tôhoku, 1928, **17**, 99—109).—See A., 1926, 1103.

Binary system manganous orthosilicate–calcium orthosilicate. L. TOKODY (Z. anorg. Chem., 1928, **169**, 51—56).—The results of Kallenberg's investigation of the above system (A., 1915, ii, 348) have been confirmed. R. CUTHILL.

M.-p. curves of the nitrobenzaldehydes in the presence of acetic anhydride. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 309—315).—The m.-p. curves were determined in presence of phosphorous or sulphuric acid as catalyst. Two modifications of *o*-nitrobenzylidene diacetate were found, of m. p. 56° and 75°, respectively, but they could not be isolated in the pure state. The yield of diacetate was greater when using sulphuric acid as catalyst and the product showed no discrepancy in m. p. The m.-p. curve of the *o*-compound showed only the 1 : 1 compound (m. p. 73°) to exist. This was confirmed by adding a drop of sulphuric acid to pure diacetate and setting aside in a sealed tube. With sulphuric acid as catalyst, equilibrium is established from either side after 7 days. For *m*-nitrobenzylidene diacetate, phosphorous acid is a better catalyst. Here again equilibrium between the substance and its components is reached in 7 days. Only the 1 : 1 compound (m. p. 57°) was found to exist, its existence being confirmed by catalysing the pure diacetate with phosphorous acid. The m.-p. curve of *p*-nitrobenzaldehyde–acetic anhydride also shows only the 1 : 1 compound (m. p. 126·8°) to exist, phosphorous acid being used as catalyst. R. A. PRATT.

Conductometric and cryoscopic study of the dimethylpyrone compounds of acetic and the chloroacetic acids in benzene. M. RABINOVITSCH (Z. physikal. Chem., 1928, **132**, 83—100).—The occurrence of salt formation by the action of dimethylpyrone on acetic, mono-, di-, and tri-chloroacetic acids in benzene solution has been studied conductometrically, and the cryoscopic relationships of the dimethylpyrone acetate solutions have been investigated. The maxima in the conductivity curves correspond in each case with the formation of the diacid salt. The conductivities of benzene solutions of the four acids are less than those of the pure substances. The order of the conductivities of the three chloroacetic acids in benzene solution is the same as that of their degrees of association; in presence of dimethylpyrone the order of both is reversed. As regards ionisation the rôle of dimethylpyrone in benzene is similar to that of water in aqueous solution. H. F. GILLBE.

Eutectic f.-p. depression in binary mixtures. IV. Effect of pressure on eutectic equations. E. KORDES (Z. anorg. Chem., 1928, **169**, 246—250; cf. this vol., 117).—Taking Hasselblatt's data for the effect of pressure on the m.-p. diagram of mixtures of the tetrahydrates of cadmium and calcium nitrates (A., 1922, ii, 61), and assuming that the hydrates are completely dissociated according to the equations $Cd(NO_3)_2,4H_2O=Cd(NO_3)_2,H_2O+3H_2O$, and $Ca(NO_3)_2,4H_2O=Ca(NO_3)_2,2H_2O+2H_2O$, the relation $(T_b-T_e)/T_b:(T_a-T_e)/T_c=a:b$, where T_e is the eutectic temperature, and a and b are the molecular concentrations of the two components, with m. p. T_a and T_b, respectively, in the eutectic, is true over the whole range of pressure. The equation $\{(T_b-T_e)/(T_a-T_e)\}^k=T_b/T_a$, where k is a constant (A., 1927, 1132) is also apparently independent of the pressure. R. CUTHILL.

Equilibria at high temperatures in the system iron–oxygen–carbon. R. E. GARRAN (Trans. Faraday Soc., 1928, **24**, 201—207).—The equilibria in the systems iron–ferrous oxide–carbon dioxide, carbon monoxide, and ferrous oxide–ferrosoferric oxide–carbon dioxide, carbon monoxide have been studied over the approximate range 600—1300°. The results would seem to be concordant with those for the temperature range covered by Bone, Reeve, and Saunders (cf. B, 1927, 484). L. F. GILBERT.

System calcium oxide–alumina–ferric oxide. W. C. HANSEN, L. T. BROWNMILLER, and R. H. BOGUE (J. Amer. Chem. Soc., 1928, **50**, 396—406).—The above system exhibits one ternary compound, viz., $4CaO,Al_2O_3,Fe_2O_3$, *d* 3·77, which melts congruently at 1415°, and forms with $2CaO,Fe_2O_3$ a complete series of solid solutions having a melting range of about 10°. The compounds CaO,Al_2O_3 and CaO,Fe_2O_3 form limited solid solutions. A diagram is given showing the fields in which CaO, $4CaO,Al_2O_3,Fe_2O_3$, $3CaO,Al_2O_3$, $5CaO,3Al_2O_3$, and solid solutions of $4CaO,Al_2O_3,Fe_2O_3$ with $2CaO,Fe_2O_3$ separate as primary phases. Two quadruple and four quintuple points have been established, and extensive optical data are recorded. S. K. TWEEDY.

Systems uranyl nitrate, alkali nitrate, water, at 25°. A. COLANI (Bull. Soc. chim., 1928, [iv], **43**, 194—199).—See this vol., 131.

Double salt formation. I. Formation of copper sodium sulphate. II. Formation of manganese potassium and ammonium sulphates. R. M. CAVEN and W. JOHNSTON (J. Roy. Tech. Coll. Glasgow, 1927, [4], 32—41).—See A., 1927, 1142.

Equilibria in systems containing water and chlorides of iron, cobalt, and nickel. Y. OSAKA and T. YAGINUMA (Bull. Chem. Soc. Japan, 1928, **3**, 4—10).—The systems $FeCl_3$–$CoCl_2$–H_2O and $FeCl_3$–$NiCl_2$–H_2O form neither double salts nor solid solutions. In the system $CoCl_2$–$NiCl_2$–H_2O, the hexahydrated chlorides form a complete series of solid solutions. The system $FeCl_3$–$CoCl_2$–$NiCl_2$–H_2O has also been examined. S. J. GREGG.

System potassium nitrate–calcium nitrate–sodium nitrate–water. F. FROWEIN (Z. anorg. Chem., 1928, **169**, 336—344; cf. A., 1927, 22).—Determination of the solubility isotherms for the systems sodium nitrate–calcium nitrate–water and potassium nitrate–calcium nitrate–water at 0° and 20° shows that in the latter system each salt increases the solubility of the other, the effect being greater at 0° than at 20°, whereas calcium nitrate depresses the solubility of sodium nitrate, and its own solubility is not affected by sodium nitrate. The three-salt points for the system potassium nitrate–calcium nitrate–sodium nitrate–water at 0° and 20° have also been determined. R. CUTHILL.

Plane representation of multicomponent systems. W. N. LODOČNIKOV (Z. anorg. Chem., 1928, **169**, 177—245).—The application of the method of graphical representation previously described (A., 1926, 358) to systems of four or more components is explained in detail. R. CUTHILL.

Specific heat of electrolytes. K. BENNEWITZ (Z. Elektrochem., 1927, **33**, 540—542).—Theoretical. H. J. T. ELLINGHAM.

Heats of dilution of strong electrolytes and limits of Debye and Hückel's theory. E. LANGE and G. MESSNER (Naturwiss., 1927, **15**, 521—522; Chem. Zentr., 1927, ii, 790).—The heats of dilution of 0·01*M*-potassium, sodium, and lithium chlorides, lithium bromide, and potassium nitrate, 0·001*M*-calcium nitrate, 0·002*M*-sodium and magnesium sulphates, and 0·00236*M*-calcium sulphate solutions have been accurately measured by means of an adiabatic differential calorimeter. The results are all positive. For original concentrations below $0{\cdot}01M$ for the uni-univalent halides, or $0{\cdot}002M$ for the uni-bivalent electrolytes the experimental values are slightly below the theoretical. Potassium nitrate, however, in $0{\cdot}01M$-solution, exhibits a large negative deviation from the theoretical value. With bi-bivalent electrolytes the heats of dilution for original concentrations of $0{\cdot}002M$ vary, and are greater than the theoretical values. A. A. ELDRIDGE.

Heat of dilution of moderately concentrated solutions. S. M. NAUDÉ (Z. Elektrochem., 1927, **33**, 532—534).—The theory put forward recently by Nernst (this vol., 127) is further developed and heats of dilution of solutions of sodium chloride, potassium chloride, sodium nitrate, and potassium nitrate are shown to be represented by $W=-U(1-\alpha)+B\alpha\sqrt{\alpha c}$, where α is the true degree of dissociation of the electrolyte, U the heat of dissociation, and B is the Debye–Hückel coefficient which is now shown to increase linearly with temperature. Data are given for concentrations, c, ranging from 0·004 to 0·333 g.-mol./litre. With increasing concentration W increases to a maximum and then decreases again, becoming negative at high concentrations. These variations are represented very closely by the above formula.

H. J. T. ELLINGHAM.

Vapour pressure and heat of dilution. V. Activity. E. P. PERMAN (Trans. Faraday Soc., advance proof, Jan., 1928).—At 80°, solutions of sucrose up to 500 g. per litre behave as perfect solutions. The lower the temperature, the lower is the concentration up to which the solution remains perfect. For dilute solutions of carbamide at 80° and 60° the activity is slightly higher than unity, and this is attributed to the formation of traces of ammonia by hydrolysis at these temperatures. Allowing for this error carbamide solutions remain perfect at these temperatures up to a concentration $n/N=0{\cdot}8$.

To calculate the activity of potassium chloride, it was assumed that $a_2/N_2=1$ at a dilution of $N_1/N_2=10{,}000$. The activity of the solute reaches a high value in concentrated solution, and is greater at 60° than at 80°. The activity coefficient γ for a molal solution is 0·52 at 80° and 0·60 at 60°. The activities have been calculated in a similar manner for calcium chloride solutions, and are shown to reach enormously high values at high concentrations.

W. A. RICHARDSON.

Heat of vaporisation and number of molecules [in unit volume]. W. HERZ (Z. anorg. Chem., 1928, **169**, 173—176).—For non-associated liquids, and many associated liquids, the value of $Z/\sqrt{L}$, where Z is the number of molecules in unit volume at a particular temperature (calculated from the molecular volume and Avogadro's number), and L the latent heat of vaporisation at that temperature, is approximately constant over a wide range of temperature although a very flat minimum is usually present. The value for liquefied gases falls slowly but continuously with rise in temperature, but data are available over only a small range of temperature. For hydrocarbons and esters, but not for associated compounds such as alcohols and fatty acids, $\sqrt{Z/L}$ for the normal b. p. has a value about $8{\cdot}5\times10^8$. R. CUTHILL.

Reversible mixing of substances in the condensed state at the absolute zero of temperature. R. D. KLEEMAN (Science, 1927, **61**, 216—217).—The internal heat of mixing a number of substances is zero at 0° Abs. if the substances and resultant mixture are under the pressures of their vapours. Near 0° Abs. the internal heat of mixing is proportional to the cube of the absolute temperature.

A. A. ELDRIDGE.

Errors in the determination of heat of combustion. E. BERNER (Tidskr. Kemi Bergv., 1927, **7**, 31—34; Chem. Zentr., 1927, i, 3211).—A discussion of the precision of the temperature measurement and of the computation of the heat exchange with the surroundings. A. A. ELDRIDGE.

Determination of heat of combustion with Féry's calorimeter. F. KARAS (Chem. Obzor, 1926, **1**, 121—125; Chem. Zentr., 1927, ii, 1373).—The maximum deviation of results obtained with Féry's and the Berthelot–Mahler–Kroeker calorimeters is 1·21%; Féry's method occupies half the time of the latter method. Errors may arise from the radiation from incandescence lamps; day- and night-values may differ by 2%. A. A. ELDRIDGE.

Heat of combustion of some secondary and tertiary amides. A. PARTS (Z. physikal. Chem., 1928, **131**, 405—408).—The following heats of combustion, in kg.-cal./mol., have been determined: diacetamide 518·9, dipropionamide 809·2, acetylbenzamide 1065·1, dibenzamide 1634·8, tribenzamide 2425·5. H. F. GILLBE.

Methods in use at the International Bureau of Physico-Chemical Standards. II. Calorimetric precision measurements. L. MARICQ and M. BECKERS (Bull. Soc. chim. Belg., 1928, **37**, 1—32).—A detailed description is given of a calorimetric method for the determination of heats of combustion. The experimental error does not exceed 1 part in 4000 and might be further reduced by using a more sensitive thermometer, *e.g.*, a resistance thermometer instead of a mercury thermometer. The applicability of Regnault's correction is discussed. The heat of combustion of pure benzoic acid prepared by Poulenc was found to be identical with that of the benzoic acid standard supplied by the U.S. Bureau of Standards (cf. Dickinson, Bull. Bur. Standards, 1915, **11**, 192—203). M. S. BURR.

Electrochemistry of the system benzamide–bromine–nitrobenzene. W. FINKELSTEIN and O. KUDRA (Z. physikal. Chem., 1928, **131**, 338—346).—The specific conductance of the additive compound bromobenzamide, NH_2Bz,Br_2, in nitrobenzene solution increases with increase of concentration up to 52%. The curves at 25° and 35° are parallel, the temperature coefficient being negative. The molecular conductivity–dilution curves at 35° have a maximum at about 900 c.c. dilution. The relationship between the conductivity and the ratio benzamide : bromine confirms the existence of the complex as a true electrolyte; on electrolysis bromine is liberated quantitatively at the anode. The decomposition potential cannot be measured on account of the thermal decomposition products.

H. F. GILLBE.

Electrical conductivity of solid sulphide mixtures. P. FISCHER (Z. Elektrochem., 1927, 33, 571—577).—Following work on mixtures of salts and of oxides (A., 1926, 478; 1927, 23), the electrical conductivity of compressed mixtures of powdered sulphides has been determined for direct and for alternating current at various temperatures. For mixtures of two sulphides the conductivity does not vary in a simple manner with the percentage composition of the mixture. With silver sulphide and lead sulphide the conductivity increases with increasing proportion of lead sulphide, but eventually reaches a maximum at about 90% PbS. Although the conductivity of silver sulphide is essentially electrolytic and that of lead sulphide electronic, migration experiments on a 50% mixture indicate that only about 1% of the conductivity is electrolytic. For mixtures of silver sulphide with ferrous sulphide, which is practically a non-conductor, the conductivity–composition curve exhibits a minimum and a maximum. Mixtures of ferrous sulphide and lead sulphide are practically non-conducting up to 50% PbS, but with higher proportions the conductivity increases rapidly. Mixtures containing sulphides of copper, zinc, cadmium, and barium were also examined. It appears that the type of conductivity exhibited by a solid substance may be modified by certain conditions. The observed phenomena are attributed to distortion of the crystal lattices and electron orbits as a result of compression.

H. J. T. ELLINGHAM.

Conductivity cells with electrodes of "brominated silver" instead of platinum. W. A. ROTH (Z. Elektrochem., 1927, 33, 508—511).—Pure silver covered with a very thin film of silver bromide by exposure to bromine vapour or by dipping in a solution of bromine in hydrobromic acid, is recommended as a cheap substitute for platinum in the construction of electrodes for conductivity cells. Such electrodes give, in conductivity measurements, a balance point about as definite as is obtained with smooth platinum electrodes, whilst, if covered with a thin deposit of platinum-black, the minimum is as sharp as with platinised platinum electrodes. For dilute solutions of silver salts or of formic acid, brominated silver electrodes give better results than platinised platinum. A number of demonstration experiments using a conductivity apparatus fitted with an amplifier and a loud speaker are described. These illustrate the relative solubility of sparingly soluble salts, the relative adsorption of sodium and potassium chlorides by soils, and of potassium chloride and nitrate by precipitated barium sulphate, and the principle of conductometric titration. For the last-mentioned purpose a simple type of apparatus with vertical electrodes of brominated silver is described. Reference is made to the conductometric determination of chlorides, bromides, or iodides of heavy metals by titration with thallium hydroxide solution in the presence of alcohol; of metals with insoluble fluorides with silver fluoride solution; of potassium with lead fluosilicate or barium perchlorate solutions in the presence of alcohol; and of sulphates of heavy metals, including double ammonium sulphates, with barium hydroxide solution.

H. J. T. ELLINGHAM.

Conductivities and p_H values of mixtures of acids in solution. J. A. CRANSTON and J. DUNCAN (J. Roy. Tech. Coll. Glasgow, 1927, 4, 41—47).—The hydrogen-ion concentration (measured by a hydrogen electrode) and the conductivity of hydrochloric acid solutions containing varying amounts of acetic, oxalic, citric, tartaric, and orthophosphoric acids have been determined. Replacement of water in $0{\cdot}5N$-hydrochloric acid by solutions of acetic, citric, or tartaric acid results in an increase of the hydrogen-ion concentration as determined by the *E.M.F.* method, whereas the conductivity falls. When phosphoric acid solution is substituted, the p_H value increases, whilst the conductivity rises to a maximum and falls. It is suggested that some of the hydrogen ions supplied by the added acid are sufficiently free to contribute to the potential of a contiguous hydrogen electrode, but are insufficiently free to contribute to the conductivity of the solution. When hydrochloric acid solutions of greater than N-concentration are used, substitution of water by solutions of varying oxalic acid concentration has no effect on the conductivity; when solutions of phosphoric acid are substituted, the conductivity of the hydrochloric acid solution is diminished. It is suggested that the hydrogen ions from the hydrochloric acid may not only prevent the dissociation of the phosphoric or oxalic acid into ions, but in the case of the former acid, may also attach themselves transiently to undissociated phosphoric acid molecules, since in phosphoric acid there is an oxygen atom possessing a "lone" pair of electrons, which may be shared by the hydrogen nucleus.

L. M. CLARK.

Potential of the saturated calomel electrode between 0° and 40°. E. VELLINGER (Arch. phys. biol., 1927, 5, 119—122; Chem. Zentr., 1927, ii, 674).—The relation $E=0{\cdot}2622-0{\cdot}00066t$ holds.

A. A. ELDRIDGE.

Potentials and activities of the metals in zinc amalgam cells. J. N. PEARCE and J. F. EVERSOLE (J. Physical Chem., 1928, 32, 209—220).—*E.M.F.* measurements of zinc amalgam concentration cells have been made at 18°, 25°, and 30°, with amalgam concentrations ranging from a mol. fraction of zinc equal to 0·0003024 up to saturation. The changes in free energy, heat content, and entropy on dilution, and the activities of the zinc and the mercury in the amalgams have been calculated. The deviation between the observed and ideal potentials increases continuously with an increase in concentration of the zinc and approaches zero at infinite dilution. Hildebrand's equation (A., 1913, ii, 470) expressing the *E.M.F.* of a zinc amalgam concentration cell applies throughout a large portion of the range studied. The present results decide in favour of the work of Richards and Forbes (A., 1907, ii, 424) and against that of Crenshaw (A., 1910, ii, 258).

L. S. THEOBALD.

Palladium diffusion electrodes. C. DRUCKER (Z. Elektrochem., 1927, 33, 504—507).—Two solutions, A and B, are separated by a thin plate of palladium which is charged with hydrogen by cathodic polarisation, using as anode a platinum wire in solution *A*. By means of standard electrodes arranged with their tips close to the two sides of the plate respectively, the *P.D.* on both sides can be measured, and hence, if the hydrogen-ion concentration of *A* is known, that of *B* can be determined. By using a rotating commutator the polarisation circuit is broken when the potentiometer circuits are made, and *vice versa*. With a polarisation current of 0·07—0·10 milliamp. at a plate with surface area 20—80 sq. mm. and thickness 0·004 mm., reproducible values were obtained, although the effective pressure of hydrogen in the palladium was only about 0·01 atm. Preliminary experiments in which *A* and *B* were both 0·1*N*-hydrochloric acid showed that under these conditions the effective hydrogen pressures on both sides of the plate become equal after about 20 min. and direct measurements are then possible. In any case determinations can be made by making a measurement with solutions *A* and *B*, and then making a further measurement when a solution *B'* of known hydrogen-ion concentration has been substituted for *B*. The method has the great advantage of being applicable to the determination of the hydrogen-ion concentration of solutions which change in composition if a stream of hydrogen gas is passed through them, and of solutions which are mild reducing agents. Measurements on solutions of sodium hydrogen carbonate and of sodium hydrogen sulphite are recorded. The second dissociation constant of sulphurous acid is thus estimated to be about 5×10^{-7}. Again, a blood-serum was found by the diffusion electrode to have a hydrogen-ion concentration of $1{\cdot}4\times10^{-7}$, whereas the value obtained by means of the ordinary hydrogen electrode was $3{\cdot}3\times10^{-9}$. H. J. T. Ellingham.

Solution tension of silver in non-aqueous solvents. F. K. V. Koch (J.C.S., 1928, 269—280).—The solution tension of silver has been measured in solutions of silver nitrate in pyridine, aniline, methyl and ethyl alcohols, acetone, and various nitriles with the view of correlating the results with the dielectric constants of the solvents and also to ascertain whether the solution tension in different solvents runs parallel with the solubility of the salt in these liquids. There appears to be no kind of regularity in the series of corresponding values of dielectric constant, solution tension, and solubility, but the general result of the investigation shows that in solvents of ammoniacal or nitrile character the metal has a higher solution tension than in those containing hydroxyl or ketonic groups. H. Ingleson.

Silver nitrate concentration cells in acetonitrile and benzonitrile. F. K. V. Koch (J.C.S., 1928, 524—527; cf. A., 1927, 420, and preceding abstract).—Previous work on the validity of the Nernst formula applied to concentration cells containing non-aqueous solutions is reviewed. Experimental results on the measurements at 0° and 25° of *E.M.F.* of concentration cells of silver nitrate in acetonitrile and in benzonitrile are recorded and compared with the values calculated from the formula $E=2(1-n_c)RT/F\ \log_e \kappa_1/\kappa_2$, where n_c is the transport number of the silver ion, and κ_1 and κ_2 are the specific conductivities of the two electrode solutions. Very good agreement was shown. The results for such concentration cells support the Nernst formula, and also show that the solution laws are obeyed in these solvents at least as nearly as in water. R. A. Pratt.

Modifications of the Sand auxiliary electrode. T. B. Smith (Trans. Faraday Soc., 1928, **24**, 216—225; cf. J.C.S., 1911, **91**, 373).—By the use of a porous diaphragm instead of the special " conducting " tap of the Sand electrode, and by other modifications, the working resistance of the auxiliary electrode can be reduced to about one tenth of the former value. This enables the potentiometer voltmeter to function also as a null-point detector without causing any appreciable error on account of concentration polarisation of the half-cell. A second modification is described in which the use of either special taps or diaphragm in the electrical circuit is avoided. It has about the same resistance as the first pattern, but permits the use of connecting liquids of high conductivity. The null-point detection is thus brought within the range of a voltmeter of relatively low sensitivity. This modification is to be preferred for most purposes, but the diaphragm pattern has the advantage that it may be used for a considerable time without refilling with electrolyte. The second modification can be employed conveniently as a quinhydrone electrode. Use is made in the electrical circuit of the better class of radio apparatus, the compact design of which facilitates the enclosure of parts most easily attacked by acid fumes. L. F. Gilbert.

***E.M.F.* of electrolytic thermocouples and thermocells and the entropy of transfer and absolute entropy of ions.** E. D. Eastman (J. Amer. Chem. Soc., 1928, **50**, 292—297).—Electrolytic thermocouples of the type: electrode(T)/soln.I(T)/soln.II($T+dT$)/soln.I(T)/electrode(T) are discussed, the solutions containing uni-univalent electrolytes with a common anion, and the equations previously given for thermocells are modified by considering the entropy of transfer of the ions. Utilising previously published data and the principles of the preceding paper (this vol., 365), the entropy of transfer of some ions in a 0·02*N*-solution at 25° is calculated, as well as the partial molal entropy of the chloride ion. S. K. Tweedy.

Haber's glass cell. W. S. Hughes (J.C.S., 1928, 491—506; cf. A., 1909, ii, 785; 1925, i, 1201).—The influence of the composition of the glass used for a Haber cell on the reproducibility of results was studied. The best results were obtained with a glass of small alumina content but of high sodium content. The manufacture of a modified Haber cell is described. Such a cell showed no evidence of the " mixed electrode function " in acid solution described by some workers. An explanation is put forward of the means whereby the hydrogen-ion concentration in the glass phase is maintained relatively constant when that of the solution changes. It is considered that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action of the sodium silicate in the glass. If, however, in a cell Hg|HgCl|KCl(satd.)|NaOH|glass|N-HCl|HgCl|Hg the concentration of the sodium hydroxide is increased to 0·1N, the buffer action breaks down. At p_H 9, the buffer action becomes less effective, and this p_H value corresponds with the p_H of a sodium acid silicate buffer mixture half neutralised with respect to the first hydrogen ion of silicic acid (dissociation constant 10^{-9}). Beyond p_H 13, the glass surface is rapidly attacked owing to neutralisation of the second hydrogen ion of silicic acid (dissociation constant 10^{-13}), and the *E.M.F.* falls rapidly. It is shown that the glass is partly acting as a hydrogen electrode in alkaline solution. The extent to which the glass cell *E.M.F.* departs from the value it would have if the glass had a perfect hydrogen electrode function was also studied.

Since the glass cell can be used to measure hydrogen-ion concentration under conditions which render the hydrogen electrode useless, by measuring the p_H of half-neutralised buffer mixtures, the following dissociation constants were determined: the second-stage constants of arsenic and chromic acids ($8·3\times10^{-8}$ and $1·0\times10^{-7}$ respectively), the first-stage constant of arsenious acid (6×10^{-10}), and the constants of azoimide ($2·56\times10^{-5}$) and hydrazine hydrate ($1·4\times10^{-6}$).

The hydrogen-ion activity of copper sulphate solutions was measured, 0·05M-solutions having a p_H of 4·24. It was shown that hydrolysis of the sulphate is a slow reaction at the ordinary temperature. The basic copper sulphate formed by addition of alkali has the composition $3CuO,CuSO_4,xH_2O$.

The p_H of an iodide–iodate mixture was found to be about 6·9 after two thirds of the iodate had been decomposed by the addition of hydrochloric acid.

R. A. Pratt.

Reducing power of dextrose. S. A. Schou and R. Wurmser (Compt. rend., 1928, **186**, 367—369).—The production of the stable potential gradually set up when a platinum or gold electrode is placed in a solution of dextrose protected from the air (A., 1927, 1218) may be followed by means of the ultra-violet absorption spectrum of the solution, the constant maximum potential corresponding with a maximum absorption band at 2650 Å. The nature of the reducing substance responsible for this is discussed. It is not methylglyoxal, but may be the result of an enolic transformation. J. Grant.

[Influence of gelatin on the potential and discharge potential of zinc in zinc sulphate solution.] E. Rabald (Z. Elektrochem., 1927, **33**, 532).—A reply to Isgarischev and Titov (A., 1927, 833). H. J. T. Ellingham.

Decomposition potential of zinc sulphate and ferrous sulphate. B. Kamienski (Przemysl Chem., 1927, **11**, 374—381; Chem. Zentr., 1927, ii, 547).—The decomposition potential of zinc sulphate for a sulphide anode is 1·8 volts and 2·62 volts with a lead dioxide anode; when powdered zinc blende on a carbon rod is employed as anode zinc is deposited at 2 volts. A. A. Eldridge.

Overpotential at metallic cathodes. Silver in neutral and alkaline solutions. J. Grant (Trans. Faraday Soc., 1928, **24**, 225—233; cf. A., 1927, 317).—Polarisation data for silver cathodes in solutions of neutral and alkaline electrolytes have been determined. A fixed value for the overvoltage is attained for a particular current density after a certain time peculiar to each electrolyte. This time decreases as the electrolytes approach the neutral point. The phenomenon is independent of the current density except with regard to the final constant value attained. The overvoltages as measured by both the "commutator" and the "direct" method increase rapidly with the current density when this is low. With the former method a constant value is finally attained, but with the latter method the overvoltage increases at a lesser rate after a critical higher value. This value is close to the constant overvoltages obtained by the commutator method. The decay of polarisation was investigated by varying the interval of the commutator. The decay curves of polarisation sink to values which remain nearly constant over a considerable time, and usually approximate to the constant overvoltages otherwise attained. The voltage between a saturated calomel electrode and a hydrogen electrode placed in the solution varies approximately linearly with the overvoltage. The deviations may be due to secondary influences. The conditions of the formation of a black deposit on the silver and the effect of this on the overvoltages have been investigated. In general, the results are analogous to those already obtained for an antimony cathode. L. F. Gilbert.

"Anode effect." H. von Wartenberg (Z. Elektrochem., 1927, **33**, 526—527).—The author maintains his theory as to the origin of the "anode effect" in the electrolysis of fused salts (A., 1926, 912) against the views of Arndt (B., 1927, 659).

H. J. T. Ellingham.

Maxima on current–voltage curves. Electrolysis of nickel salt solutions with the mercury dropping cathode. N. V. Emelianovna and J. Heyrovský (Trans. Faraday Soc., advance proof, Feb., 1928).—The prominent maxima sometimes shown on polarisation curves of electro-reductions obtained with the mercury dropping cathode have been studied in electro-deposition from nickel salt solutions. The effect of oxygen is to inhibit the appearance of maxima, which become developed only after long bubbling of hydrogen through the solutions. This influence of oxygen appears to operate by the formation of mercurous ions, as the addition of mercurous ions decreased the maximal currents by amounts which were direct functions of their concentrations. That the stability of maxima is greatest in the presence of iodides, less in chlorides, and least in sulphates, when the concentration of mercurous ions can be the greatest, is thus explained. The suppressive effect of other substances was studied. Cations suppress maxima by degrees which run in the same order as the coagulating powers on negative sols. The influence of anions was not specially examined, as it seemed to matter little. Fuchsin hydrochloride and dextrose solutions are also very effective in suppressing maxima. The phenomena of the formation of the maximum and its suppression are considered to be due to adsorption of the reducible matter at the mercury-solution interface and to the replacement of the reducible ions by other adsorbable matter, respectively. The sudden fall of current after the maximum is explained by concentration polarisation, which starts when the velocity of deposition of ions becomes greater than the velocity of adsorption in the surface film at the mercury dropping cathode. L. F. Gilbert.

Maxima on current–voltage curves. II. Maxima on the polarisation curves of uranyl salt solutions. P. Herasymenko (Trans. Faraday Soc., advance proof, Feb., 1928; cf. preceding abstract).—The current–voltage curves of the first reduction stage of uranyl ions in aqueous solution at the mercury dropping cathode have been investigated with special reference to the maxima developed. The maximal currents in pure uranyl salt solutions are nearly proportional to the concentrations of uranyl ions. Added salts reduce the maximal current by amounts depending only on the total number of electric charges in solution, so that equivalent quantities of ions of different valencies produce the same effect. Some non-electrolytes also give an appreciable effect. This difference as compared with the behaviour of added ions on the maxima for nickel salts may be ascribed to the presence of products of reduction of uranyl salts, *i.e.*, of quinquevalent uranium ions (see following abstract), which accumulate in the interfacial layer and are preferentially adsorbed. With increase of the polarisation voltage the current falls, after the maximum, to a constant value which is almost independent of the concentration of other electrolytes in solution, and is proportional to the concentration of uranyl ions. From measurements of the interfacial tension between cathodically polarised mercury and solutions of uranyl salts in presence of different concentrations of potassium chloride it is deduced that the cathode potential varies only slightly with the polarising voltage, but the decrease of current after a maximum is accompanied by a sharp increase in the polarisation of the cathode. L. F. Gilbert.

Electro-reduction of uranyl salts by means of the mercury dropping cathode. P. Herasymenko (Trans. Faraday Soc., advance proof, Feb., 1928; cf. preceding abstract).—The reduction of uranyl salts at the dropping mercury cathode proceeds in three stages, in which quinquevalent, quadrivalent, and tervalent ions are formed successively. At still greater potentials hydrogen ions deposit. The first reduction potential depends only on the concentration of uranyl ions, being uninfluenced by the concentration of hydrogen ions. Quinquevalent but not quadrivalent uranium ions readily form complexes with neutral salts. L. F. Gilbert.

Simultaneous reactions of the type $A \rightleftharpoons B \rightleftharpoons C$. F. E. C. Scheffer and (Miss) A. E. Korvezee (Rec. trav. chim., 1928, 47, 235—247).—Theoretical. If the relative concentrations of the substances A, B, and C taking part in a reaction of the type $A \rightleftharpoons B \rightleftharpoons C$ are designated by x, $1-x-y$, and y, the composition of the mixture can be expressed by an equation $f(y,x)=0$. The form of this equation and the direction of the corresponding reaction curves are discussed. By choosing the initial concentrations suitably, the reaction can give rise to the maximum and minimum concentrations of all the reactants. By solving the equations, $dy/dt=f(y,x)$ and $dx/dt=f(y,x)$, the time taken to reach these maxima and minima can be found. R. A. Pratt.

Homogeneous gas reactions. I. L. S. Kassel (J. Physical Chem., 1928, 32, 225—242).—Lewis' definition of energy of activation as the minimum internal energy which must be possessed by molecules in order to react (A., 1925, ii, 799) is considered to be preferable to the definition given by Tolman (A., 1925, ii, 799). Further, it is shown that the activation by collision theory as treated by Hinshelwood (A., 1927, 26, 212), and further developed by Rice and Ramsperger (A., 1927, 833), in which all activated molecules have the same specific reaction rate regardless of their energy content, whilst agreeing with experimental data for propaldehyde, disagrees with such data in the decompositions of diethyl ether, dimethyl ether, and azomethane. An expression is now developed showing the variation of the specific reaction rate of activated molecules with their energy content, and from this is derived an equation which gives this rate for a unimolecular reaction at any pressure. This equation agrees with Ramsperger's experimental results for the decomposition of azomethane (A., 1927, 737). The differences between the present theory and that of Rice and Ramsperger (*loc. cit.*) are considered (cf. also Fowler and Rideal, A., 1927, 114). L. S. Theobald.

Pressures developed in gaseous explosions. W. T. David and B. H. Thorp (Nature, 1928, **121**, 420).—The non-variation of the specific heat of steam over a wide range of maximum temperatures (Maxwell and Wheeler, this vol., 248) is doubted; the apparent value, calculated from explosions of air with excess of hydrogen, is practically constant, but this result is ascribed to incomplete combustion. Minimal values of the percentage of incomplete combustion for various mixtures of hydrogen, nitrogen, and oxygen are tabulated. It is believed that combustion is far from complete even when excess of hydrogen is present. A. A. Eldridge.

Effect of anti-knock materials on the condenser-discharge-spark energy required to ignite a mixture of air with the vapour of ethyl ether. Y. Nagai (Proc. Imp. Acad. Tokyo, 1927, 3, 670—671).—Values are given for the energy required to ignite a mixture of 4·25% of ethyl ether and 95·75% of air by means of a spark, when various amounts up to 1·5 mol.-% of diethyl selenide, tin tetramethyl, and lead tetramethyl are present. The energy is increased by about 50% for 1 mol.-% in each case. C. J. Smithells.

Effect of anti-knock materials on the limits of inflammability of ethyl ether and hydrocarbons. Y. Nagai (Proc. Imp. Acad. Tokyo, 1927, 3, 664—669).—The effect of lead tetramethyl and tin tetramethyl on the limits of inflammability of mixtures of air and ethyl ether or hydrocarbons was determined. A straight-line relation was found between the molecular percentage of the tetramethyl compounds and the upper and lower limits of composition of the mixtures. A similar explanation is given to that previously advanced (cf. A., 1926, 1106). The theoretical flame propagation temperatures of the lead and tin compounds are both 1680°, that of diethyl selenide is 1750°, and that of ethyl ether and hydrocarbons 1450°. This value is raised to that of the anti-knock material when a small percentage is present. C. J. SMITHELLS.

Chemically induced "chain reactions" in mixtures of a halogen with hydrogen or methane. S. VON BOGDANDY and M. PÓLÁNYI (Z. Elektrochem., 1927, **33**, 554—559).—Previous work (Beutler and Pólányi, Naturwiss., 1925, **13**, 711) has indicated that the vapour of the alkali metals reacts with a halogen according to the equation $Na+Cl_2=NaCl+Cl$. Experiments have now been made to determine the reactivity of free halogen atoms liberated in this way. Hydrogen at 5—10 mm. pressure was passed over molten sodium at 150—250°, whereby it took up sodium vapour at $0{\cdot}5-5\times10^{-4}$ mm. pressure. On meeting a stream of chlorine at 0·2—0·3 mm. pressure, sodium chloride is deposited, but hydrochloric acid is produced in enormously greater amounts. It is considered that this is due to a reaction chain of the type postulated by Nernst for the photochemical formation of hydrochloric acid, viz., $Cl+H_2=HCl+H$; $H+Cl_2=HCl+Cl$; etc. In the present case the number of reactions in a chain is estimated to vary from 700 to 10,000, according to conditions. Increase of the pressure of the sodium vapour decreases the length of the chain. But even under given conditions the length of the chain may vary greatly, probably owing to impurities or the condition of the wall of the reaction vessel. Thus, if the pressure of sodium vapour is increased and then decreased again to its initial value, the length of the reaction chain may be much greater than it was originally: the sodium chloride deposited may prevent combination of chlorine atoms on the wall of the vessel. With potassium instead of sodium the results were similar but the reaction chains shorter. With methane instead of hydrogen, the essential product was methyl chloride, but the number of reactions in a chain was only 100—300. With hydrogen, bromine, and sodium vapour very little action occurs and even when the sodium was heated to 385° only very short reaction chains were obtained. The influence of bromine vapour mixed with chlorine in inhibiting the reaction of the latter with hydrogen in the presence of sodium vapour was also investigated. From probability considerations it is concluded that if α is the ratio of the partial pressure of bromine to that of chlorine and W the ratio of the velocity coefficients for the combination of hydrogen with bromine and chlorine, respectively, the number of reactions in a chain will be $2(\alpha W+1)/\alpha W(\alpha+1)$. The experimental results are in reasonable agreement with this relation, if W is put equal to 0·13. The fact that hydrochloric acid does not inhibit the reaction between chlorine and electrolytic gas has been quoted as an objection to the Nernst reaction chain theory. In a discussion of the subject it is shown that this objection may be invalid. H. J. T. ELLINGHAM.

Explosion temperature and sensitivity to shock of liquid and solid explosives. G. TAMMANN and C. KRÖGER (Z. anorg. Chem., 1928, **169**, 1—32).—Experiments with a variety of liquid and solid explosives have shown that the temperature at which explosion occurs on heating usually increases in a linear manner with the rate of heating, and decreases with increase in the amount of explosive. For substances exploding below their m. p., the lines representing the effect of rate of heating on the explosion temperature for different quantities of explosive are parallel, but with explosives which melt and are appreciably volatile below their m. p. and explode above it the lines tend to converge at high rates of heating. With explosives of the former group, such as lead azide and mercury fulminate, the explosion limit, *i.e.*, the minimum amount which will explode with any particular rate of heating, is considerably depressed by heating in an inert atmosphere, oxidation thus being avoided, and increase in the coarseness of grain has the same effect. The explosion limits of the more volatile explosives, on the other hand, may be lowered by increasing the pressure. By varying the factors determining the rate at which the heat of reaction is lost, *e.g.*, by compressing a powder into a tablet, the effect of rate of heating and amount of explosive on the explosion temperature may be partly annulled. With small amounts of lead azide, the relation between explosion temperature and rate of heating is abnormal, apparently owing to the formation of an explosive basic azide. The explosion temperature of silver azide does not vary in any regular manner with the rate of heating and amount of explosive. From heating curves, 2 : 4 : 6-trinitrotoluene is found to begin to decompose at 150°, and 2 : 4 : 6-trinitro-*m* cresol at 180°. If the former is heated at a steady temperature for some time, there are formed decomposition products, which raise the explosion temperature. A liquid explosive can be caused to explode by the uniform propagation through it of a shock. A shock applied to a solid explosive by actual contact with a solid is more effective than an equal shock applied indirectly through hydrostatic pressure over all its surface. Under certain conditions, crystalline explosives may explode when flowing through an orifice. R. CUTHILL.

Velocity of ionic reactions. II. R. N. J. SAAL (Rec. trav. chim., 1928, **47**, 264—285; cf. this vol., 248).—The reaction constant of the reaction $CO_2+OH'\longrightarrow HCO_3'$ was found to be $3{\cdot}7\times10^3$ at 13·7° from conductivity measurements, the hydroxyl-ion concentration being so chosen that the amount of hydrogen carbonate in the solution was negligible. The total concentration of the solution was found to have no influence on the reaction constant, thus agreeing with Brönsted's theory (cf. A., 1922, ii, 699; 1925, ii, 681). Determinations were made of both the conductivity and the hydrogen potential of the equilibrium $H_2CO_3\rightleftharpoons H^{\cdot}+HCO_3'$ and of the reaction $H_2CO_3\longrightarrow CO_2+H_2O$; but it was not possible to decide whether the carbon dioxide originates from carbonic acid or whether it is the result of interaction of hydrogen and hydrogen carbonate ions. The reaction constant of the reaction $H^{\cdot}+HCO_3{}' \rightleftharpoons H_2CO_3 \longrightarrow CO_2+H_2O$ is 8 at 13·5°. The equilibrium constant of the reaction $H_2CO_3 \rightleftharpoons CO_2+H_2O$ is $1{\cdot}1\times10^3$ at 13·7°. It was possible to follow the behaviour of the p_H during acidimetric titrations with alkali containing carbon dioxide.

The reaction dichromate ⟶ chromate was also studied; the equilibrium $Cr_2O_7{}''+H_2O \rightleftharpoons 2HCrO_4{}'$ exists with an equilibrium constant of $0{\cdot}019\pm0{\cdot}001$. The decomposition of dichromate to chromate may take place in three ways: (i) In the alkaline region, $Cr_2O_7{}''+OH' \longrightarrow CrO_4{}''+HCrO_4{}'$. (ii) In the acid and neutral region, $Cr_2O_7{}''+H_2O \longrightarrow 2HCrO_4{}'$. (iii) On large dilution with acid and water, $Cr_2O_7{}''+H^{\cdot}+H_2O(\rightleftharpoons HCr_2O_7{}'+H_2O) \longrightarrow 2HCrO_4{}'+H^{\cdot}$.

R. A. Pratt.

Primary salt effect in a zero type reaction. M. Kilpatrick, jun. (J. Amer. Chem. Soc., 1928, 50, 358—362).—The reaction $6H_2O+Cr[CO(NH_2)_2]_6{}^{\cdot\cdot\cdot} \longrightarrow Cr(H_2O)_6{}^{\cdot\cdot\cdot}+6CO(NH_2)_2$ is investigated, the rate of disappearance of the first-named ion being measured by precipitation with potassium cobalticyanide. The reaction serves as a critical test of theories of reaction rate; the results are in agreement with Brönsted's theory. S. K. Tweedy.

Activation of chemical reactions by neutral salts. II. Activation of the dissolution [in acids] of marble by neutral salts. N. Isgarischev and S. Schapiro (Z. physikal. Chem., 1928, **131**, 442—445; cf. A., 1927, 945).—The velocity of dissolution of marble in hydrogen chloride solutions in presence of chlorides and in acetic acid solutions in presence of acetates has been determined by measurement of the rate of evolution of carbon dioxide. In the former case the velocity is in general increased, but there is no relationship between the velocity and the p_H of the solution. In the acetate solutions the velocity is proportional to the p_H. The results are in agreement with the Debye–Hückel theory.

H. F. Gillbe.

Kinetics of the decomposition of nitrous acid. I and II. E. Abel and H. Schmid (Z. physikal. Chem., 1928, **132**, 55—77).—The mode of decomposition of nitrous acid has been studied, regarding as the essential factor the reaction between nitrogen tetroxide and water. If supersaturation of the solution with nitric oxide is not prevented the rate of disappearance of nitrous acid is not a measure of the progress of the reaction $3HNO_2 \longrightarrow H^{\cdot}+NO_3{}'+2NO+H_2O$. H. F. Gillbe.

Reactivity of dextrose in hydrochloric acid. E. A. Moelwyn-Hughes (Trans. Faraday Soc., advance proof, Feb., 1928).—The change of rotation of solutions of dextrose (10—50 g. per 100 c.c.) in N-hydrochloric acid at 60° and 70° has been investigated. The observed increase in positive rotation, which is distinct from the ordinary mutarotation, is complete in about 200 hrs. Following Harrison (A., 1914, i, 498), the change in rotation is ascribed to a condensation product "diglucose." The relative hydrogen-ion activities in N-hydrochloric acid solutions containing 10—50 g. of dextrose in 100 c.c. are given, and it is shown that the value of k calculated from the equation for unimolecular reactions, divided by the relative hydrogen-ion activity, is constant for all the solutions. The van 't Hoff method also indicates that the reaction is of the first order. The critical increment of the reaction is 33,500 g.-cal. The order of the reaction is explained by assuming the condensation of dextrose under these conditions to be a pseudo-unimolecular change, in which the concentration of one of the reactants (normal dextrose) far exceeds that of the other (active dextrose). The nature of this active form is discussed. W. A. Richardson.

Kinetics of the hydrolysis of glucosides (salicin, arbutin, and phloridzin). E. A. Moelwyn-Hughes (Trans. Faraday Soc., advance proof, Feb., 1928).—The rates of hydrolysis at 60° and 70° of salicin, arbutin, and phloridzin by N-hydrochloric acid have been determined polarimetrically. By using dilute solutions (about 5%) the production of "diglucose" (cf. preceding abstract) is negligible under these conditions. The critical increment of the hydrolysis of disaccharides and glucosides is a more significant quantity than the velocity itself, as it lends itself more readily to comparative treatment. The mean critical increment for three fructosides (sucrose, raffinose, and melezitose) is 25,700 g.-cal. (±1%); for three glucosides (maltose, salicin, and arbutin) it is 31,600 g.-cal. (±1%), and for the galactoside lactose it is 27,100 g.-cal., whilst the velocity coefficients show no simple relationships. The experimental value of the critical increment appears to depend on the nature (whether fructosidic or glucosidic) of the linking ruptured, and to be independent of the stereochemical (α or β) character of the linking. The critical increment for phloridzin, 23,100 g.-cal., is abnormally low.

W. A. Richardson.

Mutarotation. IV. Consecutive reactions in the mutarotation of dextrose and galactose. F. P. Worley and J. C. Andrews (J. Physical Chem., 1928, 32, 307—315; cf. A., 1927, 631, 736; this vol., 25).—The mutarotation of α- and β-glucose and of α- and β-galactose in aqueous solution has been studied polarimetrically at 0° in order to examine the initial stages of the action. In each case, an initial divergence from the subsequent unimolecular nature of the change has been observed. With α-galactose an initial retardation is observed followed by an acceleration. In the case of β-galactose mutarotation is arrested for 30 min. With α-glucose there is an initial retardation, and with β-glucose an acceleration. None of these changes can be ascribed wholly to a temperature effect. These divergences are said to show that mutarotation is not a simple unimolecular reaction, but involves two stages, *e.g.*, α-sugar $\rightleftharpoons$ X $\rightleftharpoons$ β-sugar, with the formation of an intermediate substance, X, the varying nature of the divergence being determined by the magnitude of the rotation of X, and the relative values of the velocity coefficients. For a rise of 10°, the velocity of mutarotation is increased 2·8 and 2·9 times for dextrose and galactose, respectively. L. S. Theobald.

Sulphite addition to unsaturated compounds. II. E. HÄGGLUND and A. RINGBOM (Z. anorg. Chem., 1928, **169**, 96—98; cf. A., 1926, 363).—The velocity coefficients at 80° of the reactions between sulphite and methylpropiolic and phenylpropiolic acids are considerably less than those of the reactions between sulphite and the corresponding ethylenic acids. With phenylpropiolic acid, the velocity coefficient falls continuously during the course of the reaction, apparently owing to decomposition.

R. CUTHILL.

Kinetics of chemical reactions between one solid and one gaseous component which result in the formation of complex compounds. A. PREDVODITELEV and A. WITT (Z. physikal. Chem., 1928, **132**, 47—54).—A micro-balance has been constructed by the aid of which the kinetics of the reaction between anhydrous cupric sulphate and gaseous ammonia at the ordinary temperature and at various pressures have been studied. The reaction follows the equation $dc/dt=qp(B-C)(C_0-C)$, where C is the concentration of the cuprammonium sulphate, p the pressure, and q, B, and C_0 are constants.

H. F. GILLBE.

Decomposition of water and aqueous chloride solutions by powdered iron. S. MICEWICZ (Przemysl Chem., 1927, **11**, 501—511; Chem. Zentr., 1927, ii, 1551).—The speed of reaction with powdered iron in aqueous solution increases in the series: sodium, potassium, calcium, magnesium chloride. Nitrobenzene is readily reduced to aniline by iron powder and magnesium chloride solution; the compound $2NH_2Ph,MgCl_2,6H_2O$ appears to be formed intermediately. A. A. ELDRIDGE.

Action of acids on metals under pressure. G. TAMMANN and K. BOCHOV (Z. anorg. Chem., 1928, **169**, 33—41).—When dilute sulphuric or hydrochloric acid acts on metals such as iron and zinc in a closed vessel, the reaction comes to an end some time before all the metal has been attacked. Measurements of the resistance afford no indication of the existence of a protective film of hydrogen, but *E.M.F.* determinations show that the potential of the metal becomes more electronegative, owing to the dissolution of hydrogen in the metal. The potential of the hydrogen also becomes more electronegative, but to a smaller extent, so that under favourable conditions the reaction ceases. In the action of sulphuric acid on magnesium, a coating of basic salts appears to be formed.

R. CUTHILL.

Corrosion. J. CZOCHRALSKI and E. SCHMID.—See B., 1928, 160.

Passivity and protective oxide films. U. R. EVANS (Nature, 1928, **121**, 351—352).—A discussion of the conditions influencing the thickness of protective oxide films. The *X*-ray method of examination, employed by Krüger and Nahring, is unsuitable. Air-passivity appears to be a property of the pure metal. A. A. ELDRIDGE.

Passivity limit in mixed crystals. G. TAMMANN (Z. anorg. Chem., 1928, **169**, 151—156).—If it is assumed that in mixed crystals of iron and chromium each atom of the latter is able to impart its power of becoming passive when brought into contact with dilute solutions of electrolytes to one atom of iron, a consideration of the crystal structure leads to a value for the minimum amount of chromium necessary to produce passivity which is considerably greater than that actually found. It therefore appears that other factors, such as the presence of foreign substances, are also involved. Van Liempt appears to have been under a misapprehension as to the true nature of resistance limits, and the values given by him for mixed crystals of molybdenum and tungsten (A., 1927, 196) are therefore to be rejected.

R. CUTHILL.

Effect of catalysts on the speed of flame, infrared emission, and ionisation during the combustion of carbon monoxide and oxygen. W. E. GARNER and C. H. JOHNSON (J.C.S., 1928, 280—298; cf. A., 1927, 184; Johnson, this vol., 353).—Measurements were made of the rate of emission of radiation, the duration and magnitude of ionisation, and the speed of flame for mixtures of carbon monoxide and oxygen to which various catalysts were added. It being already known that the loss of radiant energy increases with the introduction of water-vapour into such mixtures, the effect of introducing other substances containing hydrogen into the reaction mixture was observed. A new experimental arrangement was devised whereby the emission of radiation, the ionisation, and the speed of flame could be measured simultaneously. The standard mixture was 2 vols. of carbon monoxide with 1 vol. of oxygen, dried for 2 hrs. over commercial phosphorus pentoxide. Its mean radiation on explosion was $6{\cdot}00\times10^6$ g.-cal., and its mean speed of flame 100 cm. per sec. Addition of 1·95% of water vapour reduced the radiation to $1{\cdot}63\times10^6$ g.-cal., but increased the flame speed more than tenfold. Similar results were observed with the addition of ethyl nitrate, ethyl iodide, ethyl bromide, and chloroform. Carbon tetrachloride acted as a negative catalyst, the radiation being increased and the flame speed decreased. Nitrogen peroxide was an anomalous case, behaving as a feebly positive catalyst in a dried mixture, but as a negative catalyst in an imperfectly dried mixture.

Analysis of the total radiation records showed that, except for small residues, radiation ceases abruptly at times dependent on the nature of the catalyst present. Evidence is adduced pointing to a possible connexion between this residual radiation and the persistence of ions in the gases after explosion.

The duration of steady radiation was correlated with the duration of flame within the bomb. The bulk of the radiant energy has its origin in the wave-front where chemical change is proceeding, and not in the hot products of reaction.

In the dry gases, two waves of ionisation accompany the explosion wave. The first wave corresponds with the explosion wave itself, but the second is associated with processes occurring some distance behind the wave-front. The persistence of the ionisation associated with the second maximum increases as the flame passes along the bomb. It is suggested that the secondary emission of radiation in explosions of carbon monoxide and oxygen discovered by Ellis and Wheeler is caused by the recombination of ions produced behind the wave-front. These phenomena disappear in the presence of hydrogen. Substances containing hydrogen increase the rate of attainment of thermal equilibrium both in, and behind, the explosion wave.

R. A. Pratt.

Catalysis of hydrolytic reactions by acids and bases. H. von Euler and A. Ölander (Z. Elektrochem., 1927, **33**, 527—532).—A detailed reply to Skrabal's criticisms (A., 1927, 942) of the theoretical principles put forward by Euler (cf. A., 1921, ii, 498; 1926, 580). H. J. T. Ellingham.

Complex homogeneous catalysis of hydrogen peroxide by sodium molybdate. E. Spitalski and A. Funk (J. Russ. Phys. Chem. Soc., 1928, **60**, 47—74).—See A., 1927, 426.

Catalytic decomposition of sodium hypochlorite solutions. I. Mechanism. J. R. Lewis (J. Physical Chem., 1928, **32**, 243—254; cf. Howell, A., 1923, ii, 634; Chirnoaga, A., 1926, 916).—The mechanism of the decomposition of sodium hypochlorite solutions using the oxides of cobalt, copper, and iron as catalysts has been studied by two methods, one at 35° and the other at 30°, the first being that used by Walton (A., 1904, ii, 319). The values obtained by this method for $k=x/t$, where x is the volume of oxygen evolved, remain constant at first and then decrease after 20—30% of the reaction has been completed; those for the usual unimolecular coefficient increase as the reaction proceeds, whilst the greatest constancy is given when k is of the form of the Freundlich equation given by Chirnoaga (*loc. cit.*). The second method, in which a fresh supply of hypochlorite solution is passed over a fixed amount of catalyst, gives constant values for $k=x/t$ over a wide range of concentration (46·5—34·2 g./litre), after which k diminishes with decreasing concentrations of the hypochlorite. The rate of reaction is proportional to the concentration of the catalyst, and the values of k_{45}/k_{35} by the first method and k_{40}/k_{30} by the second are 2·02 and 2·0, respectively. The decomposition of the hypochlorite is considered to be due to the formation of a catalyst–hypochlorite complex with subsequent decomposition, and the rate of decomposition remains constant so long as the catalyst surface is completely covered by the reactant.

L. S. Theobald.

Experiments on the theory of heterogeneous reactions. G. Adhikari and J. Felman (Z. physikal. Chem., 1928, **131**, 347—362).—Iodine reacts but slowly with the surface of pure mercury, although considerable adsorption takes place. The production of mercuric iodide is autocatalytic, combination taking place with appreciable velocity only at the interface between the three phases. H. F. Gillbe.

Decomposition of carbon monoxide in presence of reduced nickel. S. Horiba and T. Ri (Bull. Chem. Soc. Japan, 1928, **3**, 18—25).—An improved apparatus is described whereby reaction velocities as well as equilibrium quantities can be measured. The rapid pressure measurements necessary were made possible by a special quartz spring manometer, and precautions were taken to avoid contamination by grease from stopcocks. At 230° the reaction became unimolecular after 15 min., whilst the rapid initial fall in pressure is explained by the adsorption of carbon monoxide on the reduced nickel.

S. J. Gregg.

Hydrocarbon synthesis from carbon monoxide and hydrogen. O. C. Elvins.—See B., 1928, 178.

Catalytic activity of metallised silica gels. IV. Oxidation of methane. L. H. Reyerson and L. E. Swearingen (J. Physical Chem., 1928, **32**, 192—201; cf. Berl and Fischer, A., 1923, i, 641; Tropsch and Roelen, A., 1924, i, 253; this vol., 252).—Oxidation of methane by oxygen in the presence of metallised silica gels, prepared as previously described, has been studied over the temperature range 200—400°. The copper, platinum, and palladium gels, but not the silver gel, act catalytically, promoting complete oxidation of methane to carbon dioxide and water. No partly oxidised products were found. Both the silver and copper catalysts remove oxygen from the gas stream in the initial stages of the reaction without oxidation of the methane, and then the copper or copper oxide acts as a catalyst initiating the reaction at 200°. The platinised gel which is the most active catalyst for this reaction acts at 240°, the palladised gel at 330°, and the efficiency of these two catalysts depends on the oxygen content of the gas mixture. An optimum concentration ratio of methane to oxygen apparently exists. L. S. Theobald.

Behaviour of methyl alcohol over aluminium and zinc oxides. H. Adkins and P. D. Perkins (J. Physical Chem., 1928, **32**, 221—224).—The dehydration of methyl alcohol over the temperature range 240—440° has been investigated by the methods and with the catalysts previously described (A., 1925, i, 626). With the alumina catalyst, an almost quantitative conversion of the methyl alcohol into dimethyl ether results up to 350°. This is followed by a slight decomposition of the ether between 350° and 380°, after which decomposition is rapid. With the zinc oxide catalyst, ether formation is negligible and decomposition becomes marked above 325°. The optimum concentration of water vapour for maximum hydration of the dimethyl ether varies, at a constant rate of flow, with the amount of catalyst present. L. S. Theobald.

Corrosion phenomena. XII. Apparent contradiction between the catalytic influence of silver on the dissolution of zinc in acids and its position in the overvoltage series. A. Thiel and J. Eckell (Z. physikal. Chem., 1928, **132**, 78—82).—The anomaly is ascribed to poisoning of the silver by zinc salts. H. F. Gillbe.

Activation of the dissolution of marble by neutral salts. N. Isgarischev and F. S. Schapiro (J. Russ. Phys. Chem. Soc., 1928, **60**, 127—137).—See A., 1927, 945.

Acitivty of a nickel catalyst. E. J. Lush.—See B., 1928, 182.

Electrolytic preparation of magnesium from fused fluorides containing magnesium oxide. G. Grube [with J. Jaisle] (Z. Elektrochem., 1927, **33**, 481—487).—The f. p. of mixtures of the fluorides of sodium, barium, and magnesium in various proportions have been determined and the results are expressed on a triangular diagram. The compound NaF,MgF_2 has m. p. about 1030° and the existence of a compound, BaF_2,MgF_2, is also indicated. Three ternary eutectics are recognised: MgF_2–BaF_2,MgF_2–NaF,MgF_2 (850°); BaF_2,MgF_2–BaF_2–NaF,MgF_2 (800°); and BaF_2–NaF–NaF,MgF_2 (750°). Fused mixtures of various compositions containing excess of magnesium oxide were electrolysed using an iron cathode and a graphite anode. The mixture corresponding with the 750° eutectic dissolves most magnesium oxide, but only sodium is obtained on electrolysis. The 800° eutectic mixture gives sodium and magnesium, the current efficiency for the deposition of the latter being 22—25%. Electrolysis of the 850° eutectic mixture yields only magnesium at 900°; the current efficiency is about 50%, the loss being attributed to volatilisation and formation of "anode fog." Absence of sodium deposition in this case is regarded as due to the compound NaF,MgF_2 dissociating into $Mg^{\cdot\cdot}$ and NaF_3'' ions in the presence of free magnesium fluoride. H. J. T. ELLINGHAM.

Preparation of a catalyst by the electrolytic corrosion of nickel. S. IKI (J. Soc. Chem. Ind. Japan, 1928, **31**, 1—9).—An active nickel catalyst is prepared by the electrolytic corrosion of nickel in alkali hydroxide or carbonate solution (0·05—0·1*N*) containing a small amount of alcohol. When only an alkali salt is used the current efficiency of corrosion is very low and the product is oxidised from the nickelous to the nickelic state. By addition of 3—5 c.c. of alcohol to 1 litre of the solution the current efficiency increases remarkably and the product is nickelous hydroxide. Acetaldehyde acts in the same way as alcohol. When the hydroxide is used the nickelous hydroxide produced tends to adhere to the surface of the nickel anode, increasing the resistance; this tendency is small when the carbonate is used. A current density of 0·01—0·05 amp./cm.^{2} at 3—5 volts is used. The current efficiency of corrosion decreases with increase of current density. Alternating current alone has but slight effect on the anode. The nickelous hydroxide produced is easily separated from the alkali. The efficiency of corrosion is 78%. K. KASHIMA.

Electrodeposition of indium with dropping-mercury cathode. S. TAKAGI (J.C.S., 1928, 301—306; cf. A., 1923, ii, 119; 1924, ii, 598; 1925, ii, 673, 678).—The behaviour of acidified indium trichloride solutions when electrolysed with a dropping-mercury cathode was investigated, the results being applied to the determination of indium in the presence of zinc and gallium. The electrodeposition from solutions of indium trichloride in 0·1*M*-hydrochloric acid proceeded reversibly in conformity with the Nernst logarithmic equation. The normal deposition potential of the indium ion in this concentration of acid is −0·500 volt, with reference to the normal calomel electrode. This value depends on the concentration of the hydrochloric acid, being more negative the higher the concentration. The sulphate ion in presence of an insufficient concentration of hydrogen ions appears to remove indium ions, probably in the form of a basic salt. For the detection and determination of indium in metallic gallium and zinc, the metals were dissolved in hydrochloric acid, the free acid concentration being 0·1*M*, when as little as 10^{-5} mol. of indium chloride per litre could be detected and determined. The deposition potential of gallium could not be determined in acid solution. R. A. PRATT.

Electrolytic oxidation of formic acid. E. MÜLLER [with G. HINDEMITH] (Z. Elektrochem., 1927, **33**, 561—568; cf. A., 1923, i, 743).—Further investigation has been made of the relations between anode potential and current density in the electrolysis of a *M*-formic acid–*M*-sulphuric acid solution, using as anode material (*a*) rhodium, (*b*) platinised platinum, (*c*) platinum coated with finely-divided rhodium, or (*d*) palladium coated with finely-divided palladium. At anodes (*a*) and (*b*) the current–potential curves exhibit two distinct branches, one (*A*) lying at potentials about 1 volt less positive than the other (*B*). The transition from *A* to *B* occurs by a sudden jump. With electrode (*d*) there is evidence of three branches of the current–potential curve, and with (*c*) and (*d*) the *A* branch is broken by pulsations between normal values of the potential and values as much as 0·4 volt less positive. In all cases, however, curves obtained by decreasing the current follow the *B* branch until the current is practically zero. In order to explain these complex relations, a theory is developed based on the supposed reactions of formic acid and formate ions adsorbed in a polar manner on the electrode surface. The transition from the *A* to the *B* branch is regarded as due to superficial oxidation of the anode material. Rise of temperature, or addition of sodium formate instead of sulphuric acid, causes the *A* branches of the curves to extend to higher current densities. In special experiments with 10*M*-formic acid–*M*-sodium formate solution at 0·015 amp./cm.^{2} at anode (*c*), the anode potential fluctuated periodically between −0·11 and +0·33 volt (against the *N*-calomel electrode), whereas with a 2*M*-formic acid–*M*-sodium formate solution at 0·21 amp./cm.^{2} the anode potential of +1·290 volts remained steady when once established. In both cases, however, the products of electrolysis were hydrogen and carbon dioxide in amounts corresponding exactly with the equation $H\cdot CO_2H + 2\text{ faradays} = H_2 + CO_2$. H. J. T. ELLINGHAM.

Anodic oxidation of free propionic acid. F. MÜLLER [with H. SCHWAB] (Z. Elektrochem., 1927, **33**, 568—571).—Contrary to statements in the literature, free propionic acid can readily be oxidised electrolytically. Using solutions of the acid in 2*N*-sulphuric acid in a diaphragm cell fitted with smooth platinum electrodes, the current efficiency of oxidation is found to increase with the current density and the concentration of propionic acid, and reaches about 98% in a 10*M*-solution at 0·09 amp./cm.^{2} The main products of oxidation are carbon dioxide and ethyl propionate, but small amounts of ethylene, carbon monoxide, and pyruvic acid are also formed. Two main processes appear to occur. In the more important, complete oxidation to carbon dioxide and water is believed to occur by way of lactic acid and pyruvic acid. In the other, ethyl propionate is produced either by direct oxidation or through the intermediate formation of ethyl alcohol. It is shown that oxidation of lactic acid or pyruvic acid in 2*N*-sulphuric acid occurs at a lower oxidising potential at smooth platinum electrodes than is required for the oxidation of propionic acid, so that the former acids do not accumulate in the solution during the electrolysis of the latter. H. J. T. Ellingham.

Photochemical yields with complex light. V. M. Padoa and N. Vita (Gazzetta, 1928, **58**, 3—6; cf. A., 1926, 1014).—From a further survey of their own experiments and of those of Berthoud and Béraneck (A., 1927, 528) the authors consider their view justified, that the sum of the photochemical effects produced by the component radiations is different from and in general greater than that of the resulting complex light, not only owing to variations in the intensity of the light, but also, and in some cases solely, on account of specific effects due to variations in the frequency of the light. The reactions discussed are the bromination of cinnamic acid, the oxidation of hydriodic acid, and the decomposition of ferric oxalate. O. J. Walker.

Photochemistry of the halogens. Action of bromine on ethyl alcohol. A. Berthoud and J. Béraneck (J. Chim. phys., 1928, **25**, 28—39; cf. Bugarszki, Z. physikal. Chem., 1910, **71**, 705).—The rate of reaction of ethyl alcohol and bromine in the presence of potassium bromide has been studied in the dark and under various intensities of blue and violet light. Bugarszki's results for the influence of the concentrations of alcohol and bromine are confirmed, but the retarding influence of potassium bromide is less than stated by him. Potassium bromide retards also in light. It is considered that the effect of light is to dissociate bromine molecules, and that, probably, an intermediate compound, EtO, is formed. The reaction is too complex to be analysed thoroughly from the data obtained.

L. F. Gilbert.

Photochemistry of the halogens. Action of bromine on α-phenylcinnamonitrile. A. Berthoud and G. Nicolet (J. Chim. phys., 1928, **25**, 40—64; cf. preceding abstract).—This reaction has been studied in the dark and in light; it is reversible. In the dark, however, the inverse reactions are slower than found by Bauer and Moser (A., 1907, i, 307), whose reaction vessels (of brown glass) did not exclude light completely. The photochemical results disagree entirely with those of Plotnikov ("Lehrbuch der Photochemie," 1920, 250). Expressions are derived which describe the rate and equilibrium of the reaction under different conditions.

L. F. Gilbert.

Photochemical union of hydrogen and chlorine. L. Harris (Proc. Nat. Acad. Sci., 1928, **14**, 110—112).—Hydrogen and chlorine were carefully freed from oxygen. Chlorine together with an excess of hydrogen was exposed to blue light and the quantum efficiency of the union measured. A minimum yield of 6×10^5 molecules of hydrogen chloride per quantum was obtained. W. E. Downey.

Photochemical decomposition of hydrogen iodide; mode of optical dissociation. B. Lewis (J. Physical Chem., 1928, **32**, 270—284; cf. A., 1927, 428; this vol., 31).—Details are given of the results previously announced on the photochemical dissociation of hydrogen iodide at pressures low enough for the collision frequency to be comparable with the mean life of the excited state. Under these conditions the quantum efficiency is still about two, which is the same as that found by Warburg for higher pressures. Hence, hydrogen iodide is considered to dissociate in an elementary act as a result of the absorption of radiation without the necessity of a collision (cf. Stern and Volmer, A., 1920, ii, 461). Further, the continuous spectrum shows dissociation to take place into a normal hydrogen atom and an excited atom of iodine in the metastable $2P_1$ state, any excess energy being dissipated as kinetic energy. The time which elapses between absorption and dissociation is less than 2×10^{-10} sec. The decomposition of hydrogen iodide is discussed on the basis of results already published. L. S. Theobald.

Measurements of velocity, reaction per quantum, and effect of intensity of radiation in reactions between chromic acid and organic acids. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1928, **169**, 381—393).—The orders of the reactions between chromic acid and the following acids in sunlight and in the dark, respectively, are: citric acid, 2, 2·5; tartaric acid, 2, 3; lactic acid, 3, 3. Manganous sulphate accelerates most of the reactions, and, except with the reaction with tartaric acid in light, reduces the order. With decrease in the order of the reaction, the temperature coefficient of the velocity coefficient usually rises. The temperature coefficient for the reaction in the light is always greater than unity, and less than that of the corresponding reaction in the dark. In all the reactions, numerous molecules react for each quantum of light absorbed, the number increasing with increase in concentration and also with rise in temperature. It is therefore concluded that Einstein's law of photochemical equivalence is not valid for exothermic photochemical reactions. The rate of reaction in either presence or absence of manganous sulphate is directly proportional to the intensity of the incident radiation, except in the reactions with citric acid and tartaric acid in absence of manganous sulphate, the rates of which are proportional to the square root of the intensity of radiation. R. Cuthill.

Luminescence of mercurous chloride of standard purity. J. Křepelka (Nature, 1928, **121**, 457).—Pure, dry mercurous chloride exhibits a greenish-white luminescence when stirred with a glass rod; the effect lasts for about 5 sec., and cannot be again produced unless the rod is first cleaned. Luminescence is also produced if the soiled rod is lightly rubbed with a dry cloth.

A. A. Eldridge.

Tentative hypothesis of the latent image. II. A. P. H. Trivelli.—See B., 1928, 212.

Action of sulphuric acid on copper. J. G. F. Druce (Chem. News, 1928, **136**, 81—83).—The main reaction which occurs when copper is heated at 130—170° with twice its weight of concentrated sulphuric acid is represented by the equation $6Cu+6H_2SO_4=4CuSO_4+Cu_2S+SO_2+6H_2O$. With excess of acid at 270°, the reaction is $Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$. R. Cuthill.

Reduction of magnesium pyrophosphate by carbon. K. D. Jacob and D. S. Reynolds (J. Assoc. Off. Agric. Chem., 1928, **11**, 128—132).—Mixtures of equal weights of pure finely-powdered magnesium pyrophosphate and carbon were heated in a current of nitrogen at the desired temperatures for definite periods. The residues, after burning off the carbon below 800°, were analysed for magnesium oxide and phosphorus pentoxide, and the percentage of phosphorus lost by volatilisation was calculated from the change of the ratio $P_2O_5:MgO$ of the residues, as compared with that found for the pyrophosphate used. The loss of phosphorus was negligible below 975°. Heating for 1 hr. at 1000° resulted in a loss of 2·5%, at 1050° of 12·5%, and at 1100° of 32% of the total phosphorus originally present.

F. R. Ennos.

Composition of bleaching powder. C. T. Kingzett (J.C.S., 1928, 528).—Calcium hypochlorite prepared from bleaching powder and rapidly dried between sheets of filter-paper has the composition $Ca(ClO)_2,4H_2O$, being mechanically associated with some water. This formula does not represent its constitution as a hydrate of calcium hypochlorite (cf. O'Connor, B., 1928, 88). R. A. Pratt.

Bleaching powder. VII. Decomposition of calcium hypochlorite by heat in presence of calcium chloride. S. Urano (J. Soc. Chem. Ind. Japan, 1928, **31**, 46—52).—The decomposition of calcium hypochlorite in presence of large amount of calcium chloride, occurs chiefly according to the equation: $Ca(OCl)_2+CaCl_2=2CaO+2Cl_2$ (i) and partly according to the equations $Ca(OCl)_2=CaCl_2+O_2$ (ii) and $3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2$ (iii). The evolution of chlorine is caused by the mutual reaction between hypochlorite and chloride, but not by expulsion of chlorine monoxide; reaction (i) is reversible. The phenomena attending the decomposition of bleaching powder result from these three reactions. K. Kashima.

Production of carbon by the decomposition of carbon monoxide. von Wangenheim.—See B., 1928, 146.

Production of pure carbon at low temperatures. F. Fischer and P. Dilthey.—See B., 1928, 146.

Graphitic acid and the varieties of carbon obtained by its decomposition. U. Hofmann (Ber., 1928, **61**, [*B*], 435—441).—Graphitic acids, prepared by treatment of very finely-divided Ceylon graphite with a mixture of nitric and sulphuric acids and potassium chlorate (cf. Kohlschütter, A., 1919, ii, 151), is crystalline and yields a characteristic, well-defined Röntgen spectrum somewhat similar to that of graphite. When heated cautiously to about 200° it decomposes explosively with formation of voluminous "carbon I," which is incipiently crystalline but differs from graphite in the extreme smallness of its crystallites and the distinctly closer proximity of the interference lines (002) and (111). When strongly compressed it becomes denser and more suitable for Röntgen investigation without changing the position of the lines (cf. Lowry and Morgan, A., 1925, ii, 1053; Ruff and others, A., 1927, 1138). When graphitic acid is heated at 200° under pressure, the "carbon II" thus produced is more distinctly crystalline and its Röntgen spectrum closely approximates to that of lustre carbon prepared at 900° except that the interference lines (002) and (111) are closer. When the graphitic acid is decomposed under sulphuric acid at 150°, a more highly crystalline "carbon III" is obtained in which the arrangement is similar to that in retort graphite. All the types of carbon derived from graphitic acid differ from lustre carbon and retort graphite in the remarkable sharpness of their interferences. H. Wren.

Gaseous silicon monoxide. K. F. Bonhoeffer (Z. physikal. Chem., 1928, **131**, 363—365).—Ultraviolet absorption spectra indicate the formation of considerable quantities of gaseous silicon monoxide during the reduction of the dioxide by carbon at 1500°. H. F. Gillbe.

Compounds of hydrated silica and ammonia. W. Biltz (Z. Elektrochem., 1927, **33**, 491—497).—Preparations of hydrated silica prepared by methods described by Schwarz (A., 1924, ii, 753; 1925, ii, 222) were treated with liquid ammonia in a special extraction apparatus, until no more water could be extracted. The composition and vapour pressure of the products were examined at various temperatures. From metasilicic acid the product had the composition $6SiO_2,2H_2O,4NH_3$ at −78·5°, but with rise of temperature it loses ammonia in stages of one molecule, and finally yields the compound $6SiO_2,2H_2O,NH_3$ which is stable at the ordinary temperature. This result supports the view that the minimum molecular formula for metasilicic acid is $6SiO_2,6H_2O$. Partly dehydrated metasilicic acid preparations gave on treatment with ammonia the same compounds as the original substance yielded. Treatment of disilicic acid with ammonia yielded the additive product $2SiO_2,H_2O,NH_3$. Since this loses ammonia in a continuous and not a step-wise manner when examined in the tensimeter, there is no evidence that the molecular formula of disilicic acid is more complex than $2SiO_2,H_2O$. From similar experiments with the so-called "granitic acid," $3SiO_2,2H_2O$, and with a preparation having the composition of "trisilicic acid," $3SiO_2,H_2O$, it is concluded that these are not definite compounds but mixtures of meta- and di-silicic acids and of disilicic acid and silica, respectively (cf. Schwarz, A., 1926, 1112). *X*-Ray examination supports these conclusions. A few experiments on the extraction of silica gels with ammonia did not lead to the isolation of any definite compounds. Hence only two definite silicic acids appear to exist. To prepare these substances the corresponding sodium salts must be used as the starting material, since subsequent conversion of one acid into the other has not been observed to occur. The wider application of the ammonia extraction process to the study of the constitution of hydrates is referred to. H. J. T. Ellingham.

Preparation and properties of some germanous salts. J. Bardet and A. Tchakirian (Compt. rend., 1928, **186**, 637—638).—Brown germanous oxide is produced with small quantities of germanous hydride, by the reduction of germanic salts with zinc and 25% sulphuric acid. It is stable when dry and almost insoluble in hydrochloric or sulphuric acid, and may be used for the detection of 0·1 mg. of germanium by means of titration with a solution of potassium permanganate. By reduction with hypophosphorous and hydrochloric acids at 100° for 2 hrs., followed by neutralisation in the cold with ammonia, the orange-yellow hydroxide is produced. It is very soluble in alkalis and in hydrochloric or hydrobromic acid, but not in hydrofluoric acid, whilst sulphuric acid dehydrates it and forms the soluble brown oxide. Hydriodic acid and oxidising agents convert it into a red, insoluble iodide, and into the dioxide, respectively. The hydrochloric acid solution yields the chloride ($GeCl_2$), which is hydrolysed by water to a white oxychloride, and is a strong reducing agent. The bromide behaves similarly, but the fluoride is stable towards water. Hydrogen sulphide precipitates the orange-red sulphide (GeS) from solutions of the above salts. J. Grant.

Oxidation of hydrazine. VIII. Mono-de-electronators and di-de-electronators. R. E. Kirk and A. W. Browne (J. Amer. Chem. Soc., 1928, 50, 337—347; cf. A., 1916, ii, 245).—Oxidation is regarded as a process of de-electronation, and the similarity in behaviour of various oxidising agents towards hydrazine is explained on the ground that mono-de-electronators—*i.e.*, oxidising agents which accept one electron only per active unit—yield ammonia as the only by-product, whereas di-de-electronators yield both ammonia and azoimide. Many examples are considered in detail from this point of view. S. K. Tweedy.

Sodium pyrophosphates. J. R. Partington and H. E. Wallsom (Chem. News, 1928, **136**, 97—100).—Repetition of the work of Salzer (A., 1895, ii, 14) and Giran (A., 1902, ii, 549) confirms the existence of the salts $Na_3HP_2O_7$, $Na_3HP_2O_7,H_2O$, $Na_3HP_2O_7,4H_2O$, and $NaH_3P_2O_7$ and establishes the existence of the *salt* $Na_3HP_2O_7,5H_2O$. The salt formed on heating trisodium pyrophosphate has the composition $Na_6P_4O_{13}$ and is possibly a polymerised metaphosphate. For analysis, pyrophosphates are boiled with a large excess of dilute hydrochloric acid for 2 hrs., and for a further 10 min. with magnesia mixture. J. S. Carter.

Sodium thiopyrophosphates. H. E. Wallsom (Chem. News, 1928, **136**, 113—115).—*Sodium thiopyrophosphates*, $Na_2H_2P_2S_7$, $Na_3HP_2S_7$, $Na_4P_2S_7$, $Na_6P_4S_{13}$, and Na_2HPS_4, have been prepared by the action of sodium sulphide or hydrosulphide on phosphorus pentasulphide. They are easily decomposed by water with the production of hydrogen sulphide and generally also of sulphur.
C. W. Gibby.

Vanado-vanadates. G. Canneri (Gazzetta, 1928, 58, 6—25).—A study was made of the compounds containing quinquevalent and quadrivalent vanadium obtained by fusing in the required proportions vanadic anhydride with salts of the alkali metals, and especially of the evolution of oxygen which accompanies the cooling of such molten systems (cf. Prandtl, A., 1905, ii, 170). This evolution occurs appreciably only when salts of the alkali metals or of thallium are used, and is independent of the anion with which the metal is combined. The systems V_2O_5–Na_2O, V_2O_5–K_2O, V_2O_5–Li_2O, and V_2O_5–Tl_2O have been investigated thermally and diagrams of state constructed. These show that vanadic anhydride forms with the oxides of the alkali metals and of thallium three definite compounds corresponding with the meta-, pyro-, and ortho-vanadates. The evolution of oxygen is accompanied by the formation of compounds of vanadic anhydride with its reduction product V_2O_4 of the type xV_2O_5,yV_2O_4,zM_2O, where M=Na or K (vanado-vanadates). By fusing vanadic anhydride with the alkali carbonates, the *compounds* having the following values of x, y, and z, respectively, have been obtained for sodium and potassium: 5, 1, 1; 4, 1, 1; 4, 1, 2; 1, 1, 1, and in addition for sodium the compound 5, 1, 3. O. J. Walker.

Antimonic acid. A. Lottermoser (Z. Elektrochem., 1927, **33**, 514—518).—So-called "soluble antimonic acid" was prepared by gradual addition of antimony pentachloride to water at 0°, and solutions of the filtered and washed product were made. During dissolution to a clear liquid, the electrical conductivity increases; afterwards, it decreases rapidly and then more slowly, approaching a limiting value, whilst the solution gradually becomes opalescent. Rise of temperature raises the limiting value somewhat and greatly increases the rate at which it is approached, but varying the initial concentration of the solution has practically no effect on the limiting value, unless the concentration is below about 0·1%. It is concluded that the more concentrated solutions become saturated with a mixture of complex hydrated acids, whereas more dilute solutions remain unsaturated with respect to this mixture. Determinations of the p_H value of the solutions by means of indicators gave similar results, and ultramicroscopical examination showed that, whereas in the more concentrated solution ageing led to a notable increase in the number of colloidal particles, no such increase was observed in the more dilute solutions. Conductometric titrations of concentrated fresh solutions with lithium, sodium, or potassium hydroxides (MOH) gave breaks in the titration curves when the ratio M : Sb was 1 : 3 and 1 : 2. With the corresponding aged solutions, however, the breaks occurred at different points with different alkalis and these points did not in general correspond with simple ratios of M : Sb. With very dilute solutions the titration curves are unchanged by ageing and exhibit only one break, the position of which is independent of the nature of the alkali used, but does not represent a simple ratio of M : Sb. Conductometric titrations of potassium pyroantimonate solutions with hydrochloric acid are also recorded.
H. J. T. Ellingham.

Change in composition of compressed air after long storage in a steel cylinder. A. F. Sereque (J. Amer. Chem. Soc., 1928, 50, 419).—The percentages of oxygen and of carbon dioxide in compressed air decreased by 0·6 and 0·01, respectively, after 17 years' storage in a steel cylinder. S. K. TWEEDY.

Higher polythionic acids. I. Hexathionic acid. E. WEITZ and F. ACHTERBERG (Ber., 1928, **61**, [*B*], 399—408).—*Potassium hexathionate* is prepared by the addition of a solution of potassium nitrite (1 mol.) and potassium thiosulphate (about 3 mols.) to well-cooled hydrochloric acid. The mixture is vigorously shaken until the colour passes through brown and green to yellow, after which the nitrous fumes are removed in a current of air, leaving a solution having an odour of sulphur dioxide; it is preserved in a freezing mixture until it becomes almost colourless. Precipitated potassium chloride is removed and the filtrate concentrated under diminished pressure, whereby potassium hexathionate, mixed with potassium chloride, separates. The chloride is removed by water and the residue washed with alcohol and ether. The mother-liquors from the hexathionate contain considerable quantities of potassium tetrathionate. The production of the latter compound is readily explained either by the intermediate formation of nitrosylthiosulphuric acid or as a simple oxidation of the thiosulphate, but the mode of formation of the hexathionate is obscure. The smallest proportion of nitrite required to prevent precipitation of sulphur when the solution is acidified depends on the presence or absence of air and on the concentration of nitrite and thiosulphate in the solution. Potassium hexathionate is stable when dry, but readily decomposes in aqueous solution with formation of sulphur or a higher polythionate. Addition of acid stabilises the solutions. It crystallises with difficulty from aqueous or feebly acidic solutions, most readily from such as contain considerable amounts of mineral acid; from these solutions it can be salted out. Like the pentathionates, it deposits sulphur when treated with alkali, gives yellow and yellowish-white precipitates with mercurous nitrate and mercuric chloride, no reaction with copper sulphate, and a brown coloration passing into a black precipitate with ammoniacal silver solution. It is more rapidly decomposed than pentathionates by dilute ammonia, tetrathionate being the first isolable product; sodium carbonate solution behaves similarly. Alkali sulphite rapidly converts hexathionate into trithionate. Potassium hexathionate gives crystalline *precipitates* with hexammine-cobaltic and -chromic chlorides and nitrates and with *trans*-dichlorodiethylenediaminecobaltic chloride; this behaviour is also shown by the lower polythionates towards the last-mentioned reagent. The anhydrous *benzidine* salts of hexa-, penta-, tetra-, and tri-thionic acids are described. Preliminary examination of Wackenroder's solution discloses the absence of hexathionic acid and presence of acids containing a larger proportion of sulphur. H. WREN.

Reactions in liquid hydrogen sulphide. III. Thiohydrolysis of chlorides. A. W. RALSTON and J. A. WILKINSON (J. Amer. Chem. Soc., 1928, **50**, 258—264; cf. Quam and Wilkinson, A., 1925, ii, 542).—Metallic chlorides are mostly insoluble in liquid hydrogen sulphide, except those of zinc, bivalent mercury, aluminium, and tervalent iron, the last-named forming a white precipitate of ferrous chloride. Mercuric chloride is thiohydrolysed to the black sulphide which later turns red; the iodide crystallises out in the yellow form, which becomes red. Insoluble mercurous chloride reacts to give mercurous hydrogen sulphide as a brown, gelatinous mass; cuprous chloride and silver chloride are also thiohydrolysed. Boron trichloride yields white *crystals* of $BCl_3,12H_2S$. Chlorides of non-metallic elements which are readily hydrolysed by water are either soluble in liquid hydrogen sulphide in all proportions without change (*e.g.*, carbon tetrachloride; silicon tetrachloride, which, however, produces a little silicon disulphide when kept for several weeks at the ordinary temperature; and tin tetrachloride, which slowly produces stannic sulphide at the ordinary temperature) or else form thiohydrates, additive products, or sulphides (*e.g.*, titanium tetrachloride, which forms the *compound* $2TiCl_4,H_2S$; cf. Biltz and Keunecke, A., 1925, ii, 986), possibly together with a thiohydrate; phosphorus trichloride, which produces trisulphide at the ordinary temperature; phosphorus and antimony pentachlorides, which form the respective thiochlorides, $PSCl_3$ $SbSCl_3$; bismuth trichloride, which yields an orange-red *solid*, $BiSCl,BiCl_3$). The conductivities of some saturated solutions of metal chlorides in liquid hydrogen sulphide are recorded; the specific conductivity of the pure solvent is 1×10^{-11} ohm^{-1} at about $-80°$. S. K. TWEEDY.

Molybdates of lanthanum and sodium. G. CAROBBI (Gazzetta, 1928, **58**, 53—56; cf. Carobbi and Tancredi, following abstract).—At 25° the following two *compounds* are formed:

$$La_2(MoO_4)_3,Na_2MoO_4,2H_2O \text{ and}$$
$$La_2(MoO_4)_3,2Na_2MoO_4,3H_2O.$$

O. J. WALKER.

Tungstates of cerium and sodium. G. CAROBBI and G. TANCREDI (Gazzetta, 1928, **58**, 45—52; cf. A., 1926, 810).—The system $Ce_2(WO_4)_3$–Na_2WO_4–H_2O has been studied at 25°. The three *compounds*

$$Ce_2(WO_4)_3,Na_2WO_4,11H_2O;$$
$$Ce_2(WO_4)_3,3Na_2WO_4,16H_2O, \text{ and}$$

$Ce_2(WO_4)_3,5Na_2WO_4,23H_2O$ are shown to exist. They are crystalline and stable in air. The dehydration of these salts by means of calcium chloride or sulphuric acid is not effected at a constant velocity; this fact points to the possible existence of other hydrates.

O. J. WALKER.

Tungsten carbides and their applications. F. SKAUPY (Z. Elektrochem., 1927, **33**, 487—491).—The products obtained by heating tungsten powder with lamp-black in hydrogen or in a vacuum at 1400° or 2000° by means of a carbon-tube furnace or a tungsten-wire furnace have been examined by chemical analysis and by *X*-ray methods. The carbides W_2C and WC are recognised. These compounds are also produced by heating a tungsten wire electrically in an indifferent gas (hydrogen or a mixture of hydrogen and nitrogen) containing a small proportion of methane. Wires carburised in this way have their carbon content removed again if the methane concentration falls below a certain critical value dependent on the temperature and the composition of the indifferent

gas. The graph of the critical concentration of methane in hydrogen against temperature exhibits three branches, of which two correspond with WC and W_2C, respectively, whilst the third, which lies above 2400°, may correspond with the carbide W_3C found by Ruff. The development of the alloy "Widiametall" (tungsten, cobalt, carbon) now produced by Fried. Krupp A.-G. is referred to.
H. J. T. ELLINGHAM.

Oxidations with fluorine. F. FICHTER (Z. Elektrochem., 1927, **33**, 513—514).—Mainly a review of published work. W. Bladergroen has shown that fluorine reacts with phosphoric acid or phosphate solutions giving perphosphates. E. Brunner finds that in the oxidation of chromic, thallous, or manganous salts with fluorine, the reaction proceeds smoothly only when the sulphates are used; this is regarded as due to the intermediate formation of sulphur tetroxide. It is concluded that all oxidations with fluorine are almost completely paralleled by electrolytic oxidations at platinum anodes.
H. J. T. ELLINGHAM.

Black nickel oxide. G. LUNDE (Z. anorg. Chem., 1928, **169**, 405—406).—A reply to Le Blanc and Sachse (this vol., 142). R. CUTHILL.

Oxidation states of ruthenium in its halide compounds. W. R. CROWELL and D. M. YOST (J. Amer. Chem. Soc., 1928, **50**, 374—381).—Ruthenium compounds in hydrochloric acid solution are reduced by potassium iodide to the tervalent state, in agreement with the conclusions of Ruff and Vidic (A., 1925, ii, 480). Ruthenium hydroxide prepared by the method of Krauss and Kükenthal (A., 1924, ii, 196) contains both tervalent and quadrivalent ruthenium. If the hydrochloric acid solution of the hydroxide is chlorinated, all the ruthenium is converted into the quadrivalent state, and electrometric titration of the solution with titanous sulphate, both before and after chlorination, shows an end-point when all the ruthenium is reduced to the tervalent and not the bivalent state (cf. Zintl and Zaimis, A., 1927, 533). The dark blue compounds formed when the titanous sulphate is in slight excess are compounds of bivalent ruthenium. If ruthenium chloride is digested with bromine and hydrobromic acid, and evaporated with potassium bromide, a black *salt* containing quadrivalent ruthenium is obtained, probably K_2RuBr_5OH. S. K. TWEEDY.

Iridium fluorides. O. RUFF and J. FISCHER (Z. Elektrochem., 1927, **33**, 560—561).—For the preparation of iridium hexafluoride and pentafluoride by the passage of pure gaseous fluorine over heated finely-powdered iridium, the metal was contained in a boat of calcined fluorspar supported in a tube of the same material and heated electrically. Vessels of fluorspar calcined at 1280° are resistant to fluorine at high temperatures and are readily worked mechanically by means of an emery wheel. For analysis of the hexafluoride, reaction with sodium carbonate in a platinum crucible was carried out at the temperature of liquid air. Subsequent heating to redness yielded insoluble iridium oxide, which was reduced to the metal and weighed. The atomic ratio of iridium to fluorine obtained in this way was 1 : 6·08. Some properties of iridium hexafluoride and pentafluoride are described.
H. J. T. ELLINGHAM.

Magnitude of observation errors in chemical analysis. B. D. HARTONG (Chem. Weekblad, 1928, **25**, 105—106; cf. Goudriaan, this vol., 262).—A criticism of the calculations in the earlier paper. The employment of approximated atomic weights does not necessarily lead to errors as serious as appears; the error introduced by using 107·9 for the atomic weight of silver, for example, is only 0·02 and not 0·1. The method of calculating the cumulative effect of errors is also criticised.
S. I. LEVY.

Drop reactions. F. FEIGL (Mikrochem., 1928, **6**, 50—62).—A claim for priority. Many of the drop reactions recently described by Tananaev and his co-workers (A., 1925, ii, 324; 1927, 223, 1159) had been described by Feigl and his co-workers several years previously. A. R. POWELL.

Determination of dissolved gases in water. H. RICHTER.—See B., 1928, 214.

Measurement of gases dissolved in water. L. DUNOYER (J. Phys. Radium, 1928, [vi], **9**, 1—12).—A more detailed account of work already published (A., 1927, 845).

Determination of hydrogen-ion concentration in very small volumes of liquid. S. GIRGOLOV and J. SCHUKOV (Z. ges. exp. Med., 1927, **56**, 710—713; Chem. Zentr., 1927, ii, 1869).—An iridium electrode, made by depositing an iridium mirror on a fine glass capillary, is employed in place of a platinised platinum wire. A. A. ELDRIDGE.

Applicability of the quinhydrone electrode in electrometric titration. A. RABINOVITSCH and V. KARGIN (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 3—33; Chem. Zentr., 1927, ii, 1054).—Strong acids can be titrated with the quinhydrone electrode in all concentrations; with dilute weak acids the quinhydrone electrode shows at $p_H>6$ smaller p_H values than does the hydrogen electrode. The inflexion point of the titration curve is reached with greater quantities of alkali than when the hydrogen electrode is employed. Presumably the hydrogen-ion concentration of the solution is increased by dissociation of the quinol, atmospheric oxidation of the quinol in alkaline solution tending to reduce it. The deviation is maximal at p_H 10, and is smaller in the presence of buffers.
A. A. ELDRIDGE.

[Theory of end-point in electrometric titration.] Correction. E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 418).—An algebraical error in the previous paper (A., 1925, ii, 594) is corrected. The result obtained by Roller (this vol., 262) concerning the limiting strength of acid necessary for an inflexion point to appear during titration with a strong base is confirmed. S. K. TWEEDY.

Simple continuous-reading method of electrometric titration with bimetallic electrodes. N. H. FURMAN and E. B. WILSON, jun. (J. Amer. Chem. Soc., 1928, **50**, 277—283).—Platinum and tungsten wires are dipped into (*e.g.*) the reducing solution, and connected in series through a variable high resistance and a galvanometer. The oxidising agent is added a drop at a time; the graph of the galvanometer readings (ordinate) against volume of reagent added is exactly analogous to the graphs obtained potentiometrically, there being a sudden permanent change in *P.D.* at the end-point. This "galvanometer method" is as accurate as the potentiometric method. S. K. TWEEDY.

Simple bimetallic electrode systems for potentiometric titrations. I. Application of platinum–gold amalgam system to certain oxidation–reduction titrations. II. Notes on the use of the platinum–gold electrode system. N. H. FURMAN (J. Amer. Chem. Soc., 1928, **50**, 268—273, 273—277).—I. Amalgamated gold electrodes behave like calomel electrodes in solutions containing chloride and like mercurous sulphate electrodes in solutions containing sulphate. The construction of small amalgamated gold electrodes is described; they are suitable for use as reference electrodes in oxidation–reduction titrations (ferrous iron with potassium permanganate and dichromate, and with vanadic acid) in solutions as dilute as 0·05N; they also serve as indicator electrodes for certain precipitation reactions, and for following the neutralisation of hydrochloric and sulphuric acids.

II. A sharp change in *E.M.F.* occurs at the end-point of some oxidation–reduction reactions (*e.g.*, potassium permanganate and ferrous sulphate) in 0·1 or 0·05N-solutions. The chief disadvantage of the amalgamated gold electrode system is the variable nature of the readings for the same type of titration.
S. K. TWEEDY.

Determination of combined water in natural sulphates. O. ŠEBELÍK (Chem. Obzor, 1927, **2**, 46—49; Chem. Zentr., 1927, ii, 962).—Minerals containing alunite, a colloidal mixture of silica and alumina, quartz crystals, and water lose water at 350° upwards, complete elimination being effected only at white heat. Sources of error are discussed; the methods of Kurizianov and of Dittrich give good results. A. A. ELDRIDGE.

Bromometric determination of chlorates. K. PETERS and E. DEUTSCHLÄNDER (Apoth.-Ztg., 1926, **41**, 594—595; Chem. Zentr., 1927, ii, 1055).—The chlorate (0·05 g. ClO_3) is dissolved in 0·1N-arsenious oxide solution (25 c.c.) and dilute hydrochloric acid (10 c.c.) and gently boiled for 10 min. after addition of potassium bromide (0·05—0·1 g.); the solution is then diluted to about 100 c.c. and titrated hot (using methyl-orange) with 0·1N-potassium bromate solution until colourless. A. A. ELDRIDGE.

Direct oxidimetric determination of perchlorate in presence of large amounts of chlorate and chloride. E. SPITALSKI and S. JOFA (Z. anorg. Chem., 1928, **169**, 309—318, and J. Russ. Phys. Chem. Soc., 1928, **60**, 75—84).—By treatment of a solution containing perchlorate and a large amount of chlorate with sulphur dioxide, the chlorate is completely reduced to chloride, and after removing the excess of sulphur dioxide by passing a current of air or carbon dioxide through the solution near its b. p., the perchlorate may be determined by boiling with an excess of titanous chloride and titrating back with permanganate (Rothmund, A., 1909, ii, 434). Provided that the solution is not too concentrated, this titration is not affected by the presence of chlorides, and the addition of manganous sulphate is actually disadvantageous. Small amounts of chromate do not interfere with the determination. R. CUTHILL.

Electro-analytical methods. III. Potentiometric titration. J. GILLIS (Natuurwetens. Tijds., 1927, **9**, 129—148; cf. *ibid.*, **8**, 37, 115).—The changes of value in the silver-ion concentration and the potential of a silver electrode immersed in the solution are calculated for the titration of chlorides, iodides, and cyanides, by means of silver nitrate, and shown to agree with the values determined by measurement during actual titrations. S. I. LEVY.

Analysis of bromine. KUBIERSCHKY.—See B., 1928, 190.

Determination of iodide in mixtures of halides. H. BAINES.—See B., 1928, 190.

Determination of hydrogen sulphide in sea-water. G. DRUCKER (Internat. Rev. Hydrobiol. Hydrogr., 1926, **16**, 130—133; Chem. Zentr., 1927, ii, 1189).—The sea-water is run directly into 15 c.c. of 0·01N-iodine solution acidified with 1—2 c.c. of concentrated hydrochloric acid. A. A. ELDRIDGE.

Determination of sulphate in chromic acid. W. H. D. (Chemist-Analyst, 1927, **16**, No. 2, 8).—The sample (10 g. in 200 c.c. of water) is treated with hydrochloric (10 c.c.) and acetic acids (15 c.c.) before precipitation with barium chloride (10% solution, 5 c.c.), and the barium sulphate washed at least 5 times with 1% hydrochloric acid.
CHEMICAL ABSTRACTS.

Iodometric determination of selenium. R. BERG and M. TEITELBAUM (Chem.-Ztg., 1928, **52**, 142).—The reduction of selenious acid by hydriodic acid to give the equivalent amount of iodine may be carried out quantitatively when the reaction takes place in the presence of carbon disulphide. The iodine is then completely dissolved by the organic solvent and is not partly adsorbed on the precipitated selenium as in the method of Muthmann and Schäfer (A., 1893, ii, 318). It is determined in the usual way by titration with sodium thiosulphate solution.
L. M. CLARK.

Detection of selenium in decolorised bottle glasses. E. J. C. BOWMAKER and J. D. CAUWOOD.—See B., 1928, 192.

[Micro-]determination of nitrogen. R. EHRENBERG (Z. ges. exp. Med., 1927, **56**, 466—469).—The Kjeldahl-ammonia is distilled in a silica vessel into a 10 c.c. flask containing 5 c.c. of 0·001N-lead nitrate solution; the mixture, diluted to 10 c.c., is centrifuged, and 1 c.c. of the solution is treated with 0·5 c.c. of a radioactive (thorium-*B*) 0·001N-lead nitrate solution and 0·5 c.c. of 0·001N-potassium chromate solution. After removal of lead chromate by the centrifuge, 1 c.c. of the solution is evaporated, and its activity after 9 hrs. is determined with the electrometer. The activity of the solution is inversely proportional to the ammonia content.
A. A. ELDRIDGE.

Determination of small quantities of phosphorus by Denigès' method. V. V. Ciurea (Bul. Soc. Chim. România, 1927, 9, 86—89).—Small quantities of phosphorus may be accurately determined by a volumetric method involving the oxidation of the blue compound obtained in the usual Denigès colorimetric method with chlorine water, the quantity of the latter required for decolorisation being directly proportional to the phosphorus present. The phosphorus solution (5 c.c.) is shaken with 4 drops of the sulphomolybdic reagent, 4 drops of a freshly-prepared stannous chloride solution are added, and the solution is left for 10 min. for the colour to reach a maximum. The solution is then diluted with 10—15 c.c. of water and chlorine water added from a microburette until the colour is just destroyed. The operations are repeated on a solution of known phosphorus content and the volume of chlorine water used in each case is directly proportional to the phosphorus present. In no case did the error exceed 4·1%, a value much smaller than the errors in the colorimetric or nephelometric methods. J. W. Baker.

Influence of sulphates on the volumetric method for the determination of phosphorus. C. M. Bible (J. Assoc. Off. Agric. Chem., 1928, 11, 126—128).—The A.O.A.C. volumetric method for the determination of phosphorus is unsatisfactory in presence of sulphates, which may be derived either from the original material or from the extraction solvent. Accurate results may be obtained without removal of the sulphate by careful control of the temperature when precipitating the ammonium phosphomolybdate. F. R. Ennos.

Iodometric determination of phosphorous acid and the use of sodium hydrogen carbonate in iodometry. P. Carré (Compt. rend., 1928, 186, 436—438).—The production of iodate is shown to be the cause of errors obtained in the determination of phosphorous acid by oxidation with $0\cdot1N$-iodine solution in the presence of sodium hydrogen carbonate (5—15 mols. per mol. of acid), the excess of iodine being titrated after 1·5 hrs. with sodium thiosulphate. If, however, the solution is acidified with hydrochloric acid before the final titration, the iodate is reduced and the iodine regenerated; otherwise the thiosulphate is oxidised to sulphate. A large excess of hydrogen carbonate should be avoided in such cases, and loss of iodine in the carbon dioxide spray is prevented by the use of a closed vessel. Phosphorous acid may be determined in the presence of phosphorous esters, $P(OH)_2\cdot OR$, by this method. J. Grant.

Comparison of two methods used in determination of phosphorus pentoxide as magnesium ammonium phosphate. W. M. McNabb (J. Amer. Chem. Soc., 1928, 50, 300—304).—The ammonium acetate method (Schmitz, A., 1925, ii, 67) is compared with the method in which this substance is not used (Treadwell and Hall, "Analytical Chemistry," 1924, 2, p. 380). In each case a final washing of the precipitate with a saturated ammoniacal solution of ammonium nitrate previously to ignition is recommended in order completely to oxidise any organic material which may be present. The two methods give average errors of +0·02%, −0·02%, respectively (ignition over a Méker burner); in presence of molybdate ions the average error ranges from 0·1 to 0·3%, although if the ignition is carried out in an electric muffle at 1000° the error is −0·05%. In the absence of molybdate ions the acetate method more easily produces a crystalline precipitate. S. K. Tweedy.

Reinsch's test. H. Leffmann and M. Trumper (Bull. Wagner Free Inst. Sci., 1927, 2, 89—92).—The closed tube containing the copper strip should be heated for a short time only with a spirit-lamp. Chemical Abstracts.

Gutzeit method for the determination of arsenic. H. Heidenhain (J. Assoc. Off. Agric. Chem., 1928, 11, 107—112).—In the A.O.A.C. method as modified by the U.S. Bureau of Chemistry, the length of the arsenic stain is shown to be affected by changes of temperature both of the generating and of the absorption apparatus. Lower temperatures of the former produce shorter and more intense stains than higher temperatures, the opposite effect being observed on varying the temperature of the latter. By immersing the whole apparatus in a water-bath at constant temperature, *e.g.*, 30°, the stains obtained with definite quantities of arsenic are uniform both in length and intensity, thus rendering the use of permanent standards possible. A modified Gutzeit method including in addition several minor changes in the preparation of the solution is suggested. F. R. Ennos.

Separation of arsenic from antimony. L. W. McCay (J. Amer. Chem. Soc., 1928, 50, 368—373).—If excess of silver nitrate solution is added to a hydrofluoric acid solution of arsenic and antimonic acids which has been made slightly alkaline with ammonia, the arsenic is quantitatively precipitated as silver arsenate, free from antimony. The arsenic is determined by dissolving the precipitate in nitric acid and determining the silver by Volhard's method. If the filtrate from the silver arsenate is treated with the minimum amount of hydrochloric acid for precipitation of silver, mixed with concentrated sulphuric acid, evaporated to fuming point, and then boiled with a piece of sulphur, the antimony may be determined by titrating the resulting solution with potassium permanganate or bromate (cf. Petriccioli and Reuter, A., 1902, ii, 177; Györy, A., 1893, ii, 554). S. K. Tweedy.

Volumetric determination of antimony in presence of lead, tin, and copper. A. Vassiljev and W. Kargin (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 143—156; Chem. Zentr., 1927, ii, 1055—1056).—The reaction (Györy): $KBrO_3+3SbCl_3+6HCl=3SbCl_5+KBr+3H_2O$, using as indicator methyl-orange, which is decolorised by excess of bromate, is employed. When the liquid contains lead sulphate, low (1—3%) values are obtained; the solution is therefore siphoned off, the lead sulphate dissolved in concentrated hydrochloric acid, and the diluted solution titrated with bromate. The presence of tin does not affect the results. Low (0·3—1·7%) values are obtained in presence of copper. In presence of lead and copper 96—97% of the antimony is found; treatment of the precipitate (as above) indicates a further 2% of antimony. With the pure metals, but not with technical alloys, tartaric acid is not oxidised by the bromate.

A. A. Eldridge.

Determination of sodium borate. M. François and (Mlle.) L. Seguin.—See B., 1928, 156.

Volumetric determination of sodium. A. Nau (Bull. Soc. Pharm. Bordeaux, 1927, 65, 67—76; Chem. Zentr., 1927, ii, 467).—Blanchetière's method is modified in that the uranyl compound is reduced with zinc and sulphuric acid, and then titrated with permanganate.

A. A. Eldridge.

Determination of small quantities of sodium. Weiland (Mitt. Kali-Forsch.-Anst., 1927, 21—28; Chem. Zentr., 1927, ii, 1871).—Manipulative details are given for the method preferred, viz., the precipitation of sodium ions by a concentrated uranyl magnesium acetate solution, with the production of the compound $3(UO_2)(C_2H_3O_2)_2,Mg(C_2H_3O_2)_2,NaC_2H_3O_2,9H_2O$, which is practically insoluble in alcohol.

A. A. Eldridge.

Uranyl acetate as a reagent in microscopic qualitative analysis. E. M. Chamot and H. A. Bedient (Mikrochem., 1928, 6, 13—21).—In applying the uranyl acetate test for sodium the best procedure consists in evaporating the solution to be tested on a microscope slide until a dry film is formed, placing a drop of the reagent close to the edge of the film, and drawing a platinum wire through the drop, thence across the film. The formation of isotropic tetrahedra indicates the presence of sodium; fine clusters of hair-like crystals the presence of the alkaline earths or of lead; tetragonal prisms potassium, rubidium, cæsium, silver, thallium, or ammonium; square plates barium, and orthorhombic plates or prisms manganese, magnesium, zinc, cadmium, iron (ferrous), nickel, cobalt, or copper. The presence of sodium together with a member of the last-named group results in the separation of monoclinic triple acetates in the form of polysynthetic twins of somewhat indefinite chemical composition. In the absence of metals other than alkalis the formation of sodium zinc uranyl acetate is probably the most sensitive test for the presence of sodium; so sensitive is this reaction that silica object slides should be used to avoid possible contamination from sodium of the ordinary glass slide.

A. R. Powell.

Potash charge removal from platinum crucibles [in alkali determinations]. T. C. Green (Chemist-Analyst, 1927, 16, No. 2, 16).—In the Lawrence Smith method of determining alkali in silicates the crucible is charged through a cork-borer, the space between this and the walls of the crucible being filled with calcium carbonate.

Chemical Abstracts.

Capillary analysis. R. Dubrisay (Mon. Prod. chim., 1927, 9, No. 90, 4—7; Chem. Zentr., 1927, ii, 1180).—The volume of 40 drops of 1/600*N*-sodium hydroxide solution (free from carbonate), dropped from a constricted tube into "vaseline" oil containing 1% of oleic acid, was 1·20 c.c., whilst if to the solution an equal volume of 1/800 or 1/80*N*-sodium chloride solution was added, the volume of 40 drops was 0·98 or 0·20 c.c. The method should be applicable to the determination of alkali halide in 0·0002*M*-solution.

A. A. Eldridge.

Influence of impurities arising from glass vessels on the titre of alkali hydroxides. K. Seiler (Schweiz. Apoth.-Ztg., 1927, 65, 229—233; Chem. Zentr., 1927, ii, 852).—A study of "fixanal" sodium hydroxide ampoules; silica, boric acid, and calcium were detected, but not antimony, arsenic, or iron.

A. A. Eldridge.

Alkaline-earth metals in "saccharate" solutions and their use in alkalimetry. A. C. Shead (J. Amer. Chem. Soc., 1928, 50, 415—416).—Metallic calcium of known purity may be weighed out directly in air and dissolved in sucrose solution in order to prepare a carbonate-free standard alkali solution with a single weighing. Warm calcium does not tarnish readily, and in any case the film formed is too thin to affect the accuracy of the method. The chief impurity is magnesium, which, together with its oxide, is almost insoluble in 30% sucrose solution.

S. K. Tweedy.

Qualitative separation of calcium, barium, and strontium. O. Macchia (Notiz. chim.-ind., 1927, 2, 311—312; Chem. Zentr., 1927, ii, 853).—The mixed carbonates are dissolved in a little dilute hydrochloric acid, and the solution is evaporated to 5—8 c.c. One portion is neutralised with ammonia, and 4—5 vols. of saturated potassium ferrocyanide solution are added; the precipitate of the compound $K_2Ca[Fe(CN)_6],3H_2O$ is collected, the barium in the diluted filtrate being precipitated as chromate, and (after filtration) the strontium as carbonate. The other portion is slightly warmed and stirred with malonic acid (0·5 g.) and a slight excess of concentrated aqueous ammonia solution; the filtrate after removal of precipitated barium malonate is warmed with 4—5 vols. of methyl alcohol to precipitate strontium and some calcium, calcium being precipitated from the filtrate as carbimide.

A. A. Eldridge.

Rapid determination of calcium and magnesium. C. J. Schollenberger (Chemist-Analyst, 1927, 16, No. 2, 6—7).—Calcium and magnesium are precipitated together as oxalate and ammonium arsenate, respectively; the precipitate is dissolved in dilute sulphuric acid, the oxalate determined volumetrically with permanganate, and the arsenate determined iodometrically.

Chemical Abstracts.

Detection and determination of small quantities of beryllium by means of 1:2:5:8-tetrahydroxyanthraquinone. H. Fischer (Z. anal. Chem., 1928, 73, 54—64; cf. A., 1927, 36).—Further details of the method previously described are given and the method is extended to the rapid determination of beryllium in alloys and minerals. Copper and nickel alloys (0·1 g.) are dissolved in hydrochloric acid and "perhydrol," the solution is evaporated to dryness on the water-bath, and the residue dissolved in a little warm water. The solution is treated with sufficient potassium cyanide to convert the copper and nickel into soluble double cyanides, then with sodium hydroxide until the alkalinity is at least 0·25*N*. An aliquot part of the clear solution is used for the volumetric determination with a 0·05% solution of quinalizarin in 0·25N-sodium hydroxide. For the determination of beryllium in beryl, 0·2 g. of mineral is fused with sodium carbonate and the silica removed by evaporation with hydrochloric acid and filtration. The filtrate is treated with sodium hydroxide to 0·25N and the determination finished as usual. The use of tartaric acid to retain aluminium and other metals in solution in the alkali leads to high results, as under these conditions aluminium reacts similarly to beryllium. A. R. POWELL.

Detection of traces, and colorimetric determination, of beryllium. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1928, **50**, 393—395).—One drop of a 0·01% solution of curcumin in alcohol, 0·5 c.c. of 4N-ammonium chloride, and 6 drops of 4N-ammonia solution are added to the solution. A red or an orange-red flocculent precipitate is obtained, the sensitivity of this reaction extending to 0·05 mg. of beryllium per litre. By comparison with a standard which has been kept for the same length of time after precipitation a good quantitative determination may be made. Magnesium decreases the sensitivity somewhat; aluminium and ferric iron must be first precipitated by addition of sodium fluoride. It is suggested that curcumin may be useful for detecting amounts of magnesium between 1 and 10 mg. per litre in strongly alkaline solution. The indicator 1 : 2 : 5 : 8-tetrahydroxyanthraquinone was unsuitable for the colorimetric determination of beryllium. S. K. TWEEDY.

Pyrophosphate method for the determination of magnesium and [of] phosphoric anhydride. (MISS) A. W. EPPERSON (J. Amer. Chem. Soc., 1928, **50**, 321—333).—A critical examination of the published directions for carrying out the above analyses leads to the formulation of standard procedures, which are detailed in the original. A second precipitation under specified conditions is essential. In the first case, when excess of potassium chloride is present a third precipitation is necessary. S. K. TWEEDY.

[Detection of zinc and calcium.] R. W. HUFFERD (Proc. Indiana Acad. Sci., 1926, **36**, 183—184).—(*a*) Zinc is precipitated as sulphide with sulphur after addition of potassium dichromate, and the hot hydrochloric acid extract of the precipitate is tested with potassium ferrocyanide or hydrogen sulphide.

(*b*) After removal of barium as chromate, the filtrate is evaporated to 15 c.c., and diluted with 45 c.c. of hot water; to half, one drop of saturated calcium sulphate solution is added. Ammonium oxalate solution (5 drops) is added to each, and a precipitate smaller in quantity than that produced in the control is ignored. CHEMICAL ABSTRACTS.

Determination of the free acidity of solutions of heavy metal salts. E. MÜLLER and F. MÜLLER (Z. anal. Chem., 1928, **73**, 47—51).—Potentiometric titration with sodium hydroxide of the free acidity of solutions containing the sulphates of zinc, copper, manganese, cadmium, or nickel yields accurate results using a hydrogen or quinhydrone indicator electrode, the end-point being marked by a very pronounced change of potential. If a hydrogen electrode is used a further sharp change of potential occurs when the metal is entirely precipitated as hydroxide, but the results obtained are accurate only to 1—2% owing to adsorption. The use of methyl-orange as indicator for the determination of the acidity of solutions containing the above-named sulphates gives results which agree with those obtained potentiometrically. A. R. POWELL.

Sensitive microchemical reactions of cadmium salts. A. MARTINI (Mikrochem., 1928, **6**, 1—4).—Solutions of cadmium salts yield characteristic white, microcrystalline precipitates with sodium bromide and brucine acetate and with sodium bromide and a concentrated acetic acid solution of quinine sulphate. These reactions serve for the microchemical detection of cadmium, a distinct precipitate being obtained with 1 drop of a solution containing 0·3 mg./c.c. A. R. POWELL.

Precipitation of copper with sodium thiosulphate. M. G. ROEDER (Tidskr. Kemi Berg., 1927, **7**, 94—95; Chem. Zentr., 1927, ii, 1740).—Precipitation of copper with sodium thiosulphate is complete in the presence of nitric, hydrochloric, or sulphuric acid. The cuprous sulphide is washed with cold sulphurous acid solution. A. A. ELDRIDGE.

Gravimetric separation of copper and mercury. G. SPACU (Bul. Soc. Stiinte Cluj, 1927, **3**, 171—174; Chem. Zentr., 1927, ii, 2087).—The neutral or slightly acid solution containing copper and mercury is heated to boiling, excess of pyridine is added with production of an intense blue colour, and then, with vigorous shaking, solid ammonium thiocyanate. After 1 hr. the precipitate is collected, washed with a cold solution containing ammonium thiocyanate (0·5%) and pyridine (5 c.c. per litre), dried at 140—150°, heated slowly, and finally ignited to cupric oxide. After acidification of the filtrate with hydrochloric acid, the mercury is precipitated as sulphide. Solutions containing much nitric acid are first evaporated to dryness, the residue is dissolved in hot water, and the solution mixed with much pyridine. If too little pyridine is employed, the copper is precipitated, and must be redissolved by addition of a few drops of nitric acid.

A. A. ELDRIDGE.

Micro-determination of mercury in organic compounds and the determination of carbon and hydrogen in such compounds. A. VERDINO (Mikrochem., 1928, **6**, 5—12).—The destruction of the organic matter by heating with concentrated sulphuric and nitric acids leads to a small loss of mercury, but good results are obtained by heating for 2 hrs. at 250—270° with fuming nitric acid in a sealed tube. The mercury may be recovered from the solution by electrolysis with 2·5—3·2 volts, using a gold-plated platinum gauze cathode.

A. R. POWELL.

Potentiometric determination of cerium. K. SOMEYA (Sci. Rep. Tôhoku, 1928, **17**, 93—97).—See this vol., 146.

Quantitative microscopic analysis of commercial felspar. H. INSLEY.—See B., 1928, 193.

Action of hexamethylenetetramine on solutions of salts of metals of the third group, and

quantitative separation of iron from manganese, zinc, nickel, and cobalt. P. RÂY and A. K. CHATTOPADHYA (Z. anorg. Chem., 1928, **169**, 99—112).—Iron, aluminium, chromium, and titanium are precipitated as hydroxides from boiling solutions of their salts containing ammonium salts by hexamethylenetetramine. Under the same conditions, manganese, zinc, cobalt, and nickel are not precipitated, because the hydrogen-ion concentration resulting from the hydrolysis of their salts is not great enough to furnish by hydrolysis of the precipitant a hydroxyl-ion concentration sufficient for precipitation. In order to separate iron from manganese, cobalt, nickel, or zinc, ammonium chloride is added to the solution, which is then almost neutralised with ammonium carbonate, and the iron is precipitated at the b. p. with a 10% solution of the reagent. It is not possible to separate chromium from zinc, cobalt, and nickel in this way. Kollo's method of separating iron and manganese with hexamethylenetetramine (A., 1921, ii, 218) does not seem to give satisfactory results, and his explanation of the mechanism of the process is apparently incorrect. R. CUTHILL.

Determination of cobalt as Co_3O_4. R. CERNATESCO and (MME.) VASCAUȚANU (Ann. Sci. Univ. Jassy, 1928, **15**, 69—70).—The hydroxide is precipitated from boiling solution by potassium hypobromite, filtered, dried, and ignited with the filter-paper in a Rose crucible in a current of oxygen. The temperature is raised as soon as the carbon is burnt, and the conversion into Co_3O_4 is complete. Any remaining alkali can be washed out, and the ignition repeated. C. W. GIBBY.

Microchemical reactions [with hexamethylenetetramine sulphate and with piperazine]. A. MARTINI (Mikrochem., 1928, **6**, 28—33).—Addition of hexamethylenetetramine sulphate and ammonium thiocyanate solutions to a solution of cobalt chloride yields glistening, blue, triclinic prisms of a complex, non-ionised compound. Under similar conditions copper chloride yields light yellow, triclinic tables, zinc chloride a mass of thin, white needles, ferrous chloride light red crystals, vanadyl chloride light red hexagons, indium chloride reddish-white, tetragonal prisms, and ammonium molybdate red, hexagonal crystals or yellow prisms. A mixture of antimonious chloride and sodium iodide yields with an acetone solution of piperazine microscopic, monoclinic, yellow tablets and prisms. Under similar conditions bismuth chloride gives intense red crystals isomorphous with the antimony compound. Auric chloride, sodium bromide, and piperazine produce orange-yellow to red microscopic prisms. A. R. POWELL.

Analysis of chrome iron ore. E. DITTLER.—See B., 1928, 195.

Metal complexes with pyrocatechol and their use in microchemical analysis. A. MARTINI (Mikrochem., 1928, **6**, 63—66).—Addition of 1 drop of a saturated solution of pyrocatechol acetate followed by 1 drop of aniline or of a saturated solution of piperazine to solutions of sodium molybdate, tungstate, or vanadate produces characteristic precipitates of the type $[OM(OH)(O\cdot C_6H_4O)_2]$,AcOB, where M is quinquevalent molybdenum, tungsten, or vanadium, and B is aniline or piperazine. The respective colours of the precipitates are red, yellow, and black; those containing aniline crystallise in triclinic prisms and plates, whilst those with piperazine separate out in tufted clusters of needles. A. R. POWELL.

Separation of tungsten from silicon and tin. J. CIOCHINA (Z. anal. Chem., 1927, **72**, 429—434).—Tungstic acid may be separated from a freshly-precipitated mixture of tungstic and metastannic acids or from a mixture of tungstic acid and silica dehydrated at 130° by treating the mass with a warm, concentrated solution of sodium tungstate, in which it dissolves with the formation of metatungstate. Prolonged digestion of the mixture may cause dissolution of part of the silica to form silicotungstate, but a good separation is obtained by treating the mixed acids on the filter-paper with a warm 20—30% solution of sodium tungstate and washing the residual silica or metastannic acid with hot water, hydrochloric acid, and hot water successively. For the determination of silica in ferrotungsten the finely-divided metal is heated for 3—4 hrs. with bromine at 50°, the solution evaporated to dryness, the residue heated at 130°, cooled, and extracted with 10% hydrochloric acid, and the insoluble tungstic acid–silica mixture is collected, washed, and treated as described above. For the alkalimetric determination of tungstic acid it is recommended to wash the precipitated acid with a saturated solution of sodium chloride until the wash water ceases to react acid, transfer the filter and precipitate to a beaker containing an excess of $0{\cdot}1N$-sodium hydroxide, and titrate the excess of alkali with $0{\cdot}1N$-sulphuric acid using phenolphthalein as indicator. A. R. POWELL.

Precipitation of earth-acids by sodium compounds and quantitative separation of tungsten from tantalum and niobium. W. R. SCHOELLER and K. JAHN (Z. anorg. Chem., 1928, **169**, 321—335).—See A., 1927, 32, 1047.

Titration of tin with "chloramine." E. RUPP (Z. anal. Chem., 1928, **73**, 51—53).—Chloramine (the sodium salt of *p*-toluenesulphonylchloroamide) may be used instead of iodine in the titration of stannous chloride provided that the acidity of the solution does not exceed 3—5%; a small crystal of potassium iodide is added to the tin solution together with the usual starch indicator. Solutions containing stannic salts are reduced by means of zinc filings and the spongy tin is dissolved in warm concentrated hydrochloric acid, the excess of which is neutralised by the addition of a solution of sodium hydroxide and carbonate just prior to titration. A. R. POWELL.

Use of liquid amalgams in volumetric analysis. X. Determination of vanadium, chromium, and nitro-compounds. K. SOMEYA (Z. anorg. Chem., 1928, **169**, 293—300; cf. A., 1927, 746).—Ammonium vanadate may be determined by reducing in concentrated hydrochloric acid solution with lead amalgam, then titrating after removal of the amalgam with a $0{\cdot}1M$-solution of cupric sulphate, the acid concentration being maintained at 10—12N. Safranine or neutral-violet is used as indicator, 10 c.c. of a 0·1% solution being added to the vanadate when it has been reduced to the vanadous state, and reduced to the leuco-compound by further treatment with amalgam. The completion of the re-oxidation in the subsequent titration is then indicated by the reappearance of the original colour of the indicator. If zinc amalgam is substituted for lead amalgam, iodine may be used instead of copper sulphate for the titration, and the method is then a convenient one for the determination of vanadium in ferrovanadium, as ferric salts do not interfere. Chromic salts may be determined by reduction to the chromous state with zinc amalgam (cf. *ibid.*, 333) followed by titration with iodine, iodate, or bromate, the indicator for the first two of these being starch, and for the third starch and potassium iodide. A solution of chromous chloride prepared in this way may also be employed to reduce *p*-nitroaniline or *p*-nitrophenol, which is then titrated with ferric alum, with ammonium thiocyanate as indicator. The results obtained in the determination of picric acid by this method are, however, about 1% too low. R. CUTHILL.

Determination of bismuth as oxyiodide. R. STREBINGER and W. ZINS (Z. anal. Chem., 1927, 72, 417—429; cf. this vol., 39).—The microchemical method previously described has been modified for the determination of larger quantities of bismuth as follows: The solution of the nitrate is evaporated to dryness on the water-bath, the residue dissolved in 1 c.c. of 1 : 1 nitric acid and 10—15 c.c. of water, and the solution treated with crystals of potassium iodide until the liquid above the black precipitate is pale golden in colour; a further 50 c.c. of water are added and the solution is heated on the water-bath until the black precipitate changes to copper-coloured scales of the oxyiodide. Hot water is added until the liquid becomes almost colourless, followed by a solution of sodium acetate (25 g./litre) until the colour entirely disappears. The precipitate is collected in a glass filtering crucible, washed with hot water, dried at 105°, and weighed as BiOI. Small amounts of lead do not interfere, but in the presence of much lead a preliminary separation of the bismuth must be made; the boiling slightly acid solution of the metals is treated with a few drops of methyl-orange followed by 2*N*-sodium formate solution until the liquid becomes yellow. The precipitate of basic bismuth formate, containing only traces of lead, is collected on a glass filtering crucible, washed with hot water, and dissolved in nitric acid for the iodide precipitation. A. R. POWELL.

Potentiometric determination of gold. E. MÜLLER and F. WEISBROD (Z. anorg. Chem., 1928, 169, 394—398).—In determining gold by the method previously described (A., 1926, 1117), the concentration of free hydrochloric acid in the solution should be small, as otherwise the auric ion combines to a large extent to form chloroauric acid, and the change in potential corresponding with the completion of the reaction $Au^{\cdots}+3Fe^{\cdot\cdot} \longrightarrow Au+3Fe^{\cdots}$ is therefore indistinct. Nitric acid has an even more marked effect, but this may in a large measure be overcome by adding to the solution potassium sulphate before the titration commences, and alcohol when the reduction of the chlorine is complete. Copper, mercury, and lead, even at high concentrations, and solid silver chloride do not affect the determination, but appreciable amounts of palladium or platinum make the titration impossible, although the effect of palladium may be partly overcome by addition of alcohol and potassium sulphate. When gold is titrated with titanous chloride after being oxidised with potassium bromate in hydrochloric acid solution, according to Zintl and Rauch's method (A., 1925, ii, 1005), any excess of bromate may give rise to errors by causing the solution to attack the platinum electrode.
R. CUTHILL.

Osmium. II. Determination. E. FRITZMANN (Z. anorg. Chem., 1928, 169, 356—364; cf. A., 1927, 742).—Sufficient of the material for analysis to give about 0·1 g. of metallic osmium is heated with a mixture of 5 c.c. of concentrated sulphuric acid, 10 c.c. of water, and 5 c.c. of a 10% solution of chromium trioxide, a further 5 c.c. of this solution being added 10 min. after boiling commences, and again after 20 min., and after 30 min. 5 c.c. of water are added. Osmium tetroxide distils over, and is condensed into a solution of sodium hydroxide. Sodium sulphide is then added to the distillate, and the mixture acidified at 90° with hydrochloric acid, ammonium chloride being added to cause the precipitated sulphide to coagulate satisfactorily. The precipitate is ignited in a current of hydrogen, and weighed as the metal. This method cannot be used for the determination of osmium in osmiridium, or in presence of ruthenium. R. CUTHILL.

Mercury spectrum tube. E. RUMPF (Z. physikal. chem. Unterr., 1927, 40, 205—206; Chem. Zentr., 1927, ii, 1869).

Ultra-violet refractometry. L. C. MARTIN (Trans. Opt. Soc., 1927—1928, 29, 1—21).—A critical-angle method is described for determining the refractive indices of small quantities of liquid for ultra-violet light. Two quartz hemispheres, between which is a thin film of the liquid, are rotated in a beam of approximately parallel radiation, and the critical angles for various wave-lengths are measured by means of a quartz spectrograph. A detailed procedure is described and discussed. C. W. GIBBY.

Simple form of photo-electric photometer. J. H. J. POOLE (Nature, 1928, 121, 281—282).—The phenomenon of the intermittent discharge through a neon lamp is applied to the measurement of small illuminations with a vacuum photo-electric cell. The cell and the neon lamp are connected in series with a high-tension battery, and the lamp is shunted with a condenser; the frequency of the intermittent flashes increases with the illumination. A. A. ELDRIDGE.

Adiabatic microcalorimeter for radiological researches. W. SWIENTOSLAWSKI and (MLLE.) A. DORABIALSKA (Rocz. Chem., 1927, 7, 559—566).—See A., 1927, 1163.

Micro-determination of mol. wt. H. JÖRG (Mikrochem., 1928, 6, 34—49).—An apparatus is described and illustrated diagrammatically for the micro-determination of the mol. wt. of organic substances by the depression of f.-p. method. It consists essentially of two thermostats containing tubes holding the liquid used as solvent and provided with copper–constantan thermocouples either of which may be connected through a resistance to a sensitive galvanometer by means of a throw-over switch. One of the vessels serves for standardising the galvanometer, which is adjusted to zero at the f. p. of the solvent, and the other vessel is used for determining the f. p. of the solution. When both solution and solvent are just melting the difference between the galvanometer readings corresponds with the depression of the f. p. Several examples are given of the results obtained and the method of calculation is explained. A. R. Powell.

Resistance wire for use in the laboratory. J. Piccard (J. Amer. Chem. Soc., 1928, 50, 406—408).—"White gold," an alloy of nickel and gold, is a suitable non-corrosive material for the measuring wires of Wheatstone bridges. The alloy is hard and ductile, and has a tensile strength greater than that of steel. The resistance, temperature coefficient of resistance, and thermoelectric force against copper are recorded for two commercial specimens of "white gold," and for platinum and constantan. S. K. Tweedy.

Pipette for micro-analyses. A. T. Shohl (J. Amer. Chem. Soc., 1928, 50, 417).—Van Slyke and Neill's modified Ostwald pipette is fitted with a hypodermic needle (made of platinum if necessary). Drops of the order 0·00015 c.c. can be removed from such a tip. S. K. Tweedy.

Modified weighing pipette. G. Edgar (Ind. Eng. Chem., 1928, 20, 158).—A Lunge weighing pipette contains three bulbs of definite volume with graduation marks between them. It enables triplicate weighings of nearly the same quantity of material to be conveniently made. C. Irwin.

Apparatus for micro-filtration. A. T. Shohl (J. Amer. Chem. Soc., 1928, 50, 417—418).—The liquid is filtered by suction through a thin layer of asbestos packed over a glass bead in a filter funnel. The precipitate can be washed five or ten times with 1 c.c. of solution. S. K. Tweedy.

Suction flask for quantitative analysis. G. W. Kühl (Chem.-Ztg., 1928, 52, 131).—The suction funnel is carried in a stopper which fits into a tubulure on the top of a spherical container. The tubulure carries a side tube connected through a 3-way cock either to the vacuum pump or to the atmosphere. Another tube provided with a stopcock is connected to the lower end of the spherical container. S. I. Levy.

Laboratory cooling device using liquid sulphur dioxide. A. F. Gill (Ind. Eng. Chem., 1928, 20, 212).—The "cold test" of castor oil for use in aircraft engines requires the maintenance of a temperature of −10° for 10 days. This is conveniently obtained by placing the test-tube containing the oil in a small Dewar flask charged with slowly-boiling liquid sulphur dioxide (b. p. −10°). The only attention required was addition of 100 c.c. of sulphur dioxide every second day. C. Irwin.

Electrical solution-mixing device. K. Hickman and D. Hyndman (Ind. Eng. Chem., 1928, 20, 213—216).—The automatic control of the proportions in which two solutions are being mixed is effected by carrying forward in a current of air a gas which is either a participant in the reaction or is added as an indicator, into a conductivity cell. Ammonia may be used either in the neutralisation of sulphuric acid with ammonia, or in the neutralisation of this acid with sodium hydroxide, a trace of ammonia being added in the last case. Other indicators are sulphur dioxide and chlorine. The resistance of the cell used with tap water was 2000 ohms. This is coupled to a 110-volt A.C. supply and the variable current produced actuates a solenoid which is capable of rotating a hollow drum pivoted axially through a few degrees. In the sides of the drum are two outlets for the liquor under regulation, one a feed and the other a by-pass. In effect, a frictionless valve controls the feed actuated by the conductivity of the indicator cell. C. Irwin.

Extraction apparatus for liquids. J. Friedrichs (Chem Fabr., 1928, 91).—A new apparatus is described in which the usual glass spiral is replaced by a porous filter plate. C. W. Gibby.

Metallographic etching. M. Schneider (Z. physikal. chem. Unterr., 1927, 40, 175—176; Chem. Zentr., 1927, ii, 1001).—A lecture demonstration. A. A. Eldridge.

Geochemistry.

[Variation of] the layer of ozone in the upper atmosphere during the night. D. Chalonge (Compt. rend., 1928, 186, 446—448).—The thickness of the layer of ozone encircling the upper atmosphere of the earth (Dobson and Harrison, A., 1926, 493) was determined for a few days and nights from the spectral intensities of the radiations (up to 3050 Å.) from the sun and moon, respectively. It remained constant during a particular night (about 3 mm.) but was less during the day (about 2·2 mm.). A longer series of measurements is required to confirm this. J. Grant.

Nitrate in the sea. II. H. W. Harvey (J. Marine Biol. Assoc., 1928, [ii], 15, 183—189).—The nitrates in the sea-water south-west of Plymouth are used up by the phytoplankton during the summer but reappear during the autumn as their synthesis during this period is more rapid than their decomposition. Nitrates from land drainage cannot be detected more than a few miles from the land. W. O. Kermack.

Seasonal variations in the phosphate and silicate content of sea-water during 1926 and 1927 in relation to the phytoplankton crop. W. R. G. Atkins (J. Marine Biol. Assoc., 1928, [ii], 15, 191—205).—The silicate and phosphate contents of sea-water undergo rapid reduction during the late spring and early summer as a result of the rapid proliferation of diatoms. The silicates may show a rise in late summer which is not exhibited by the phosphate, and comparing various seasons a high phosphate minimum may accompany a low silicate minimum and *vice versa*. The date of the fall of the phosphates in spring varies from season to season and is correlated chiefly with the amount of sunlight.

W. O. Kermack.

Photosynthesis of diatom cultures in the sea. S. M. Marshall and A. P. Orr (J. Marine Biol. Assoc., 1928, [ii], **15**, 321—360).—With increasing depth photosynthesis by diatoms, as determined by the oxygen production (Winkler's method), reaches a maximum and then decreases. This maximum occurs very near the surface in winter or in the absence of direct sunlight, and occurs at a depth of 20—30 metres in the summer, but under similar conditions is nearer the surface in the more turbid waters nearer the coast than in the open sea. W. O. Kermack.

p_H of the Black Sea compared with that of the salt lake Tékir-Ghiol. N. L. Cosmovici (Ann. Sci. Univ. Jassy, 1928, **15**, 131—132).—p_H values have been determined colorimetrically in July in the Black Sea and in the adjacent salt lake Tékir-Ghiol. For the former, values between 8·3 and 8·5 were found in all cases, independent of temperature, wind, and the nature of the sea bed. The presence of algæ increased the p_H. The p_H of the lake Tékir-Ghiol was 8·6 under all observed conditions.

C. W. Gibby.

Comparison of the absorptive powers of Russian and other clay. A. Monosson (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 169—173; Chem. Zentr., 1927, ii, 1009).—The absorptive power of clays for ozokerite in kerosene is increased by heating the material at 350—400°, but not at 105° or 700°. Treatment with acid, and pulverisation, also often increase the absorptive power. A. A. Eldridge.

Kaolin content of clays. H. Boege (Chem. Erde, 1927, **3**, 341—369).—Chemical analyses are given of eight clays from German localities. By digesting the material in hydrochloric acid (d 1·1) for 2 hrs. from 6·00 to 14·08% $Al_2O_3+Fe_2O_3$ passed into solution, this representing the colloidal portion of the aluminium silicate. After ignition of the material at 700° hydrochloric acid extracted more (up to 36·82%) alumina, the additional amount representing the broken-down kaolin. From these results the amount of kaolin in the clay can be calculated. The amount of kaolin present in each of these clays was also determined by the dehydration method of Calsow (A., 1927, 38). L. J. Spencer.

Mineralogical constitution of clays. G. Linck (Chem. Erde, 1927, **3**, 370—374).—Remarks on the paper by Boege (preceding abstract).

L. J. Spencer.

Kaliophylite. O. Mügge (Z. Krist., 1927, **65**, 380—390; Chem. Zentr., 1927, ii, 1140).—Kaliophylite from Mt. Somma contained SiO_2 39·04, Al_2O_3 31·96, Fe_2O_3 0·98, CaO 0·33, MgO 0·15, K_2O 22·84, Na_2O 3·89, H_2O (>105°) 0·60%, but no carbon dioxide, chlorine, or sulphur; ω 1531_6, ε 1527_3, d 2·61.

A. A. Eldridge.

Mineral phosphates in the province of Lecce. G. Tarulli and A. Marcucci (Annali Chim. Appl., 1928, **18**, 40—46).—The whole of the subsoil of the heel of Italy appears to contain higher or lower proportions of phosphates at varying depths, in some cases capable of economic utilisation. T. H. Pope.

Chemical and provincial relations of the younger eruptive rocks of Germany and northern Bohemia. H. Jung (Chem. Erde, 1927, **3**, 137—340).—A large number of chemical analyses of Tertiary igneous rocks from Germany and northern Bohemia, collected from the literature, are tabulated and plotted on diagrams. Variation curves are given for each of the constituent oxides. The rocks of the "Oligocene province" are all alkali-rocks of the "Atlantic type," whilst in the "Miocene province" there are also lime-alkali-rocks of the "Pacific type."

L. J. Spencer.

Mineralogy of Western Australia. I. E. S. Simpson (J. Roy. Soc. W. Australia, 1927, **12**, 57—66).—Lithiophilite (from near Wodgina) contained: P_2O_5 45·99, MnO 30·80, FeO 10·44, CaO 2·78, MgO 0·94, Li_2O 7·87, Na_2O 0·34, K_2O —, H_2O (<110°) 1·11, total 100·27%; d 3·39, hardness 5. Leucite (from Fitzroy valley) contained: SiO_2 52·45, Al_2O_3 8·64, Fe_2O_3 5·48, FeO 0·94, MnO 0·13, MgO 6·42, CaO 2·01, Na_2O 0·38, K_2O 10·42, H_2O (<110°) 1·99, H_2O (>110°) 2·89, TiO_2 5·85, P_2O_5 1·58, BaO 1·19, total 100·37%; d 2·6. Ferrimolybdite (Mulgine) contained: Fe_2O_3 17·87, MoO_3 62·90, H_2O (over calcium chloride) 10·20, H_2O (250°) 9·95, total, 100·92%; d 2·99. The formula $(Fe_2O_3,4MoO_3,5H_2O),5H_2O$ is proposed. Kyanite and staurolite are described. Chemical Abstracts.

Crystals of cornetite, and their refractive indices. A. Schoep (Natuurwetens. Tijds., 1927, **9**, 125—128).—Very well formed crystals, distributed in a layer of chrysocolla covering a brown sandstone, probably from the Star of the Congo mine at Katanga, are found to have the angles and axial ratios already measured by Cesàro and by Hutchinson and Macgregor (A., 1921, ii, 701); besides the forms m (100) and v (221), a new form a (100) is recorded. Measurement of the refractive indices by the immersion method, using the powdered mineral, gives $\alpha=1\cdot765\pm0\cdot003$, $\beta=1\cdot79-1\cdot80$, $\gamma=1\cdot83-1\cdot84$. S. I. Levy.

Structure of millerite. H. W. V. Willems (Physica, 1927, **7**, 203—207).—Millerite, NiS, is ditrigonal–bipyramidal, space-group C_{3v}^{5}, the co-ordinates being Ni $(u, 0, 0)$ $(0, u, 0)$ $(0, 0, u)$, S (x, x, z) (z, x, x) (x, z, x), where $u=0\cdot265$, $x=0\cdot75$, $z=0\cdot41$; hence one sulphur atom is surrounded by three nickel atoms distant 2·24 Å., two nickel atoms at 2·43 Å., and one nickel atom at 3·45 Å. The elementary rhombohedron has α 116° 35′, r 5·65 Å., and contains 3 mols., $d_{calc.}$ 5·25. Chemical Abstracts.

Association of water with serpentine. P. G. Nutting (J. Washington Acad. Sci., 1928, **18**, 81—89).—An attempt is made to distinguish between dissolved, adsorbed, and chemically combined water. The material used for the experiments consisted of clear homogeneous yellowish-green grains of serpentine sieved to 0·15—0·05 mm., and gave on analysis

SiO_2 35·56, Al_2O_3 2·46, Fe_2O_3 4·62, MgO 39·88, FeO 2·02, NiO 0·22, CaO 0·10, H_2O (at 110°) 0·88, H_2O (over 110°) 15·04, corresponding with the ratios $SiO_2 : R^{III}{}_2O_3 : R^{II}O : H_2O = 1{\cdot}73 : 0{\cdot}16 : 3{\cdot}00 : 2{\cdot}59$ [differing appreciably from the formula $3MgO,2SiO_2,2H_2O$]. The weights of this material at temperatures of 26°, 36°, and 46° are plotted against the humidities of the atmosphere; the curves show greater variations in the more arid and more humid regions. The dehydration (weight–temperature) curve shows no break, but the logarithmic curve shows breaks at 368° (corresponding with $2H_2O$) and at 620° (corresponding with $1{\cdot}25H_2O$).

L. J. Spencer.

Bolivianite and Silesite. F. Ahlfeld (Zentr. Min. Geol., 1927, A, 320—321; Chem. Zentr., 1927, ii, 1807—1808).—Polemical against Pauly (Zentr. Min. Geol., 1926, A, 43). A. A. Eldridge.

Blue rock-salt. K. Przibram (Kali, 1927, 21, 253—255; Chem. Zentr., 1927, ii, 1807).—Radioactivity develops a blue colour in rock-salt similar to that in the natural substance, especially under pressure (400 kg./cm.^{2}). Under a pressure of 100 kg./cm.^{2} a yellow colour develops. Potassium may be the origin of radioactivity. A. A. Eldridge.

Mud from lake Tékir-Ghiol [Romania]. A. Burada (Ann. Sci. Univ. Jassy, 1928, 15, 129—130).—A detailed analysis of wet mud from this salt lake shows 63·36% of solids, of which 4·43% consists of soluble salts (mainly sodium chloride and sulphate).

L. J. Spencer.

Granite of Cicurova [Romania]. D. M. Cadere (Ann. Sci. Univ. Jassy, 1928, 15, 81—88).—A petrographical description and a chemical analysis are given of this hornblende-granite, and the analytical results are plotted on diagrams of various kinds. It is an alkali-granite bordering on syenite.

L. J. Spencer.

Chemical constitution of natural hydrated iron oxide. N. S. Kurnakov and E. J. Rode (Z. anorg. Chem., 1928, **169**, 57—80).—See this vol., 41.

Meteoric irons from Bolivia, W. Arkansas, and Michigan. G. P. Merrill (Proc. U.S. Nat. Mus., 1927, 72, Art. 4, 1—4).—The Bolivian specimen (21·25 kg.) contained Fe 94·212, Ni 5·626, Co 0·320, Cu 0·0004, S 0·014, P 0·261, Pt trace, insol. 0·042, total 100·475%. The Arkansas specimens (1·75 kg.) contained Fe 94·858, Ni 5·121, Co 0·353, Cu 0·013, P 0·020, S 0·009, insol. 0·013, Mn trace, total 100·387%. The Michigan specimen (11·5 kg.) contained Fe 87·77, Ni 11·41, Co 0·26, Cu 0·01, S 0·05, P 0·15, total 99·65%. Chemical Abstracts.

Oxidation of meteoric irons. New examples of magnetic iron oxides from terrestrial sources. E. V. Shannon (Proc. U.S. Nat. Mus., 1927, 72, Art. 21, 1—15).—In the oxidation of meteoric iron, magnetite is formed in relatively small quantities as a transitory and unstable stage; the magnetite and the iron are rapidly converted into limonite. The formation of ferromagnetic trevorite, NiO,Fe_2O_3, and of analogous cobalt and copper compounds, seems established. Chlorides promote the formation of amorphous hydrated ferric oxide. Terrestrial ferromagnetic iron oxide is not analogous to the oxidation product of meteorites. Chemical Abstracts.

Connexion between commercial oil deposits and major structural features with special reference to Asiatic fields. L. D. Stamp (J. Inst. Petrol. Tech., 1928, **14**, 28—63).—A critical examination of the occurrence of oilfields shows their frequent association with geosynclinal areas of deposition and occurrence round the margins where the deposits are of a deep-water type, or in the centre in the case of shallow-water deposits. No genetic connexion between oil and belts of folding or between oil and vulcanicity can be traced. H. S. Garlick.

Telegdite, a fossilised resin. L. Zechmeister and V. Vrabély (Z. Min. Geol. Palaont., 1927, A, 287—290; Chem. Zentr., 1927, ii, 1461).—The resin, formerly regarded as succinite, and now named *telegdite*, was found at Szászcsór; it has *d* 1·09, hardness 2½, n_D^{22} 1·5416, and contains C 76·93, H 10·17, S 1·71, O 11·17%; acid value 0, saponification and ester value 180. Decomposition with alkali yields a crystalline acid. A. A. Eldridge.

Proportion of barium in arable soil. G. Bertrand and L. Silberstein (Compt. rend., 1928, **186**, 477—480; cf. this vol., 336).—Barium in soil (20 g.) is determined after destruction of organic matter by heat, by fusion for 30 min. with 60 g. of an equimolecular mixture of sodium and potassium carbonates. The washed, water-insoluble residue is reheated and extracted with hydrochloric acid, the remaining residue re-fused and again extracted, and the combined acid filtrates (125 c.c.) are precipitated with 10 drops of 10% sulphuric acid. The barium sulphate is stirred frequently, and filtered after 2 days. A number of soils from various parts of France were found to contain 0·082—0·829 g. (in an exceptional case, that of Langlade, Gard, 1·717 g.) of barium per kg. If it is assumed that all the barium is present in the soil as sulphate, these values account for 10—38% (80·5% in the exceptional case) of the total sulphur available for nutritive purposes. J. Grant.

"Fossil" soils and tropical weathering. P. W. E. Vageler (Z. Pflanz. Düng., 1928, **10A**, 193—205).—A formal statement of the author's views in which a plea is entered against the too loose use of the term "fossil" soils. Laterite soils can be formed only under certain well-defined climatic conditions. They can become "fossilised" by two processes only; (*a*) by becoming covered with a humus layer, and (*b*) by becoming covered by a hard crust formed by the precipitation of material brought to the surface by capillary action. Fossil loess soils also undoubtedly exist. H. J. G. Hines.

Organic Chemistry.

Röntgen rays and organic chemistry. A. Karssen (Chem. Weekblad, 1928, **25**, 114—127).—An account of the results achieved in the elucidation of structure of organic compounds by *X*-ray analysis.

S. I. Levy.

Theory of the meso-structure of organic compounds. I. I. Kotjukov (Bull. Siberian Inst. Tech., 1927, **48**, 1—35).—The basis of the arguments developed in this theoretical paper is the great, often dominant, importance of hydrogen in structural organic chemistry. The more stable are the carbon–carbon linkings, the less stable is the carbon–hydrogen linking and hence the greater the residual affinity of the carbon, this being termed meso-valency and being identical with Werner's secondary valency. With halogens the reverse is the case, this explaining the formation of linkings between halogens and hydrogen and also the specificity of the linking of halogen with carbon. Linkings formed as a result of the reciprocal saturation of meso-valencies are termed meso-linkings.

Benzene has no central linkings, its carbon linkings representing a peculiar whole, in consequence of which the hydrogen atoms exhibit marked meso-valency. In the benzene hexachlorides the chlorine is united, not with carbon, but with hydrogen. Substitution reactions proceed so that the meso-linkings formed in the initial product of combination remain undisturbed in the final product. Every substituent entering the benzene nucleus combines, not only with the carbon of the nucleus, but also with the neighbouring *ortho*-hydrogen atoms with formation of meso-linkings, unless the entering radical possesses unsaturated atoms. Introduction of a substituent is accompanied by redistribution of the affinity, which in one case causes loosening of the *ortho–para*, and in another that of the *meta*-hydrogen atom; initiation of meso-linkings enhances this phenomenon. Radicals possessing unsaturated atoms connected directly to the nucleus are *ortho–para*-dirigents, whilst *meta*-dirigents are those with unsaturated atoms not combined with the nucleus; the cause of the directing influence lies in the unequal distribution of the affinity. These views furnish explanations for a number of problems, such as the velocity of reaction of substitution, the varying stability of radicals in the nucleus, etc. A meso-formula is suggested for naphthalene.

The phenomenon of steric hindrance is founded, not on the magnitude of the radical, but on the appearance of meso-linkings between the radical and the neighbouring *ortho*-hydrogen atoms and on uneven distribution of the affinity. Physical isomerism is structural isomerism and is encountered only when more than one meso-linking is possible; in the great majority of cases the number of isomerides known corresponds with the possible number. The isomerism of benzophenone, β-dinaphthyl ketone, benzil, and phenylmethylpicramide is discussed from this point of view, meso-formulæ being suggested for these compounds.

The isomerism of ethylene compounds rests, not on the presence of double linkings as such and on their rigidity, but on the presence of hydrogen atoms with meso-valency and of atoms having affinity towards them. Isomerism arises only when the possibility of forming meso-valencies exists. Ethylenic isomerism is never observed when the radicals at the double linkings are aliphatic and saturated, hydrogen atoms with meso-valencies being absent from such radicals. This isomerism is annulled by replacement of the hydrogen atoms with meso-valency by other radicals, even if these contain double linkings and different radicals. The isomerism of fumaric and maleic acids, stilbene, nitrobenzylidenedeoxybenzoin, cinnamic acid, and hydroxylepidine is considered, and meso-formulæ are given. The isomerism of β-butene and allylpropenyl is doubtful.

The isomerism of the oximes is conditioned by the setting-up of meso-linkings between the oxygen of the oximino-group and the hydrogen of the radical situate at the carbon atom. If this radical has an unsaturated atom, the hydrogen and the oximino-groups take part in the isomerisation. The isomerism is completely annulled by replacement of the hydrogen atom with meso-valency or of the hydroxyl of the oximino-group by any inert radical. Here, too, the number of known isomerides is in accord with the meso-theory and not with the requirements of the classical theory. Both isomerides of acetylacrylic acid are regarded as *anti*-compounds. The isomerism of the diazo-compounds is also explainable by the author's theory.

T. H. Pope.

Slow combustion of hydrocarbons. S. Landa (Compt. rend., 1928, **186**, 589—591).—Slow combustion of paraffin, m. p. 51°, at 280—300° yields the following identified products: methyl and ethyl alcohols, acetone, methyl ethyl ketone, acetaldehyde, propaldehyde, hexaldehyde, heptaldehyde, octaldehyde, nonaldehyde, and undecaldehyde. The identification of the alcohols amongst the products of combustion is important in relation to the hydroxylation theory of Bone (J.C.S., 1902, **81**, 535).

G. A. C. Gough.

[Preparation of] Δ^{β}-pentene. J. F. Norris (Org. Syntheses, 1927, **7**, 76—77).

Decomposition of methyl chloride at high temperatures. K. Wiesler (Chem.-Ztg., 1928, **52**, 182—183).—Methyl chloride decomposes at high temperatures, giving an equivalent quantity of hydrogen chloride. Decomposition is appreciable at 500° and nearly complete at 900°. The presence of methane has no effect on the equilibrium, but the decomposition is slightly increased by water vapour and to a much greater extent by carbon dioxide.

C. J. Smithells.

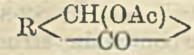
Catalytic oxidations in aqueous solutions. II. Oxidation of primary alcohols. N. A. Milas (J. Amer. Chem. Soc., 1928, **50**, 493—499; cf. A., 1927, 973).—Addition of a solution of sodium chlorate (73 g.) in aqueous 2·5% sulphuric acid (130 c.c.) to methyl alcohol (64 g.), water (50 c.c.), and vanadium pentoxide (0·3 g.), at 75—80°, with stirring, with subsequent heating for 10 hrs., addition of 6*N*-sulphuric acid (36 c.c.), and continued heating for 36 hrs. affords methyl formate, formic acid, a trace of chloroform, and an unidentified product. Similar oxidation of ethyl alcohol affords ethyl acetate in 60—61% yield, together with acetaldehyde and acetic acid. Acetal (100 g.) yields similarly ethyl acetate (45 g.), acetic acid (36 g.), and ethyl alcohol, whilst an equimolecular mixture of paracetaldehyde and ethyl alcohol (total 102·3 g.) yields ethyl acetate (54 g.) and acetic acid (21·3 g.). Acetaldehyde alone yields paracetaldehyde, which then remains unattacked. *n*-Propyl alcohol yields similarly propyl propionate (48—51%), together with propionic acid and small proportions of propaldehyde and a chlorinated ester; *n*-butyl alcohol yields *n*-butyl butyrate (47—49%); *iso*butyl alcohol yields *iso*butyl *iso*butyrate (46—48%), together with carbon dioxide, acetone, *iso*butaldehyde, and chlorinated products, whilst *iso*amyl alcohol affords *iso*amyl *iso*valerate (45—48%), *iso*valeraldehyde, chlorinated products, acetone, and carbon dioxide. It is concluded that aldehydes are the primary oxidation products, these then condensing with unchanged alcohols to form semi-acetals, the secondary alcoholic groups of which are then oxidised with formation of esters; any free acid present in the product is derived from the latter by hydrolysis. F. G. WILLSON.

Catalytic dehydration of *iso*propyl alcohol. W. J. ALLARDYCE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 315—321).—The catalytic dehydration of *iso*propyl alcohol at 360° has been studied in presence of tertiary, secondary, and primary calcium phosphates, tertiary and secondary magnesium phosphates, and aluminium phosphate and sulphate. In all cases the reaction was almost entirely represented by the equation $CHMe_2{\cdot}OH \longrightarrow CHMe{:}CH_2+H_2O$. The catalyst improved with use at first, but ultimately attained constant values which were much closer to one another than the initial values. Treatment of the aluminium sulphate with ammonia gas, or with hydrogen chloride, decreased its efficiency by about 2%. In the former case the reactivity of the catalyst could be restored by treatment with carbon dioxide. Treatment of fresh samples of aluminium sulphate or primary calcium phosphate with carbon dioxide gave initial yields 2—3% higher than those given by the untreated samples, but had no effect on the yields after the constant value was reached. The yield of propylene was varied over a range of 3% by changing the rate at which the alcohol was passed over aluminium sulphate. The catalyst darkens with time and the darkening is not confined to the surface. Its extent varies with the catalyst. M. S. BURR.

Preparation of sodium formaldehydesulphoxylate. N. BACH-NIKOLAJEVA (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 92—100; Chem. Zentr., 1927, ii, 1014).—The reduction according to G.P. 276,984 is complete in 2—3 hrs.; long boiling decomposes the product. A. A. ELDRIDGE.

Electrolytic oxidation of formic acid. E. MÜLLER.—See this vol., 377.

Decomposition of acid anhydrides. Preparation of anhydrides by direct dehydration of acids. J. CAMPARDOU and M. SÉON (Compt. rend., 1928, **186**, 591—593).—Acid anhydrides are converted into ketones by passage over heated thoria more easily than the corresponding acids; thus at 300° acetic acid yields acetone, and a mixture of acetic and benzoic anhydrides yields acetophenone. At 400° acetic anhydride yields some mesityl oxide. In the synthesis from acids it is suggested that it is more probable that the ketones arise from the intermediate formation of the acid anhydrides than through the formation and decomposition of a thorium salt. This view is supported by the preparation of acetic anhydride from acetic acid by passage over titanic oxide at 300°. G. A. C. GOUGH.

Action of acetic anhydride on carboxylic acids. A. W. VAN DER HAAR (Rec. trav. chim., 1928, **47**, 321—328).—The action of acetic anhydride on simple monocarboxylic acids yields only the simple acid anhydride (which often crystallises with 1 mol. of acetic anhydride of crystallisation) and not a mixed anhydride as stated by Autenrieth (A., 1888, 230) and by Askenasy and Meyer (A., 1895, i, 506). Mol. wt. determinations of the products were made, since the empirical formula of the simple anhydride containing 1 mol. of acetic anhydride of crystallisation is the same as that of the mixed anhydride. Thus when benzoic acid is heated with acetic anhydride for 0·75 hr. and the resulting solution concentrated over potassium hydroxide in a vacuum, the crystalline product has the composition $Bz_2O,C_4H_6O_3$, m. p. 100—105°. The crystals effloresce with loss of acetic anhydride, and by warming with 5% sodium carbonate solution the whole of the acetic anhydride is removed, leaving benzoic anhydride, m. p. 40—42°. By similar treatment *p*-dimethylaminobenzoic acid yields its anhydride with 1 mol. $C_4H_6O_3$, m. p. 109°, to which the structure $(NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot})_2O{:}OAc_2$ is assigned, but by heating above its m. p. acetic anhydride is expelled, and the anhydride has m. p. 218°. Thus with increasing mol. wt. of the acid the acetic anhydride of crystallisation is more firmly held, confirming the composition previously assigned to the compounds obtained similarly from the sugar saponins (this vol., 68). When aldehydo- or keto-acids are heated with acetic anhydride the acid is converted into the enol lactone form and the resulting hydroxyl group is acetylated,  $R<\genfrac{}{}{0pt}{}{CH(OAc)}{—CO—}>O$. Thus opianic acid yields acetyl-*ψ*-opianic acid, m. p. 125°, which can be crystallised from water without loss of its acetyl group (cf. Liebermann and Klerman, A., 1887, 47). J. W. BAKER.

Aromatic properties of some aliphatic compounds. Local anæsthetics derived from aliphatic carboxylic acids. H. GILMAN, L. C. HECKERT, and R. MCCRACKEN (J. Amer. Chem. Soc., 1928, **50**, 437—439).—The following compounds were prepared by treating diethylaminoethyl alcohol with the appropriate acid chlorides in benzene or ether: *diethylaminoethyl acrylate hydrochloride*, m. p. 93°; *diethylaminoethyl* ββ-*dimethylacrylate hydrochloride*, m. p. 128·5—130°; *diethylaminoethyl trichloroacetate hydrochloride*, m. p. 144—145°, and *diethylaminoethyl acetate hydrochloride*, m. p. 116—117°. Taking the relative pharmacological activities of cocaine, apothesin (diethylaminopropyl cinnamate), diethylaminoethyl thiophen-2-carboxylate, and diethylaminoethyl furan-2-carboxylate as 10, 8, 1, and <1, respectively, those of the above compounds, in that order, are 1, 1, <1, and 0, from which it is deduced that pharmacological activity ascribed to aromatic groupings can be approached by suitable unsaturated aliphatic structures (cf. Gilman and Pickens, A., 1925, i, 333). β-*Chloroethyl* αβ-*dibromopropionate*, b. p. 153°/20 mm., n^{30} 1·9080, d_4^{20} 1·5241, is described. F. G. Willson.

Anodic oxidation of free propionic acid. F. Müller.—See this vol., 377.

Allyl hexoate and octoate. V. Deulofeu (J.C.S., 1928, 528).—Allyl iodide reacts with silver hexoate and silver octoate, yielding, respectively, *allyl hexoate*, b. p. 186—188°, and *allyl octoate*, b. p. 225—230°. M. Clark.

Oxidation of unsaturated acids by chlorates in presence of osmium tetroxide. I. Oleic and elaidic acids. S. Medvedev and E. Alexéeva (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 128—142; Chem. Zentr., 1927, ii, 1012).—The oxidation was effected with aqueous sodium chlorate and osmium tetroxide in presence or absence of sodium carbonate or hydrogen carbonate. Crotonic acid (10 hrs. at 80°) afforded oxalic acid (13% of crotonic acid) and dihydroxybutyric acid. Cinnamic acid (15 hrs. at 80°) gave phenylglyceric acid (50%), benzaldehyde (20%), and a liquid of styrene-like odour. Oleic acid yielded dihydroxystearic acid, m. p. 132°, and elaidic acid ; elaidic acid gave dihydroxystearic acid, m. p. 95°, and oleic acid. It is curious that only one dihydroxystearic acid is produced in each case, although both acids are present; experiments show, however, that one acid does not inhibit the oxidation of the other.
A. A. Eldridge.

Chemical constitution of selacholeic acid. M. Tsujimoto (J. Soc. Chem. Ind. Japan, 1927, **30**, 868—873).—Selacholeic acid, $C_{21}H_{46}O_2$, m. p. 42·5—43°, was first found from *Alizame* liver oil (cf. B., 1926, 712). A mixture of equal parts of hydrogenated selacholeic acid, m. p. 83·5°, and synthetically prepared *n*-tetracosoic acid, m. p. 84°, melts at 83·8°, so the former has the straight carbon-chain structure. The normal ozonide, $C_{21}H_{46}O_5$, gave *n*-nonoic acid and tridecane-αν-dicarboxylic acid, m. p. 113°. Selacholeic acid, $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{13}\cdot CO_2H$, is identical with nervonic acid (cf. Klenk, A., 1927, 691).
K. Kashima.

Esters of orthoacetic acid. P. P. T. Sah (J. Amer. Chem. Soc., 1928, **50**, 516—518).—Triethyl orthoacetate, b. p. 144—146°, d_4^{25} 0·8847, n_D^{25} 1·39485, is obtained by keeping acetimidoethyl ether hydrochloride in absolute alcohol for 2 weeks, with occasional shaking, and fractionating the filtrate from the precipitated ammonium chloride under reduced pressure. The following orthoacetates were prepared by condensation of alcohols as above with appropriate acetimidoalkyl ether hydrochlorides: *trimethyl*, b. p. 107—109°, d_4^{25} 0·94375, n_D^{25} 1·38585; *dimethyl ethyl*, b. p. 123—126°, d_4^{25} 0·91915, n_D^{25} 1·38885; *methyl diethyl*, b. p. 135—136°, d_4^{25} 0·90085, n_D^{25} 1·39185; *ethyl di*-n-*propyl*, b. p. 190—194°, d_4^{25} 0·87129, n_D^{25} 1·40635; and *ethyl di*-n-*butyl orthoacetate*, b. p. 220—225°, d_4^{25} 0·86461, n_D^{25} 1·41485. When the alkyl radicals of the imido-ether and the alcohol are not the same, the mixed orthoacetate is always accompanied by the simple orthoacetate derived by replacement of the lower alkyl radical by the higher (cf. Pinner, A., 1883, 1089). F. G. Willson.

Configurational relationships of β-hydroxyvaleric and lactic acids, and of methylethyl- and ethyl-*n*-propyl-carbinols. P. A. Levene and H. L. Haller (J. Biol. Chem., 1928, **76**, 415—422; cf. A., 1927, 643, 1053).—*d*-*n*-Butane-αβ-diol gave *l*-α-bromobutan-β-ol, $[\alpha]_D^{22}$ $-10{\cdot}2°$, which yielded d-α-*cyanobutan*-β-*ol*, b. p. 110—112°/12 mm., $[\alpha]_D^{21}$ $+13{\cdot}1°$ in alcohol; this gave *l*-β-hydroxyvaleric acid, $[\alpha]_D^{23}$ $-15{\cdot}2°$ (*sodium* salt, $[\alpha]_D^{23}$ $-9{\cdot}3°$). *d*-Δ^{ϵ}-Hexen-γ-ol, $[\alpha]_D^{22}$ $+0{\cdot}3°$, gave, on reduction, d-*hexan*-γ-*ol*, b. p. 132—134°, $[\alpha]_D^{22}$ $+1{\cdot}35°$; by means of ozone this was oxidised to *d*-β-hydroxyvaleric acid, $[\alpha]_D^{22}$ $+2{\cdot}3°$ (*barium* salt, $[\alpha]_D^{22}$ $+1{\cdot}25°$). From these and earlier results it follows that *l*-butan-β-ol and *d*-hexan-γ-ol are configurationally related, which is in disagreement with the conclusions of Pickard and Kenyon (J.C.S., 1914, **105**, 830).
C. R. Harington.

[Preparation of] β-hydroxypropionic acid. R. R. Read (Org. Syntheses, 1927, 7, 54—56).

[Preparation of] ethyl *n*-butylacetoacetate. C. S. Marvel and F. D. Hager (Org. Syntheses, 1927, 7, 36—38).

[Preparation of] ethyl bromomalonate. C. S. Palmer and P. W. McWherter (Org. Syntheses, 1927, 7, 34—35).—The interaction of bromine and ethyl malonate is effected in carbon tetrachloride solution. A. A. Eldridge.

Oxidation of maleic and fumaric acids by potassium permanganate. T. Sabalitschka and H. Tietz (Continent. Met. Chem. Eng., 1927, 2, 232).—Maleic or fumaric acid can be accurately determined by adding excess of permanganate to a hot, acidified solution, decolorising with oxalate, and titrating to the end-point with permanganate. The reaction is: $5C_4H_4O_4+12MnO_4'+36H^{\cdot} \longrightarrow 20CO_2+12Mn^{\cdot\cdot}+28H_2O$ (cf. Lange and Kline, A., 1923, ii, 180). Chemical Abstracts.

Synthesis of αβγ-trimethylglutaric acid. F. E. Ray (J. Amer. Chem. Soc., 1928, **50**, 558—563).—Treatment of ethyl ethylidenedimalonate with methyl iodide and alcoholic sodium ethoxide affords *ethyl* γ-*methyl*-n-*pentane*-ββδδ-*tetracarboxylate*, b. p. 190—195°/2—3 mm., from which the corresponding *acid*, m. p. 190°, is obtained on hydrolysis with boiling aqueous hydrochloric acid. When heated at 190—200°, the latter loses approximately the expected amount of carbon dioxide, but the residue is a mixture. Condensation of ethyl tiglate with ethyl cyanoacetate affords *ethyl* α-*cyano*-βγ-*dimethylglutarate*, b. p. 150—170°/30 mm., from which *ethyl* α-*cyano*-αβγ-*trimethylglutarate*, b. p. 140—150°/1—2 mm., is obtained on methylation. The latter yields α-*carboxy*-αβγ-*trimethylglutaric acid*, m. p. 144—145°

(decomp.), on hydrolysis with boiling concentrated aqueous potassium hydroxide, and this, when heated at 150—160°, affords αβγ-*trimethylglutaric acid*, m. p. 134°. Condensation of ethyl malonate with ethyl tiglate affords analogously *ethyl γ-methyl*-n-*pentane-*βδδ-*tricarboxylate*, b. p. 121°/25 mm., from which the trimethylglutaric acid is obtained by hydrolysis and decomposition of the resulting acid. The "αββ-trimethylglutaric acid" obtained by Noyes and Skinner (A., 1918, i, 65) from *iso*aminocamphonanic acid is shown to be identical with Perkin and Thorpe's ααβ-trimethylglutaric acid (J.C.S., 1899, **75**, 65). F. G. Willson.

α-*iso*Propylglutaconic acid. K. V. Hariharan, K. N. Menon, and J. L. Simonsen (J.C.S., 1928, 431—438).—Ethyl sodiodicarboxyglutaconate condenses with *iso*propyl iodide at 140—160°, yielding ethyl trimesate. Ethyl *iso*propylcyanoacetate condenses with ethyl β-iodopropionate in presence of sodium ethoxide, yielding *ethyl* α-*cyano*-α-iso*propylglutarate*, b. p. 195°/32 mm., which is hydrolysed by 50% sulphuric acid, giving α-*iso*propylglutaric acid. Bromination of α-*iso*propylglutaryl chloride yields, as main product, α-bromo-α-*iso*propylglutaryl chloride (cf. A., 1925, i, 358), since esterification of the bromination product yields an acid ester, converted by treatment with alkali into the lactone of γ-hydroxy-β-methylpentane-γε-dicarboxylic acid. Treatment of ethyl potassioacetonedicarboxylate with *iso*propyl iodide in alcoholic solution gives *ethyl* α-iso*propylacetonedicarboxylate*, b. p. 142—143°/9 mm., converted by prolonged reduction with a large excess of sodium amalgam into *ethyl* β-*hydroxy*-α-iso*propylglutarate*, b. p. 145—146°/10 mm. The hydroxy-ester reacts with phosphorus pentachloride, giving *ethyl* β-*chloro*-α-iso*propylglutarate*, which is converted by treatment with diethylaniline at 180—190° into *ethyl* α-iso*propylglutaconate*, b. p. 148—150°/15 mm. Hydrolysis yields the acid, separated by treatment with acetyl chloride into cis-α-iso*propylglutaconic acid*, m. p. 101° (*calcium*, *barium*, and *copper* salts; *potassium* salt of *hydroxy-anhydride*), and trans-α-iso*propylglutaconic acid*, m. p. 132° (*barium* salt). Neither acid is identical with the acid obtained from *d*-Δ³-carene by oxidation with potassium permanganate in acetone solution (J.C.S., 1923, **123**, 553). Reduction of the monomethyl ester of caronic acid with sodium and alcohol yields the *lactone* of δ-*hydroxy*-ββ-*dimethylvaleric acid*, b. p. 137°/43 mm., 232—235°/685 mm., converted by treatment with potassium cyanide at 275°, followed by hydrolysis of the resulting nitrile, into ββ-dimethyladipic acid. M. Clark.

Salts of mesotartaric acid. I. F. Heckele (Österr. Chem.-Ztg., 1928, **31**, 28—32).—The following salts of mesotartaric acid are described: disodium salt; additive *compound*, $C_4H_5O_6Na,C_4H_6O_6$ (unaltered by crystallisation from water); dipotassium salt ($2H_2O$); potassium hydrogen salt (this salt forms many soluble additive compounds with metallic hydroxides); sodium potassium salt (H_2O); diammonium salt; ammonium hydrogen salt; potassium ammonium salt (H_2O); dilithium salt; lithium hydrogen salt (H_2O); potassium lithium salt (H_2O); calcium salt ($3H_2O$); barium salt (H_2O); strontium salt; magnesium salt ($2H_2O$); zinc salt ($2H_2O$); lead salt, $PbC_4H_4O_6,2PbO$; cadmium salt ($2H_2O$); normal aluminium salt (from which the aluminium is not precipitated by ammonia); normal manganese salt ($3H_2O$). The copper, nickel, and iron salts could not be obtained in a state of purity. The solubilities of many of the salts are recorded. G. A. C. Gough.

Inhibition of the precipitation of calcium tartrate by salts. M. E. Stas (Pharm. Weekblad, 1928, **65**, 107—108).—The commoner sodium, ammonium, and magnesium salts inhibit the precipitation, especially in warm solutions; 0·1 g. of sodium chloride in 4 c.c. completely prevents precipitation if not more than 10 mg. of tartaric acid is present. For small quantities, therefore, the acid should be extracted by means of ether before applying the test. S. I. Levy.

Composition of a series of bismuth sodium tartrates. W. F. von Oettingen and Y. Ishikawa (J. Amer. Pharm. Assoc., 1928, **17**, 124—134).—The preparation of bismuth tartrate by the addition of sodium tartrate solution to an acetic acid solution of bismuth nitrate and of soluble sodium bismuth tartrate has been examined. Both preparations pass through different compounds. The following *compounds* were isolated: $C_4H_1O_6Bi{\cdot}OAc$, $C_4H_5O_6Bi$, $C_4H_2O_6NaBi$, $C_4H_2O_8NaBi_2$, $O(C_4H_2O_7NaBi)_2$, $C_4H_2O_7ClNaBi_2$, $C_4H_2O_7Bi_2$, $C_4H_2O_9NaBi_3$, $C_4H_3O_9Bi_3$. E. H. Sharples.

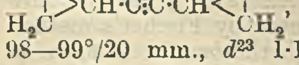
Optically active copper compounds. W. Wahl (Soc. Sci. Fennica Comm. Phys. Math., 1927, **4**, (14), 1—5).—Diethylenediaminediaquocupric tartrate has been prepared from barium tartrate and the complex sulphate which is obtained when aqueous solutions of cupric sulphate and ethylenediamine are mixed and evaporated to dryness. After filtration from barium sulphate the copper complex salt is precipitated by the addition of alcohol to the solution. The salt has $[M]$ +28·3°. After two extractions with alcohol the residual compound has $[M]$ −59·4°. When obtained by vacuum evaporation of the aqueous solution, the salt has $[M]$ −38·3°, and of the residue after alcoholic extraction −134°. The *l*-diaquodiethylenediaminecupric ion must have $[M]$ at least 190°. A series of optically active iodides has been prepared from the tartrates. Nickel yields corresponding tartrates of varying activity, the highest observed value being about +420°. H. F. Gillbe.

Preparation and properties of *l*-mannono- and *d*-glucono-lactones. F. W. Upson, L. Sands, and C. H. Whitnah (J. Amer. Chem. Soc., 1928, **50**, 519—525).—Crystalline *l*-gluconolactone, m. p. 134—135°, $[\alpha]_D$ −68·7°, to −13·7° in 15 days, subsequently increasing (cf. Hedenburg, A., 1915, i, 76), has now been obtained from *l*-arabinose by Fischer's method (cf. A., 1890, 1389), through the *brucine* salt, m. p. 181—182°, $[\alpha]_D^{20}$ −25·43°. l-*Gluconophenylhydrazide*, m. p. 200°, $[\alpha]_D^{20}$ −11·7°, is described. l-*Mannono-γ-lactone*, m. p. 150·5—151°, $[\alpha]_D^{20}$ −51·8°, obtained from *l*-mannonolactone by Nef's method (A., 1914, i, 490) was converted by methyl iodide and silver oxide into *methyl tetramethyl*-l-*mannonate*, from which, on hydrolysis, *tetramethyl*-l-*mannono-γ-lactone*, m. p.

109°, $[\alpha]_D^{20}$ $-65{\cdot}51°$, to $-47{\cdot}4°$ in 18 days, was obtained. The slow change in rotation, together with the slow titration with alkali at the ordinary temperature, supports the δ-lactonic structure. *Tetramethyl*-d-*mannono-γ-lactone*, m. p. 151°, $[\alpha]_D^{20}$ $+66{\cdot}6°$, was obtained analogously. Treatment of calcium *l*-mannonate with oxalic acid affords an l-*mannonolactone*, m. p. 160—162°, $[\alpha]_D^{20}$ $-113{\cdot}6°$, to $-30{\cdot}9°$ in 32·5 hrs., subsequently increasing, to which, as well as to the corresponding *d*-mannonolactone of Hedenburg (*loc. cit.*), the δ-lactonic structure is ascribed, from theoretical evidence presented. Oxidation of tetramethyl-*d*-mannose with bromine affords a *tetramethyl*-d-*mannonolactone*, liquid, $[\alpha]_D^{20}$ $+132{\cdot}3°$, to $+59{\cdot}5°$ in 6 days, subsequently increasing, which also appears to be a δ-lactone. F. G. WILLSON.

Semiacetal formation and the refractive indices and densities of mixtures of certain alcohols and aldehydes. H. ADKINS and A. E. BRODERICK (J. Amer. Chem. Soc., 1928, 50, 499—503).—The refractive indices and densities of certain alcohol–aldehyde mixtures, taken over the range from pure alcohol to pure aldehyde, indicate that condensation takes place in all cases, presumably with formation of semiacetals. In the cases of acetaldehyde–ethyl alcohol, heptaldehyde–ethyl alcohol, and acetaldehyde–*iso*propyl alcohol, semiacetal formation appears to be almost quantitative. F. G. WILLSON.

Action of chloroacetaldehyde on the mixed dimagnesium derivative of acetylene. Acetylenic glycol and erythritol. R. LESPIEAU (Bull. Soc. chim., 1928, [iv], 43, 199—210).—When chloroacetal is treated with oxalic and sulphuric acids there is produced, in addition to polymerised chloroacetaldehyde, some βδ-dichlorocrotonaldehyde, b. p. 80°/15 mm., d^{20} 1·361, n^{20} 1·512, which with ethyl orthoformate, alcohol, and a trace of hydrochloric acid yields βδ-*dichlorocrotonaldehyde diethyl acetal*, b. p. 101—102°/15 mm., d^{23} 1·128, n^{23} 1·4601, *R* 51·73. This compound yields with sodium ethoxide β-*chloro*-δ-*ethoxycrotonaldehyde diethyl acetal*, b. p. 117°/13 mm., d^{21} 1·033, n^{21} 1·446. The action of chloroacetaldehyde on the product of reaction of acetylene and magnesium ethyl bromide is to give α-*chloro*-β-*hydroxy*-Δ^{γ}-*butinene*, b. p. 157°/760 mm., 62—63°/14 mm., d^{21} 1·171, n^{21} 1·475, and αζ-dichloro-Δ^{γ}-hexinene-βε-diol (not isolated) [*dibromide*, m. p. 141—142·5° (crystallographic data given)]. The former compound when treated with dry potassium hydroxide in ether yields *ethinylethylene oxide*, b. p. 86—87°/760 mm., d^{23} 0·945, n^{23} 1·427, hydrolysed to Δ^{γ}-*butinene*-αβ-*diol*, m. p. 39·5—40·5° (*diphenylcarbamate*, m. p. 134—134·5°; *dibromide*, m. p. 47—48°), whilst the latter furnishes the *dioxide*,



$\underset{H_2C}{\overset{O}{|}}\!\!>CH\cdot C{:}C\cdot CH<\!\!\underset{CH_2}{\overset{O}{|}}$, b. p. 87·5—88·5°/10 mm., 98—99°/20 mm., d^{23} 1·1189, n^{23} 1·4871 (cis- and trans-*dibromides*, m. p. 57—58° and 101—102·5°). Ethyl αβ-dichloroethyl ether furnishes two stereoisomeric αζ-*dichloro*-βε-*diethoxy*-Δ^{γ}-*hexinenes*, having b. p. 136—137°/11—12 mm., m. p. 12—14°, d^{21} 1·110, n^{21} 1·4705 (*dibromide*, m. p. 107—108°), and b. p. 138—139°/13 mm., m. p. 21°, d^{21} 1·112, n^{21} 1·471 [*dibromide*, m. p. 71—72° (crystallographic data given)], respectively, when regenerated from the dibromides. When the form of m. p. 12—14° is treated with acetic acid and acetic anhydride at 150°, there is produced a *diacetate*, b. p. 160—162°/11 mm., d^{21} 1·144, n^{21} 1·4669, hydrolysed by cold alcoholic sodium hydroxide to βε-*diethoxy*-Δ^{γ}-*hexinene*-αζ-*diol*, b. p. 125—128°/3·5 mm., d^{18} 1·026, n^{18} 1·4503. The form of m. p. 21° is unaffected by similar treatment. The above dioxide is acted on by methyl alcohol and a small amount of sulphuric acid, forming αζ-*dimethoxy*-Δ^{γ}-*hexinene*-βε-*diol*, b. p. 143—143·5°/3·5 mm., d^{23} 1·122, n^{23} 1·477 (*dibromide*, m. p. 150—151·5°), and by water, yielding Δ^{γ}-*hexinene*-αβεζ-*tetraol*, m. p. 113—114·5° (*dibromide*, m. p. 184—185°). H. BURTON.

Condensing action of mixed magnesium alkyloxides. V. GRIGNARD and M. FLUCHAIRE (Ann. Chim., 1928, [x], 9, 5—54; cf. Grignard and Dubien, A., 1923, i, 896).—Magnesium alkyloxyhalides, RO·MgHal, for use as condensing agents (cf. Meerwein and Schmidt, A., 1925, i, 1239) are prepared by treating magnesium alkyloxides with etherated magnesium halides (Menschutkin, A., 1906, i, 131, 552). The etherated halides themselves are inactive as condensing agents, whilst the alkyloxides have a smaller reactivity than the mixed derivatives. During condensations of aldehydes two reactions usually proceed simultaneously, (*a*) aldol formation, (*b*) ester formation, $2R\cdot CHO \longrightarrow R\cdot CO_2CH_2R$, whilst with ketones only aldol condensation takes place.

Acetaldehyde and magnesium butoxyiodide react in presence of ether to form ethyl acetate, aldol, and butyl acetate, this being obtained from the interaction of ethyl acetate and the magnesium derivative. *n*-Butaldehyde and magnesium butoxyhalides give *n*-butyl butyrate, γ-hydroxy-β-ethyl-*n*-hexaldehyde, and αγ-*dihydroxy*-β-*ethyl*-n-*hexyl butyrate*, b. p. 255°, 148—149°/15 mm., d_4^{15} 0·9473, n_D^{15} 1·4452, *R* 60·72. β-*Ethyl*-n-*hexane*-αγ-*diol* has b. p. 116°/5 mm., 133—134°/15 mm., d_4^{15} 0·9367, n_D^{15} 1·4535. Benzaldehyde reacts slowly, forming benzyl benzoate and benzyl oxide, whilst furfuraldehyde affords furfuryl alcohol, b. p. 75—76°/15 mm., d_4^{16} 1·1359, n_D^{16} 1·4940, *R* 25·12, together with α-furfurylidenebutaldehyde, b. p. 234—235°, 114—115°/15 mm., d_4^{12} 1·061, n_D^{12} 1·5668.

Benzaldehyde and acetone condense in presence of magnesium butoxybromide to form benzylidene- and dibenzylidene-acetones.

Condensation of methyl alkyl ketones proceeds $2R\cdot COMe \longrightarrow R\cdot CO\cdot CH_2\cdot CMeR\cdot OH$. The alcohols formed are dehydrated by distillation either alone or with traces of iodine and anhydrous oxalic acid to the unsaturated ketones, $R\cdot CO\cdot CH{:}CMeR$. Magnesium butoxybromide causes the conversion of acetone into diacetone alcohol (cf. Grignard and Dubien, *loc. cit.*), but prolonged treatment or the use of magnesium bromodiacetone alcoholate gives phorone, *iso*phorone, and βζ-*dimethyl*-Δ^{ϵ}-*hepten*-β-*ol*-δ-*one*, b. p. 95—96°/5 mm., d_4^{15} 0·9432, n_D^{15} 1·4577. Methyl ethyl ketone furnishes γ-*methyl*-n-*heptan*-γ-*ol*-ε-*one*, b. p. 85°/15 mm., d_4^{15} 0·9315, n_D^{15} 1·4367, dehydrated to γ-methyl-Δ^{γ}-hepten-ε-one, d_4^{15} 0·8511, n_D^{15} 1·4469 (*semicarbazone*, m. p. 115°). Methyl propyl ketone gives δ-*methylnonan*-δ-*ol*-ζ-*one*, b. p. 110°/15 mm., d_4^{15} 0·9076, n_D^{15} 1·4424, dehydrated to δ-methyl-Δ^{δ}-nonen-ζ-one, b. p. 90°/14 mm., 202°/755 mm., d_4^{12} 0·8494, n_D^{12} 1·4512 (*oxime*, b. p. 130°/14 mm.). Methyl butyl ketone yields ε-*methylundecan*-ε-*ol*-η-*one*, b. p. 111°/4 mm., d_4^{16} 0·8975, n_D^{16} 1·4445, dehydrated easily to ε-*methyl*-Δ^{ϵ}-*undecen*-η-*one*, b. p. 120°/16 mm., d_4^{17} 0·8472, n_D^{17} 1·4541 (*oxime*, b. p. 149—150°/12 mm.). From methyl *iso*butyl ketone there are obtained βδ0-*trimethylnonan*-δ-*ol*-ζ-*one*, b. p. 99°/3 mm., d_4^{11} 0·8962, n_D^{11} 1·4427, and βδθ-trimethyl-Δ^{δ}-nonen-ζ-one, b. p. 108°/15 mm., d_4^{12} 0·8447, n_D^{12} 1·4543 (*oxime*, b. p. 145°/14 mm.). Methyl amyl ketone gives ζ-*methyl*-Δ^{ζ}-*tridecen*-0-*one*, b. p. 115°/4 mm., d_4^{12} 0·8510, n_D^{12} 1·4592, *R* 67·48 (*oxime*, b. p. 165°/12 mm.), which when ozonised yields methyl amyl ketone and probably amylglyoxal. The molecular refractions of the above unsaturated ketones show exaltation, due to conjugation.

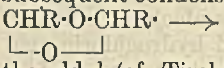
Condensation of diethyl and dipropyl ketones proceeds with difficulty (cf. Ekeley and Carpenter, A., 1924, i, 369) under the influence of magnesium butoxybromide. There are formed δ-*methyl*-γ-*ethylheptan*-γ-*ol*-ε-*one*, b. p. 105°/14 mm., d_4^{18} 0·9175, n_D^{18} 1·4435, dehydrated to δ-methyl-γ-ethyl-Δ^{γ}-heptenε-one, b. p. 92°/14 mm., d_4^{17} 0·8515, n_D^{17} 1·4509, and ε-*ethyl*-δ-*propyl*-Δ^{δ}-*nonen*-ζ-*one*, b. p. 224°/755 mm., d_4^{11} 0·8506, n_D^{11} 1·4569, respectively.

Magnesium butoxybromide converts ethylidene- and propylidene-acetone into δ-*methyl*-$\Delta^{\beta\delta\eta}$-*nonatrien*-ζ-*one*, b. p. 102°/4 mm., d_4^{12} 0·9187, n_D^{12} 1·4871, and ε-*methyl*-$\Delta^{\gamma\epsilon\theta}$-*undecatrien*-η-*one*, b. p. 120°/4 mm., 138°/18 mm., d_4^{18} 0·9103, n_D^{18} 1·4899, respectively. When ethylideneacetone is treated with a deficit of magnesium ethyl bromide there is formed in addition to the above condensation product some γ-*methyl*-Δ^{δ}-*hepten*-γ-*ol*, b. p. 62°/15 mm., d_4^{17} 0·8477, n_D^{17} 1·4421. Improved methods of preparation of ethylidene-, propylidene-, and butylidene-acetones, methyl butyl and methyl *iso*butyl ketones are given. *n*-Hexan-δ-ol-β-one has b. p. 83°/15 mm., d_4^{13} 0·9639, n_D^{13} 1·4353, *R* 31·42 (cf. Pastureau and Zamenhof, A., 1926, 272). βδ-*Dimethylhexane*-βδ-*diol*, prepared from magnesium ethyl bromide and diacetone alcohol, has b. p. 94—95°/5 mm., d_4^{15} 0·9212, n_D^{15} 1·4437.

When methyl *iso*butyl ketone is treated with magnesium butoxybromide and benzoyl chloride there is formed in addition to the above trimethylnonenone, the *benzoate*, b. p. 123°/15 mm., d_4^{14} 0·9706, n_D^{14} 1·4898, of the enolic form of the initial ketone. The same benzoate is produced, together with methylethyl*iso*butylcarbinyl benzoate, from magnesium ethyl bromide and benzoyl chloride. These results demonstrate the enolisating effect of the organo-metallic compound.

It is shown that magnesium butoxyiodide has a greater condensing action on butaldehyde than either the chloride or the bromide, whilst in a series of alkoxy-iodides the greatest effects are shown by Pr, Bu, and *iso*amyl. The benzyloxy-compound is of the same order as the butoxy-derivative, and the best results are obtained by using primary alcoholates. The corresponding ketolates are much less reactive.

The formation of esters from the aldehydes is explained by the production of a semi-acetal (I) (cf. Verley, A., 1925, i, 783) (probably isolated from benzaldehyde and magnesium butoxybromide) thus: $\mathrm{R{\cdot}CHO+BuO{\cdot}MgBr \longrightarrow BuO{\cdot}CHR{\cdot}OMgBr}$ (I), with subsequent condensation of 2 mols. into $\mathrm{2BuO{\cdot}MgBr}+$ $\underbrace{\mathrm{CHR{\cdot}O{\cdot}CHR{\cdot}}}_{\text{-O-}} \longrightarrow \mathrm{R{\cdot}CO_2CH_2R}$. The production of the aldol (cf. Tischtschenko, A., 1907, i, 282, 284) is formulated $\mathrm{CHO{\cdot}CHR{\cdot}H+BuO{\cdot}CH(O{\cdot}MgBr){\cdot}CH_2R \longrightarrow BuOH+CHO{\cdot}CHR{\cdot}CH(OMgBr){\cdot}CH_2R}$. When the aldehyde is reduced to the alcohol the following change takes place: $\mathrm{CH_2PrO{\cdot}CHR{\cdot}OMgBr \longrightarrow CH_2R{\cdot}OMgBr+Pr{\cdot}CHO}$, and the formation of the enol form of the ketone is postulated as $\mathrm{BuO{\cdot}CR'(CH_2R){\cdot}OMgBr \longrightarrow BuOH+CHR{:}CR'{\cdot}OMgBr}$. H. BURTON.



Reactions of nitrosyl chloride. H. RHEINBOLDT and M. DEWALD (Annalen, 1928, **460**, 305—307).—It has been found (A., 1927, 229) that whilst some aldoximes and nitrosyl chloride gave crystalline chloronitrosohydrocarbons, higher aldoximes and *iso*valer- and phenylacet-aldoxime gave oils. Some higher aldoximes have now been converted into crystalline products, although the two other oximes named have not. With increase of mol. wt., the stability of the dimeric form of chloronitroso-compounds increases. (The higher members have only a feeble colour in benzene solution.) Again, the higher members pass much less readily than the lower into hydroxamic chlorides. α-*Chloro*-α-*nitroso*-n-*octane*, -n-*nonane*, -n-*decane*, and -n-*dodecane* melt, respectively, at 42°, 50—51°, 62°, and 63°. The last-named compound was obtained from *dodecaldoxime*, m. p. 73°. E. E. TURNER.

[Preparation of] methyl *n*-amyl ketone. J. R. JOHNSON and F. D. HAGER (Org. Syntheses, 1927, **7**, 60—62).

Mechanism of carbohydrate oxidation. VII. Action of potassium hydroxide on dihydroxyacetone. W. L. EVANS and W. R. CORNTHWAITE (J. Amer. Chem. Soc., 1928, **50**, 486—492; cf. A., 1926, 1226).—The action of aqueous potassium hydroxide on dihydroxyacetone under conditions precisely comparable with those previously applied to glyceraldehyde (*loc. cit.*) gives the same products, and the similarity between the variations of proportions of the different products with alkali concentration and temperature in the two cases is brought out by graphical methods. These results indicate that glyceraldehyde and dihydroxyacetone exist in alkaline solution in equilibrium with the same enediol. In presence of phenylhydrazine, the maximum production of pyruvaldehyde from glyceraldehyde and dihydroxyacetone occurs at the same alkali concentration, but the yields of pyruvaldehyde (as osazone) are not identical, from which it is concluded that the proportions of components present at equilibrium vary with the triose used, as previously noted by de Bruyn and van Eckenstein for dextrose, mannose, and lævulose. This is supported by the observation that the formation of pyruvaldehyde is a unimolecular reaction in each case, but that the rates of reaction are not identical.

F. G. WILLSON.

Catalytic hydrogenation of oximes and their transformation into β-hydroxylamines. G. Vavon and Krajcinovic (Bull. Soc. chim., 1928, [iv], **43**, 231—237).—Hydrogenation of dipropyl ketoxime (1 mol.) in 70% aqueous-alcoholic solution in presence of platinum-black and hydrochloric acid (1 mol.) yields δ-*hydroxylaminoheptane*, m. p. 52°. When the *hydrogen oxalate*, m. p. 115°, of this base is treated with benzaldehyde in presence of aqueous-alcoholic sodium hydrogen carbonate, there is formed N-*benzylideneheptane*-δ-*nitrone*, m. p. 53—54°. β-*Hydroxylamino*-δ-*methylpentane*, m. p. 63° (*hydrogen oxalate*, m. p. 132—133°), and β-*hydroxylamino*-β-*phenylethane* (*hydrogen oxalate*, m. p. 150°), are obtained from methyl *iso*butyl ketoxime and acetophenoneoxime, respectively.

When aldoximes are hydrogenated by the same method, the main products are secondary hydroxylamines, probably formed thus: $R{\cdot}CH{:}N{\cdot}OH \longrightarrow R{\cdot}CH_2{\cdot}NH{\cdot}OH \xrightarrow{R\cdot CHO} R{\cdot}CH_2{\cdot}NO{:}CHR \longrightarrow (CH_2R)_2N{\cdot}OH$. Thus heptaldoxime furnishes *diheptylhydroxylamine* (90%), m. p. 74° (*hydrogen oxalate*, m. p. 137°); *iso*valeraldoxime yields *di*-γ-*methylbutylhydroxylamine* (*oxalate*, m. p. 167—168°); benzaldoxime affords dibenzylhydroxylamine, m. p. 123°, and piperonaloxime gives *dipiperonylhydroxylamine*, m. p. 123—124° (*hydrochloride*).

H. Burton.

First phases of the chemistry of the dissimilation of the hexoses. A. J. Kluyver and A. P. Struyk (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 871—884).—The effect of the addition of disodium hydrogen phosphate on the rate of fermentation of dextrose by yeast juice varies with the sample of yeast employed; in one case (*A*) a rapid rise to a maximum velocity is followed by a fairly rapid and constant fall to the initial value, whilst in the other (*B*) the increase produced is smaller in magnitude but extends over a longer period. Isolation of the phosphoric ester produced by the method of Robison (A., 1923, i, 86) shows that in case *B* almost the whole of the phosphate is present as a hexose monophosphoric ester, but in case *A* a larger proportion of the diphosphoric ester is present. Attempts to prove the presence of a triose phosphoric ester were unsuccessful, although the application of the triose reaction of Neuberg, (A., 1918, i, 91) yielded methylglyoxal, isolated as its *p*-nitrophenylosazone. These results are shown to confirm the authors' theory of hexose dissimilation (A., 1926, 978). A critical summary of the literature is also given. J. W. Baker.

Determination of reducing sugars by the ferricyanide method. A. Ionesco-Matiu (Bul. Soc. Chim. România, 1927, **9**, 68—75).—Dextrose and other reducing sugars may be rapidly and accurately determined by titration with potassium ferricyanide using picric acid as an indicator, the method employed varying in the case of relatively large or small sugar contents. In the former case 10 c.c. of the ferricyanide solution (46 g. of potassium ferricyanide and 46 g. of potassium hydroxide per litre, standardised by titration against a 5% solution of pure dextrose and diluted so that 10 c.c. are equivalent to 0·05 g. of dextrose), 20 c.c. of water, and 10 drops of a 1% solution of picric acid are heated to boiling and the sugar solution (approximately 5%) is added from a burette until the yellow colour changes to red. When the sugar content is less than 2% an indirect method must be employed. The ferricyanide solution (4 c.c.), 6 c.c. of water, and a measured volume (1—6 c.c.) of the sugar solution are boiled together for exactly 1 min., rapidly cooled, 100 c.c. of water and 5 c.c. of 20% sulphuric acid added, and the ferrocyanide produced is titrated with a 1% solution of potassium permanganate, the titre being compared with that of a 1% dextrose solution similarly treated. The method is applied to the following cases: invert-sugar, obtained by hydrolysis of a 5% sucrose solution with 1% hydrochloric acid and subsequent neutralisation before titration; 10 c.c. of ferricyanide solution = 0·0467 g. of sucrose or 0·0491 g. of invert-sugar; maltose, 10 c.c. = 0·637 g.; lactose, 10 c.c. = 0·0676 g. (the technique for the determination of lactose in milk is described); sugar in urine, previously defecated with lead acetate and diluted until the sugar content is 0·5%; blood-sugar previously treated with 20% trichloroacetic acid solution to remove albuminous matter, and subsequently neutralised. Reducing material in normal blood varies from 0·80 to 1·2%. J. W. Baker.

Pentabenzoates of dextrose. P. A. Levene and G. M. Meyer (J. Biol. Chem., 1928, **76**, 513—519).—Repetition of the work of Fischer and Freudenberg (A., 1912, i, 887) and of Schlubach and Huntenburg (A., 1927, 858) led to the preparation of α-*pentabenzoylglucose*, m. p. 187°, $[\alpha]_D^{20}$ +138·5° in chloroform, β-*pentabenzoylglucose*, m. p. 157°, $[\alpha]_D^{20}$ +24° in chloroform, α-*pentabenzoyl*-γ-*glucose*, m. p. 118°, $[\alpha]_D^{20}$ +79° in chloroform, β-*pentabenzoyl*-γ-*glucose*, m. p. 146—147°, $[\alpha]_D^{20}$ −82° in chloroform. These new values support the previous suggestion that the difference between the molecular rotations of the α- and β-forms of a sugar differs with the ring structure, and, further, that the sum of these rotations is less with a five-membered than with a six-membered ring. C. R. Harington.

β-Acetylchloroglucose. II. H. H. Schlubach, P. Stadler, and I. Wolf (Ber., 1928, **61**, [*B*], 287—293; cf. A., 1926, 600).—The use of a particularly active form of silver chloride enables the time required for the conversion of acetylbromoglucose into β-acetylchloroglucose to be reduced from 3—4 hrs. to 8—10 min. with consequent increase in the yield of β-product on which silver chloride has an isomerising action. The lowest value observed with the product is $[\alpha]_D^{20}$ −17·4° in carbon tetrachloride (Hudson's use of pharmaceutical chloroform in this connexion is adversely criticised); this datum differs by about 30° from that calculated by Hudson. A similar discrepancy is found with β-nitroacetylglucose, for which the values, m. p. 96°, $[\alpha]_D^{20}$ −8·4° in carbon tetrachloride, are now recorded. It is suggested that the principle of optical superposition is not valid in these cases and consequently that Hudson's methods of calculation cannot be applied.

The dielectric constant of the solvent appears to be intimately concerned with the rate of isomerisation of β-acetylchloroglucose into dextrorotatory acetylchloroglucose in solution, but secondary reactions not involving the production of equilibrium mixtures inhibit mathematical treatment of the data. Ether is a potent stabiliser, whereas alcohols accelerate isomerisation; alkyl halides and acetonitrile occupy an intermediate position. Addition of small quantities of water, acids, or bases to the ethereal solution does not cause marked acceleration of the change, but silver chloride is a strong, positive catalyst. The formation of β-acetylchloroglucose in small amount by Fischer and Armstrong's method (A., 1901, i, 257, 671) is confirmed, as is its isomerisation when shaken in ethereal solution with sodium carbonate; the conversion of the crude material into tetramethyl-α-methylglucoside appears very improbable. Indications of the production of β-acetylbromoglucose by Fischer and Armstrong's method could not be observed. H. WREN.

α-Methylmannoside. C. S. HUDSON (Org. Syntheses, 1927, 7, 64—66).—The preparation of α-methylmannoside from "vegetable ivory" waste is described. A. A. ELDRIDGE.

Mannan acetate. I. Preparation of mannan acetate and some of its properties. R. SHINODA and C. ASHIZAWA (J. Cellulose Inst. Tokyo, 1928, 4, 3).—Mannan triacetate is prepared by treating raw Japanese konjaku powder (*Amorphophallus Konjac*) with an aqueous solution of chlorine peroxide, and heating the product (in the form of threads) with glacial acetic acid at 100°. It is claimed that the method is economical, the time of reaction is short, and that no decomposition of mannan takes place. Mannan triacetate may be used as a cellulose acetate substitute, since it yields a strong film; a 1% solution in a mixed solvent containing tetrachloroethane 40%, methyl acetate 40%, methyl alcohol 20% has a suitable viscosity. W. J. POWELL.

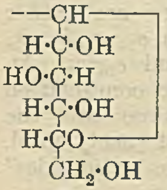
Epirhamnitol, reduction product of epirhamnose. E. VOTOČEK and J. MIKŠIČ (Bull. Soc. chim., 1928, [iv], **43**, 220—224).—When epirhamnose (*iso*rhamnose) is reduced with sodium amalgam and acidulated water there is obtained *epirhamnitol*, a syrup, having $[\alpha]_D^{20}$ +9·18° in water when purified through the *dibenzylidene* derivative, $C_6H_{10}O\left(<^{O}_{O}>CHPh\right)_2$, m. p. 196°, $[\alpha]_D^{20}$ −36·7° in chloroform. Epirhamnitol and *iso*rhodeitol (following abstract) are optical antipodes. H. BURTON.

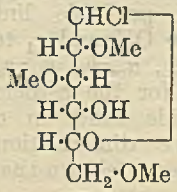
***iso*Rhodeitol, reduction product of *iso*rhodeose.** E. VOTOČEK and F. VALENTIN (Bull. Soc. chim., 1928, [iv], **43**, 216—220).—Reduction of an aqueous solution of *iso*rhodeose, $[\alpha]_D$ +30·3° (cf. A., 1910, i, 274), with sodium amalgam gives iso*rhodeitol*, a syrup, $[\alpha]_D$ −8·3° in water. When distilled in a high vacuum the alcohol has $[\alpha]_D$ −9·7°, and its rotation is lowered when mixed with sodium borate. The crude alcohol reacts with benzaldehyde in presence of 50% sulphuric acid, yielding a *monobenzylidene* derivative, $C_6H_{12}O_3<^{O}_{O}>CHPh$, m. p. 158°, whilst the redistilled alcohol gives a *dibenzylidene* derivative, m. p. 196—197°, $[\alpha]_D^{18}$ +35·1° in chloroform. H. BURTON.

Cellulose formate. I. Formation [from hydrocellulose and cellulose regenerated from viscose]. Y. UEDA and K. HATA (J. Cellulose Inst. Tokyo, 1928, 4, 1—2).—Hydrocellulose with anhydrous formic acid and sulphuric acid yields a product containing 22·90% of formic acid (theory for monoformate 24·21%), whilst the product from cellulose regenerated from viscose contains 50·50% (cellulose triformate requires 56·09%). The ester is readily soluble in pyridine, but only sparingly soluble in other organic solvents. Results showing the effect of variations in the amount of sulphuric acid on the degree of esterification are given. W. J. POWELL.

Lignin and cellulose. II. Methylcellulose. K. FREUDENBERG and E. BRAUN (Annalen, 1928, **460**, 288—304).—It was shown recently by Urban (cf. B., 1926, 531) that the methylation of cotton at 20° gives a trimethylcellulose essentially different from previously obtained trimethylcelluloses. It dissolves to a clear and very viscous solution in chloroform, tetrachloroethane, and glacial acetic acid, whilst the specimens of Denham (J.C.S., 1921, **119**, 81) and of Irvine and Hirst (J.C.S., 1923, **123**, 529) did not. Further, it differs from the product obtained by Hess (A., 1924, i, 142; 1927, 44) in being quite insoluble in water and not crystallising from other solvents. It is formed in 93% yield from unbleached cotton, whilst previous preparations were obtained only in about 75% yield. With methyl-alcoholic hydrogen chloride it gives a 91% yield of 2 : 3 : 6-trimethyl-methylglucoside and 9% of dimethyl-methylglucoside, corresponding with the original methoxyl content (44·4%) of the sample used (the highest OMe content obtained was almost 45% instead of calc. 45·6%). No trace of tetramethylglucose was found. This establishes the structural identity and stereochemical similarity of all the glucose units (I) present in the cellulose molecule.

When trimethylcellulose (for the preparation of which a few further details are given) is treated with hydrogen chloride in presence of ether (sealed tube, 35°) 1-*chloro*-2 : 3 : 6-*trimethylglucose* (II or III) is formed. This gives a crystalline *pyridinium* salt, decomp. 180°, $[\alpha]_D^{15}$ +26·6° in water.


(I.)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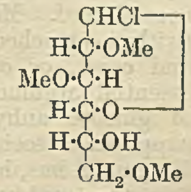
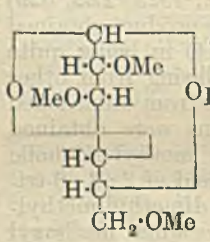

(III.)

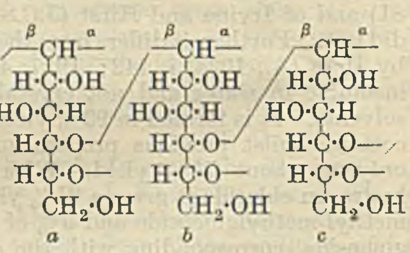
Powdered sodium converts the chloro-derivative in cold ethereal solution into 2 : 3 : 6-*trimethylglucose anhydride* (IV ?), a mobile oil, b. p. 83—85°/0·1 mm., $[\alpha]_D^{16}$ −10·1° (in water, +16·5°, in chloroform +14·6°), d^{15} 1·1593, n_D^{14} 1·4656. The anhydride contains no hydroxyl groups, is stable to Fehling's solution, to permanganate, and to bromine water, and when boiled with dilute hydrochloric acid gives 2 : 3 : 6-trimethylglucose, $[\alpha]_D^{15}$ +90·7°, mutarotating to +70·2° (cf. Irvine and Hirst, J.C.S., 1922, **121**, 1216).

The complete dissimilarity of trimethylcellulose and trimethylglucose anhydride (the latter gives a filtrable mobile solution in chloroform and has a normal mol. wt. in benzene; a 2% chloroform solution of the former is too viscous to be poured and the mol. wt. is immeasurably large) shows that trimethylcellulose is not a trimethylglucose anhydride and therefore that cellulose is not a unimolecular glucose anhydride as suggested by Hess.

The results of Micheel and Hess (A., 1927, 1056) for the preparation of two 2 : 3 : 6-trimethylglucose anhydrides could not be confirmed. The anhydride had a considerable b.-p. range and two fractions obtained from it had $[\alpha]_D$ +23° and +50° respectively, the former giving rise to a trimethylglucose with $[\alpha]_D$ only +63·5°.

1-*Dimethylamino*-2 : 3 : 6-*trimethylglucose*, from trimethylglucose and dimethylamine in methyl alcohol, has b. p. 109°/0·1 mm., $[\alpha]_D$ +18·6° in water and +7·2° in methyl alcohol. The corresponding *quaternary ammonium iodide* and chloride had $[\alpha]_D^{15}$ −41·2° and $[\alpha]_D^{18}$ −9·4° in water, respectively, whereas the chloride prepared by Micheel and Hess had $[\alpha]_D$ −8·7°.


(IV.)


(V.)

A survey of the main facts shows that there can be no reversible interconversion of trimethylcellulose and trimethylglucose anhydride. Moreover, cellobiose must be a product of degradation of cellulose, not a product of re-synthesis from glucose. In short, ordinary co-valency linkings unite the glucose units in cellulose, which is probably (V). If cellulose contains the linkings $a_{1\alpha}$–a_5, $b_{1\alpha}$–b_5, and $c_{1\alpha}$–c_5, degradation would lead to reducing and tetramethylglucose fragments. With linkings $a_{1\alpha}$–b_5, $b_{1\alpha}$–c_5, and $c_{1\alpha}$–d_5, etc., the same might apply, but is not necessitated. More probable linkings are either (with a_β attached to OH and c_4 to H), $a_{1\alpha}$–a_5, $b_{1\alpha}$–b_3, and $c_{1\alpha}$–c_5, or $a_{1\beta}$–a_5, $a_{1\alpha}$–b_5, $b_{1\alpha}$–c_5, and $c_{1\alpha}$–c_4. An essential argument for the associative combination of glucose anhydride units in cellulose was the supposed associative dimerisation of acetylaldol. Bergmann has, however, shown that the " dimeride " is a structural unit.

2 : 3 : 6-Trimethylglucose is converted by phosphorus pentachloride in ether into the *compound* $(C_9H_{16}O_6)_2PCl_3$, decomp. 160°. Trimethyl-methylglucoside reacts with phosphorus pentachloride in chloroform to give a syrupy *chlorohydrin*, $C_{10}H_{19}O_5Cl$ (Cl in position 4?), b. p. 88—95°/0·1 mm., $[\alpha]_D^{20}$ +16·4° in chloroform. The latter, when heated with hydrochloric acid, affords 2 : 3 : 6-*trimethylglucose*-4(?)-*chlorohydrin*, syrupy, b. p. 140—150°/0·1 mm., $[\alpha]_D^{20}$ +27·5° in chloroform. This in turn is converted by sodium into a 2 : 3 : 6-*trimethylhexose anhydride*, b. p. 84°/0·1 mm., $[\alpha]_D^{20}$ +106·8° (in water, +112·8°). Hydrolysis of the latter with hydrochloric acid gives a *trimethylhexose* with $[\alpha]_D$ +95·2° in water. Methylation of this gives a *methylhexoside* with $[\alpha]_D$ +33°, which when hydrolysed affords a *tetramethylhexose*, $[\alpha]_D$ +55°, not identical with tetramethylgalactose. The hexose anhydride, however, is not a derivative of glucose. E. E. TURNER.

Oxidation of amino-acids with sugars. S. AKABARI (Proc. Imp. Acad. Tokyo, 1927, 3, 672—674).—When *l*-leucine is heated with *d*-glucose at 120—130° in glycerol there are formed carbon dioxide, *iso*valeraldehyde (15%), and a brown substance, probably melanoidin (cf. Maillard, A., 1912, i, 169). *l*-Phenylalanine and *dl*-alanine afford phenylacetaldehyde (*semicarbazone*, m. p. 154—155°) and acetaldehyde, respectively. Ammonia is not evolved during the reaction, probably because it is used in the formation of melanoidin. The glycerol solution of the brown substance contains a small amount of hydroxymethylfurfuraldehyde. The oxidation is formulated $NH_2{\cdot}CHR{\cdot}CO_2H+O=R{\cdot}CHO+CO_2+NH_3$. H. BURTON.

Crystallisation of lysine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **76**, 437—443).—Lysine was recovered from the carefully purified picrate, m. p. 266° (decomp.), by shaking the latter with dilute sulphuric acid and ether; the sulphuric acid was for the most part removed by addition of barium hydroxide, and the solution concentrated; with precautions against access of carbon dioxide, the remaining sulphuric acid was removed and the concentration continued; lysine separated in needles, darkening at 210°, m. p. 224—225° (decomp.), $[\alpha]_D^{20}$ +14·6°. C. R. HARINGTON.

Alkylation of α-cyano-β-alkylacrylic esters and of α-phenyl-β-alkylacrylonitriles. J. A. MCRAE and R. H. F. MANSKE (J.C.S., 1928, 484—491).—*Ethyl* α-n-*butyl*-Δ^1-cyclo*hexenylcyanoacetate* (I), b. p. 163—164°/15 mm., *ethyl* α-*ethyl*-Δ^1-cyclo*hexenylcyanoacetate* (II), b. p. 168°/22 mm., and *ethyl* α-*cyano*-α-n-*butyl*-Δ^β-*nonenoate* (III), b. p. 154—156°/11 mm., are prepared by treatment of ethyl *cyclo*hexylidenecyanoacetate or of ethyl heptylidenecyanoacetate with sodium ethoxide and the appropriate alkyl iodide. Ozone is rapidly absorbed by these compounds. Decomposition of the ozonisation products gives, in the three cases, ethyl *n*-butylcyanoacetate and adipic acid, adipic acid only, and hexaldehyde, formic acid, and *n*-butylmalonic acid. The compounds are therefore unsaturated in the βγ-position (cf. J.C.S., 1908, 93, 1956), whereas the parent esters are unsaturated in the αβ-position (J.C.S., 1922, **121**, 274). The structural difference is further exemplified by the ease with which the alkyl derivatives take up bromine and by their failure to react with potassium cyanide or sodium hydrogen sulphite. Heptaldehyde condenses with phenylacetonitrile, giving α-*phenyl*-β-n-*hexylacrylonitrile* (IV), b. p. 168—170°/13 mm. Alkyl derivatives could not be prepared from the compound (IV) or from *cyclo*hexylidenephenylacetonitrile, m. p. 28°, b. p. 176—178°/12 mm. (cf. J.C.S., 1923, **123**, 2446). The last-named compound combines with hydrogen cyanide, giving 1-*cyano*cyclo*hexylphenylacetonitrile*, softening at 258°, decomp. above 264°. Combination of the compound (IV) with hydrogen cyanide, followed by hydrolysis, gave *α-phenyl-α′-n-hexylsuccinic acid* and an *acid*, m. p. 170°. M. CLARK.

[Preparation of] chloroacetamide. W. A. JACOBS and M. HEIDELBERGER (Org. Syntheses, 1927, 7, 16—17).

Butenoic acid amides. P. BRUYLANTS and A. CASTILLE (Bull. Acad. Roy. Belg., 1927, [5], **13**, 767—781).—The amides of crotonic and *iso*crotonic acids have been prepared by the action of 66% sulphuric acid on the corresponding nitriles for several days at the ordinary temperature. The nitrile of b. p. 121° thus treated yields exclusively crotonamide (*trans*), m. p. 159—160°, whilst that of b. p. 108° yields a mixture of this amide and *iso*crotonamide, m. p. 100—101°. The nitrile of lower b. p. is therefore related to *iso*crotonic acid (*cis*), the reverse conclusion to that obtained by a comparative study of the ultra-violet absorption spectra and heats of combustion of the nitriles and acids. Physical evidence of the latter type is therefore untrustworthy as a basis for the determination of configuration (cf. Errera and Henri, A., 1925, ii, 1137; Auwers, A., 1923, i, 295). The same conclusion probably applies to the nitriles of α-methylcrotonic acids. In agreement with Stoermer (A., 1920, i, 614) and Auwers (*loc. cit.*), the b. p. of crotononitrile (*trans*) is 13° higher than that of *iso*crotononitrile (*cis*). Vinylacetamide is similarly prepared from the corresponding nitrile if excess of alkali (which causes isomerisation to crotonamide) is avoided in working up the product, the absorption spectrum of the amide in 0·1*N*-sodium hydroxide solution after 15 days closely resembling that of crotonamide in the same medium. The absorption curves of *cyclo*propanecarboxylic acid and its amide (obtained by alkaline hydrolysis of the nitrile) are plotted, and show a greater difference than is found in the corresponding crotonic acid derivatives. The amide of methylacrylic acid, obtained by acid hydrolysis of the nitrile, readily polymerises to an amorphous mass. J. W. BAKER.

Ureides of bromovaleric acids. II. Influence of branched chains on physiological properties. E. FOURNEAU and G. FLORENCE (Bull. Soc. chim., 1928, [iv], **43**, 211—216).—The effect of branching the chain in a series of α-bromovaleric ureides is to cause an increase in the hypnotic action. Bromopivalic ureide is a powerful hypnotic and as it contains the bromine atom in the β-position it is concluded that the group R·CHBr·CO– is not specific (Tiffeneau). The following data are recorded (percentage figures indicate solubility in water, and ordinary figures partition coefficients): α-bromo-*n*-valeric ureide, m. p. 162°, 0·833%, 0·42; α-bromo*iso*valeric ureide, 1·94%, 0·95; α-bromo-α-methylbutyric ureide, m. p. 132·5°, 5·3%, 1·98; *bromopivalic ureide*, m. p. 93·5°, 5·4%, 2·02. *n*-Valeric acid is obtained from magnesium butyl bromide and carbon dioxide in 78% yield. H. BURTON.

Additive compounds of allylthiocarbamide and silver halides. S. E. SHEPPARD and H. HUDSON (Z. wiss. Phot., 1928, **25**. 113—120).—See A., 1927, 755.

[Preparation of] guanidine nitrate. T. L. DAVIS (Org. Syntheses, 1927, 7, 46—48).

[Preparation of] nitroguanidine. T. L. DAVIS (Org. Syntheses, 1927, 7, 68—69).

[Preparation of] anhydrous hydrogen cyanide. K. ZIEGLER (Org. Syntheses, 1927, 7, 50—52).

Reaction of carbylamines and hydrocyanic acid with magnesium phenyl bromide. H. GILMAN and L. C. HECKERT (Bull. Soc. chim., 1928, [iv], **43**, 224—230).—Magnesium phenyl bromide reacts with methylcarbylamine forming a small amount of benzaldehyde (cf. Sachs and Loevy, A., 1904, i, 307). Definite reaction products were not obtained from hydrocyanic acid or ethyl-, *tert.*-butyl-, or *p*-tolyl-carbylamine. H. BURTON.

Preparation of magnesium *tert.*-butyl chloride. H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1928, **50**, 425—428; cf. A., 1924, i, 23).—Magnesium *tert.*-butyl chloride is obtained in 70% yield by adding *tert.*-butyl chloride (0·5 mol.) in ether (7 mols.) to magnesium powder (200-mesh), with stirring, during 3 hrs., the ether being maintained in gentle ebullition. F. G. WILLSON.

Lead tetraethyl. Y. TANAKA and T. KUWATA (Rep. Aeronautical Res. Inst., Tokyo, 1927, 2, 409—417).—Crude lead tetraethyl, prepared from lead chloride and magnesium ethyl chloride, is best purified by the passage of air through a solution in dilute hydrochloric acid. This treatment converts the contaminating lead triethyl into crystalline *lead triethyl chloride*, which in turn affords lead tetraethyl with magnesium ethyl chloride (total yield 74%). Magnesium and ethereal ethyl chloride react readily if small amounts of iodine and ethyl iodide or bromide are added. Pure lead tetraethyl, b. p. 85·4—85·7°/13 mm., d_4^{18} (vac.) 1·6600, n_D^{18} 1·5206, decomposes at 400° giving metallic lead; at the ordinary temperature in sunlight it becomes turbid and alkaline, and when neutralised with hydrochloric acid yields some lead triethyl chloride. G. A. C. GOUGH.

Auto-oxidation. I. *cyclo*Hexene peroxide. H. N. STEPHENS (J. Amer. Chem. Soc., 1928, **50**, 568—571).—When oxygen is circulated continuously at atmospheric pressure and the ordinary temperature through *cyclo*hexene for 4 months, there is formed about 0·75% of cyclo*hexene peroxide*, b. p. 54—56°/0·5 mm., together with a non-volatile syrup, which appears to be a *dimeric* form of the peroxide, containing one peroxide group. F. G. WILLSON.

Oxidation of unsaturated hydrocarbons by free oxygen in presence of osmium. S. MEDVEDEV and E. ALEXÉEVA (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 110—127; Chem. Zentr., 1927, ii, 1012).—The catalyst consisted of osmium dioxide deposited on alumina, ferric oxide, manganese sesquioxide, or cupric oxide; benzene was preferable to acetone as a solvent for the unsaturated hydrocarbon (*cyclo*hexene or Δ²-methyl*cyclo*hexene), acetone solutions exhibiting an induction period of several hours. A catalyst inactivated by air is reactivated by benzene much more quickly than by acetone. The portion of the oxidation product of *cyclo*hexene which remained dissolved in the benzene contained peroxidic compounds, an aldehyde (semicarbazone, m. p. 240—241°), and much Δ^2-*cyclo*hexenol (naphthylurethane, m. p. 156°). The portion on the catalyst contained adipic acid, and a compound, $C_6H_{10}O_2$, b. p. 108—110°/0·2 mm. A. A. Eldridge.

Volume chemistry. II. Halogen derivatives of hydrocarbons. F. Wratschko (Pharm. Presse, 1927, **32**, 130—135, 172—174, 205—209; Chem. Zentr., 1927, ii, 777).—Abnormal "*E*-values" for cyclic hydrocarbons halogenated in a side-chain are avoided by supposing that the last hydrogen atom of the side-chain is attached to a nuclear carbon atom, with ring closure. A. A. Eldridge.

Nitration by means of nitrogen peroxide. M. Battegay (Bull. Soc. chim., 1928, [iv], **43**, 109—134).—A lecture.

Hydrogenation of cyclic compounds under pressure in presence of osmium and other catalysts. V. S. Sadikov and A. K. Mikhailov (J.C.S., 1928, 438—448).—The rate of hydrogenation of benzene, quinoline, and pyridine in a modified Ipatiev apparatus has been investigated using as catalyst platinum, osmium, osmium–cerium oxide, or palladium deposited on asbestos. In every case a periodic absorption of hydrogen takes place, a period of activity being followed by a period of quiescence, whilst the activity of the catalyst gradually diminishes on account of the presence of impurities or of the formation of products of hydration inimical to the catalyst. This periodicity is attributed to removal of oxygen from the catalyst, followed by reactivation, and is compared with the periodic evolution of hydrogen when metals are dissolved in acids or alkalis (cf. Hedges and Myers, A., 1925, ii, 309). The addition of 1% of cerium oxide to a 20% osmium–asbestos catalyst for the reduction of quinoline causes considerable initial acceleration of the reaction, which proceeds throughout at a higher rate than when osmium alone is used; in the case of pyridine, the reverse effect results. In the reduction of benzene and pyridine in the presence of osmium, there is an initial period during which the rate of reaction is considerably greater for pyridine than for benzene, whilst the rate diminishes more rapidly with pyridine. The total amount of reduction over a period of hours is thus approximately the same for both (cf. this vol., 427). M. Clark.

Comparative reactivities of some chloro-, bromo-, and iodo-nitrobenzenes. Mechanism of activation of halogen atoms by a nitro-group present in the same aromatic nucleus. A. Brewin and E. E. Turner (J.C.S., 1928, 332—334, 334—337).—The comparative reactivities of a number of halogenonitrobenzenes have been measured, using piperidine in benzene solution. It is concluded that reactions involving reactive halogen compounds are, as the majority of previous workers have assumed, dependent on the initial formation of additive compounds. A mechanism of activation by nitro-groups is developed, and correlated with one for aromatic substitution. M. Clark.

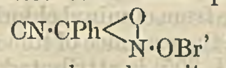
Replaceability of nitro-groups from the nucleus of various aromatic compounds. R. H. Clark and N. M. Carter (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 323—338).—Data for the effect of heat on 119 aromatic nitro-compounds containing from one to five nitro-groups are recorded, and the results discussed from the point of view of the electronic conception of positive and negative valencies developed by Fry and others. In 96 of the compounds the results are in accordance with theory, in 9 the reaction appears to be with the unstable electromeride, whilst the behaviour of the remaining 14 cannot be accounted for on this hypothesis. M. S. Burr.

Replacement of halogen atoms from the nucleus of various aromatic compounds. R. H. Clark and R. H. Hall (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 311—314).—The maximum replacement of halogen atoms, under the experimental conditions, has been determined for a number of aromatic halogen compounds, when heated under pressure with sodium methoxide of different concentrations. The yields are compared with those calculated on the basis of the electronic theory as elaborated by Fry. The results are not as conclusive as corresponding measurements on the nitro-groups. M. S. Burr.

Nature of the alternating effect in carbon chains. XXIII. Anomalous orientation by halogens, and its bearing on the problem of the *ortho-para* ratio, in aromatic substitution. C. K. Ingold and C. C. N. Vass (J.C.S., 1928, 417—425).—The reaction mixture from *m*-fluoroacetanilide and bleaching powder yields, after treatment with hydrochloric acid, a mixture of 3-*fluoro*-4-*chloroacetanilide* (I), m. p. 115°, 3-*fluoro*-6(2 ?)-*chloroacetanilide*, m. p. 143°, and 3-*fluoro*-4 : 6(2 : 6 ?)-*dichloroacetanilide*, m. p. 124°. Hydrolysis of (I) gives 3-*fluoro*-4-*chloroaniline*, m. p. 61—62°, converted through the diazo-derivative into 3-*fluoro*-4-*chloronitrobenzene* (II), m. p. 63—64°, b. p. 114—116°/24 mm. Chlorination of *p*-fluoronitrobenzene in presence of anhydrous ferric chloride gives 4-fluoro-3-chloronitrobenzene (III), m. p. 41·5°, converted by elimination of the nitro-group into *o*-fluorochlorobenzene (IV), b. p. 138—140°/758 mm. Nitration of compound (IV) yields a mixture consisting essentially of compounds (II) and (III) present in the proportion corresponding with the ratio direction by F : direction by Cl=78·7% : 21·3%. An explanation of this anomaly is based on the hypothesis that the *op*-directive efficiencies of the halogens, which vary directly with the tendency of the halogen atom to share additional electrons (+T) and inversely as its attraction for electrons, shared and unshared (−T) (cf. this vol., 164), are also influenced by a third factor. The inductive effect is regarded as originating in a contracted electron shell round the halogen atom, and it is suggested that, as well as electron displacements relayed from linking to linking, modification of the existing electric fields might also occur by direct action through space in such a way that the potentially active electrons of the benzene ring would be subjected to additional electrostatic restraint. This "direct" effect of halogens would therefore be a deactivating influence (−D) and the full expression for the directive action of halogens in halogenobenzenes (+T—I—D). The variation of D as between different directing atoms would be the same as that of the inductive effect, but, since it is propagated through space, its distribution in the ring would be, not in the order $op>m$, but in the order $o>m>p$. The working of such an hypothesis in the case under discussion as well as in other cases cited is demonstrated. M. Clark.

Nature of the alternating effect in carbon chains. XXIV. Directive action in aromatic substitution of certain groups containing triple linkings. J. W. Baker, K. E. Cooper, and C. K. Ingold (J.C.S., 1928, 426—431).—The nitration of two acetylene derivatives and two nitriles has been investigated with special reference to the proportion of *m*-isomeride formed, and the results are as follows: Phenylpropiolic acid (8% meta), ethyl phenylpropiolate (16%), benzonitrile (81%), phenylacetonitrile (14%). The results are discussed in relation to the other properties of the unsaturated groups contained in the side-chains of these compounds and an hypothesis is advanced to account for them. M. Clark.

Preparation of *p*-nitrobenzyl bromide. I. V. Hopper (J. Roy. Tech. Coll. Glasgow, 1927, (4), 58—60).—Addition of a solution of bromine in carbon tetrachloride to a boiling solution of *p*-nitrotoluene in the same solvent, in presence of a trace of iodine, and under the influence of ultra-violet light, gives excellent yields of *p*-nitrobenzyl bromide. L. M. Clark.

Laws of aromatic substitution. VII. Constitution and substitution of phenylnitromethane and some of its derivatives. B. Flürscheim and E. L. Holmes (J.C.S., 1928, 453—483).—Contrary to the findings of Baker and Ingold (A., 1926, 1131), the statement by one of the authors (A., 1903, i, 79) that phenylbromocyanonitromethane (I) yields, on brief treatment with nitric acid (*d* 1·480) and subsequent oxidation with permanganate, a mixture consisting essentially of benzoic and *p*-nitrobenzoic acids is fully confirmed. Nitric acid of the strength used by Baker and Ingold (*d* 1·49) gives a similar result. The *p*-acid, amounting to 34—38% of the weight of the total acids, arises mainly by migration of the nitro-group during oxidation, and such migration can be prevented by prior treatment with alkali. The complex changes occurring on prolonged exposure of compound (I) to nitric acid (*d* 1·480) have been quantitatively elucidated. The main change—the migration of bromine into the *m*-position—occurs to the extent of 54% in 10 days and the rate of formation of the *m*-bromophenyl compound is independent of the concentration. With nitric acid of *d* 1·52, the nitromethane undergoes *m*-nitration (92—93%) (cf. Baker and Ingold, *loc. cit.*) and *p*(and *o*?)-nitration (8—7%). The compound (I) is decomposed by heat, giving 92% of benzoyl cyanide and 8% of *p*-nitrobenzoyl cyanide. m-*Nitrophenylbromocyanonitromethane* (II), m. p. 70—70·5°, gives 93·5% of *m*-nitrobenzoyl cyanide. Both the compound (I) and phenylcyano*iso*nitromethane (sodium derivative) are decomposed by concentrated sulphuric acid, giving a blue nitroso-compound formulated as $\mathrm{CN{\cdot}CPh(NO){\cdot}O{\cdot}SO_3H}$, which breaks down into benzoyl cyanide and eventually into benzoic acid. The compound (II) undergoes analogous decomposition, yielding *m*-nitrophenylglyoxylic acid, m. p. 144·5—145° (lit. 77—78°). The compound (I) undergoes partial rearrangement in ethereal solution, a small percentage of bromine migrating to the *m*-position. The correlated behaviour of phenylcyano*iso*nitromethane (III), benzoyl cyanide (IV), and *m*-bromobenzoic acid (V) on nitration was also investigated quantitatively. The compound (III) gives more than 99% of *p*-nitrophenylcyano*iso*nitromethane in nitric acid (*d* 1·48); compound (IV) gives 87·6% of *m*-nitrobenzoyl cyanide and 12·4% of *o*- and *p*-nitrobenzoyl cyanides, using nitric acid of *d* 1·52; compound (V) gives 96% of *o*- and *p*-nitro-*m*-bromobenzoic acids and 4% of *m*′-nitro-*m*-bromobenzoic acid, using nitric acid of *d* 1·48. Migration of the nitro-group during oxidation of phenylcyanonitromethane is also shown to take place to the extent of 14 mol.-%. The mechanism of these various transformations is discussed. Both phenylbromocyanonitromethane,  $\mathrm{CN{\cdot}CPh{<}\begin{smallmatrix}O\\|\\N{\cdot}OBr\end{smallmatrix}}$, and its *m*-nitro-derivative possess a hypobromite constitution, with an oxygen bridge (cf. Willstätter and Hottenroth, A., 1904, i, 472). They react with dry ammonia with replacement of bromine by hydrogen and are quantitatively reduced by potassium iodide. Ethyl phenylbromomalonate, a true bromide, fails to give these reactions at the ordinary temperature; at 95°, however, there is equilibrium between the hypobromite and bromide forms, the latter greatly preponderating. M. Clark.

Laws of aromatic substitution. VI. Quantitative method for the rapid determination of isomeric nitro-derivatives of laterally substituted toluenes. B. Flürscheim and E. L. Holmes (J.C.S., 1928, 448—453).—Isomeric nitro-derivatives of laterally substituted toluenes show almost identical resistance to destructive oxidation either by dilute permanganate solution (1 in 60) or by dilute nitric acid. The proportions of the corresponding acids obtained from mixtures of the isomerides are therefore essentially unaltered from those of the parent nitro-derivatives. For determination of these mixtures the nitro-acids may readily be separated from any benzoic or bromobenzoic acid present by reduction in dilute hydrochloric acid solution with titanous chloride. The non-amino-acids are removed by extraction with ether. The relative proportions of the residual isomeric amino-acids are then determined by prolonged exposure of the dilute hydrochloric acid solution to bromine. *o*- and *p*-Aminobenzoic acids are converted quantitatively into tribromoaniline, separation of which from the tribromo-*m*-aminobenzoic acid simultaneously formed from *m*-aminobenzoic acid is readily effected by alkaline reagents (cf. Francis and Hill, A., 1925, ii, 163). M. Clark.

The parachor and chemical constitution. VII. Semipolar double bonds. A. Freiman and S. Sugden (J.C.S., 1928, 263—269).—Measurements have been made of the surface tension and density of *p*-toluenesulphonyl chloride, ethyl *p*-toluenesulphonate, benzyl methyl sulphone, diphenyl sulphone, phenyl benzyl sulphone, chromyl chloride, sulphonal, and trional. Calculations of the parachor for the five simple sulphones, all of which are solid crystalline substances which can readily be purified, confirm the value −1·6 obtained in an earlier investigation (A., 1925, ii, 936) for the effect of the semipolar double bond on the parachor. Measurements for chromyl chloride give a parachor for chromium of 54 units, assuming that the oxygen atoms in this compound are held by semipolar double bonds. This value is confirmed by calculation of the parachor for potassium dichromate from the observations of Jaeger (A., 1918, ii, 33). The parachor values for sulphonal and trional are 10—20 units lower than those predicted by theory. It is suggested that this is due to the production of a cyclic phase by the formation of singlet linkings between oxygen atoms of the SO_2 groups.

M. CLARK.

Houben's reaction. L. BERT (Compt. rend., 1928, **186**, 587—588).—The production of 1-benzyl-4-*iso*propylbenzene in the preparation of 1-propyl-4-*iso*propylbenzene from cuminyl chloride and magnesium ethyl iodide in the presence of toluene by Houben's method (A., 1903, i, 805) is attributed to the catalytic action of the magnesium halides which causes a Freidel–Crafts reaction to take place between the toluene and the cuminyl chloride. This conclusion is verified by substituting *cyclo*hexane or petroleum (b. p. 70—90°) for toluene; under these conditions the desired product (yield 50%) is obtained alone. In extending the modified reaction to the interaction of benzyl chloride with various magnesium alkyl bromides (yields 26—70%), concurrent reactions involving the production of dibenzyl, ethylene, and ethane (in the case of magnesium ethyl bromide) are noted.

G. A. C. GOUGH.

Aromatic compounds containing a *tert*.-butyl group. A. TSCHITSCHIBABIN, S. ELGASINE, and V. LENGOLD (Bull. Soc. chim., 1928, [iv], **43**, 238—242).—Bromination of *tert*.-butylbenzene in presence of a trace of iodine or iron gives mainly *p*-bromo-*tert*.-butylbenzene, b. p. 104—106°/14 mm., m. p. 10°. Hydrolysis of the reaction product of magnesium *p-tert*.-butylphenyl bromide and ethyl orthoformate yields p-tert.-*butylbenzaldehyde* (30—40%), b. p. 245—246° (corr.), d_4^0 0·9877, n_4^{20} 0·9733, oxidised by potassium permanganate to *p-tert*.-butylbenzoic acid, m. p. 164°. There is formed during the Grignard reaction some 4 : 4′-*di*-tert.-*butyldiphenyl*, b. p. 190—192°/13 mm., m. p. 128—129°. The above aldehyde condenses with acetone, forming p-tert.-*butylbenzylideneacetone*, b. p. 158—160°/11 mm., m. p. 49—50°. Magnesium *p-tert*.-butylphenyl bromide and magnesium β-chloroethoxy bromide give β-p-tert.-*butylphenylethyl alcohol*, b. p. 141—143°/15 mm., d_4^{15} 0·9782, d_4^{20} 0·9749, n^{17} 1·5209, *R* 55·1. Some of the above compounds have pungent odours.

H. BURTON.

Action of sodium–potassium alloy on certain hydrocarbons. J. B. CONANT and A. H. BLATT (J. Amer. Chem. Soc., 1928, **50**, 551—558).—α-*Phenyl*-β-*methyl*-n-*propyl bromide*, b. p. 116—119°/17 mm., and α-*phenyl*-n-*amyl bromide*, b. p. 120—123°/10 mm., are obtained by treating the corresponding carbinols with hydrogen bromide at 0°. From these, by treatment with magnesium and ether and subsequently with anhydrous cupric chloride and hydrolysis, γδ-*diphenyl*-βε-*dimethyl*-n-*hexane*, m. p. 150—150·5°, and εζ-*diphenyl*-n-*decane*, m. p. 80°, were prepared, γδ-*diphenyl*-ββεε-*tetramethyl*-n-*hexane*, m. p. 180—181°, being obtained analogously. These hydrocarbons and βγ-diphenyl-*n*-butane are unaffected by liquid sodium–potassium alloy. Treatment of Δ^a-phenylamylene with sodium–potassium and ether affords a red, metallic *derivative*, which is converted by carbon dioxide into the metallic salt of αα′-*diphenyl*-ββ′-*dipropyladipic acid*, m. p. 278°. ββ-Dimethylstyrene yields similarly αα′-*diphenyl*-βββ′β′-*tetramethyladipic acid*, m. p. 238—240° (decomp.), whilst treatment of the metallic derivative of the dimethylstyrene with water affords αδ-*diphenyl*-ββγγ-*tetramethyl*-n-*butane*, m. p. 131—132°.

F. G. WILLSON.

Supposed mechanism of polymerisations by alkali metals. K. ZIEGLER and K. BAHR (Ber., 1928, **61**, [*B*], 253—263).—The action of potassium β-phenyl*iso*propyl (Ziegler and Schnell, A., 1924, i, 851) on stilbene in the presence of ether followed by treatment of the product with dry carbon dioxide affords the two stereoisomeric forms of αβγ-*triphenyl*-γ-*methylvaleric acid*, m. p. 245—246° (*silver* salt) and 215—216° (*silver* salt). The primary product is therefore the compound, $CPhMe_2\cdot CHPh\cdot CHKPh$, formed simply by addition of the metallic compound to the double linking. When similarly treated, potassium β-phenyl*iso*propyl and αα-diphenylethylene give mainly ααδ-*triphenyl*-γ-*methylvaleric acid*, m. p. 154—156° (*silver* salt), with a little ααδδ-tetraphenyladipic acid, obtained also by the action of alkali metals on αα-diphenylethylene (cf. Schlenk, A., 1914, i, 396). Anthracene and potassium β-phenyl*iso*propyl yield 9-*phenyl*iso*propyl*-9 : 10-*dihydroanthracene*-10-*carboxylic acid*, m. p. 206—207°. With phenanthrene, addition of the potassium compound does not occur and the product of the change is the acid, $C_{30}H_{22}O_4$, m. p. 223—224° (*silver* salt), apparently identical with that obtained by Schlenk by the action of alkali metal and carbon dioxide on the hydrocarbon. The possibility of addition appears to depend on the presence of conjugated double linkings or a double linking vicinal to the benzene nucleus; thus *cyclo*hexene does not react. Polymerisation of an unsaturated organic compound, *e.g.*, butadiene, by an alkali metallic compound, *RK*, is explained by the hypothesis that the primary compound, $CH_2R\cdot CHK\cdot CH\colon CH_2$, is itself an alkali metallic compound and hence can react further with another molecule of butadiene, giving the substance $CH_2R\cdot CH(CH\colon CH_2)\cdot CH_2\cdot CHK\cdot CH\colon CH_2$, and the process can continue until stopped by external agency, by process of the change in other directions, or by the increasing size of the molecule inducing extreme sluggishness in reaction. Although the additive compound from stilbene and potassium β-phenyl*iso*propyl does not further react with stilbene, it combines with styrene, giving, after treatment with carbon dioxide, αγδε-*tetraphenyl*-ε-*methylheptoic acid* (*silver* salt). Further, when potassium β-phenyl*iso*propyl is caused to react with increasing molecular proportions of styrene or βγ-dimethylbutadiene and the products are treated with carbon dioxide the isolated acids exhibit increasing mol. wt. H. WREN.

α-Benzylnaphthalene. I. Reactions of 4-benzylnaphthalenesulphonic acid. K. DZIEWOŃSKI and S. DZIĘCIELEWSKI (Bull. Acad. Polonaise, 1927, *A*, 273—286).—*Sodium 4-benzylnaphthalenesulphonate* (corresponding *barium* and *lead* salts described), prepared by sulphonation of the hydrocarbon with sulphuric acid (*d* 1·84) at the ordinary temperature followed by treatment with brine, yields 4-*benzylnaphthalenesulphonyl chloride*, m. p. 104—105° (corresponding *amide*, m. p. 164—165°). The constitution of this substance follows from the fact that 4-*benzyl-α-naphthol*, m. p. 125—126° (*acetyl* derivative, m. p. 87—88°; *benzoyl* derivative, m. p. 103°; *methyl* derivative, m. p. 85—87°), prepared by fusion of the sodium sulphonate with potassium hydroxide at 240°, is identical with that prepared directly from α-naphthol and benzyl chloride in the presence of zinc chloride and chloroform. 4-Benzyl-α-naphthol affords *nitro*-1-*benzyl*-4-*naphthol*, m. p. 130—132°, with nitric acid (*d* 1·43) in acetic acid solution, *nitroso*-4-*benzyl-α-naphthol*, m. p. 170° (decomp.), with aqueous alcoholic zinc chloride and sodium nitrite, followed by decomposition of the resultant *zinc* salt with sodium hydroxide and the following arylazo-compounds on coupling with the appropriate diazotised amine: *benzeneazo*-, m. p. 191—193°; p-*nitrobenzeneazo*-, m. p. 252—253°; α-*naphthaleneazo*-, m. p. 201—203°; β-*naphthaleneazo*-, m. p. 207—208°. By heating 4-benzyl-α-naphthol at 240° with anhydrous calcium chloride saturated with ammonia, 4-*benzyl-α-naphthylamine*, m. p. 114·5° (*acetyl* derivative, m. p. 208—209°), is obtained.

G. A. C. GOUGH.

Replaceability of the halogen atom in 1-chloro-2 : 4-dinitro- and -2 : 4 : 5-trinitro-naphthalenes. H. W. TALEN (Rec. trav. chim., 1928, 47, 329—345).—The velocities of replacement of the chlorine atom by the action of sodium methoxide and ethoxide in 1-chloro-2 : 4-dinitrobenzene, 1-chloro-2 : 4-dinitronaphthalene, -2 : 4 : 6- and -2 : 4 : 5-trinitronaphthalene, and 2-chloro-1 : 6 : 8-trinitronaphthalene at 0°, 15°, and 25° have been determined. The values of the coefficients for a bimolecular reaction are constant except in the cases of 1-chloro-2 : 4 : 5-trinitronaphthalene and 1-chloro-2 : 4 : 6-trinitrobenzene, in which the value of the coefficient is initially very large and rapidly decreases, the reaction ceasing long before it is complete. It is assumed (cf. van de Vliet, A., 1924, i, 1293) that this is due to the occurrence of the concurrent reactions $RCl + NaOMe \longrightarrow ROMe + NaCl$; $ROMe + NaOMe \longrightarrow ROMe,NaOMe$ [$R = C_{10}H_4(NO_2)_3$ or $C_6H_2(NO)_3$], followed, in the latter case, by the slow reaction $ROMe,NaOMe + RCl \longrightarrow 2ROMe + NaCl$. An approximate value for this case, in which replacement is very rapid, was determined at −50°. The values of the velocity coefficient for the replacement of chlorine in 1-chloro-2 : 4-dinitrobenzene agree with those of Hollemann and Ter Weel (A., 1916, i, 22) and of Luloffs (A., 1902, i, 87), whose values must be halved, but the value obtained for k^{25}_{NaOEt} deviates from that found by Mattaar (A., 1922, ii, 275). At 0°, 15°, and 25°, the ratio k_{NaOMe}/k_{NaOEt} in this case is about 1 : 3. The chlorine atom in 1-chloro-2 : 4-dinitronaphthalene is much more reactive than in the corresponding benzene derivative, the ratio of the velocity coefficients for the two reactions at 0°, 15°, and 25° being, with sodium methoxide, 1 : 30·8, 1 : 14·0, and 1 : 13·9, and with sodium ethoxide, 1 : 24·9, 1 : 10·3, and 1 : 8·9, respectively. The chlorine in 1-chloro-2 : 4-dinitronaphthalene is thus replaced 2—3 times as rapidly with sodium ethoxide as with the methoxide, and, moreover, its mobility is of the same order of magnitude as that in 2-chloro-1 : 6 : 8-trinitronaphthalene. The introduction of another nitro-group in position 5 in the naphthalene nucleus increases the mobility of the chlorine considerably, but not to so great an extent as does the introduction of a third nitro-group in position 6 in the corresponding benzene derivative. The velocity of replacement in the latter case (1-chloro-2 : 4 : 6-trinitrobenzene) is so great that only at −50° is it of the same order of magnitude as k^0 for 1-chloro-2 : 4 : 5-trinitronaphthalene, and k^{15} for 1-chloro-2 : 4-dinitronaphthalene. The mobility of the chlorine in the chloro-di- and -tri-nitronaphthalenes investigated is thus intermediate between that in 1-chloro-2 : 4-dinitro- and -2 : 4 : 6-trinitrobenzene. The solubility of 1-chloro-2 : 4-dinitronaphthalene at 0° and 25°, is, in methyl alcohol, 0·1056 g. and 0·2378 g., and in ethyl alcohol, 0·0752 g. and 0·1780 g., in 100 c.c., respectively. J. W. BAKER.

Replacement of the halogen atom or the alkoxy-group in 1-chloro-, 1-methoxy-, or 1-ethoxy-2 : 4-dinitro- and -2 : 4 : 5-trinitronaphthalenes by various other groups. W. H. TALEN (Rec. trav. chim., 1928, 47, 346—362).—By the action of amines and similar substances on 1-chloro-2 : 4-dinitro- and -2 : 4 : 5-trinitro-naphthalenes and on the corresponding 1-methoxy- and 1-ethoxy-derivatives a large number of α-naphthylamine derivatives have been prepared. From a review of the literature it is shown that by nitration of α-chloro- or α-bromo-naphthalenes the nitro-group first enters position 4 and subsequently positions 5 and 8, whilst in the case of α-alkoxy-derivatives the nitro-group is directed towards the 2-, 4-, and 5-positions. Thus nitration of α-naphthyl methyl ether yields 1-methoxy-2 : 4 : 5-trinitronaphthalene, m. p. 153° (Staedel, A., 1883, 861, gives 128°), identical with the product obtained by the action of sodium methoxide on the corresponding 1-chloro-compound. Similarly, nitration of α-naphthyl ethyl ether yields 1-ethoxy-2 : 4 : 5-trinitronaphthalene, m. p. 151° (Staedel, *loc. cit.*, gives 148°), identical with the product obtained from the 1-chloro-compound. The following derivatives of 2 : 4-dinitronaphthalene are obtained by heating 1-chloro- (or sometimes 1-alkoxy-)2 : 4-dinitronaphthalene with the calculated quantity of the appropriate amine in alcohol solution at 100° for several hours: α-2 : 4-dinitronaphthyl-amine, m. p. 242° (Ullmann and Bruck, A., 1909, i, 21) (*acetyl* derivative, m. p. 258—259°; $+1CH_3{\cdot}CO_2H$, m. p. 117°); -*methylamine*, m. p. 167·5° and 179—180°, the two modifications not being interconvertible and depressing each other's m. p.; -ethylamine, m. p.

172° (Meldola, J.C.S., 1906, **89**, 1435, gives 169—170°: *acetyl* derivative, m. p. 86—87°); -n-*propylamine*, m. p. 129°; -n-*butylamine*, m. p. 89°; -n-*amylamine*, m. p. 74°; -n-*heptylamine*, m. p. 58°. By similar methods are obtained 2 : 4-*dinitronaphthyl*-1-*semicarbazide*, decomp. 185—187°; and -1-*semioxamazide*, decomp. 227—228°. By nitration of 1-chloro-2 : 4-dinitronaphthalene the chief product is 1-chloro-2 : 4 : 5-trinitronaphthalene, m. p. 147—148° (Rindl, J.C.S., 1913, **103**, 1911, gives 143—144°), together with some 2 : 4 : 8-trinitro-compound. The 1-chloro- (or alkoxy-) group in the 2 : 4 : 5-trinitronaphthalene derivative is similarly replaced by amino-groups and thus are obtained α-2 : 4 : 5-*trinitronaphthyl-amine*, m. p. 310° (*acetyl* derivative, m. p. 275°); -*methylamine*, m. p. 206°; -ethylamine, m. p. 160° (Rindl, *loc. cit.*, gives 157—159°); -n-*propylamine*, m. p. 139°; -n-*butylamine*, m. p. 121°; -n-*amylamine*, m. p. 144—145°; -n-*heptylamine*, m. p. 99·5—100·5°; 2 : 4 : 5-*trinitronaphthyl*-1-*semicarbazide*, exploding 173°, and -1-*semioxamazide*, exploding 236°. The m. p. of the 1-*n*-alkylamino-derivatives of 2 : 4-dinitro- and 2 : 4 : 5-trinitro-naphthylamine decrease gradually with an increasing number of carbon atoms in the chain in a similar manner to that observed by Kam (A., 1926, i, 1240) in the case of the analogous derivatives obtained from 1-chloro-2 : 4-dinitrobenzene. J. W. Baker.

Supposed stereoisomerism in the fluorene series. J. Cerezo (Anal. Fís. Quím., 1927, **25**, 567—587; cf. Wieland and Cerezo, A., 1927, 1183).—The alleged isomerism in the fluorene series is discussed and evidence put forward which demonstrates that no such isomerism is shown by 9-acetoxyfluorene, 9-aminofluorene, or 9-methylfluorenol. J. S. Carter.

***meso*-Alkylanthracenes and "transannular tautomerism." IV.** E. de B. Barnett and J. W. Cook (Ber., 1928, **61**, [*B*], 314—319; cf. A., 1926, 1030; 1927, 140; this vol., 52).—1 : 5-Dichloroanthrone is converted by methyl iodide and potassium hydroxide at 100° into a mixture of approximately equal amounts of 1 : 5-dichloro-9-methoxyanthracene, m. p. 105°, and 1 : 5-*dichloro*-9-*methylanthrone*, m. p. 184°. The presence of the methyl group in the *meso*-position in the latter compound appears to hinder conversion into the enolic form, since 1 : 5-dichloro-9-methylanthrone cannot be etherified by treatment with potassium hydroxide and methyl toluene-*p*-sulphonate and only slowly yields an *acetate* with boiling acetic anhydride and pyridine. By treatment with the requisite Grignard reagent, 1 : 5-dichloro-9-methylanthrone is converted into the following substances: 1 : 5-*dichloro*-9-*methyl*-10-*methylene*-9 : 10-*dihydroanthracene*, m. p. 143°; 1 : 5-*dichloro*-9-*methyl*-10-*ethylidene*-9 : 10-*dihydroanthracene*, m. p. 153°; 1 : 5-*dichloro*-9-*methyl*-10-iso*propylidene*-9 : 10-*dihydroanthracene*, m. p. 134°; 1 : 5-*dichloro*-9-*methyl*-10-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 165°. 1 : 5-*Dichloro*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthran*-10-*ol*, m. p. 144°, is converted by treatment with acetic acid containing hydrochloric acid at 100° into 1 : 5-*dichloro*-10-*phenyl*-9-*methylanthracene*, m. p. 104°. Further treatment of the latter compound with the same reagent produces 1 : 5-dichloro-10-phenyl-9-methylene-9 : 10-dihydroanthracene, m. p. 151°, thus placing beyond doubt the possibility of "transannular tautomerism." The constitution of the methylene derivative is established by its almost quantitative oxidation to 1 : 5-dichloro-9-phenylanthrone and conversion into 1 : 5-*dichloro*-9 : 10-*dibromo*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 122°. H. Wren.

9-Iodophenanthrene. J. Salkind and F. Lubinskaja (Ber., 1928, **61**, [*B*], 269—271).—9-*Iodophenanthrene*, m. p. 87° (*picrate*, m. p. 137°), is prepared by the action of iodine on magnesium phenanthryl bromide in the presence of ether. It is oxidised to phenanthraquinone by chromic acid in glacial acetic acid. H. Wren.

Chlorination of anilides. II. Decomposition of *N*-chloroacetanilide by heat. A. E. Bradfield (J.C.S., 1928, 351—352).—In order to show that, contrary to the statement of Porter and Wilbur (A., 1927, 1041), the re-arrangement of fused *N*-chloroacetanilide at 100° is a two-stage process involving the intermediate production of chlorine, the reaction has been carried out with pure material in an open vessel in an air-bath, and in a sealed tube in boiling water. From the products 7·0% and 4%, respectively, of 2 : 4-dichloroacetanilide were isolated, in addition to *p*-chloro-, 41·0%, 50·7%; *o*-chloro-, 18·2%, 16·5%, and acetanilide, 6·3%, 0·0%.
H. E. F. Notton.

[Preparation of] benzanilide. C. N. Webb (Org. Syntheses, 1927, **7**, 6—7).

Interaction of sulphur and *p*-toluidine in presence of litharge: thio-*p*-toluidine and related compounds. M. T. Bogert and L. Smidth (J. Amer. Chem. Soc., 1928, **50**, 428—436; cf. A., 1924, i, 166).—Separation of the products of the reaction between *p*-toluidine, sulphur, and litharge at 140° is conveniently effected by dissolution in 10% hydrochloric or sulphuric acid, followed by dilution to precipitate weakly basic resins, and fractional precipitation with ammonia solution. Purification of the products is effected by repeating this process. In this way 535 g. of *p*-toluidine afforded 70 g. of resins, 80 g. (17%) of dithio-*p*-toluidine, and 121 g. (26%) of monothio-*p*-toluidine, 167 g. of *p*-toluidine being recovered. Only small amounts of impure dithio-*p*-toluidine could be obtained by Hodgson's process (B.P. 15,466 of 1911). When heated at 205—210°, thio-*p*-toluidine evolves ammonia, hydrogen sulphide, and *p*-toluidine, leaving a brown, amorphous residue. Thio-*p*-toluidine yields only a small amount of *p*-toluidine when heated with concentrated hydrochloric acid or 25% sulphuric acid for 6 hrs. at 200°, and remains undecomposed when fused with sulphur. It is only slowly decomposed, with formation of basic tars, when heated with sulphur and litharge at 140—150°. Thio-*p*-toluidine could not be coupled with diazotised sulphanilic acid. Oxidation of the diacetyl derivative to the corresponding sulphone is conveniently effected by treatment with concentrated nitric and sulphuric acids (75 : 30) at the ordinary temperature. Treatment of thio-*p*-toluidine with acetic anhydride, glacial acetic acid, and hydrogen peroxide affords *bis*-2-*acetamido*-5-*methylphenylsulph*-

oxide, m. p. 212°. *Bis-2-chloro-5-methylphenylsulphone*, brown, amorphous, decomp. above 95°, is obtained by heating diazotised thio-*p*-toluidine with hydrochloric acid and copper powder, with subsequent oxidation with nitric and sulphuric acids; replacement of the copper powder in this process by potassium iodide affords analogously *bis-2-iodo-5-methylphenylsulphone*, pale brown, amorphous, decomp. about 82°. When diazotised thio-*p*-toluidine is kept over-night in excess of concentrated hydrochloric acid, and the solution then boiled, 2-*chloro*-5 : 5′-*dimethyldiphenylsulphide*-2 : 2′-*oxide*, b. p. 265°/80 mm., is obtained. 2-*Bromo*-5 : 5′-*dimethyldiphenylsulphone*, brown, amorphous, decomp. 69—72°, is obtained by diazotising thio-*p*-toluidine in aqueous sulphuric acid, with subsequent treatment with potassium bromide and copper powder, and oxidation as above. Thio-*p*-toluidine is not obtained when dithio-*p*-toluidine is heated with *p*-toluidine and litharge, or with sulphur and litharge, at 140—165° (cf. Hodgson, A., 1924, i, 1188). Diazotised and coupled with H-acid, dithio-*p*-toluidine yields a *dye* producing purplish shades on wool. *Dithio*-p-*toluidine picrate*, yellow, was prepared. Reduction of dithio-*p*-toluidine affords 2-*amino*-5-*methylphenyl mercaptan* (*zinc* salt). F. G. Willson.

Condensation of ethyl cyanoacetate with some aryl- and alkyl-amines. Preparation of some aryl- and alkyl-substituted cyanoacetamides. K. G. Naik and Y. N. Bhat (J. Indian Chem. Soc., 1927, 4, 547—551).—The following new compounds are described: *cyanoaceto*-o-*toluidide*, m. p. 125°; *cyanoaceto*-m-*toluidide*, m. p. 132°; *cyanoaceto*-α-*naphthylamide*, m. p. 175°; *cyanoaceto*-β-*naphthylamide*, m. p. 174°; *cyanoaceto*-vic-m-*xylidide*, m. p. 107°; *cyanoacetomethylamide*, m. p. 101°; *cyanoacetoethylamide*, m. p. 74°. C. D. Langford.

Properties of 2 : 5- and 2 : 8-naphthylaminesulphonic acids. H. I. Waterman and J. Groot (Chem. Weekblad, 1928, 25, 40—42).—The four possible sulphonated β-naphthylamines having one sulphonic acid radical in the nucleus not containing the amino-group have been prepared in the pure condition. The solubilities in water at 20° are: 2 : 8- and 2 : 5-acids, as anhydrous, 1 part in 1680 and 3025 parts, respectively; 2 : 7- and 2 : 6-acids, as monohydrates, 1 in 5040 and 7790, respectively. The solubility products of the 2 : 5- and 2 : 8-acids are calculated from these data and from the dissociation constants recorded by Ebersbach (cf. A., 1893, ii, 450) as $1{\cdot}08\times10^{-7}$ and $2{\cdot}63\times10^{-7}$, respectively. These values are in accordance with the fact that the 2 : 5-acid separates first when an equimolecular mixture of the sodium salts of the two acids in solution is acidified; the solubility products calculated from the solubilities given by Forsling (A., 1887, 962) and the work of Levi (cf. B., 1921, 503A) indicate erroneously that the 2 : 8-acid separates first.

S. I. Levy.

Manufacture of anthracene derivatives [alkylaminoanthracenes] and of benzanthrene. I. G. Farbenind. A.-G.—See B., 1928, 151.

Manufacture of aromatic oxamic acid halides. I. G. Farbenind. A.-G.—See B., 1928, 151.

Transformation of diazoaminobenzene into aminoazobenzene. E. Rosenhauer and H. Unger (Ber., 1928, 61, [*B*], 392—398).—Evidence in favour of the view that the conversion of diazoaminobenzene into aminoazobenzene is due to primary fission into diazonium salt and aniline followed by nuclear coupling and not to isomerisation is found in the following observations. Dimethylaminoazobenzene is obtained from diazoaminobenzene, dimethylaniline, and dimethylaniline hydrochloride. The conversion of diazoaminobenzene into aminoazobenzene is effected by glacial acetic acid, dilute aqueous acetic acid, or formic acid in satisfactory yield. Quinoline and its hydrochloride may replace aniline and aniline hydrochloride under the conditions usually employed, but reaction then occurs much more slowly. The weak point in the explanation appears to be in the assumption of nuclear coupling. This reaction is, however, general. Thus benzenediazonium chloride and aniline hydrochloride at 0° afford aminoazobenzene hydrochloride without intermediate formation of diazoaminobenzene. Further, crude diazoaminobenzene, obtained from diazotised aniline and aniline in aqueous solution containing acetic acid, sodium carbonate, or sodium hydroxide, invariably contains about 2% of aminoazobenzene, the proportion of which increases with rise of temperature. Coupling of diazotised aniline with aniline in neutral, feebly basic, or weakly acidic solution consists of two independent changes leading respectively to diazoaminobenzene and aminoazobenzene. Increasing acidity favours the production of the latter compound, which becomes exclusive at a certain degree of acidity. Beyond this point coupling does not occur. The yields of aminoazobenzene are better when aniline hydrochloride and aniline are used than when aqueous or alcoholic solutions are employed owing to the stabilising action on the diazonium salt of the aniline and its large excess. About 70% of aminoazobenzene can be obtained in acetic acid solution if 3—4 mols. of aniline are added.

The volatility of diazoaminobenzene with steam is incidentally recorded. H. Wren.

Sulphonation of phenolic ethers by means of aminosulphonic acid. A. Quilico (Atti R. Accad. Lincei, 1927, [vi], 6, 512—517).—Like anisole (cf. Hofmann and Biesalski, A., 1912, i, 444), both phenetole and phenyl ether are converted by the action of aminosulphonic acid into the ammonium salts of the corresponding *p*-sulphonic acids. Probably the first product of the reaction is an additive compound with the hydroxyl group of the aminosulphonic acid in the 1-position and the $NH_2{\cdot}SO_2{\cdot}$ in the 2-position, this then giving the ammonium salt of the *o*-sulphonic acid, which undergoes isomerisation into the salt of the *p*-acid. *Ammonium phenoxybenzene*-p-*sulphonate*, $OPh{\cdot}C_6H_4{\cdot}SO_3{\cdot}NH_4$, the *barium* ($+H_2O$), *sodium*, and *potassium* salts, the free *acid*, m. p. 80°, the *sulphonyl chloride*, and the *sulphonamide*, m. p. 125° (? 88°), are described. T. H. Pope.

Fries' transformation. K. von Auwers [with W. Mauss] (Ber., 1928, 61, [*B*], 416—421; cf. A., 1926, 608).—The observation that *p*-chloroacetylphenol is not produced by the action of aluminium chloride at 130—140° on a mixture of phenyl acetate and *p*-tolyl chloroacetate, whereas it is relatively freely produced from phenyl chloroacetate under precisely similar conditions, is strong evidence against Skraup's conception of the course of the Fries transformation (cf. A., 1925, i, 143; 1927, 659). Attempts to prepare the *o*-ββ-dimethylacrylylphenol, m. p. 88°, of Skraup and Beng (A., 1927, 560) were unsuccessful.

Phenyl *iso*valerate is converted by aluminium chloride at 130—140° into a mixture of *o-isovalerylphenol*, b. p. 138—140°/20 mm. (p-*nitrophenylhydrazone*, m. p. 121—122°; *methyl ether*, b. p. 142—144°/12 mm.; *acetate*, b. p. 164—166°/20 mm.), and *p-iso*valerylphenol, m. p. 95·5—96·5°. Phenyl ββ-dimethylacrylate and aluminium chloride at 130—140° afford 7-*hydroxy*-3 : 3-*dimethylhydrindone*, b. p. 138—142°/16 mm., d_4^{20} 1·098, n_{He}^{20} 1·5519 (*semicarbazone*, m. p. 261—263°). *o*-Dimethylacroyl-*p*-cresol is converted by protracted boiling with acetic anhydride into the corresponding *acetate*, m. p. 63—64°; the ketone is transformed by zinc chloride at 140° into 2 : 2 : 6-trimethylchromanone, identified as the *p*-nitrophenylhydrazone, m. p. 199—200°.

H. WREN.

Nitrosation of phenols. V. An *o*-nitrosophenol. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1928, 329—332).—5 - Chloro - 3 - hydroxyanisole is readily nitrosated to dark green 5-*chloro*-4-*nitroso*-3-*hydroxyanisole*, m. p. 132°, and nitrated to 5-*chloro*-4-*nitro*-3-*hydroxyanisole* (I), m. p. 105°, which is also formed by oxidising the nitroso-derivative with alkaline ferricyanide. 3 : 5-Dichloro-2-nitroanisole and 3 : 5-dichloro-4-nitroanisole yield with sodium methoxide 5-*chloro*-2-*nitroresorcinol dimethyl ether*, m. p. 171°, and 5-*chloro*-4-*nitroresorcinol dimethyl ether*, m. p. 123°, respectively. The constitution of (I) follows from its conversion by methyl sulphate and potassium carbonate into the latter ether. Oily 5-*chloro*-3-*methoxydimethylaniline*, prepared by heating 5-chloro-3-methoxyaniline with methyl sulphate and methyl alcohol at 165°, is nitrosated to green 5-*chloro*-4-*nitroso*-3-*methoxydimethylaniline*, decomp. 155° (*hydrochloride*), which forms methylamine and products of profound decomposition when boiled with 10% potassium hydroxide.

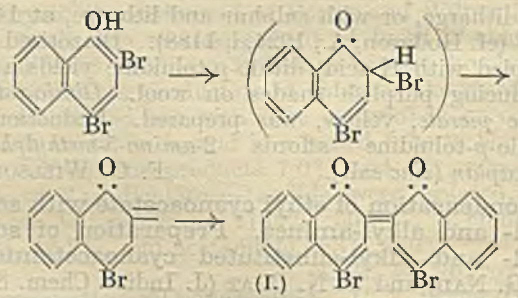
H. E. F. NOTTON.

Colour reactions of phenacetin. L. EKKERT (Pharm. Zentr., 1928, 69, 98—100).—A series of colour changes, obtained when phenacetin is warmed with resorcinol and sulphuric acid, and the mixture cooled, diluted, and treated with alkalis, with subsequent extraction, is described. S. I. LEVY.

[Preparation of] 3 : 5-dinitroanisole. F. REVERDIN (Org. Syntheses, 1927, 7, 28—29).

Action of niobium and tantalum pentachlorides on organic compounds. H. FUNK and K. NIEDERLÄNDER (Ber., 1928, 61, [*B*], 249—253; cf. Lindner and Feit, A., 1924, ii, 320).—Phenol is converted by niobium pentachloride in carbon disulphide solution and in absence of atmospheric moisture into the *compound* $Nb(OPh)_4Cl$, m. p. 233—235°; the analogous *substance* $Ta(OPh)_4Cl$, m. p. 240°, is described. β-Naphthol affords the *compounds* $Nb(O·C_{10}H_7)_3Cl_2$, m. p. 215° (apparent decomp.), $Ta(O·C_{10}H_7)_3Cl_2$, m. p. 210° (decomp.), and $Ta(O·C_{10}H_7)_5$, m. p. 180°, if the action is very prolonged. From anthranol, the *products* $Nb(O·C_{14}H_9)_2Cl_3$ and $Ta(O·C_{14}H_9)_2Cl_3$ are derived. Careful regulation of the reaction between anthranol and tantalum pentachloride permits the isolation of the unstable, primary *adduct*, $C_{10}H_{14}O,TaCl_5$, and the intermediate *product*, $Ta(O·C_{14}H_9)Cl_4$. The assumption that the metal in these compounds is united to oxygen is supported by their properties, analogies with known compounds such as those of zinc, and the established strong affinity of the metals for oxygen. H. WREN.

Formation of indigoid compounds from halogenated naphthols. R. WILLSTÄTTER and L. SCHULER (Ber., 1928, 61, [*B*], 362—372).—Halogenated α-naphthols readily pass into indigotin-like compounds owing to loss of hydrogen halide; for 2 : 4-dibromo-α-naphthol the scheme is suggested:

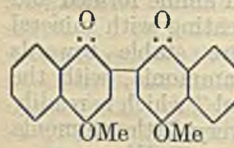


2 : 4-Dibromo-α-naphthol dissolves readily in solutions of alkali hydroxides or carbonates and an indigo-blue precipitate rapidly separates. Atmospheric oxygen takes no part in the change, but the product absorbs oxygen; it is decomposed by an excess of alkali, so that its formation is not observed in concentrated solution. It is also produced when solutions of 2 : 4-dibromo-α-naphthol in acetone, ether, or benzene are poured on to aqueous solutions of sodium carbonate or hydroxide, by contact of alcoholic solutions of the naphthol with metallic copper, and, most satisfactorily, by preserving the naphthol in cold pyridine. The *dye* does not appear to be quite homogeneous, but analyses indicate the composition $C_{20}H_{10}O_2Br_2$ (cf. I). Determinations of mol. wt. are untrustworthy, since the compound is unstable in solution. When suspended in ether and reduced with zinc dust and a little glacial acetic acid it gives *dibromo-α-dinaphthol* (constitution not decided), m. p. 219° (decomp.) (corresponding *diacetate*, $C_{24}H_{18}O_4Br_2$, m. p. 239°; *dimethyl ether*, $C_{22}H_{16}O_2Br_2$, m. p. 225—226°). α-Dinaphthol, obtained from α-naphthol and ferric chloride, is converted by bromine in glacial acetic acid solution into a *tribromo*-compound, transformed by boiling acetic acid into the dibromo-α-dinaphthol, m. p. 219—220° (decomp.). 2 : 4-Dichloro-α-naphthol is converted by alkali carbonate or hydroxide but not by pyridine into an analogous *dye*, $C_{20}H_{10}O_2Cl_2$.

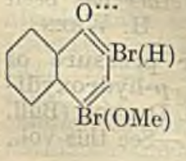
1 : 5-Dihydroxynaphthalene, in cold glacial acetic acid, is converted by chlorine into 4 : 8-*dichloro*-1 : 5-*diacetoxynaphthalene*, m. p. 154° (corr., decomp.), hydrolysed to 4 : 8-*dichloro*-1 : 5-*dihydroxynaphthalene*, m. p. 189—190° (corr.). The main product of

the action of a small excess of bromine on 1 : 5-dihydroxynaphthalene under similar conditions is the *monoacetate* of 4 : 8-dibromo-1 : 5-dihydroxynaphthalene, m. p. 165·5° (corr.), from which the *diacetate*, m. p. 131°, is obtained by pyridine and acetic anhydride. 4 : 8-*Dibromo*-1 : 5-*dihydroxynaphthalene* has m. p. 147·5° (decomp.). 4-*Bromo*-1 : 5-*dihydroxynaphthalene*, m. p. 116°, and its *diacetate*, m. p. 138°, are described. The colour reactions of certain halogenated naphthols are described in detail. 2-*Chloro*-4-*bromo*-α-*naphthol*, m. p. 112°, prepared by bromination of 2-chloro-α-naphthol, yields a blue dye with alkali hydroxide or carbonate with loss of hydrogen chloride and bromide. 4-*Chloro*-2-*bromo*-α-*naphthol*, m. p. 96°, behaves similarly to 2 : 4-dibromo-α-naphthol, but loses a little hydrogen chloride and mainly hydrogen bromide. 2-*Bromo*-1 : 4-*dihydroxynaphthalene*, m. p. 113—114°, is prepared by reduction of 2-bromo-α-naphthaquinone. H. Wren.

***oo*′-Diquinones of the naphthalene series.** S. Goldschmidt and H. Wessbecher (Ber., 1928, **61**, [*B*], 372—377).—4-Methoxy-α-naphthol dissolved in boiling benzene is readily oxidised by lead dioxide to a blue compound, m. p. 258°, for which Russig has established the formula $C_{22}H_{16}O_4$. Reduction of the product with zinc dust and glacial acetic acid in the presence of benzene affords the *leuco-compound*, $C_{22}H_{18}O_4$, m. p. 205° in an atmosphere of carbon dioxide (corresponding *diacetate*, m. p. 180°; mol. wt. 440 in boiling chloroform), readily reconverted by air into the dye, for which the quinonoid structure is thus established. Distillation of the dye with zinc dust yields two *hydrocarbons*, m. p. 257° and 175°, respectively (*picrate* of latter, m. p. 145°), which do not correspond with any of the expected products. Oxidation of the dye with nitric acid affords 2 : 2′-di-α-naphthaquinonyl, identical with the product obtained by Meldola and Hughes (J.C.S., 1890, **57**, 393, 631, 808) from 2 : 4-dibromo-α-naphthol, thus establishing the constitution (I). It is probable that the very unstable, violet-blue solutions obtained by the oxidation of α-naphthol contain *oo*′-dinaphthaquinone. Similarly, the substance obtained by the oxidation of 2 : 4-dibromo-α-naphthol by air in alkaline solution or by lead dioxide in benzene is probably constituted analogously to (I) (Br instead of OMe), since the change occurs with loss of bromine and the compound is oxidised to the product obtained by Meldola and Hughes. Reduction of it gives a leuco-compound and not the original material, and the amount of hydrazobenzene required to decolorise the violet solution is approximately that required theoretically. 4-Bromo-α-naphthol also appears to yield the same quinone. Production of *oo*′-dinaphthaquinones appears to be preceded by dehydrogenation of the naphthol to the radical (II) followed by rapid polymerisation to the bimolecular product (III). The very ready elimination of the bromine atom in position 2 can be explained only on the assumption that it is not aromatically combined during the change. It cannot be removed by powerful reducing agents from 2 : 4-dibromo-α-naphthol itself. H. Wren.



(I.)



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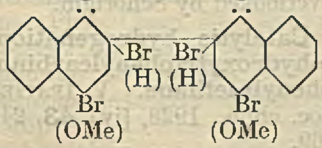


(III.)

Action of bromine on naphtholsulphonic acids. A remarkable colour reaction in solution. G. Heller [with W. Eisenschmidt, G. Reichardt, and H. Wild] (Z. angew. Chem., 1928, **41**, 171—177).—On treatment with 2 mols. of bromine in cold acetic acid solution naphthasultone gives 4-*bromonaphthasultone*, m. p. 199°; sodium naphthasultone-4-sulphonate and sodium 1-naphthol-4 : 8-disulphonate afford the same product when bromine in acetic acid is added to their aqueous solutions acidified with sulphuric acid. When treated with alkali in saturated solution in presence of excess of solid, undissolved crystals of *sodium* 2 : 4-*dibromo*-1-*naphthol*-8-*sulphonate* (obtained by brominating sodium 1-naphthol-8-sulphonate in a freezing mixture) develop a reddish-blue colour which diffuses through the solution and after some minutes fades to olive-brown. The coloration is due to the formation of the *quinhydrone* of 2-*bromo*-1 : 4-*naphthaquinone*-8-*sulphonic acid* (*sodium* salt, reddish-brown crystals with green reflex), the latter being also produced by the addition of potassium ferricyanide to the filtered solution of the dibromonaphtholsulphonate, and when the solution of sodium 1-naphthol-8-sulphonate is only cooled with ice for bromination. 1-Naphthol-2 : 4 : 8-trisulphonic acid affords the same quinhydrone. With excess of bromine (4 mols.) sodium 1-naphthol-8-sulphonate, -2 : 4 : 8-trisulphonate, and -3 : 8-disulphonate all afford *sodium* 2 : 3-*dibromo*-α-*naphthaquinone*-8-*sulphonate*, yellow, which is readily reduced to a colourless quinol, and with *p*-toluidine in alcohol yields 3-*bromo*-2-p-*toluidino*-α-*naphthaquinone*-4-p-*methylanil*-8-*sulphonic acid*, carmine-red, anthranilic acid giving an analogous *derivative*. With 1 mol. of bromine, sodium 1-naphthol-3 : 8-disulphonate gives *sodium* 4-*bromo*-1-*naphthol*-3 : 8-*disulphonate*, which couples with diazotised *p*-toluidine to give 4-*bromo*-2-p-*tolueneazo*-1-*naphthol*-3 : 8-*disulphonate*, and on treatment with a further mol. of bromine affords *sodium* 2-*bromo*-α-*naphthaquinone*-3 : 8-*disulphonate*, red needles, and traces of *sodium* 3 : 4-*dibromo*-1-*naphthol*-8-*sulphonate*, which forms no quinone. Bromination of sodium 1-naphthol-3 : 6-disulphonate gives the readily soluble *sodium* 2-*bromo*-α-*naphthaquinone*-3 : 6-*disulphonate*, yellow, which could not be obtained pure. Treatment of zinc 1-naphthol-4-sulphonate with 1 mol. of bromine affords 2-bromo-1-naphthol-4-sulphonic acid (*potassium* salt), the constitution of which follows from its inactivity towards alcoholic *p*-toluidine and diazonium salts. With a further mol. of bromine this potassium salt gives *potassium* 2 : 3-*dibromo*-1-*naphthol*-4-*sulphonate*. With 4 mols. of bromine zinc 1-naphthol-4-sulphonate gives 2-bromo-1 : 4-naphthaquinone, m. p. 127·5—128° (Zincke and Schmidt, A., 1895, i, 56), together with a little 2 : 3-dibromonaphthaquinone, m. p. 216—217°.

4-Bromonaphthasultone is converted by 10% sodium hydroxide into *sodium* 4-*bromo*-1-*naphthol*-8-*sulphonate*, which with 3 mols. of bromine gives sodium 2 : 3-dibromo-α-naphthaquinone-8-sulphonate, and with diazotised *p*-toluidine, *sodium* 4-*bromo*-2-p-*tolueneazo*-1-*naphthol*-8-*sulphonate*, analysis indicating displacement of bromine and coupling in the 4-position to a slight extent. *Sodium* 1-*naphthol*-2-p-*tolueneazo*-8-*sulphonate* is described.

Sodium 2-naphthol-6-sulphonate yields *sodium* 1-*bromo*-2-*naphthol*-6-*sulphonate* and a *dibromo*-2-*naphthol*-6-*sulphonate*. 2-Naphthol-3 : 6-disulphonic acid similarly affords mono- and di-bromo-derivatives, and 2-naphthol-6 : 8-disulphonic acid an easily soluble *sodium tribromo-2-naphtholsulphonate*. Sodium 2-naphthol-3 : 6 : 7-trisulphonate with 1 mol. of bromine gives *sodium* 1-*bromo*-2-*naphthol*-3 : 6 : 7-*trisulphonate* (sparingly soluble p-*toluidine* salt; does not couple with diazonium salts). In no case was quinone formation observed in the bromination of β-naphtholsulphonic acids. The quinone formation observed by Armstrong and Graham (J.C.S., 1881, **39**, 137) was probably due to the presence of α-naphthol in their β-naphthol. R. BRIGHTMAN.

***iso*Eugenol.** SCHIMMEL & Co. (Bericht, 1927, 138; Chem. Zentr., 1927, ii, 1472).—*iso*Eugenol was obtained in large crystals, m. p. 32°, stable at the ordinary temperature in absence of air. Structural isomerism is presumed. A. A. ELDRIDGE.

Molecular rearrangement in the *cyclo*heptane series. M. GODCHOT and (MLLE.) CAUQUIL (Compt. rend., 1928, **186**. 375—377).—Monochlorocarbamide reacts with *cyclo*heptene (cf. Detœuf, A., 1922, i, 236, 327) to form 2-*chloro*cyclo*heptanol*, b. p. 98°/16 mm., d^{19} 1·1351, n_D^{19} 1·4948, which when treated with magnesium methyl iodide (A., 1926, 164) yields *cyclo*hexylmethylcarbinol, b. p. 189·5° (corr.), together with a small amount of ethylidene*cyclo*hexane (nitrosate, m. p. 140°; nitrosochloride, m. p. 130°; *nitrosopiperidide*, m. p. 108—109°). A mechanism explaining the formation of a six- from a seven-membered ring is postulated. H. BURTON.

Colour reactions of cholesterol. L. EKKERT (Pharm. Zentr., 1928, **69**, 97—98).—The colorations obtained by treating alcoholic solutions of cholesterol with an alcoholic solution of an aldehyde and shaking with sulphuric acid are described. Using 0·1 mg. of cholesterol in 2 c.c. of alcohol, 2 drops of a 1% solution of furfuraldehyde in alcohol, and 2 c.c. of sulphuric acid, the alcohol layer becomes blue, and the acid layer rose. S. I. LEVY.

Sterol group. II. Formation of ψ-cholestene and cholestenone in the dry distillation of cholesterol. I. M. HEILBRON and W. A. SEXTON (J.C.S., 1928, 347—351).—Distillation of cholesterol in a carbon dioxide atmosphere at the ordinary pressure yields principally cholestenone and ψ-cholestene, with water, hydrogen, and a complex mixture of low-boiling hydrocarbons (cf. Diels and Linn, A., 1908, i, 164; Fischer, A., 1926, 399; Fantl and Kabos, A., 1927, 53; Windaus, A., 1927, 557). It is concluded that cholestenone and cholesterilene are the primary products, the hydrogen evolved in the formation of the former reducing the latter to ψ-cholestene. H. E. F. NOTTON.

Allophanates of certain sterols. U. TANGE and E. V. McCOLLUM (J. Biol. Chem., 1928, **76**, 445—456).—*Allophanates* of the following sterols were prepared by passing cyanic acid vapour into the cold benzene solution of the sterol; cholesterol, m. p. 235—236°, *iso*cholesterol, dihydrocholesterol, m. p. 255—256°, sitosterol, m. p. 246—247°, coprosterol, m. p. 210—211°; the esters, except that of *iso*cholesterol, are sparingly soluble in fat-solvents; they are very stable towards mineral acids but are fairly readily hydrolysed by alcoholic potassium hydroxide. C. R. HARINGTON.

Action of Grignard reagent on amino-acids. XIV. Decomposition of amino-alcohols by alkalis. F. BETTZIECHE (Z. physiol. Chem., 1928, **172**, 69—71).—The decomposition of amino-alcohols into ketone and amine by heating with alkali (cf. A., 1926, 154) has been investigated more fully. The small amount of ammonia formed under the influence of alkali at high temperatures is due to the side-reaction, $R{\cdot}CH(NH_2){\cdot}CR'_2{\cdot}OH \longrightarrow R{\cdot}CO{\cdot}CHR'_2+NH_3$, which accompanies the main reaction, $R{\cdot}CH(NH_2){\cdot}CR'_2{\cdot}OH \longrightarrow R{\cdot}CH_2{\cdot}NH_2+CO{\cdot}R'_2$. Thus two ketones, ammonia, and an amine are formed. No significant amount of ammonia is produced when the decomposition is effected by water at high temperatures and for this side-reaction alkali is necessary. The amounts of amine+ammonia, ammonia, and the different ketones formed from various aminols with sodium hydroxide are given, and a general relationship is found between the relative amounts of ammonia and amine formed and the decomposition effected by heating with mineral acids. Amino-alcohols which are stable towards mineral acids give little or no ammonia, with the exception of "glycinephenylaminol" which is readily decomposed by acid but gives very little ammonia by decomposition with alkali. A. WORMALL.

***p*-Tolyl triphenylmethyl ether and its reaction with zinc chloride.** J. VAN ALPHEN (Ber., 1926, **61**, [*B*], 276—277).—Repetition of the author's experiments (A., 1927, 660) has confirmed the production of *p*-tolyl triphenylmethyl ether, m. p. 81°, by the action of *p*-cresol on triphenylmethyl chloride in pyridine (contrast Schorigin, this vol., 59). Probably the ether is trimorphous, giving forms of m. p. 81°, 95°, and 114°, respectively. The formation of triphenylmethane in addition to triphenylcarbinol by the action of zinc chloride on the ether has been overlooked by Schorigin. H. WREN.

Catalytic hydrogenation under pressure of *p*-hydroxytriphenylcarbinol and *p*-hydroxydiphenylmethane. V. IPATIEV and B. DOLGOV (Bull. Soc. chim., 1928, [iv], **43**, 242—248).—See this vol., 169.

Action of Grignard reagent on amino-acids. XIII. Phenylserine derivatives. F. BETTZIECHE and R. MEYER (Z. physiol. Chem., 1928, **172**, 64—

68; cf. A., 1927, 137).—By the action of magnesium phenyl bromide on phenylserine ester hydrochloride, β-*amino-ααγ-triphenylpropane-αγ-diol*, m. p. 154—155°, is obtained in 40% yield (N-*benzoyl* derivative, m. p. 174·5°). Magnesium benzyl bromide and phenylserine ester hydrochloride yield β-*amino-γ-phenyl-αα-dibenzylpropane-αγ-diol*, m. p. 126·5° (yield 13%; *hydrochloride*, difficult to obtain pure, m. p. of crude product, 115°). These aminols are not decomposed to any appreciable extent by heating with 12% hydrochloric acid or 20% sodium hydroxide.

A. Wormall.

Permanganate oxidation in alkaline media. R. Cornubert and H. Le Bihan (Bull. Soc. chim., 1928, [iv], **43**, 248—255; cf. A., 1921, i, 422).—Oxidation of 2-methyl-2-allyl*cyclo*hexanone with potassium permanganate in presence of sodium or potassium hydroxide, or sodium hydroxide and calcium oxide, yields in each case a glycol, m. p. 103° (corr.), together with an oil, probably a mixture of isomeric glycols (cf. A., 1927, 1075). The solid glycol when heated for 1 hr. in a vacuum yields the corresponding ethylene oxide, also formed in small quantity during the oxidation, which exists in a monomeric form, b. p. 110°/32 mm., and also in various polymeric forms. Dilute sodium hydroxide solution has practically no action on the monomeric oxide, and it is concluded that this compound is not an intermediate in the production of the glycol.

H. Burton.

Union of benzoylacetonitrile with organic bases in presence of salicylaldehyde. II. P. Krishnamurti (J.C.S., 1928, 415—417).—In presence of traces of salicylaldehyde and piperidine, benzoylacetonitrile combines (yield 40%, 20%, and 50%, respectively, of the theoretical) with aniline, *m*-4-xylidine, and *p*-, but not *o*- or *m*-toluidine. These compounds, unlike the corresponding piperidine derivative (A., 1927, 766), easily afford dibenzoyl derivatives, and their oximino-derivatives are decomposed by benzoylation, yielding the benzoyl derivative of the amine. The p-*toluidine* compound, $C_{16}H_{16}ON_2$, m. p. 182° (*hydrochloride*, m. p. 194—195°; *dibenzoyl* derivative, m. p. 166°), gives an orange *oximino*-derivative, m. p. 158° (*silver* salt). The *aniline* compound, $C_{15}H_{14}ON_2$, has m. p. 163° (*hydrochloride*, m. p. 94—96°; *dibenzoyl* derivative, m. p. 168°; red *oximino*-derivative, m. p. 182°), and the m-4-*xylidine* compound, $C_{17}H_{18}ON_2$, m. p. 145—146° (*benzoyl* derivative, m. p. 153°; *oximino*-derivative, m. p. 150—151°).

H. E. F. Notton.

Condensation of nitriles with thioamides. VI. Action of sulphur acid chlorides on thioamides. VII. Toluonitrile with thiotoluamide, naphthonitrile with thionaphthamide, and others. S. Ishikawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 237—248, 277—292; cf. A., 1925, 917, 1149).—VI. Thionyl chloride or sulphur monochloride reacts with thiobenzamide to give benzimino-*iso*thiobenzamide, 2 : 5-diphenyl-1 : 3 : 4-thiodiazole (dibenzenylsulphime), and sulphur; and with thioacetamide to yield acetamide and sulphur. Thionyl chloride reacts with thiobenzanilide to yield dibenzanilide sulphide, m. p. 111°, and aniline; with thioacetanilide to yield acetanilide, aniline, and sulphur. Sulphur monochloride reacts with α-benznaphthalide to yield dibenznaphthalide sulphide and α-benznaphthalide; with thiobenzanilide to yield benzanilide, sulphur, and dibenzanilide sulphide. The properties of the last-named compound uphold the formula ascribed by Rivier and Schneider (A., 1920, i, 229); it is very stable towards alkalis, and easily hydrolysed by acids to thiobenzanilide and benzanilide. Treatment with mercuric oxide yields only benzanilide, whilst it is easily reduced by sodium amalgam and alcohol to phenylbenzylamine. It is suggested that an ester of thiosulphuric acid is the unstable intermediate through which it is formed. Benzenesulphonyl chloride reacts with thiobenzamide to afford 1 : 5-diphenyl-1 : 3 : 4-thiodiazole, sulphur, and a red condensation compound; with thiobenzanilide to form dibenzanilide sulphide; with sodium thiobenzanilide to form benzenesulphonyl monosulphide, m. p. 101—102°, and benzenesulphonyl trisulphide, m. p. 133°. Hydrogen sulphide was detected in the last condensation only.

VII. Since the condensation of benzonitrile with *p*-thiotoluamide in the presence of hydrogen chloride proceeds normally to afford *benzimino*-p-iso*thiotoluamide* (*hydrochloride*, m. p. 132°; *picrate*, m. p. 116°; oxidised by iodine to *phenyl*-p-*tolyl*-1 : 3 : 4-*thiodiazole*, m. p. 56°), whereas a similar experiment with *p*-toluonitrile and thiobenzamide affords benzonitrile and the same benzimino-*p*-*iso*thiotoluamide, it is suggested that, in the latter condensation, an interchange of the aryl radicals takes place through the intermediate formation of the unstable di-iminosulphides, only part of which are converted into the benzimino-compound. The following condensations confirm this view: *p*-toluonitrile and *p*-thiotoluamide yield p-*toluimino*-p-iso*thiotoluamide*, m. p. 108° [*hydrochloride*, m. p. 161°; *picrate*, m. p. 160°; action of ethyl iodide affords S-*ethyl*-p-*toluimino*-p-iso*thiotoluamide hydriodide*, m. p. 154° (free base decomposes to give mercaptan and tri-*p*-tolylguanidine); 2 : 5-*di*-p-*tolyl*-1 : 3 : 4-*thiodiazole*, m. p. 129° (*hydrochloride*, m. p. 161°)]; *m*-toluonitrile and *m*-thiotoluamide yield m-*toluimino*-m-iso*thiotoluamide* (23%), m. p. 58° [*hydrochloride*, m. p. 114°; *chloroplatinate* (not obtained pure), m. p. about 121°; S-*ethyl*-m-*toluimino*-m-iso*thiotoluamide hydriodide*, m. p. 136° (corresponding *picrate*, m. p. 145°); corresponding *thiodiazole*, m. p. 49·5°]. The *S*-ethyl compound can be reduced by alcoholic hydrogen chloride and zinc to m-*methylbenzyl*-m-*toluamidine hydrochloride*, m. p. 199°.

p-Toluonitrile and *m*-thiotoluamide, β-naphthonitrile and thiobenzamide, and α-naphthonitrile and thioacetamide yield typical condensation compounds which were not further examined; benzonitrile and *m*-thiotoluamide yield probably a mixture of the possible products, from which a *hydrochloride*, m. p. 135° [corresponding *picrate* (B_2A), m. p. 140°; *hydrobromide*, m. p. 136°; corresponding *thiodiazole picrate*, m. p. 88°)], is obtained; *m*-toluonitrile and thiobenzamide yield a similar mixture from which a *hydrochloride*, m. p. 135°, a *hydrobromide*, m. p. 136°, and a *picrate*, m. p. 140°, are isolated.

G. A. C. Gough.

Condensation of nitriles with thio-acids. I. S. Ishikawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 7, 293—300).—These condensations, carried out in ether saturated with hydrochloric acid, result in the production of the thio-amide from the nitrile and of the normal acid chloride from the thio-acid, together with the secondary condensation products of these substances. It is suggested that the reaction proceeds through the intermediate formation of a compound of the type R·C(:NH)·S·CO·R. In this way benzonitrile and thioacetic acid yield thiobenzamide, benziminoisothiobenzamide, and acetic acid; *p*-nitrobenzonitrile and thioacetic acid yield *p-nitrothiobenzamide*, m. p. 157°; *m*-nitrobenzonitrile and thioacetic acid yield *m-nitrothiobenzamide*, m. p. 130—131°; benzonitrile and thiobenzoic acid yield benzamide, benziminoisothiobenzamide, and benzoyl chloride. Nitriles react with hydrogen sulphide in ethereal hydrogen chloride to afford the aryliminoisothioarylamides, through the intermediate formation of the diarylimino-sulphide. Thus benzonitrile gives benziminoisothiobenzamide, also produced under similar conditions by the use of potassium, calcium, or zinc sulphide; and β-naphthonitrile gives β-thionaphthamide. G. A. C. Gough.

Action of metallic salts on thioamides and their derivatives. I. Mercuric chloride in ethereal solution. S. Ishikawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 7, 301—312).—Mercuric chloride additive *compounds* of the type $B_2,HgCl_2$, are quantitatively formed when ethereal solutions of the following thioamides are titrated with ethereal mercuric chloride: thiobenzamide, m. p. 194—197° (decomp. with the liberation of mercuric chloride and hydrogen sulphide); *m*-thiotoluamide, m. p. 183—186° (decomp.); *p*-thiotoluamide, m. p. 191—194° (decomp.); *m*-nitrothiobenzamide, darkening at 206°; *p*-nitrothiobenzamide, m. p. 183° (decomp.); thioacetamide, m. p. 183°; phenylthioacetamide, m. p. 160° (decomp.); α-thionaphthamide, m. p. 184° (decomp.); β-thionaphthamide, m. p. 221° (decomp.); thiobenzanilide, m. p. 100—101° (re-solidifying at about 180° and unmelted at the b. p. of sulphuric acid); α-thioacetonaphthalide, decomp. 222° (previous darkening); β-thioacetonaphthalide, decomp. 225° (with previous darkening). β-*Thiobenznaphthalide mercuric chloride* has m. p. 184—187°. The following form additive compounds of the type $B,HgCl_2$: benziminoisothiobenzamide, m. p. 149° (decomp.): *p*-toluimino-*p*-isothiotoluamide, m. p. 118° (decomp. 163°); *m*-toluimino-*m*-isothiotoluamide, m. p. 110° (changing to a yellow solid at 159°); *acetophenonethiosemicarbazone mercuric chloride.* The first-named is decomposed by potassium hydroxide into potassium chloride, mercury, water, and the thiodiazole. G. A. C. Gough.

***p*-Iodobenzoic acid.** F. C. Whitmore and (Miss) G. E. Woodward (Org. Syntheses, 1927, 7, 58—59).—*p*-Iodobenzoic acid is prepared in 72—81% yield by the interaction of *p*-chloromercuribenzoic acid and iodine in alcoholic solution. A. A. Eldridge.

2-Bromo-3-nitrobenzoic acid. P. J. Culhane (Org. Syntheses, 1927, 7, 12—14).—Interaction of anhydro-2-hydroxymercuri-3 nitrobenzoic acid, sodium bromide, and bromine, under conditions described in detail, produces sodium 2-bromo-3-nitrobenzoate. A. A. Eldridge.

Constitution of elemic acid. K. H. Bauer (Ber., 1928, 61, [*B*], 343—344).—Determination of the iodine value of α-elemic acid, $C_{27}H_{42}O_3$ (cf. Tschirch and Cremer, A., 1902, i, 812; Buri, A., 1878, ii, 439; Lieb and Schwarzl, A., 1924, i, 1312), indicates the presence of a double linking which is confirmed by its catalytic hydrogenation in alcohol in presence of palladised kieselguhr to *dihydroelemic acid*, $C_{27}H_{44}O_3$, m. p. 238°. The *methyl* esters of elemic and dihydroelemic acid could not be caused to crystallise. H. Wren.

Addition of bromine to ethylenic compounds in non-hydroxylic solvents. D. M. Williams and T. C. James (J.C.S., 1928, 343—347; cf. Sudborough and Thomas, J.C.S., 1910, 97, 715, 2450).—Three distinct types of reaction have been observed in dilute solutions in dry chloroform or carbon tetrachloride at 13° in the dark: (*a*) Addition to *cis*- and *trans-o*-methoxycinnamic acids, cinnamylideneacetic acid and its methyl ester, α-phenylcinnamylideneacetic acid, β-furfurylacrylic acid, oleic acid, and elaidic acid proceeds rapidly and is accompanied by substitution and formation of hydrogen bromide. The bimolecular velocity coefficient decreases as the reaction proceeds. (*b*) After an inhibition period addition to cinnamic acid, its methyl ester, crotonic acid, and methyl cinnamylidenemalonate proceeds slowly with increasing velocity. (*c*) No measurable addition to maleic anhydride, coumarin, and α-phenylcinnamonitrile is observed under these conditions. Reactions of type (*a*) are probably catalysed by the hydrogen bromide formed, since addition of this substance greatly accelerates those of type (*b*). In each case the inhibition period disappears and the reaction becomes bimolecular. Water and hydrogen chloride are less efficient catalysts. Reactions of type (*c*) are not accelerated by these substances. H. E. F. Notton.

Isomerism of phenylphthalimide [phthalanil] and a study of the nitro- and chloro-derivatives. M. L. Sherrill, F. L. Schaeffer, and E. P. Shoyer (J. Amer. Chem. Soc., 1928, 50, 474—485).—By extraction with chloroform, Gabriel and Thorpe's "phthalanilic acid," m. p. 192° (cf. A., 1893, i, 466), can be separated into phthalanil (soluble) and phthalanilic acid, m. p. 169°. It is also shown that whilst van der Meulen's phthalphenylisoimide is the true *as*-phenylphthalimide (A., 1897, i, 414), Kuhara's βα-phenylphthalimide is a mixture of phthalphenylisoimide and phthalanilic acid (cf. A., 1911, i, 205), and his α-phenylphthalimide is a mixture of the normal and isophthalanils. The "*p*-isonitrophenylphthalimide" of Kuhara and Dobreff (A., 1895, i, 360) is identical with *p*-nitrophthalanilic acid (*ammonium* salt; *disilver* salt, brown); the "*m*-isonitrophenylphthalimide" is a mixture of *m*-nitrophenylphthalamide and *m*-nitrophenylphthalimide, whilst the "*o*-isonitrophenylphthalimide" is *o*-nitrophthalanilic acid, contaminated with *o*-nitrophthalanil and *o*-nitroaniline hydrochloride. *p*-Chlorophthalanilic acid is obtained by treatment of *p*-chloroaniline with phthalic anhydride in chloroform. m-*Chlorophthalanilic acid*, m. p. 183—184° (decomp.), and o-*chlorophthalanilic acid*, m. p. 147—148°, decomp. 155°, obtained analogously, are described. Fusion of phthalic anhydride with chloroanilines affords the respective *o*-, m. p. 132—140°, *m*-, m. p. 183—184° (decomp.), and *p*-chlorophenylphthalimide (cf. Gabriel, A., 1879, 323). F. G. WILLSON.

[Preparation of] 3-nitrophthalic acid. P. J. CULHANE and (MISS) G. E. WOODWARD (Org. Syntheses, 1927, 7, 70—72).

[Preparation of] 3-nitrophthalic anhydride. B. H. NICOLET and J. A. BENDER (Org. Syntheses, 1927, 7, 74—75).

[Preparation of] ethyl phthalimidomalonate. A. E. OSTERBERG (Org. Syntheses, 1927, 7, 78—79).

[Preparation of] β-bromoethylphthalimide. P. L. SALZBERG and J. V. SUPNIEWSKI (Org. Syntheses, 1927, 7, 8—10).

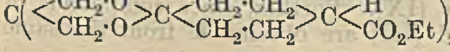
[Preparation of] α-cyano-β-phenylacrylic acid. A. LAPWORTH and W. BAKER (Org. Syntheses, 1927, 7, 20—22).

[Preparation of] diphenic acid. E. H. HUNTRESS (Org. Syntheses, 1927, 7, 30—33).—Vorländer and Meyer's method is applied to the preparation of large quantities. A. A. ELDRIDGE.

Hydroxyamino-acids. II. F. BETTZIECHE and R. MENGER (Z. physiol. Chem., 1928, **172**, 56—63; cf. A., 1926, 154).—*Benzoylphenylserine* (*α-benzamido-β-hydroxy-β-phenylpropionic acid*), m. p. 158°, when subjected to steam distillation in 8% sodium hydroxide yields benzaldehyde, benzoic acid, and glycine, but no ammonia or hippuric acid. *Hippurylphenylserine* (*α-hippurylamino-β-hydroxy-β-phenylpropionic acid*), m. p. 143°, in the same way yields benzoic acid, benzaldehyde, glycine, and traces of hippuric acid, but no ammonia; thus no splitting of the acid into hippurylamide and phenylpyruvic acid occurs. Toluenesulphonylphenylserine when heated with 3% sodium hydroxide for 5 hrs. at 200° is partly decomposed into benzaldehyde and toluenesulphonylglycine and partly into toluenesulphonamide and phenylpyruvic acid, the products of both changes being isolated; the yields, however, are minimal on account of the high temperature. By the action of benzoyl chloride on benzoylphenylserine in sodium hydrogen carbonate solution, the azlactone of benzamidocinnamic acid is formed and not the diacyl compound, which has not yet been obtained. The azlactone of benzamidocinnamic acid does not react with ethyl alcohol, but with methyl alcohol an almost quantitative yield of the *methyl* ester of the azlactone, m. p. 140°, is obtained. Benzamidocinnamic acid, in contrast with its azlactone, is indifferent to both methyl and ethyl alcohols.

A. WORMALL.

Triple spiran. P. PFEIFFER and P. BACKES (Ber., 1928, **61**, [*B*], 434—435).—Pentaerythritol is converted when heated with ethyl *cyclo*hexanone-4-carboxylate into the triple *spiran*



$\mathrm{C}\left(<\begin{matrix}\mathrm{CH_2\cdot O}\\ \mathrm{CH_2\cdot O}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{H}\\ \mathrm{CO_2Et}\end{matrix}\right)_2$, m. p. 139·5—140·5°, which is expected to afford an example of molecular asymmetry. H. WREN.

Auto-oxidation of benzaldehyde. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 286—300; cf. A., 1926, 519).—The oxidation of benzaldehyde to perbenzoic acid has been studied, using various metals and solvents. Iron powder considerably accelerates the oxidation, tin and aluminium powders having no particular accelerating action. On exposing benzaldehyde dissolved in acetone, carbon tetrachloride, benzene, or chloroform to diffuse light or to sunlight in the presence of oxygen, the formation of varying quantities of perbenzoic acid was observed, a conversion of 43% (determined by oxidation of iodide) being recorded with acetone solution. No perbenzoic acid was formed in pyridine solution. The oxidation of benzaldehyde in benzene solution produced a substance of sharp, penetrating odour and having the properties of a peroxide. The auto-oxidation being assumed as taking place in two stages: (i) $\mathrm{Ph\cdot CHO} \longrightarrow \mathrm{Ph\cdot CO_3H}$, (ii) $\mathrm{Ph\cdot CO_3H+Ph\cdot CHO} \longrightarrow \mathrm{Ph\cdot CO_2H}$, stabilisation of the intermediate product was necessary; acetone gave the best results (63·4% yield). A dilution of 10 vols. of benzaldehyde in 80 vols. of acetone should not be exceeded; the yield is then about 50%. Admission of water to the reaction greatly decreases the yield. Pure perbenzoic acid was obtained by oxidising a 10% acetone solution of benzaldehyde with oxygen until absorption ceased. After removal of acetone by distillation, the peroxide was isolated either by distillation at low pressure, or by removal of benzoic acid from the acetone solution with dilute sulphuric acid, followed by extraction with chloroform.

By oxidising benzaldehyde in carbon tetrachloride solution, it is shown that perbenzoic acid is not the first product of oxidation, since carbonyl chloride, hydrogen chloride, and carbon dioxide are formed. R. A. PRATT.

Auto-oxidation of benzaldehyde in presence of acetic anhydride. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 301—308).—Equal volumes of benzaldehyde and acetic anhydride were mixed with the addition of one drop of phosphorus trichloride as catalyst, the mixture being kept over-night at a low temperature in the dark. Snow-white crystals of benzylidene diacetate, m. p. 40°, were formed in large yield. M.-p. curves, obtained by a method avoiding oxidation of benzaldehyde, were determined after the mixtures had been kept for 62 hrs. in an atmosphere of carbon dioxide. Two maxima were found, one corresponding with the *compound* $\mathrm{2Ph\cdot CHO,Ac_2O}$, m. p. about 17°, and the other with $\mathrm{Ph\cdot CHO,Ac_2O}$, m. p. 40°. Despite attempts to isolate the new compound in the pure state, it was impossible to preserve a solid substance with m. p. other than 45—46°. Apparently the new compound decomposes during purification into benzylidene diacetate and benzaldehyde. The addition of a trace of phosphorus trichloride to the pure diacetate, the reaction mixture being kept for some months in a sealed glass tube, also produces a compound of m. p. 40°, indicating that the reaction benzaldehyde+

acetic anhydride $\rightleftharpoons$ benzylidene diacetate proceeds to an equilibrium. R. A. PRATT.

Mechanism of substitution of bromine in aromatic hydrazones. II. M. VANGHELOVICI (Bul. Soc. Chim. România, 1927, **9**, 59—67).—Bromination or chlorination of the phenylhydrazones of aromatic aldehydes occurs in accordance with the scheme $CHPh{:}N{\cdot}NHPh \longrightarrow CHPh{:}N{\cdot}NH{\cdot}C_6H_4X(p) \longrightarrow CHPh{:}N{\cdot}NH{\cdot}C_6H_3X_2(2:4) \longrightarrow [CHXPh{\cdot}NX{\cdot}NH{\cdot}C_6H_3X_2] \longrightarrow CXPh{:}N{\cdot}NH{\cdot}C_6H_3X_2$ (X=Br or Cl), since the third halogen atom readily reacts with potassium cyanide to yield the corresponding cyano-derivative or with phenylhydrazine to yield intensely coloured azo-derivatives which are not isolated. The product, m. p. 114°, obtained by bromination of benzaldehydephenylhydrazone in glacial acetic acid has the structure $CBrPh{:}N{\cdot}NH{\cdot}C_6H_3Br_2$ (I), and is not p-*bromobenzaldehyde*-2 : 4-*dibromophenylhydrazone* as stated by Ciusa (A., 1916, i, 437). The latter, m. p. 125·5°, is synthesised from *p*-bromobenzaldehyde and 2 : 4-dibromophenylhydrazine. By treatment with potassium cyanide in boiling alcohol (I) yields α-*cyanobenzylidene*-2 : 4-*dibromophenylhydrazine*, m. p. 138°. By similar methods are prepared *salicylidene*-p-*bromophenylhydrazine*, m. p. 175°; α-*bromobenzylidene*-2-*bromo*-4-*nitrophenylhydrazine*, m. p. 169°; α-*chlorobenzylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 87°, from which is obtained α-*cyanobenzylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 128°; α-*chloroanisylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 111°; the corresponding α-*cyano*-derivative, m. p. 150°.

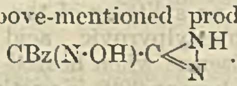
J. W. BAKER.

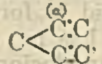
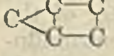
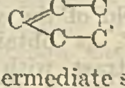
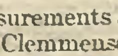
Nitration of benzaldoxime and some derivatives. O. L. BRADY and B. E. M. MILLER (J.C.S., 1928, 337—342).—With nitric and sulphuric acids at 0° and 5°, respectively, benzaldoxime and its *N*-methyl derivative give exclusively *m*-nitro-derivatives, the yields being diminished by hydrolysis and oxidation. α-*O*-Methylbenzaldoxime is attacked by nitrating agents only with difficulty, even on warming, giving small amounts of the *m*-nitro-derivative. The absence of *o*- and *p*-derivatives is in accordance with Vorländer's rule (A., 1919, i, 319), but not with the suggestion of Ingold (Ann. Reports, 1926, **23**, 131; A., 1927, 236) that introduction of unsaturated carbon atoms between a positive pole and the nucleus should decrease the *m*-directing effect. When other strongly directive groups are present, nitration occurs more readily and the orienting effect of the aldoximino-group is not apparent. Thus, α-4-methoxybenzaldoxime yields a 3-nitro-derivative, and its *O*-methyl ether a 3-nitro- and a 3 : 5-*dinitro*-, m. p. 129°, derivative; α-3 : 4-methylenedioxybenzaldoxime and its *O*-methyl ether give 6-nitro-derivatives and α-4-hydroxy-3-methoxybenzaldoxime gives quantitatively a 5-nitro-derivative. H. E. F. NOTTON.

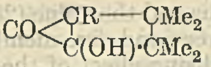
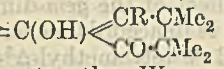
Dioximes. XLVI. G. PONZIO and C. CERRINA (Gazzetta, 1928, **58**, 26—35).—By the action of ammonia solution on dibenzoylglyoxime peroxide, Holleman (A., 1893, i, 206) obtained a substance, $C_9H_7O_3N_3$, (I), m. p. 135°, which Böeseken and van Lennep (A., 1912, i, 723) regarded as 5-amino-3-benzoyl-1 : 2 : 4-oxadiazole. The product (II) of the action of potassium ethoxide on (I) was considered to be the 5-hydroxy-compound. The latter has, however, been prepared (Ponzio, A., 1926, 1159), and has different properties. Actually, the action of ammonia solution in the cold yields benzamide and α-*benzoylaminoglyoxime*, m. p. 127° (decomp.), which forms a *silver* salt (explodes about 130°), and a *dibenzoyl* derivative $CBz(N{\cdot}OBz){\cdot}C(N{\cdot}OBz){\cdot}NH_2$, m. p. 158—159°; some 5-hydroxy-3-benzoyl-1 : 2 : 4-oxadiazole and benzoylmetazonic acid are also formed. On heating the above α-compound with dilute acetic acid, β-*benzoylaminoglyoxime*, m. p. 187° (decomp.), is obtained; the precipitates with nickel and copper acetate are described, as is the *dibenzoyl* derivative, m. p. 198°.

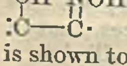
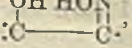
The compound (I) is obtained by the first-mentioned reaction only when the temperature rises, or by the action of acetic anhydride in the cold on the α-compound, or by heating the α- or the β-compound with ammonia solution; it is to be regarded as 3-amino-4-benzoyl-1 : 2 : 5-oxadiazole (derived through the intermediate formation of benzoyloximinoacetonitrile oxide). Its N-*oxide* ("benzoylaminoglyoxime peroxide"), m. p. 145° (decomp.), from which it can be obtained by reduction, is prepared by oxidation of α-benzoylaminoglyoxime by, *e.g.*, bromine water. Contrary to the statement of Böeseken, the compound (I) easily yields a *benzoyl* derivative, m. p. 139—140°.

Similarly, di-*p*-toluoylglyoxime peroxide yields α- and β-p-*toluoylaminoglyoximes*, m. p. 114° and 188° (each decomp.), respectively. 3-*Amino*-4-p-*toluoyl*-1 : 2 : 5-*oxadiazole* N-*oxide* ("*p*-toluoylaminoglyoxime peroxide") has m. p. 145° (decomp.), and can be reduced to the oxadiazole. The compounds regarded by Böeseken as 5-amino-3-*p*-toluoyl- and -3-*p*-anisoyl-1 : 2 : 4-oxadiazoles, m. p. 165° and 144° respectively, are renamed 3-amino-4-*p*-toluoyl- and -4-*p*-anisoyl-1 : 2 : 5-oxadiazoles.

The above-mentioned product (II) may have the structure  $CBz(N{\cdot}OH){\cdot}C{<}\begin{smallmatrix}NH\\ |\\ N\end{smallmatrix}$. E. W. WIGNALL.

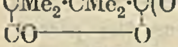
Possibility of ring-chain valency tautomerism, and of a type of mobile-hydrogen tautomerism analogous to the Wagner–Meerwein re-arrangement. I. Derivatives of phorone. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1928, 365—410).—Further evidence (cf. Francis and Willson, *ibid.*, 1913, **103**, 2238) is adduced to show that, whilst phorone has an open-chain structure (I)  $C{<}\begin{smallmatrix}\overset{(\alpha)}{C}{:}C\\ C{:}C\end{smallmatrix}$, its acyloxy- and alkyloxy-derivatives have cyclic formulæ, (II)  $C{<}\begin{smallmatrix}C-C\\ |\quad\ |\\ C-C\end{smallmatrix}$ or (III)  $C{\leqslant}\begin{smallmatrix}C-C\\ \quad\ |\\ C-C\end{smallmatrix}$, and its halogeno-derivatives are in an intermediate state, (IV)  $C{<}\begin{smallmatrix}C{=}C\\ |\\ C{=}C\end{smallmatrix}$. A formula of type (IV) for dichloro- and dibromophorone is favoured by refractivity measurements and by the reduction of the latter by Clemmensen's method to phorone and deoxyphorone, and by phosphorus and hydriodic acid to 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone (IX). Further, since compounds of types (II) and (III) are obtainable from the same

hydroxyphorone, the latter must be capable of a tautomerism, 
$\mathrm{CO}{<}\begin{array}{l}\mathrm{CR{-}{-}CMe_2}\\ \mathrm{C(OH){\cdot}CMe_2}\end{array}$ (V, R=Br; VI, R=H)$\rightleftharpoons$ 
$\mathrm{C(OH)}{<}\begin{array}{l}\mathrm{CR{\cdot}CMe_2}\\ \mathrm{CO{\cdot}CMe_2}\end{array}$ (VII, R=Br; VIII, R=H), similar to the Wagner–Meerwein transformation. The electronic interpretation of these and analogous reactions is discussed, and it is shown that the tendency of a phorone derivative to undergo the changes (I) ⟶ (IV) ⟶ (II), which are accompanied by a decrease in unsaturation and visible colour, and by depression of the mol. refractivity and parachor (cf. Sugden, this vol., 416), runs parallel with the *op*-directing power in aromatic substitution of the group in position (*a*). The structure of the ketone (IX) (cf. Farmer and Kracovski, A., 1927, 447) has been confirmed by its synthesis by heating βγ-dibromo-βγ-dimethylbutane and ethyl acetonedicarboxylate with sodium ethoxide and hydrolysing the product with hydrochloric acid. It gives a *di*-3 : 4-*methylenedioxybenzylidene* derivative, m. p. 125°, and a 2 : 5-*dioximino*-derivative, m. p. 223°, which is hydrolysed by hydrochloric acid in presence of formaldehyde to oily *tetramethyl*cyclo*pentane*-1 : 2 : 3-*trione* (*trioxime*, m. p. 168—169°). The ketone (IX) absorbs bromine (3 mols.) in anhydrous solvents, forming probably 2 : 5-dibromo- and 2 : 2 : 5-tribromo-3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone. The latter is decomposed by water to bromohydroxyphorone (V) or (VII) (d-*bromocamphorsulphonyl* derivative, m. p. 150°; p-*nitrobenzyl ether*, m. p. 111°). This is reduced by zinc dust and acetic acid to the hydroxyphorone (VI) or (VIII) and the products of direct alkylation and acylation of the latter are also preparable by this method from the corresponding derivatives of (V) or (VII). The ethers and esters described below fall into two groups, (i) derivatives of (V) or (VI), which are fairly stable towards reduction, oxidation, and bromination, and (ii) derivatives of (VII) or (VIII), which yield dihydro-derivatives and are easily oxidised and brominated.

(i) Bromohydroxyphorone does not form ketonic derivatives, but hydroxyphorone (VI) gives a *semicarbazone*, m. p. 211—213°, an *anil*, m. p. 104°, a p-*dimethylaminoanil*, m. p. 90°, and an α-*oxime*, m. p. 96° [*monohydrate*, m. p. 76°; *sodium* salt, m. p. 200° (decomp.); *hydrochloride*, m. p. 189—190° (also +CCl$_4$, m. p. 174—175°); *benzoyl* derivative, m. p. 134—135°], which is converted by cold ethereal hydrogen chloride into the *hydrochloride*, m. p. 69—70°, of a β-*oxime*, m. p. 114—115°. The α- and β-forms are readily interconvertible, and since the latter gives by the Beckmann reaction a *substance* [(?) 2 : 3-*diketo*-4 : 4 : 5 : 5-*tetramethylpiperidine*], m. p. 113°, not identical with ααββ-*tetramethylglutarimide*, m. p. 200—202°, they are probably stereoisomerides, 
$\begin{array}{ll}\mathrm{OH} & \mathrm{NOH}\\ \mathrm{:C{-}{-}} & \mathrm{C{\cdot}}\end{array}$ and 
$\begin{array}{ll}\mathrm{OH} & \mathrm{HON}\\ \mathrm{:C{-}{-}{-}} & \mathrm{C{\cdot}}\end{array}$, respectively. The α-oxime is shown to be a derivative of (VI) by its reduction by sodium amalgam and acetic acid or palladium and hydrogen to 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentylamine*, m. p. 100—102° [*picrate*, m. p. 255°; *chloroaurate*, m. p. 230° (decomp.); *hydrochloride*, m. p. 308° (decomp.); *acetyl* derivative, m. p. 95°], which is obtained by the same methods from 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanoneoxime*, m. p. 107° (*hydrochloride*, m. p. 119°), or its *acetyl* derivative. On further treatment with hydroxylamine, the α-oxime yields 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentane*-1 : 2-*dionedioxime*, m. p. 211°, dehydrated by heating with aqueous ammonia to a *furazan*, m. p. 209°. The hydroxyketone (VI) and *o*-phenylenediamine yield in boiling glacial acetic acid a *quinoxaline*, $C_{15}H_{18}N_2$, m. p. 100°. The benzoate (X) of hydroxyphorone (VI) is converted by hydroxylamine into the (γ)-*oxime* (2-*oximino*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*), m. p. 115°, of (VIII), which is also formed on regulated nitrosation of the ketone (IX) in chloroform. In methyl-alcoholic solution (IX) yields a δ-*oxime*, m. p. 170—172° (*monohydrate*, m. p. 83°; *sodium* salt, m. p. 200°), which is probably stereoisomeric with the γ-oxime, since it affords with hydrochloric acid and formaldehyde ααββ-tetramethylglutaric acid. The γ-oxime is converted by hydroxylamine into the above dioxime, m. p. 211°, by sodium and alcohol into (?) 5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentylamine*, isolated as the *picrate*, m. p. 220—221°, and by the Beckmann reaction into (?) 2 : 3-*diketo*-5 : 5 : 6 : 6-*tetramethylpiperidine*, m. p. 200°. If the oximino-group directly displaces the benzoyl group in (X), the latter has thus been shown to be a derivative of (VI). Bromohydroxyphorone is converted by sodium ethoxide and *p*-bromobenzyl bromide into an oily *by-product* (XI) and the p-*bromobenzyl ether*, m. p. 65°, of (V), which is reduced by zinc dust and acetic acid to the p-*bromobenzyl ether*, m. p. 86°, of (VI). This is fairly stable towards bromine and alkaline permanganate and does not yield a dihydro-derivative (cf. the methyl ether, below). With boiling hydriodic acid it gives (IX) and with ozone, bromine, and an ozonide which is hydrolysed to *p*-bromobenzaldehyde and tetramethylsuccinic acid. The *acetyl* derivative, m. p. 84°, of its *oxime*, m. p. 175° (*hydrochloride*, m. p. 133°), is reduced to (?) 2-*hydroxy*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentylamine* [*picrate*, m. p. 215° (decomp.)], besides neutral *substances*, m. p. 161—162°, and oils. 1-*Cyano*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (V or VII, R=CN) has m. p. 172—173°.

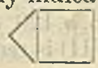
(ii) The constitution of the acetate (1-bromo-5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*penten-4-one) (Francis and Willson, *loc. cit.*) of bromohydroxyphorone is established as follows: it is reduced by zinc and acetic acid, first to 5-*acetoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*, b. p. 120°/15—16 mm., d_4^{20} 1·0190, n_D^{20} 1·4549, then to 5-*acetoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (XII), b. p. 127°/15—16 mm. (hydrolysed to a *hydroxyketone*, $C_9H_{16}O_2$, m. p. 140°), and by sodium amalgam and acetic acid to 2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (XIII), b. p. 100°/16 mm., m. p. 119° (*semicarbazone*, m. p. 222°), and a little of the isomeride (IX). The *oxime*, m. p. 101—102° (*hydrochloride*, m. p. 125°), of (XIII) is reduced by sodium and alcohol to 2 : 2 : 3 : 3-*tetramethyl*cyclo*pentylamine* (XIV) (*picrate*, m. p. 242—243°; *acetyl* derivative, m. p. 115°), which is also obtained by oximation and reduction from (XII). Similarly, the *methyl ether* (1-*bromo*-5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*), b. p. 120°/14 mm., n_D^{20-21} 1·5131—1·5147, d_4^{20} 1·3159, of (VII) is reduced by zinc dust and acetic acid to 5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*, m. p. (on one occasion) 37°, b. p. 112—115°/21 mm., n_D^{19} 1·4687 [reducible through its *oxime*, b. p. 140—150°/22 mm. to (XIV)], and to 5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone*, b. p. 88—90°/10 mm., n_D^{19} 1·4580, which is reduced by hydriodic acid to (IX) and through its *oxime* to (XIV). The by-product (XI) appears to contain the *p*-bromobenzyl ether of (VII), since it is reduced by zinc and acetic acid to a substance, the oxime of which is reduced by sodium and alcohol to (XIV).

The oxidation and halogenation of bromohydroxyphorone are best explained in terms of formula (VII). With sodium perchlorate and osmium tetroxide it affords the lactonic acid (XV) of γγ-dihydroxy-ααββ-tetramethylglutaric acid and the lactonic acid (*dilactone anhydride*, m. p. 177—178°) of γ-hydroxy-ααββ-tetramethylglutaric acid. The methyl ether of (VII) is ozonised to bromine and ozonides which yield on hydrolysis a product containing the *lactonic* ester,



$CMe_2{\cdot}CMe_2{\cdot}C(OH){\cdot}CO_2Me$ / CO——O

, b. p. 155—165°/13 mm., and its *methyl ether*, m. p. 103°, previously regarded by Rothstein and Shoppee (A., 1927, 447) as methyl γ-keto-ααββ-tetramethylglutarate. The acetate of (VII) does not yield bromine when ozonised; it is oxidised by permanganate to (XV). Hydroxyphorone (VI) or (VIII) and the ketone (XIII) are both oxidised to ααββ-tetramethylglutaric acid. The constitution, 1 : 1 - dibromo - 2 : 2 : 3 : 3 - tetramethyl*cyclo*pentanedione, proposed by Francis and Willson for the bromination product of (VII) is supported by the observation that chlorination of (VII) and bromination of 1-*chloro*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (V or VII, R=Cl), m. p. 116° (*acetyl* derivative, m. p. 47°), yield the same 1-*chloro*-1-*bromo*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione*, m. p. 178°, which is reduced by carbamide to the chlorohydroxy-derivative. The close similarity between dibromo-, chlorobromo-, and 1 : 1-*dichloro*-, m. p. 187°, -tetramethyl*cyclo*pentanediones indicates that they are analogously constituted. H. E. F. NOTTON.

Parachor and chemical constitution. VIII. Ring-chain valency tautomerism in phorone derivatives. S. SUGDEN (J.C.S., 1928, 410—415).—The constitutions assigned to these derivatives on chemical grounds by Ingold and Shoppee (this vol., 414) are, in general, confirmed. The parachor and the calculated value for the formula, $CMe_2{:}CR{\cdot}CO{\cdot}CR'{:}CMe_2$, with two non-polar double linkings, are given for the following compounds: (*a*) phorone, 367·9, 372·2; (*b*) dichloro-, 427·7, 446·6; (*c*) dibromo-, 463·2, 474·0; (*d*) acetoxy-, 459·4, 476·0; (*e*) bromoacetoxy-, 506·4, 526·9; (*f*) bromomethoxy-, 455·3, 482·1; (*g*) benzoyloxy-, 583·9, 609·9; (*h*) bromobenzoyloxy-, 642·4, 660·8; (*i*) *p*-bromobenzyloxy-, 630·7, 655·0; (*j*) bromo-*p*-bromobenzyloxy-, 684·0, 705·9, also for distyryl ketone, 564·5, 562·0, and αα'-dibromodistyryl ketone, 650·7, 663·8. Thus, (*a*) agrees well with an open-chain structure, whereas the maximum deviations at (*f*), (*g*), and (*i*) probably indicate complete conversion into the dicyclic form  . The mean structural constant for this system is therefore 20·7. The difference between this and the value (25·2) calculated for superimposed three- and five-membered rings is ascribed to the stabilising effect of the *gem*-dimethyl groups. The anomaly of (*d*) is in accordance with the structure, 5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*-penten-4-one, and that of (*c*) with an equilibrium between cyclic and open-chain forms, which must have nearly the same energy content, since the parachor does not vary appreciably with temperature. Similarly, whilst distyryl ketone has a normal structure, its dibromo-derivative appears to exist partly in the dicyclic form. H. E. F. NOTTON.

Orientation phenomena with 2-methyl*cyclo*hexanone. R. CORNUBERT (Compt. rend., 1928, **186**, 441—442).—Alkylation of 2-methyl*cyclo*hexanone by means of sodamide yields mainly the 2 : 2-dialkyl derivative, with a small proportion of the 2 : 6-dialkyl compound (cf. Haller and Cornubert, A., 1927, 152; Cornubert and Le Bihan, *ibid.*, 1075). That this is not due to an inversion of the latter is shown by the stability of both 2 : 2- and 2 : 6-dimethyl*cyclo*hexanones towards sodium hydroxide and hydrochloric acid; also, both ketones can be isolated without using sodium hydrogen sulphite. It is concluded that sodium, unlike chlorine, substitutes in the 2- preferentially to the 6-position. The "tetrahydropyrone" compound of 2 : 6-dimethyl*cyclo*hexanone has m. p. 175°, not 197—198°, as previously stated. E. W. WIGNALL.

2 : 6-Dimethyl*cyclo*hexanones. R. CORNUBERT (Compt. rend., 1928, **186**, 585—586; cf. preceding abstract).—The mixture of dimethyl*cyclo*hexanones, obtained by the methylation of 2-methyl*cyclo*hexanone by the method of Kötz and Blendermann (A., 1913, i, 1069), is separated by crystallisation of the oximes affording the *oxime A*, m. p. 119° (hydrolysed with difficulty to yield the *ketone A*, b. p. 85°/41 mm., d^{18} 0·914, n_D^{18} 1·4486), and the *oxime B*, m. p. 64—65° (softening at 63°; easily hydrolysed to afford the *ketone B*, b. p. 80·5°/41 mm., d^{18} 0·911, n_D^{18} 1·4482). The ketone *A* gives pyrone-like *compounds*, m. p. 197—198°, 175°, and 216°, of the common formula $C_{22}H_{24}O_2$, when treated with benzaldehyde in the presence of hydrogen chloride (A., 1925, i, 1070, 1071), whilst the ketone *B* similarly affords the compound, m. p. 175°, b. p. 271°/20 mm., and the compound, m. p. 216°. Oximation of the ketones in the presence of sodium acetate yields in each case mixtures of the oximes *A* and *B*, whilst in the presence of alkali the ketone *A* gives the oxime *A* alone and the ketone *B* again gives a mixture. Both ketones give mixtures of semicarbazones (Zelinsky, A., 1897, i, 462). The results are attributed to the rapid interchange of the *cis–trans* isomerides. G. A. C. GOUGH.

Relative ease of formation of rings. II. J. VON BRAUN (Ber., 1928, **61**, [*B*], 441—443; cf. this vol., 174).—It is shown in two instances that a six-membered carbon ring is more readily allied to a benzene nucleus than a five-membered carbon ring (cf. Leuchs and others, this vol., 287).—*Benzyl-β-phenylethylacetyl chloride*, b. p. 198—202°/15 mm., is converted by aluminium chloride in presence of carbon disulphide into 1-keto-2-benzyl-1 : 2 : 3 : 4-

tetrahydronaphthalene, b. p. 220—225°/13 mm. (*oxime*, m. p. 119°), the constitution of which is established by converting it by Clemmensen's method into 2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 194—195°/13 mm., transformed by heated lead oxide into naphthalene. Benzylsuccinic acid is converted by phosphorus pentachloride into *benzylsuccinyl chloride*, b. p. 115—117°/0·5 mm., which, with aluminium chloride, affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene-3-carboxylic acid*, m. p. 144°, b. p. 218—220°/16 mm. (also obtained from benzylsuccinic anhydride and aluminium chloride); the *ethyl* ester, b. p. 175—177°/15 mm., and the *semicarbazone*, m. p. 264°, are described. The acid is reduced by amalgamated zinc and hydrochloric acid to 1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m. p. 97°.

H. Wren.

Preparation of benzophenone. G. Dougherty (J. Amer. Chem. Soc., 1928, **50**, 571—573).—*o*-Benzoylbenzoic acid (300 g.) is stirred with its *copper* salt (20 g.) at 200—260° for about 4 hrs., or until evolution of carbon dioxide has ceased, in a distilling flask, and the benzophenone then distilled from the mixture. The yield is 82—84%, calculated on the *o*-benzoylbenzoic acid, after crystallisation from alcohol, m. p. 47—48°. F. G. Willson.

Preparation of benzophenone by organo-magnesium compounds. Mechanism of the reaction between organo-magnesium compounds and their carbonated derivatives. D. Ivanoff (Compt. rend., 1928, **186**, 442—444).—When phenyl magnesium bromide is treated at –20° with half an equivalent of carbon dioxide for 8 hrs., a 60% yield of benzophenone is obtained on hydrolysis, with 2—3% of triphenylcarbinol; the reaction is unsuccessful with other ketones. From anhydrous magnesium benzoate and magnesium phenyl bromide a 35% yield of benzophenone is obtained. If the product of the first reaction is treated, before hydrolysis, with benzoyl or acetyl chloride, no trace of an ester is obtained; it is therefore concluded that the complex $CPh_2(OMgBr)_2$, is not formed, but rather the complex $Ph_2CO,MgBr_2$, from which benzophenone can be obtained by distillation, although not by extraction.

E. W. Wignall.

[Preparation of] *p*-dimethylaminobenzophenone. C. D. Hurd and C. N. Webb (Org. Syntheses, 1927, **7**, 24—26).

Wandering of alkyl groups in the Fries transformation. K. von Auwers and W. Mauss (Annalen, 1928, **460**, 240—277).—A continuation of previous work (A., 1927, 608). The Fries transformation has been effected with a number of other polyalkylphenyl acetates, using the methods of rapid or of slow heating with aluminium chloride. In order to determine whether wandering of alkyl has occurred or not during the transformation, the acetyl group is removed from the resulting hydroxyacetophenone and the new phenol identified. Phosphoric acid used formerly for this removal is often less effective than boiling glacial acetic–hydrobromic acid. In general *o*- and *p*-hydroxyacetophenones are separable by steam distillation.

The new results show that an alkyl group in the *meta*-position to the acetoxyl group favours the formation of *o*-hydroxyacetophenones. Two *meta*-groups produce an even greater tendency in the same direction. Thus, when 3 : 5-dimethyl- and 3 : 5-diethyl-phenyl acetate undergo the Fries change, no 4-hydroxyacetophenones are formed. Similarly, 3 : 5-dimethylphenyl alkyl ethers give only 2-derivatives in Friedel–Crafts reactions. When one *meta*-alkyl group is present (*e.g.*, *m*-tolyl acetate), the Fries change gives a little *p*-compound. A second methyl group in the *ortho*-position (3-*o*-xylyl acetate) does not weaken the effect of the *meta*-grouping in this respect.

Phenyl acetates with a free *ortho*-position give a Fries change only if one alkyl group is in position 2 and a second in position 5 (homologues of *p*-xylenol or ψ-cumenol, 4 : 5-dimethyl-2-ethyl-, 2 : 4-dimethyl-5-ethyl-, and 5-methyl-2 : 4-diethyl-phenyl acetates).

The ethyl group is much more readily displaced than methyl (cf. 2 : 6-dimethyl-4-ethylphenyl acetate, where the Fries change is abnormal in giving rise to a *p*-compound). When ethyl groups are present in both *ortho*- and *para*-positions, the *ortho*-group is eliminated, the displaced ethyl group wandering into the *para*-position to that it originally occupied (2-methyl-4 : 6-diethyl- and 2 : 4 : 6-triethyl-phenyl acetates). Other new facts which show the greater valency requirement of ethyl over methyl are the abnormal Gattermann aldehyde and Friedel–Crafts ketone syntheses recorded with 2-methyl-4-ethyl- and 5-methyl-2 : 4-diethylanisole.

When 2 : 4-dimethyl-6-ethylphenyl acetate undergoes the Fries change, both a methyl and an ethyl group are displaced by the entering acetyl groups, but in 2-methyl-4 : 6-diethylphenyl acetate only the ethyl is displaced. Again, whilst 2-methyl-6-ethylphenyl acetate gives mainly 4-hydroxy-3-methyl-5-ethylacetophenone, some ethyl is displaced, giving 2-hydroxy-3-methyl-4-ethylacetophenone. Yet with 2 : 6-diethylphenyl acetate no ethyl displacement occurs. A further fact showing that methyl is more firmly attached than ethyl is that acetyl groups are more readily removed from a hydroxymethyl- than from a hydroxyethyl-acetophenone, *i.e.*, ethyl takes up more of the nuclear affinity than does methyl.

2 : 4-*Dimethyl*-6-*ethylphenyl acetate*, b. p. 242°, gives a mixture of 2-*hydroxy*-3 : 5-*dimethyl*-4-*ethylacetophenone*, m. p. 52—53°, b. p. 153—155°/11 mm. (*oxime*, m. p. 157·5—158·5°; *semicarbazone*, m. p. 235—236°; p-*nitrophenylhydrazone*, m. p. 212—214°), and 2 - *hydroxy* - 4 : 5 - *dimethyl* - 3 - *ethylacetophenone* (*semicarbazone*, m. p. 219—221°, p-*nitrophenylhydrazone*, m. p. 179—183°). The former acetophenone is converted into 2 : 4-*dimethyl*-3 : 6-*diethylphenol*, m. p. 59·5—60·5°, b. p. 250—252°. 4 : 5-*Dimethyl-2-ethylanisole*, b. p. 218—220°, from the corresponding phenol, alkali, and methyl sulphate, is converted by acetyl chloride and aluminium chloride into an oil from which only 2-*hydroxy*-5 : 6-*dimethyl-3-ethylacetophenone*, a yellow oil, b. p. 143—145°/11 mm. (*oxime*, m. p. 153—154°; p-*nitrophenylhydrazone*, m. p. 251—253°), is obtained. It gives the original dimethylethylphenol when boiled with hydrobromic–acetic acid and when reduced (Clemmensen) affords 3 : 4-*dimethyl*-2 : 6-*diethylphenol*, m. p. 47—48°, b. p. 246—

248°. 3-o-*Xylyl acetate*, b. p. 226—228°, is converted only into 2-*hydroxy*-3 : 4-*dimethylacetophenone*, a steam-volatile yellow oil, b. p. 122—124°/12 mm. (p-*nitrophenylhydrazone*, m. p. 216—218°), undergoing reduction to 2 : 3-*dimethyl*-6-*ethylphenol*, m. p. 53—54°. The *methyl ether*, b. p. 216—218°, of the latter gives 4-*methoxy*-2 : 3-*dimethyl*-5-*ethylacetophenone*, steam-volatile, b. p. 138—140°/12 mm., which on reduction affords 2 : 3-*dimethyl*-4 : 6-*diethylanisole*, b. p. 234—236°, demethylated to 2 : 3-*dimethyl*-4 : 6-*diethylphenol*, b. p. 244—246°. 4 : 5-*Dimethyl*-2-*ethylphenyl acetate*, b. p. 247—249°, is converted (Fries) into a steam-volatile mixture of hydroxyacetophenones, b. p. 145—147°/12 mm., which when reduced gives 3 : 4-dimethyl-2 : 6-diethylphenol, but is not separable. Fractionation of the *p*-nitrophenylhydrazones shows the presence of 2-hydroxy-5 : 6-dimethyl-3-ethyl- and 2-hydroxy-4 : 5-dimethyl-3-ethyl-acetophenone.

2 : 4-*Dimethyl*-6-*ethylanisole*, b. p. 210—211°, slowly reacts with acetyl chloride ($AlCl_3$) to give some 2 : 4-dimethyl-6-ethylphenol, and, as the main product (semi-solid, b. p. 178—182°/15 mm.), 3-*hydroxy*-2 : 6-*dimethyl*-4-*ethylacetophenone* (possibly containing some 3-hydroxy-4 : 6-dimethyl-6-ethyl isomeride, and converted by phosphoric acid into 2 : 4-dimethyl-6-ethylphenol), the constitution of which follows from its reduction to 2 : 4-dimethyl-3 : 6-diethylphenol.

Reduction of 3-hydroxy-4 : 6-dimethylacetophenone affords 2 : 4-*dimethyl*-5-*ethylphenol*, m. p. 39—40°, b. p. 242—244°, the *acetate*, b. p. 254—256°, of which is transformed (Fries) mainly into 2-hydroxy-3 : 5-dimethyl-4-ethylacetophenone (converted in poor yield by phosphoric acid into 2 : 4-*dimethyl*-3-*ethylphenol*, m. p. 70—71°) together with some 2-hydroxy-3 : 5-dimethyl-6-ethylacetophenone, isolated only as the impure *oxime*, m. p. 120—125°.

In an attempt to synthesise 2 : 6-dimethyl-4-ethylphenol, 2-methyl-4-ethylanisole was treated with hydrogen cyanide and chloride in presence of aluminium chloride and benzene. The main product was 4-methoxy-3-methylbenzaldehyde, since it was reduced to 4-*m*-xylenol, the by-product being 2-*hydroxy*-3-*methyl*-5-*ethylbenzaldehyde*, a yellow oil, b. p. 120—122°/12 mm. (p-*nitrophenylhydrazone*, m. p. 167—169°). The dimethylethylphenol was successfully synthesised from 2-*m*-xylenol. The *acetate*, b. p. 214—216°, of the latter was treated in the cold with aluminium chloride and the mixture then slowly heated to 120° (see below). Some 2-*m*-xylenol and (mainly) 4-*hydroxy*-2 : 6-*dimethylacetophenone*, m. p. 150—151° (*sodium* salt, sparingly soluble), were formed. The latter was deacetylated normally to the original xylenol and reduced to 2 : 6-*dimethyl*-4-*ethylphenol*, m. p. 36—37°, b. p. 228—230°. The *acetate*, b. p. 245—247°, of this substance is converted (Fries) mainly into 4-hydroxy-3 : 5-dimethyl- and some 2-hydroxy-3 : 5-dimethyl-4-ethylacetophenone. Reduction of 2-hydroxy-5-methyl-3-ethylacetophenone gives 4-*methyl*-2 : 6-*diethylphenol*, m. p. 48—48·5°, b. p. 229—230° (*benzoate*, m. p. 103—103·5°), the *acetate*, b. p. 242—243°, of which affords (Fries) 2-*hydroxy*-5-*methyl*-3 : 4-*diethylacetophenone*, a yellow oil, b. p. 136—137°/12 mm. [*oxime*, m. p. (?) 108—109°; *semicarbazone*, m. p. 228—229°; p-*nitrophenylhydrazone*, m. p. 254—256°], undergoing reduction to 4-*methyl*-2 : 3 : 6-*triethylphenol*, a yellow oil, b. p. 242—244°.

5-*Methyl*-2-*ethylanisole*, b. p. 200°, gives a very little 2-*hydroxy*-6-*methyl*-3-*ethylphenol*, b. p. 137—138°/12 mm., and mainly 4-*methoxy*-2-*methyl*-5-*ethylacetophenone*, m. p. 29—30°, b. p. 139—140°/12 mm., converted by hydrobromic–acetic acid into 5-methyl-2-ethylphenol and reduced to 5-*methyl*-2 : 4-*diethylanisole*, b. p. 222—224°. The latter is demethylated normally to give 5-*methyl*-2 : 4-*diethylphenol*, b. p. 247—249° (*carbamate*, m. p. 109—110°), the *acetate*, b. p. 258—260°, of which under Fries' conditions affords a mixture of 2-hydroxy-5-methyl-3 : 4-diethylacetophenone and (?) 2-hydroxy-3 : 5-dimethyl-6-ethylacetophenone. Acetyl chloride ($AlCl_3$) and 5-methyl-2 : 4-diethylanisole give a mixture of 2-*hydroxy*-4-*methyl*-5-*ethylacetophenone*, m. p. 94—95°, and 2-*methoxy*-6-*methyl*-3 : 5-*diethylacetophenone*, a pale yellow oil, b. p. 146—148°/11 mm., the oily oxime of which when boiled with 20% hydrochloric acid gives a base (cf. A., 1924, i, 743; 1925, i, 264, 265). Reduction of the methoxyacetophenone gives 3-*methyl*-2 : 4 : 6-*triethylanisole*, b. p. 252—254°, converted by aluminium chloride into 3-*methyl*-2 : 4 : 6-*triethylphenol*, b. p. 256—258° (*sodium* salt, sparingly soluble).

Reduction of 4-hydroxy-2-methylacetophenone gives 3-*methyl*-4-*ethylphenol*, b. p. 228—230°, the *acetate*, b. p. 239—240°, of which undergoes Fries transformation into 2-hydroxy-4-methyl-5-ethylacetophenone, reduced to 5-methyl-2 : 4-diethylphenol. 2-Methyl-4-ethylphenol gives a *benzoate*, m. p. 47—49°, and an *acetate*, b. p. 238—240°. The latter is converted (Fries) into 2-*hydroxy*-3-*methyl*-5-*ethylacetophenone*, a yellow oil, b. p. 129—131°/11 mm. (p-*nitrophenylhydrazone*, m. p. 196—198°), which is reduced to 2-*methyl*-4 : 6-*diethylphenol*, b. p. 234—236°. The *acetate*, b. p. 250—252°, of the latter undergoes Fries change to 2-*hydroxy*-3-*methyl*-4 : 5-*diethylacetophenone*, m. p. 50—51° (*oxime*, m. p. 125—126°, gives no base, when boiled with hydrochloric acid; p-*nitrophenylhydrazone*, m. p. 187—190°), which on reduction affords 2-*methyl*-3 : 4 : 6-*triethylphenol*, m. p. 28—29°, b. p. 252°.

Whilst phenyl acetate under Fries' conditions gives a 50% yield of *p*- in addition to *o*-hydroxyacetophenone, the method of Wha (Diss., Kiel, 1928: acetyl chloride and aluminium chloride on phenol in nitrobenzene solution) gives a 70% yield of *p*-compound. Reduction of the latter gives *p*-ethylphenol, the acetate of which (Fries) gives 2-*hydroxy*-5-*ethylacetophenone*, a yellow oil, b. p. 119—121°/12 mm. (*oxime*, m. p. 118—119°), reduced to 2 : 4-*diethylphenol*, b. p. 228—230° (*phenylcarbamate*, m. p. 96—99°). The *acetate*, b. p. 242—244°, of this substance under Fries' conditions passes into 2-*hydroxy*-3 : 5-*diethylacetophenone*, a yellow oil, b. p. 138—140°/12 mm. (p-*nitrophenylhydrazone*, m. p. 136—138°), which is reduced to 2 : 4 : 6-*triethylphenol*, b. p. 244—246°. 2 : 4 : 6-*Triethylphenyl acetate*, b. p. 261—262°, undergoes Fries transformation into 2-*hydroxy*-3 : 4 : 5-*triethylacetophenone*, a yellow oil, b. p. 153—155°/12 mm., together with (?) some 2-hydroxy-3 : 5 : 6-triethylacetophenone, not isolated.

2-*o*-Xylyl acetate when heated rapidly with aluminium chloride at 130—140° gives only 4-hydroxy-3 : 5-dimethylacetophenone, whereas 2-*methyl*-6-*ethylphenyl acetate*, b. p. 220—222°, under Fries' conditions gives some 2-*hydroxy*-3-*methyl*-5-*ethylacetophenone*, steam-volatile, b. p. 130—132°/12 mm. (p-*nitrophenylhydrazone*, m. p. 191—195°), but chiefly 4-*hydroxy*-3-*methyl*-5-*ethylacetophenone*, m. p. 95·5—96·5°.

Fries' conditions convert *o*-ethylphenyl acetate into 2-*hydroxy*-3-*ethylacetophenone*, b. p. 213° (p-*nitrophenylhydrazone*, m. p. 213—217°), reduced to 2 : 6-diethylphenol, the *acetate*, b. p. 238—240°, of which when rapidly heated under Fries' conditions gives a little *o*-hydroxyketone (?), but mainly 4-*hydroxy*-3 : 5-*diethylacetophenone*, m. p. 92—92·5°.

3 : 5-*Diethylphenyl acetate*, b. p. 250—251°, is converted (Fries) into 2-*hydroxy*-4 : 6-*diethylacetophenone*, b. p. 140°/12 mm. (*sodium* salt, sparingly soluble), which with boiling 84% phosphoric acid gives 3 : 5-diethylphenol.

The colour reactions of the hydroxy-compounds with ferric chloride are noted. Some compounds such as 4-hydroxy-3 : 5-diethylacetophenone give no colour with this reagent. E. E. TURNER.

Benzoylmethylcarbinol and acetylphenylcarbinol. II. K. VON AUWERS and H. MAUSS (Biochem. Z., 1928, **192**, 200—229; cf. A., 1924, i, 384).—Benzoylmethylcarbinol (α-ketol) and acetylphenylcarbinol (β-ketol) furnish the same semicarbazone, m. p. 193°, thiosemicarbazone, m. p. 197°, and *phenylurethane*, m. p. 143—144°. To explain these reactions it is assumed that each ketol reacts as a mixture of OH·CPh·O·CHMe and Ph·CH·O·CMe·OH. Oxidation of the semicarbazone prepared from α-ketol with lead peroxide and acetic acid at 50° affords phenylmethylglyoxalsemicarbazone, m. p. 211° (cf. Diels and van Dorp, A., 1903, i. 862). α-Ketol (benzoate, m. p. 106—107°, cf. Zincke and Zahn, A., 1910, i, 316) reacts with *p*-nitrobenzoyl chloride in pyridine to yield *p*-nitrobenzoic anhydride and α-*ketol* p-*nitrobenzoate*, m. p. 120—121°, also formed from potassium or silver *p*-nitrobenzoate and α-bromopropiophenone. Phenyl magnesium bromide and α-ketol give αα-diphenylpropane-αβ-diol, m. p. 95—96° (*monobenzoate*, m. p. 184·5—185·5°), which when treated with boiling 10% sulphuric acid gives benzhydryl methyl ketone. From β-ketol (regenerated from the semicarbazone) and phenyl magnesium bromide there is obtained αβ-diphenylpropane-αβ-diol (*monobenzoate*, m. p. 141—142°), which, contrary to the statement of Neuberg and Ohle (A., 1922, i, 480), yields with boiling 10% sulphuric acid mainly αα-diphenylpropaldehyde, b. p. 176—178°/12 mm., which when oximated and treated with acetic anhydride affords αα-*diphenylpropionitrile*, b. p. 178—180°/12 mm. Favorsky's conversion of α- into β-ketol by treatment with alcohol and sulphuric acid at 120—130° (A., 1926, 500) has not been confirmed.

α-Anilinopropiophenone reacts with ethyl chloroformate yielding α-N-*carbethoxyanilinopropiophenone*, m. p. 81°, which when treated with alkali in ice-cold alcoholic solution gives 3 : 5-*diphenyl*-4-*methyloxazolone*, m. p. 113—114°. Similarly the N-*carbethoxy*-derivative, m. p. 56—58°, of α-*anilinobenzyl methyl ketone*, m. p. 90—91°, yields 3 : 4-*diphenyl*-5-*methyloxazolone*, m. p. 162·5°, also formed by the action of 50% sulphuric acid on a hot alcoholic solution of the above phenylurethane. Hydrolysis of this oxazolone with alcoholic potassium hydroxide regenerates α-anilinobenzyl methyl ketone. Benzoinphenylurethane affords 3 : 4 : 5-triphenyloxazolone, m. p. 214—214·5° (McCombie and Parkes, J.C.S., 1912, **101**, 1994, give m. p. 210°).

α-Bromo*iso*butyrophenone is decomposed by sodium hydroxide in dilute alcoholic solution into *benzoyldimethylcarbinol* (*semicarbazone*, m. p. 188°; *acetate*, b. p. 148—150°/14 mm., m. p. 61°). Acetylphenylmethylcarbinol (*semicarbazone*, m. p. 183—184°) is acetylated by acetyl chloride, forming the *acetate*, b. p. 152—154°/14 mm. (*semicarbazone*, m. p. 183°). *Benzoylcarbinolsemicarbazone acetate* has m. p. 148—149°. Numerous spectrochemical data for the above ketols and esters are tabulated.

H. BURTON.

Tautomerism of α-diketones. Two forms of benzylmethylglyoxal and their reversible transformation. H. MOUREU (Compt. rend., 1928, **186**, 380—382; cf. A., 1927, 246, 1173).—Distillation of the hydrolytic product of the intermediate piperidide (Dufraisse and Moureu, this vol., 180) gives *benzylmethylglyoxal* (I), yellow, b. p. 104°/10 mm., m. p. 17—18°, which when kept in a sealed tube undergoes after several hours or days spontaneous transformation into a colourless form (II), b. p. 134°/10 mm., m. p. 69—70° (Dufraisse and Moureu, *loc. cit.*). Treatment of (I) with traces of alkali in the cold causes transformation into (II), the rates of change being a few seconds for diethylamine and piperidine, 12 min. for potassium hydroxide, and 3 days for benzylamine. When (II) is heated with the same catalysts and then distilled there is formed (I).

H. BURTON.

Tautomerism of α-diketones. Constitution of the two forms of benzylmethylglyoxal. H. MOUREU (Compt. rend., 1928, **186**, 503—505).—Benzylmethylglyoxal exists in two tautomeric forms, *A* and *B*. *A* has the constitution $CH_2Ph{\cdot}CO{\cdot}COMe$. The enolic form, *B*, $CHPh{:}C(OH){\cdot}COMe$, is far more reactive than *A* with Grignard reagents, bromine, and ferric chloride; it gives an *antimony* derivative, m. p. 184—185°, and *benzoyl* derivative, m. p. 82—83°; with *o*-phenylenediamine it forms *benzylmethylquinoxaline*, m. p. 57—58°. The "α-phenylacetoacetaldehyde" of Weitz and Scheffer (A., 1921, i, 869) was in reality the above *B* tautomeride.

B. W. ANDERSON.

Influence of anti-auxochromic groups on the halochromy of ketones. P. PFEIFFER and B. SEGALL (Annalen, 1928, **460**, 123—137).—It is shown that the nitro- and sulpho-groups, and to a lesser extent halogen atoms, exert a hypsochromic effect on the halochromy of unsaturated ketones. The *meta*-directing nitro-group exerts its effect most markedly when it is in the *meta*-position with respect to the ethylenic linking, and least when it is in the *para*-position. The *ortho*–*para* directive groups, OH, OMe, and NH_2, best exert their effect, which is bathochromic, when in the *para*-position to the unsaturated side-chain.

The preparation of 3-nitro-4-methoxybenzaldehyde by the nitration of anisaldehyde is described. The nitro-compound when condensed (this and other condensations now described were carried out in aqueous-alcoholic sodium hydroxide) with acetophenone, gave *phenyl* 3-*nitro*-4-*methoxystyryl ketone*, yellow, m. p. 146°, whilst with *p*-methoxyacetophenone, p-*anisyl* 3-*nitro*-4-*methoxystyryl ketone*, yellow, m. p. 160°, resulted. The *perchlorate*, m. p. 177—180° (decomp.), of the latter is orange-red, whilst the *perchlorate* of *p*-anisyl *p*-methoxystyryl ketone is red. Condensation of *o*-nitrostyryl methyl ketone with *o*-nitrobenzaldehyde affords 2 : 2′-*dinitrodistyryl ketone*, yellow, m. p. 170·5—171°. The known 3 : 3′-isomeride is greenish-yellow, and forms an orange-yellow *perchlorate*, decomp. 143—145° (softening at about 125°). 3-*Nitro*-4 : 4′-*dimethoxydistyryl ketone*, obtained either from 3-nitro-4-methoxystyryl methyl ketone or from *p*-methoxystyryl methyl ketone, is yellow and has m. p. 158·5°. 3 : 3′-*Dinitro*-4 : 4′-*dimethoxydistyryl ketone*, yellow, has m. p. 220°, and forms an orange-red *perchlorate*, m. p. 198° (decomp.).

3-*Chloro*-4-*methoxystyryl methyl ketone*, bright yellow from aqueous alcohol or colourless from water, has m. p. 111·5° and is formed together with some of the distyryl ketone (next below) when acetone is condensed with 3-chloroanisaldehyde, m. p. 62·5—63° (prepared by the hydrogen cyanide method from *o*-chloroanisole; Gattermann gave m. p. 53°). With different proportions of reactants, 3 : 3′-*dichloro*-4 : 4′-*dimethoxydistyryl ketone*, yellow, m. p. 177·5—178·5° (*perchlorate*, chocolate-brown, subl. 153°, m. p. 205—207° decomp.), is formed. The similarly obtained *phenyl* 3-*chloro*-4-*methoxystyryl ketone*, bright yellow, has m. p. 113—114°.

3-Bromo-4-methoxybenzaldehyde, prepared by an improved method, is converted by acetone into a mixture of 3-*bromo*-4-*methoxystyryl methyl ketone*, m. p. 101°, with some 3 : 3′-*dibromo*-4 : 4′-*dimethoxydistyryl ketone*, yellow, m. p. 181° (*perchlorate*, deep brownish-red, but lighter in shade than the bromine-free compound, has m. p. 168—169°, decomp.), obtainable better from bromoanisaldehyde and bromostyryl methyl ketone. *Phenyl* 3-*bromo*-4-*methoxystyryl ketone*, bright yellow, has m. p. 112—113°, and p-*anisyl* 3-*bromo*-4-*methoxystyryl ketone*, bright greenish-yellow, has m. p. 120° (*perchlorate*, orange-red, m. p. 138—139°). E. E. Turner.

Behaviour of methoxy-compounds towards aluminium bromide. P. Pfeiffer and E. Haack (Annalen, 1928, 460, 156—179).—Previous work has shown that when perchloric acid or stannic chloride forms additive compounds with unsaturated ketones containing methoxyl groups, neither the latter nor the ethylenic linking are concerned in the compound formation, which is controlled by the carbonyl group solely. Aluminium bromide is now shown to form, with unsaturated ketones, compounds in which each methoxyl and each carbonyl group can cause the union of a molecule of bromide, although here again the ethylenic linking plays no part. 4-Methoxydiphenyl is exceptional in giving the *compound* $3C_6H_4Ph{\cdot}OMe,2AlCl_3$, the composition of which cannot be accounted for.

The aluminium bromide additive compounds of methoxylated ketones have much less deep colours than those of the methoxyl-free ketones, a result due to the depression of the bathochromic effect of the methoxyl group by its combination with aluminium bromide, and analogous to the similar depression of the bathochromic effect of an amino- or a derived amino-grouping in perchlorate formation, with unsaturated amino-ketones (Pfeiffer, Kollbach, and Haack, following abstract). The group $\cdot OMe,AlBr_3$, in fact, exerts a hypsochromic action.

The discovery that phenol ethers in general form additive compounds with aluminium bromide suggests that the probable mode of action of aluminium halides as demethylating agents is to be represented as follows: $R{\cdot}OMe \longrightarrow R{\cdot}OMe,AlBr_3 \longrightarrow R{\cdot}O{\cdot}AlBr_2+MeBr \longrightarrow R{\cdot}OH$. In actual fact, the additive compounds now described usually decompose smoothly when heated in benzene solution to give the aluminium alkyloxybromides, which with water afford the corresponding phenols. It is pointed out that aluminium bromide is probably preferable to the chloride, since it is readily soluble in benzene etc., whilst the chloride is not.

Precise directions are given for the purification of the benzene and other solvents used for the preparation of the aluminium bromide additive compounds, a special apparatus being described. Most of the additive compounds derived from methoxylated compounds lose methyl bromide merely on keeping, passing thereby into the aluminium alkyloxybromides. The same decomposition occurs more rapidly in a vacuum at 100—130°, but is accompanied by side reactions. Quantitative demethylation is effected by heating the additive compound with excess of benzene, avoiding ingress of moisture. The above additive compound of aluminium bromide and methoxydiphenyl is thus converted into a crystalline *aluminium methoxydibromide*, which with water affords 4-hydroxydiphenyl. The additive *compound* of β-naphthyl methyl ether with $1AlBr_3$ behaves similarly.

Quinol dimethyl ether forms two additive *compounds*, one with $1AlBr_3$, one with $2AlBr_3$. Decomposition of the latter in boiling benzene affords the yellow crystalline *compound*, $AlBr_2{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}AlBr_2$, from which quinol was readily obtained.

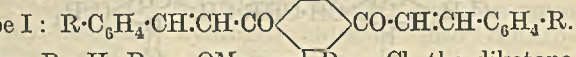
p-Methoxyacetophenone gives a *compound* with $2AlBr_3$, readily converted into *p*-hydroxyacetophenone. 4 : 4′-Dimethoxybenzophenone gives a *compound* with $2AlBr_3$. If this ketone is heated in benzene solution with aluminium bromide, the yellow $R{\cdot}O{\cdot}AlBr_2$ *compound* separates and may be converted into the corresponding phenol. 4-Methoxy-α-naphthyl methyl ketone forms yellow *compounds* (1) with $1AlBr_3$, and (2) with $2AlBr_3+C_6H_6$. The latter decomposes to give an oily $R{\cdot}O{\cdot}AlBr_2$ *compound*, convertible into the corresponding phenol.

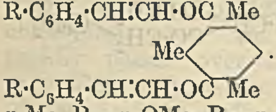
p-Methoxystyryl methyl ketone affords a red *compound* with $1AlBr_3$ and a deep yellow *compound* with $2AlBr_3$, through which demethylation was effected. Phenyl *p*-methoxystyryl ketone gives a deep red *compound* with $1AlBr_3$, decomposing in hot benzene without demethylation, and a honey-yellow *compound* with $2AlBr_3$, decomposing particularly readily in hot benzene to give the yellow *compound*, $Br_2AlO\cdot C_6H_4\cdot CH{:}CHBz,AlBr_3$, from which the *p*-hydroxy-ketone was obtained.

p-Anisyl *p*-methoxystyryl ketone forms a cinnabar-red *compound* with $1AlBr_3$, not undergoing demethylation in hot benzene, and a honey-yellow *compound* with $3AlBr_3$, demethylating with great readiness.

4 : 4′-Dimethoxydistyryl ketone forms a bright red *compound* with $1AlBr_3$, and a honey-yellow *compound* with $3AlBr_3$, the latter undergoing demethylation with moderate facility. E. E. TURNER.

Halochromic compounds of polyketones. P. PFEIFFER, K. KOLLBACH, and E. HAACK (Annalen, 1928, 460, 138—156).—An investigation devised to test Pfeiffer's theory that additive compounds of ketones and inorganic chlorides etc. are not merely "molecular" compounds but that the oxygen of the keto-group is definitely the prime factor causing combination. The theory is apparently proved, for in the case of polyketones, additive compounds with aluminium bromide have been obtained which contain as many molecules of bromide as there are keto-groups in the polyketone. In the case of unsaturated ketones, no addition occurs at the ethylenic linking. Perchlorates of the polyketones were also isolated, but their composition did not uniformly correspond with the requirements of the above theory.

Some further observations are made on the halochromy of "double chalkones," viz., compounds of type I:  $R\cdot C_6H_4\cdot CH{:}CH\cdot CO$ $CO\cdot CH{:}CH\cdot C_6H_4\cdot R$. When R=H, R=*p*-OMe, and R=*o*-Cl, the diketone is straw-yellow, bright yellow, and pale yellow, respectively; the solution in concentrated sulphuric acid is deep orange-red, deep reddish-violet, and orange-red, respectively. Paler halochromy colours are shown by compounds of type II,


$R\cdot C_6H_4\cdot CH{:}CH\cdot OC$ Me
Me
$R\cdot C_6H_4\cdot CH{:}CH\cdot OC$ Me

. Thus, when R=H, R=*p*-Me, R=*p*-OMe, R=*p*-NMe_2, R=*o*-Cl, and R=*p*-Cl, the diketone is yellowish-white, yellowish, yellowish, yellowish-green, pale straw-yellow, and pale yellow, respectively. When R=H, *o*-Cl, or *p*-Cl, the concentrated sulphuric acid solution is greenish-yellow. When R=*p*-Me, this solution is deep yellow, and when R=*p*-OMe, it is orange. In concentrated sulphuric acid solution, the bathochromic effect of a *p*-NMe_2 group is destroyed owing to salt formation, and the solution is only yellowish-brown in consequence. The halochromy colours of the "double chalkones" of the diacetylmesitylene series (II) correspond with those of the simple chalkones, whilst the colours of the "double chalkones" of the 1 : 4-diacetylbenzene series (I) are markedly deeper than those of the latter.

1 : 4-Diacetylbenzene, difficult to prepare by Ingle's method (Diss., München, 1894) from ethyl terephthaloyldimalonate, is also obtained in poor yield by the action of magnesium methyl iodide on terephthalonitrile, prepared by distilling lead terephthalate with lead thiocyanate. Benzaldehyde converts diacetylbenzene in aqueous-alcoholic sodium hydroxide solution (the condensing method used generally in this investigation) into 1 : 4-*dicinnamoylbenzene* (I, R=H), m. p. 205·5—207·5° (no perchlorate obtainable). 1 : 4-*Di*-p-*methoxycinnamoylbenzene* (I, R=*p*-OMe), prepared from anisaldehyde, has m. p. 212° (*perchlorate*, violet-black), and 1 : 4-*di*-o-*chlorocinnamoylbenzene* (I, R=*o*-Cl), from *o*-chlorobenzaldehyde, has m. p. 251°, and was not obtained quite pure.

Acetophenone-4-carboxylic acid has m. p. 210°, not 205° as lit., and is converted normally into p-*cinnamoylbenzoic acid*, pale yellow, m. p. 234°, 4-p-*methoxycinnamoylbenzoic acid*, yellow, m. p. 223° (*perchlorate*, chocolate-brown, exploding when heated), 4-o-*chlorocinnamoylbenzoic acid*, yellow, m. p. 214—215°, and 4-p-*dimethylaminocinnamoylbenzoic acid*, reddish-brown, m. p. 248°. These four substances dissolve in concentrated sulphuric acid to give reddish-orange, deep bluish-red, orange, and deep greenish-yellow solutions, respectively.

2 : 4-Diacetylmesitylene is readily converted into 2 : 4-*dicinnamoylmesitylene* (II, R=H), m. p. 135°, 2 : 4-*di*-p-*methylcinnamoylmesitylene* (II, R=*p*-Me), m. p. (+½EtOH) 97°, 2 : 4-*di*-p-*methoxycinnamoylmesitylene* (II, R=*p*-OMe), m. p. (+½EtOH) 105—106° or (+½C_6H_6) 93°, 2 : 4-*di*-o-*chlorocinnamoylmesitylene* (II, R=*o*-Cl), m. p. 161°, 2 : 4-*di*-p-*chlorocinnamoylmesitylene* (II, R=*p*-Cl), m. p. 116° (*perchlorate*, yellowish-grey, exploding when heated), and 2 : 4-*bisdimethylaminocinnamoylmesitylene* (II, R=*p*-NMe_2), m. p. 234° (*perchlorate*, yellow, exploding when heated). The six last-named ketones give, in concentrated sulphuric acid solution, the following colours, respectively: deep greenish-yellow, deep yellow, orange, greenish-yellow, greenish-yellow, and yellowish-brown.

p-Tolyl 4-diphenylyl ketone forms a lemon-yellow additive *compound* with $1AlBr_3$, xanthone a yellow additive *compound* with $1AlBr_3+1C_6H_6$, phenyl styryl ketone an orange *compound* with $1AlBr_3$, distyryl ketone a blood-red *compound* with $1AlBr_3$, αε-diphenyl-$\Delta^{\beta\delta}$-pentadien-α-one (cinnamylideneacetophenone) a blood-red *compound* with $AlBr_3$, 1 : 4-dibenzoylbenzene a *compound* with $2AlBr_3+C_6H_6$, 2 : 4-diacetylmesitylene a reddish-yellow *compound* with $2AlBr_3$, and *s*-triacetylbenzene a pale yellow *compound* with $3AlBr_3$. E. E. TURNER.

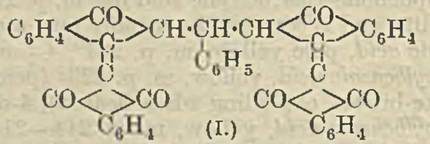
Unusual substitution reaction. I—III. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1926, 3, 54—59, 210—229, 230—239; Chem. Zentr., 1927, i, 602, ii, 69, 70).—I. Condensation of dimethyldihydroresorcinol with ethyl benzylideneacetoacetate by means of piperidine in absolute alcohol affords *benzylidenebisdimethyldihydroresorcinol*, m. p. 192°, which is also produced from dimethyldihydroresorcinol and ethyl benzylidenebisacetoacetate, and is converted by sulphuric or acetic acid into Vorländer's phenyltetramethyloctahydroxanthendione, m. p. 200—201° (A., 1900, i, 100).

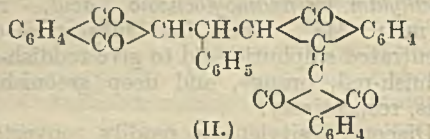
II. This substitution,

$$(CO\cdot R')_2CH\cdot CHR\cdot CH(CO\cdot R'')_2+CH_2(CO\cdot R''')_2 \longrightarrow (CO\cdot R')_2CH\cdot CHR\cdot CH(CO\cdot R''')_2+CH_2(CO\cdot R'')_2,$$

is

determined by the activity of the methylene compounds, which rises in the series: ethyl malonate, ethyl acetoacetate, acetylacetone, indandione, dimethyldihydroresorcinol, di-indone. Evidence is adduced in support of the author's view of the reaction. *Benzylidenebisdi-indone* (I), yellow, m. p. 256°, is obtained by interaction of indandione and ethyl benzylideneacetoacetate, ethyl benzylideneindandionemalonate, benzylidenebisdimethyldihydroresorcinol, or (together with benzylideneindandionedi-indone) benzylideneindandione in absolute alcohol in presence of piperidine. *Benzylideneindandionedi-indone* (II), m. p. 302°, is also obtained from ethyl benzylideneindandionemalonate and dimethyldihydroresorcinol.


(I.)

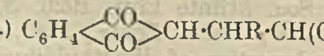

(II.)

III. [with V. N. Georgescu]. Methylenebisdi-indone, $C_{37}H_{20}O_6$, yellow, m. p. 273°, gives with alkali in boiling alcohol an indigo-blue, then reddish-violet colour. Methyleneindandionedi-indone, $C_{28}H_{16}O_5$, has m. p. 305—311° (decomp. and subl.), and gives a reddish-violet solution in alcoholic potash.

A. A. Eldridge.

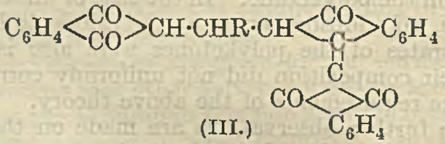
Factors disturbing valency fields. Action of substances with an active methylene group on the carbindogenides. I—II. M. V. Ionescu and S. Secareanu (Bul. Soc. Stiinte Cluj, 1926, **3**, 112—128, 250—284; Chem. Zentr., 1927, i, 601—602, ii, 71—72).—I. It has already been shown (Bul. Soc. Stiinte Cluj, 1925, **2**, 280) that the absorption spectrum of a chromogen is modified by the introduction of a co-ordinatively unsaturated group, in a measure determined by the extent of the unsaturation. According to the character of the absorption spectra, the carbindogenides (I) can be divided into (*a*) those where R=phenyl, *p*-tolyl, *m*-tolyl, or *p*-acetoxyphenyl, the absorption curve lying below 4800 Å.,

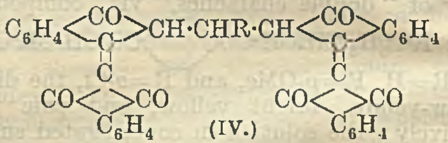
(I.) 
$C_6H_4{<}{}^{CO}_{CO}{>}C{:}CHR$

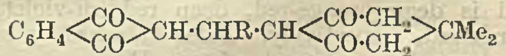
(II.) 
$C_6H_4{<}{}^{CO}_{CO}{>}CH{\cdot}CHR{\cdot}CH(CO_2Et)_2$

and (*b*) those where R=*p*-anisyl, 3 : 4-methylenedioxyphenyl, *p*-hydroxyphenyl, or *p*-dimethylaminophenyl, the curve passing 4800 Å. Only group (*a*) gives products (II) by addition with ethyl malonate on account of the presence of the co-ordinatively unsaturated groups OMe, O_2CH_2, OH, and NMe_2. The *p*-tolyl derivative, when heated at 175° or treated with cold, concentrated sulphuric acid, does not yield a lactone, but is decomposed into its components. *Ethyl* α-*carbethoxy*-β-*indandionyl*-β-*phenylpropionate*, m. p. 108°; *ethyl* β-*indandionyl*-β-*phenylpropionate*, m. p. 109°; *ethyl* α-*carbethoxy*-β-*indandionyl*-β-p-*tolylpropionate*, m. p. 111—112° [dicarboxylic *acid*, $C_{20}H_{16}O_6$, m. p. 182° (decomp.); *lead* and *copper* salts]; the *diphenylhydrazonediphenylhydrazide* from II, $C_{44}H_{40}O_2N_8$, m. p. 178°; β-*indandionyl*-β-p-*tolylpropionic acid*, m. p. 173° (*lead* and *copper* salts); *ethyl* α-*carbethoxy*-β-*indandionyl*-β-m-*tolylpropionate*, m. p. 135°, and *ethyl* α-*carbethoxy*-β-*indandionyl*-β-p-*acetoxyphenylpropionate*, m. p. 154°, are described.

II. The following compounds have been prepared: p-*toluylidene*-, m. p. 310°; p-*acetoxybenzylidene*-, m. p. 320; *anisylidene*-, m. p. 310°; m-*toluylidene*-, m. p. 340°; and p-*hydroxybenzylidene*-, m. p. 275°, -*indandionedi-indones* (cf. III); p-*acetoxybenzylidene*-, m. p. 162°; p-*toluylidene*-, m. p. 151°; m-*toluylidene*-, m. p. 156°, and α-*naphthylidene*-, m. p. 172°, -*indandiones* (cf. I); p-*toluylidene*-, m. p. 253°; m-*toluylidene*-, m. p. 236°; *anisylidene*-, m. p. 233°; *piperonylidene*-, m. p. 242°; and α-*naphthylidene*-, m. p. 230°, -*bisdi-indones* (cf. IV); the *compounds* $C_{23}H_{26}O_3$ (VII, R=Ph), m. p. 202°; $C_{24}H_{28}O_3$ (VII, R=*p*-C_7H_7), m. p. 202°; $C_{24}H_{28}O_4$ (VII, R=*p*-anisyl), m. p. 247°; *compound* (VII) (R=*p*-acetoxyphenyl), not analysed, has m. p. 234°. Inadequate boiling in the preparation of the compound $C_{23}H_{26}O_3$ leads to the production of (VI).

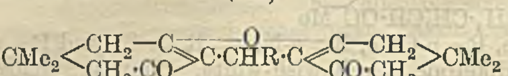

(III.)


(IV.)

(V.) 
$C_6H_4{<}{}^{CO}_{CO}{>}CH{\cdot}CHR{\cdot}CH{<}{}^{CO\cdot CH_2}_{CO\cdot CH_2}{>}CMe_2$

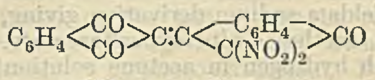

$CMe_2{<}{}^{CH_2\cdot CO}_{CH_2\cdot CO}{>}CH{\cdot}CHR{\cdot}CH{<}{}^{CO\cdot CH_2}_{CO\cdot CH_2}{>}CMe_2$

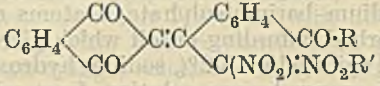
(VI.)

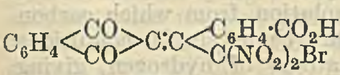

(VII.)

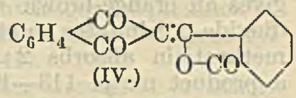
A. A. Eldridge.

Dinitrobindone and its scission products. W. Wislicenus and H. Schlichenmaier (Annalen, 1928, **460**, 278—288).—Nitric acid (*d* 1·5) converts bindone (indandionylidenehydrindone; Wislicenus, Ber., 1887, **20**, 598) in boiling glacial acetic acid solution into *dinitrobindone* (I), m. p. 183°. The latter in alcoholic potassium hydroxide affords the red *dipotassium* salt of the unstable *acid* (II, R=OH, R′=H), m. p. 94°, whilst bromine and aqueous potassium hydroxide convert (I) into *compound* (III), pale yellow, exploding at 117°. When dinitrobindone is treated with ice-cold potassium hydroxide and the red solution formed is at once acidified, *phthalideneindandione* (IV,) m. p. 253°, is formed, dinitromethane being eliminated at the acidification stage. By prolonged heating of dinitrobindone with aqueous potassium hydroxide at 100°, the *potassium* salt of dinitromethane, exploding at 204°, is obtained.

(I.)

$$C_6H_4<^{CO}_{CO}>C:C<^{-C_6H_4-}_{C(NO_2)_2}>CO$$

(II.)



$$C_6H_4<^{CO}_{CO}>C:C<^{C_6H_4\cdot CO_2H}_{C(NO_2)_2Br}$$
(III.)


(IV.)

Alcoholic potassium ethoxide converts (I) into the deep red *potassium* salt–*ethyl* ester (II, R=OEt, R′=K) (+2MeOH). Acidification of this affords the *ethyl hydrogen* ester (II, R=OEt, R′=H), m. p. initially 132°, rapidly changing to 124°. The *potassium* salt–*methyl* ester (II, R=OMe, R′=K) (+2MeOH) and the *methyl hydrogen* ester (II, R=OMe, R′=H) are formed similarly. The last-named potassium salt is converted by bromine water into the corresponding *tribromodinitro-methyl* ester, yellow, m. p. 139°.

Aqueous ammonia converts dinitrobindone into the *lactam* corresponding with (IV), m. p. 265°, and dinitromethane, whilst if ammonia gas is passed into a cold benzene solution of dinitrobindone, the red *ammonium* salt–*amide* (II, R=NH_2, R′=NH_4), decomp. 183°, results. The latter undergoes decolorisation when treated with anhydrous ether. Cold aniline slowly converts dinitrobindone into the red *phenylammonium* salt–*anilide* (II, R=NHPh, R′=NH_3Ph), transformed by anhydrous ether into the free *anilide* (II, R=NHPh, R′=H) and by warm methyl-alcoholic hydrogen chloride into dinitromethane and the *phenylimide*, orange-yellow, m. p. 234°, stable to acids and only slowly hydrolysed by alkalis. When the above lactam, m. p. 265°, is warmed with aqueous sodium hydroxide, 2-o-*carboxybenzoylindandione*, obtained anhydrous and +1MeOH, m. p. 155—160°, results (*copper* salt; *methyl* ester, m. p. 123°). Bromination of (II) in chloroform gives the 2-*bromo*-derivative, which rapidly passes over into *dibromodiketohydrindene*, m. p. 176°, which is also formed by treating a solution of the acid in sodium hydrogen carbonate with bromine water. E. E. Turner.

Tautomerism of hydroxyquinones. L. F. Fieser (J. Amer. Chem. Soc., 1928, 50, 439—465).—Tautomeric equilibrium between 2-hydroxy-α-naphthaquinone (α-form) and 4-hydroxy-β-naphthaquinone (β-form) has previously been evidenced (cf. Fieser, A., 1927, 59). Since both tautomerides yield the same trihydroxynaphthalene on reduction, the value of the tautomeric equilibrium constant (K) can be deduced from their respective normal reduction potentials, and it is shown that $\log K=(E_0^{\beta}-E_0^{\alpha})/0{\cdot}0296$. The normal reduction potentials of certain alkyl ethers of the α- and β-isomerides were determined, the values for the methyl ethers being 0·353 and 0·433 volt, respectively, and K was evaluated assuming that the difference between these two values approximates to that between those for the two tautomeric hydroxynaphthaquinones. The measured normal reduction potential of naphthapurpurin (0·243 volt) is in good agreement with that calculated from the corresponding constants of related compounds, whilst the value similarly calculated for the tautomeride of naphthapurpurin (0·308 volt) is considerably higher, thus confirming that the tautomeride of lower reduction potential predominates in the equilibrium mixture, according to the above expression, and this is also supported by available data for two indophenols (cf. Clark, A., 1924, ii, 597). From determinations of normal reduction potentials of lapachol, its derivatives, and a large number of similar compounds it is concluded that both lapachol and *iso*-β-lapachol are derivatives of α-naphthaquinone (cf. Hooker, J.C.S., 1896, 69, 1381). With regard to the influence of p_H on the position of tautomeric equilibrium, it is shown mathematically that the ratio of the equilibrium constant of the undissociated tautomeride to that of the completely ionised substance is equal to the ratio of the dissociation constants of the two tautomerides.

4-n-*Propoxy*-β-*naphthaquinone*, orange-yellow, m. p. 116°, and 2-n-*propoxy*-α-*naphthaquinone*, pale yellow, m. p. 91°, are described. The following 3-methoxy-2-alkyl-α-naphthaquinones were prepared by treating the corresponding hydroxy-derivatives with diazomethane: 3-*methoxy-2-γ-methyl-*Δ^{β}*-butenyl-*, m. p. 53°; -2-*γ-phenyl-*Δ^{β}*-propenyl-*, m. p. 90·5°; -2-*benzyl-*, m. p. 83·5°, and -2-*diphenylmethyl-α-naphthaquinone*, m. p. 112·5°. Details are given of the preparation of a number of polyhydroxynaphthaquinones (cf. Charrier and Tocco, A., 1923, i, 1028); the *barium* salt of naphthapurpurin is described. iso*Naphthazarin dimethyl ether*, yellow, m. p. 115°, is hydrolysed by aqueous 1% sodium hydroxide solution to a *monomethyl ether*, yellow, m. p. 152°, which is very resistant to further hydrolysis. 3-Hydroxy-2-β-hydroxypropyl-α-naphthaquinone yields 1-methyl-4 : 5-benzocoumaran-3 : 6-quinone (I) when treated with hydrobromic acid in glacial acetic acid, and 1-methyl-5 : 6-benzocoumaran-3 : 4-quinone (II) when treated with concentrated sulphuric acid, reverse changes being effected in each case by the action of aqueous sodium hydroxide, whilst (II) yields (I) when treated with hydrobromic acid (cf. Fieser, A., 1927, 462).

F. G. Willson.

2-Hydroxy-1 : 4-anthraquinone. L. F. Fieser (J. Amer. Chem. Soc., 1928, 50, 465—474).—When treated with aqueous sodium hydrogen sulphite, 1 : 2-anthraquinone yields *sodium* 1 : 2-*dihydroxyanthracene-4-sulphonate*, from which, by oxidation with chromic acid, *sodium* 1 : 2-*anthraquinone-4-sulphonate*, red, is obtained. The corresponding *ammonium* salt (I) is also obtained by treatment of nitroso-β-anthrol with aqueous sodium hydrogen sulphite, and oxidation, with 25% nitric acid, of the resulting 1-*amino-2-anthrol-4-sulphonic acid*, (+½H_2O), yellow. Treatment of (I) with methyl alcohol and concentrated sulphuric acid affords 2-*methoxy*-1 : 4-*anthraquinone*, yellow, m. p. 217°, which is hydrolysed by boiling aqueous sodium hydroxide to 2-*hydroxy*-1 : 4-*anthraquinone* (II), yellow, m. p. 243° (decomp.) (*sodium* salt, orange; *silver* salt, red; *acetate*, yellow, m. p. 195°). When boiled with acetic anhydride, sodium acetate, and zinc dust, (II) yields

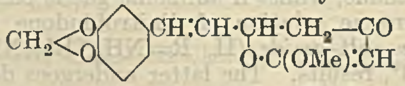
1 : 2 : 4-*triacetoxyanthracene*, m. p. 191°, which, on oxidation with chromic acid in glacial acetic acid, affords triacetylpurpurin, m. p. 202—203° (cf. Schunk and Roemer, A., 1877, ii, 624). Treatment of the silver salt of (II) with methyl iodide in benzene affords 4-*methoxy*-1 : 2-*anthraquinone*, yellow, m. p. 198°, together with about half its weight of the above 2-methoxy-1 : 4-anthraquinone, the former being completely isomerised to the latter when boiled with methyl alcohol and sulphuric acid. Allyl bromide yields, similarly, the following three derivatives, in the proportions given: 4-*allyloxy*-1 : 2-*anthraquinone* (70%), yellow, m. p. 173°, 2-*allyloxy*-1 : 4-*anthraquinone* (11%), yellow, m. p. 139°, and 3-*hydroxy*-2-*allyl*-1 : 4-*anthraquinone* (10%), yellow, m. p. 215°. The *o*-quinonoid derivative is isomerised to the *p*-quinone when heated at 175°, whilst treatment with cold, concentrated sulphuric acid affords 1-*methyl*-5 : 6-(ββ-*naphtha*)*coumaran*-3 : 4-*quinone*, orange-red, m. p. 186—187°. When treated with warm, dilute, aqueous alkali, the latter yields 3-*hydroxy*-2-β-*hydroxypropyl*-1 : 4-*anthraquinone*, yellow, m. p. 211—212°. The reduction potentials of α- and β-anthraquinones are from 81 to 101 millivolts lower than those of the corresponding naphthaquinones, whilst that of α-anthraquinone is 246 millivolts higher than that of 9 : 10-anthraquinone. It is concluded that there is complete analogy between α-anthraquinone and α-naphthaquinone, but that α-anthraquinol is analogous to 9 : 10-anthraquinol. F. G. WILLSON.

[Fritzsch's reagent.] Correction. E. BÖRNSTEIN (Ber., 1928, **61**, [*B*], 443; cf. A., 1927, 155).—The terms α- and β-methylanthracene should be interchanged. H. WREN.

Salicylic acid primeveroside. M. BRIDEL and P. PICARD (Compt. rend., 1928, **186**, 98—99).—Monotropitoside, when hydrolysed by aqueous potassium hydroxide, and then treated with the calculated quantity of sulphuric acid, yields *salicylic acid primeveroside*, α_D −61·6°, a crystalline, non-reducing substance. When hydrolysed by dilute sulphuric acid, the primeveroside yields salicylic acid and equimolecular proportions of xylose and dextrose.

B. W. ANDERSON.

Methysticin. V. LAMPE, J. ZIELINSKA, and J. MAJEWSKA (Bull. Soc. chim., 1928, [iv], **43**, 62—71; cf. Borsche, Meyer, and Peitzsch, A., 1927, 1192).—*Methyl piperoylacetate*, m. p. 132—134°, has been synthesised by boiling *methyl α-piperoylacetoacetate*, m. p. 166—167° (from piperoyl chloride, b. p. 175—185°, and methyl sodioacetoacetate), with dilute acetic acid and proved identical with ψ-methysticin. Pomeranz's structure for methysticin (A., 1889, 278; 1890, 257) is therefore abandoned. Heating at 3 atm. pressure for 3 hrs. converts methyl α-piperoylacetoacetate into piperoylacetone, m. p. 119—120°. *Ethyl α-piperoylacetoacetate*, m. p. 92—94°, with 10% ammonia affords *ethyl piperoylacetate*, m. p. 73—75° (cf. Winzheimer, A., 1908, i, 804). Potassium piperoylacetate and methyl iodide in alcoholic solution also afford ψ-methysticin, together with a substance, m. p. 156—157°. Alcoholic potassium hydroxide converts ψ-methysticin into an indefinite amorphous, orange substance; with 10% alcoholic sulphuric acid or on heating with water under 3 atm., methysticol is obtained. With sodium in anisole ψ-methysticin yields a sodium derivative giving, with acetyl chloride, methyl α-piperoylacetoacetate. On reduction with hydrogen in acetone solution in presence of palladium–barium sulphate, 4 atoms of hydrogen are absorbed, affording an oil which gives no copper salt, and agitated with 2% sodium hydroxide in ether gives an orange-brown solution from which carbon dioxide precipitates an oil. Under similar conditions methysticin absorbs 2 atoms of hydrogen, giving a product m. p. 113—115°. On bromination with the hydrobromide of pyridine dibromide in chloroform, methysticin affords a *dibromo*-derivative, m. p. 156° (decomp.); ψ-methysticin under similar conditions gives a monobromo-derivative, probably *methyl α-bromopiperoylacetic acid*, m. p. 98°, since under similar conditions cinnamoylacetone gives *α-bromo-α-cinnamoylacetone*, m. p. 93—95°, identical with the product obtained by the action of bromine on the copper salt of cinnamoylacetone in chloroform solution. These relations between methysticin and ψ-methysticin are parallel to those obtaining between the chalkones and flavones and support the 1 : 4-pyrone structure advanced for methysticin:



R. BRIGHTMAN.

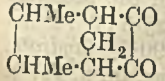
Photochemical oxidation of ergosterol. A. WINDAUS and J. BRUNKEN (Annalen, 1928, **460**, 225—235).—Ergosterol undergoes photo-oxidation in 95% alcohol solution in presence of eosin when submitted to radiation from a powerful filament lamp. Eosin may be replaced by other fluorescent substances, *e.g.*, erythrosin, methylene-blue, chlorophyll, or hæmatoporphyrin. Acridone is feebly sensitising, but rosaniline has no effect. Potassium cyanide inhibits the photo-oxidation, and the latter does not occur at all in the dark.

The product of oxidation is *ergosterol peroxide*, $C_{27}H_{42}O_3$, m. p. 178°, having a normal *M* in camphor or naphthalene, and $[\alpha]_D^{19}$ −35·7° (in chloroform, $[\alpha]_D^{18}$ −35·5°). The peroxide is very unstable in presence of acids. Its chloroform solution becomes greenish-blue, then deep blue, and finally violet when treated with arsenic trichloride. Antimony trichloride and tin tetrachloride give brownish-violet and wine-red colorations, respectively. Concentrated sulphuric acid becomes deep red when shaken with a chloroform solution of the peroxide. When distilled in a high vacuum, the latter affords a crystallisable distillate, not examined, but is for the most part unchanged up to 180—185°. Digitonin precipitates an additive *compound*, $[\alpha]_D^{15}$ −38° in pyridine, from an alcoholic solution of the peroxide; the latter is converted by acetic anhydride into *ergosteryl acetate peroxide*, m. p. 202°, also obtained by the photo-oxidation of ergosteryl acetate in alcoholic (eosin) solution. Alcoholic potassium hydroxide converts the acetate into ergosterol peroxide. The latter on reduction with sodium and alcohol affords ergosterol and then, slowly, *dihydroergosterol*, m. p. 173—174°, $[\alpha]_D^{17}$ −20·4° in chloroform (the readily hydrolysed *acetate*, m. p. 180—181°, has $[\alpha]_D^{16}$ $-20°$ in chloroform), also obtainable direct from ergosterol. Traces of the latter may be removed from dihydroergosterol by treatment with blood charcoal in alcohol, or by photo-oxidation. Dihydroergosterol gives no colour reactions with arsenic or antimony trichlorides, but sulphuric acid gives a yellow, then an orange, solution. Dihydroergosteryl acetate, when reduced with hydrogen in presence of acetic acid and platinum-black, affords γ-ergostyl acetate (Reindel, A., 1927, 241).

Ergosterol peroxide, whether irradiated or otherwise, has neither antixerophthalmic nor antirachitic action, whilst ergosterol prepared from the peroxide is still capable of activation. This suggests that it is ergosterol itself and not an impurity present in it which forms the antirachitic provitamin. Dihydroergosterol, before or after irradiation, is physiologically inactive. E. E. Turner.

Photochemical dehydrogenation of ergosterol. A. Windaus and P. Borgeaud (Annalen, 1928, **460**, 235—239).—Ergosterol dissolved in alcohol containing eosin or erythrosin (chlorophyll has a feeble sensitising action, whilst methylene-blue and rosaniline have none) undergoes photo-dehydrogenation in a glass vessel in sunlight to give *ergopinacol*, $C_{54}H_{82}O_2$, m. p. 202—203° (decomp.), $[\alpha]_D^{16}$ $-209°$ in pyridine. Concentrated sulphuric acid becomes orange when shaken with a chloroform solution of the pinacol. On distillation at 0·1 mm. (bath at 210°) the latter affords *neoergosterol*, $C_{27}H_{42}O$ ($C_{27}H_{40}O$ not impossible), m. p. 151—152°, *M* normal in camphor, $[\alpha]_D$ $-12°$ (*acetate*, m. p. 122—123°), also formed by reducing ergopinacol with zinc dust and glacial acetic acid. Neither ergopinacol nor neoergosterol possesses antirachitic action, whether previously irradiated or not. E. E. Turner.

Santenonequinone and a general method for the preparation of diketones. J. Palmén (Finska Kemistamfundets Medd., 1927, **36**, 11—21; Chem. Zentr., 1927, ii, 1691).—In the preparation of *iso*nitrosocamphor, sodamide and benzene were substituted for sodium and ether. Treatment with formaldehyde and hydrogen chloride then yields a diketone, the method being convenient for diketones having an unsubstituted CH_2-group next to the CO-group. In this way were obtained *iso*nitrososantenone and an oil, possibly a geometrical isomeride. Thence were obtained santenonequinone hydrate, m. p. 137—138°, and santenonequinone (annexed formula), m. p. 84—85° [disemicarbazone, m. p. 238° (uncorr.)]. The dioxime, $C_9H_{14}O_2N_2$, has m. p. 144—145°. Oxidation of the quinone with 2% potassium permanganate solution yields santenic acid, $C_9H_{14}O_4$. A. A. Eldridge.



Higher terpene compounds. XXXI. Second double linking in *d*-pimaric acid. L. Ruzicka, H. W. Huyser, and C. F. Seidel (Rec. trav. chim., 1928, **47**, 363—369; cf. this vol., 297, 298).—Catalytic reduction of *d*-pimaric acid with hydrogen at 220—235°/48 atm. in the presence of platinum-black for 3 days yields a mixture, m. p. 200—203°, of stereoisomeric dihydro-acids. When a platinum oxide catalyst in ethyl acetate at 15° is employed, two stereoisomeric dihydro-acids, m. p. 238—239° (less soluble) and m. p. 228—229°, can be separated by fractional crystallisation of the product from ethyl acetate. Reduction in acetic acid solution with the same catalyst at 50°, however, yields a mixture of stereoisomeric *tetrahydro*-d-*pimaric acids* from which one form, m. p. 236—237°, is isolated in a pure state, and proved by crystallographic data [by Nieuwenkamp] to be different from the dihydro-acid. Further proof of the presence of a second, unreactive, double linking in *d*-pimaric acid is obtained by comparative measurements of the velocity of oxidation, with perbenzoic acid, of *d*-pimaric and abietic acids. In each case one double linking is rapidly attacked with approximately the same velocity, whilst the second reacts only extremely slowly. Dihydroabietic acid, m. p. 167—168° (Ruzicka and Meyer, A., 1922, i, 544), as expected, reacts with only 1 mol. of perbenzoic acid, whilst the isomeric product, m. p. 130°, obtained by the action of hydrogen bromide in acetic acid on the dihydro-acid, and which later (unpublished) work has shown to be an isomeric lactone, is unattacked. J. W. Baker.

Higher terpene compounds. XXXIV. Sesquiterpene compounds of vetiver, West Indian sandalwood, and galangal oils. L. Ruzicka, E. Capato, and H. W. Huyser (Rec. trav. chim., 1928, **47**, 370—381).—The constituents of vetiver, sandalwood, and galangal oils have been investigated. The samples of vetiver oil (cf. Semmler, Risse, and Schröter, A., 1912, i, 882), obtained either from Réunion or Java stock, contain essentially the same constituents. The fraction of b. p. 110—140°/12 mm. contains mainly dicyclic sesquiterpenes together with a small quantity of tricyclic, and on dehydrogenation with sulphur yields cadalene. The fraction of b. p. 140—180°/12 mm. contains the sesquiterpene alcohols. Esterification by means of phthalic anhydride and subsequent hydrolysis of the esters separates the primary alcohols, the less volatile fraction of which is mainly dicyclic (together with small amounts of tricyclic); on dehydrogenation the alcohols yield a mixture of cadalene and eudalene. The intermediate fraction consists of a mixture of tricyclic alcohols with a little dicyclic, and the fraction of higher b. p. contains only tricyclic alcohols, $C_{15}H_{24}O$; when heated with dilute sulphuric acid these lose water to yield sesquiterpenes, but no hydrocarbon picrate could be isolated after dehydrogenation. The unesterified portion consists of a mixture of tertiary alcohols, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, which by heating with 80% formic acid afford a mixture of dicyclic sesquiterpenes, $C_{15}H_{22}$ and $C_{15}H_{24}$, and yield cadalene on dehydrogenation. The fraction of b. p. above 180°/12 mm. after hydrolysis with 10% alcoholic solution of potassium hydroxide contains the tricyclic vetivenic acid $C_{15}H_{22}O_2$ and primary sesquiterpene alcohols.

The second runnings of West Indian sandalwood oil (cf. Deussen, A., 1912, i, 368; von Soden, A., 1900, i, 401) contain no sesquiterpenes, but consist of a mixture of tertiary, dicyclic sesquiterpene alcohols, chiefly $C_{15}H_{26}O$. When they are heated with phthalic anhydride, water is eliminated and a sesquiterpene, $C_{15}H_{24}$, is produced which yields a dihydrochloride identical with that of *l*-cadinene, hence the original constituents are probably a mixture of cadinols.

The more volatile fraction of galangal oil consists of dicyclic sesquiterpenes, mainly cadalene, probably mixed with hydronaphthalene derivatives, and by dehydrogenation yields cadalene. The higher fraction yields a small quantity of a solid, m. p. 167°, and liquid sesquiterpene alcohols, $C_{15}H_{24}O$, which by heating with 90% formic acid yield sesquiterpenes which are dehydrogenated to cadalene. The original oil, therefore, probably contains hydrated hexahydrocadalenes.

J. W. Baker.

Furan. W. C. Wilson (Org. Syntheses, 1927, 7, 40—41).—Furan is obtained in 72—78% of the theoretical yield by heating furan-2-carboxylic acid at 200—205°. A. A. Eldridge.

[Preparation of] furfurylideneacetone. G. J. Leuck and L. Cejka (Org. Syntheses, 1927, 7, 42—43).

[Preparation of] 2-furylmethyl acetate. Miner Laboratories (Org. Syntheses, 1927, 7, 44—45).

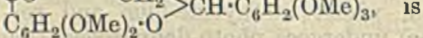
Alkylations. K. von Auwers [with T. Bahr, G. Wegener, and C. Wiegand] (Ber., 1928, 61, [*B*], 408—416; cf. A., 1912, i, 484, 486; 1921, i, 806; 1924, i, 992).—Treatment of ethyl 3-hydroxycoumarone-2-carboxylate or its 5-methyl derivative with alkyl halides shows that production of *C*-compounds is favoured by the use of halides containing an alkyl group of low valency demand (allyl or benzyl), whereas the formation of *O*-derivatives is facilitated by "true" alkyls (ethyl and propyl); the methyl group occupies an intermediate position. The particular halogen present also influences the course of the change. The observations are confirmed with 2-cyano*cyclo*hexanone, with which it is found that *C*-derivatives are produced in greater proportion when the change proceeds most rapidly. The following compounds are incidentally described: 2-*propylcoumaranone*, b. p. 125·5—126°/13 mm., d_4^{20} 1·094, n_{He}^{20} 1·5459, converted by semicarbazide acetate into the *disemicarbazone* of o-*hydroxyphenyl propyl diketone* (+H_2O), m. p. 210—211°; 3-*propoxycoumarone-2-carboxylic acid*, m. p. 154—155°; 2-*allylcoumaranone*, b. p. 132°/13·5 mm., d_4^{20} 1·101, n_{He}^{20} 1·5614; 2-*benzylcoumaranone*, b. p. 193—195°/11 mm., d_4^{20} 1·166, n_{He}^{20} 1·6034 [*disemicarbazone* of *o*-hydroxyphenyl benzyl diketone (+$2H_2O$), m. p. 219—220° (decomp.)]; 3-*benzyloxycoumarone-2-carboxylic acid*, m. p. 159—160°; 3-*propoxy-5-methylcoumarone-2-carboxylic acid*, m. p. 159—160° (decomp.); 5-*methyl-2-allylcoumaranone*, m. p. 56—57° [*disemicarbazone* (+H_2O), m. p. 200°, and *di*-p-*nitrophenylosazone*, decomp. 165—170°, of *p*-tolyl allyl diketone].

H. Wren.

Condensation of certain β-ketonic esters with *o*-hydroxymonostyryl ketones. R. Hill (J.C.S., 1928, 256—259).—In agreement with Heilbron and Hill (A., 1927, 565) it is found that the interaction of α-substituted-β-ketonic esters with *o*-hydroxymonostyryl ketones yields only γ-pyran derivatives and, contrary to the findings of Forster and Heilbron (A., 1924, i, 1323), no trace of the substituted dihydrocoumarin is detected. Interaction of the appropriate ketone with the β-ketonic ester in alcoholic sodium ethoxide at the ordinary temperature for 8 days yields 4-*acetonyl*-2 : 3-*dimethyl*-, m. p. 141°; 4-*phenacyl*-2 : 3-*dimethyl*-, m. p. 179°; 4-*acetonyl*-3-*phenyl*-2-*methyl*-, m. p. 186—187°; and 4-*phenacyl*-3-*phenyl*-2-*methyl*-, m. p. 219—221°, -1 : 4 - *benzopyran*. Ethyl cyanoacetate, ethyl oxaloacetate, and ethyl malonate do not react with *o*-hydroxymonostyryl ketones, whilst when ethyl malonate is allowed to react with 2-hydroxystyryl phenyl ketone in the presence of sodium ethoxide at the ordinary temperature for 10 weeks, coumarin-3-carboxylic acid is the sole product, scisson of the ketone occurring in the presence of the alkali. J. W. Baker.

[Preparation of] xanthydrol. A. F. Holleman (Org. Syntheses, 1927, 7, 88—89).

[Preparation of] xanthone. A. F. Holleman (Org. Syntheses, 1927, 7, 84—86).

Synthesis of myricetin. M. Nierenstein (Ber., 1928, 61, [*B*], 361—362).—The observations of Hattori (A., 1927, 883) show that the flavanone,  $\begin{matrix}CO\text{———}CH_2\\ C_6H_2(OMe)_2\cdot O\end{matrix}\!>\!CH\cdot C_6H_2(OMe)_3$, is converted by amyl nitrate into myricetin 5 : 7 : 3′ : 4′ : 5′-pentamethyl ether (cf. Dean and Nierenstein, A., 1925, i, 951) without possible isolation of the intermediate oximino-compound (contrast Sonn, A., 1925, i, 932).

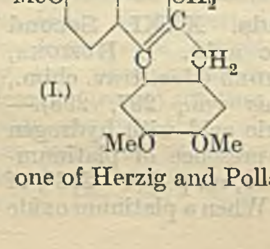
H. Wren.

Gossypol. II. Carruth's *D*-gossypol. E. P. Clark (J. Biol. Chem., 1928, 76, 229—235).—The *D*-gossypol obtained by Carruth from heated cottonseed meal (A., 1918, i, 266) gives, with aniline, dianilinogossypol. *D*-Gossypol cannot therefore be a degradation product of gossypol; it is suggested that it may be gossypol in amide linking with free amino-groups of the cottonseed proteins.

C. R. Harington.

Brazilin and hæmatoxylin. VI. Synthesis of tetramethylanhydrohæmatoxylin. P. Pfeiffer, E. Haack, and J. Willems (Ber., 1928, 61, [*B*], 294—299; cf. A., 1927, 1198).—Pyrogallol 1 : 2-dimethyl ether condenses with β-chloropropionic acid to β-2 : 3-*dimethoxyphenoxypropionic acid*, m. p. 101°, converted by phosphoric oxide in presence of benzene into 7 : 8-dimethoxychromanone, b. p. 196°/17 mm., m. p. 98—100°. The latter compound is converted by veratraldehyde and hydrogen chloride in glacial acetic acid into 7 : 8-*dimethoxy*-3 : 3′ : 4′-*dimethoxybenzylidenechromanone*, m. p. 137—137·5°, catalytically hydrogenated in acetic acid solution in the presence of spongy platinum to 7 : 8-*dimethoxy*-3 : 3′ : 4′-*dimethoxybenzylchromanone*, m. p. 90—90·5° (*hydrate*, m. p. 115°; *oxime*, m. p. 167°). Treatment of the benzyl derivative with phosphoric oxide in presence of benzene yields tetramethylanhydrohæmatoxylin (I.), m. p. 170—173° (decomp.), according to the rate of heating, identical with the tetramethyldeoxyhæmatoxylone of Herzig and Pollak (A., 1905, i, 605).

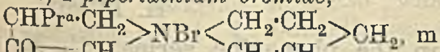
H. Wren.



(I.)

Acylation of thiophen in presence of tin tetrachloride. G. Stadnikov and V. Rakovski (Ber., 1928, **61**, [*B*], 268—269).—Addition of tin tetrachloride to a solution of acetyl chloride and thiophen in light petroleum at 0° causes immediate separation of a crystalline complex compound, decomposed by water into thiophen and 2-acetothienone, b. p. 213—214°/760 mm. [semicarbazone, m. p. 188° (cf. A., 1917, i, 278); oxime, m. p. 81°; phenylhydrazone, m. p. 94·5°]. 2-Benzothienone, m. p. 55° (oxime, m. p. 93°), is prepared similarly. H. Wren.

Bromination of tertiary β-ketonic bases and synthesis of 3-hydroxy-1-methylpyrrolidine. C. Mannich and T. Gollasch (Ber., 1928, **61**, [*B*], 263—268).—α-Dimethylaminobutan-γ-one does not react simply with bromine, whereas its hydrobromide is converted by bromine and hydrogen bromide in glacial acetic acid into δ-*bromo-α-dimethylaminobutan-γ-one hydrobromide*, m. p. 103°, in 65% yield from which potassium carbonate liberates the corresponding unstable *base*, whereas barium hydroxide converts it into 3-*keto*-1 : 1-*dimethylpyrrolidinium bromide*, m. p. 213—215° [*oxime*, m. p. 209°; 3-*keto*-1 : 1-*dimethylpyrrolidinium chloride*, m. p. 185°, and *chloroaurate*, m. p. 183° (decomp.)]. Reduction of the chloride by sodium amalgam in hydrochloric acid solution affords α-dimethylaminobutan-γ-ol, which is also produced by electrolytic reduction at a lead cathode together with small quantities of 3-*hydroxy*-1 : 1-*dimethylpyrrolidinium chloride* (*chloroaurate*, decomp. 260°), more readily prepared by catalytic hydrogenation in aqueous solution under pressure in presence of spongy platinum. 3-*Hydroxy*-1-*methylpyrrolidine*, b. p. 77°/16 mm., obtained by thermal decomposition of the above chloride in an atmosphere of nitrogen, gives a *chloroaurate*, m. p. 191° (decomp.), very hygroscopic *hydrochloride*, *methiodide*, m. p. 260°, and *benzoate hydrochloride*, m. p. 146°. γ-Piperidinomethyl-Δᵋ-hexen-β-one hydrobromide is hydrogenated in aqueous solution in the presence of palladised charcoal to γ-*piperidinomethylhexan*-β-*one hydrobromide*, m. p. 151° (corresponding *base*, b. p. 126°/16 mm.). The salt is transformed by bromine in chloroform solution into α-*bromo*-γ-*piperidinomethylhexan*-β-*one hydrobromide*, m. p. 142°, converted by barium hydroxide into spiro-1-(4′-*keto*-3′-*propylpyrrolidinium*)-1-*piperidinium bromide*,



$$\begin{array}{l}CHPr^{\alpha}\cdot CH_2\\ |\\ CO—CH_2\end{array}>NBr<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>CH_2$$

, m. p. 221°.

H. Wren.

By-products of the hydrogenation of pyridine under pressure. V. S. Sadikov and A. K. Mikhailov (Ber., 1928, **61**, [*B*], 421—427).—Hydrogenation of pyridine under pressure in presence of osmium deposited on asbestos affords ammonia, piperidine (up to 70%), and products of high b. p. from which the *compounds* $C_9H_{19}N$ and $C_{15}H_{30}O_2$ are isolated. The former compound, regarded as 1-*methyl*-3-*propylpiperidine*, b. p. 195—200°, *d* 0·8415, mol. wt. 151, yields a *picrate*, m. p. 106—107°, and *methiodide*, $(C_9H_{19}N)_2,MeI$, m. p. 81°. With hydroferrocyanic and hydrochloric acids it appears to give the *substances* $(C_8H_{17}N)_2,H_4FeC_6N_6$ and $C_8H_{17}N,HCl$, m. p. 200°. The latter compound, considered to be 2 : 2′-*dimethyl*-3-*propyl*-1 : 1′-*dipiperidyl*, b. p. 295—300°, is characterised by its *hydroferrocyanide*, $C_{15}H_{30}N_2,H_4FeC_6N_6$, *methiodide*, $C_{15}H_{30}N_2,2MeI$, m. p. 269—270°, and *picrate*, m. p. 191° (attempts to recover the base from the picrate are accompanied by extensive resinification and the volatile product gives a *hydrochloride*, $C_{15}H_{26}N_2,2HCl$, m. p. 157°); when evaporated with hydrochloric acid the base loses its methyl groups and affords the *salt*, $C_{15}H_{26}N_2,2HCl$, m. p. 258°. If asbestos impregnated with 20% of osmium and 1% of cerium dioxide is used, the hydrogenation is extraordinarily accelerated and the product contains 34·6% of piperidine, 55·8% of methylpropylpiperidine, and 9·1% of 2 : 2′-dimethyl-3-propyl-1 : 1′-dipiperidyl. If reduction is effected in an autoclave provided with a cooled side tube in which volatile products of the reaction can be condensed during the progress of the change, the less volatile bases are obtained in high yield, thus indicating that alkylation of the piperidine occurs in the early stages of hydrogenation. H. Wren.

Local anæsthetics derived from β-piperidylcarbinol. L. T. Sandborn and C. S. Marvel (J. Amer. Chem. Soc., 1928, **50**, 563—567).—3-*Piperidylcarbinol*, b. p. 106—107°/3·5 mm., d_4^{20} 1·0263, n_D^{20} 1·4964, is obtained in 40—43% yield by reduction of ethyl nicotinate with sodium and alcohol. The following alkyl derivatives were prepared by the action of the appropriate alkyl bromides or iodides in boiling benzene: N-*methyl*-, b. p. 110—112°/7 mm., d_4^{20} 1·0125, n_D^{20} 1·4988; N-*ethyl*-, b. p. 110—111°/6·5 mm., d_4^{20} 0·9904, n_D^{20} 1·4911; N-iso*propyl*-, b. p. 93—94°/3·5 mm., d_4^{20} 0·9881, n_D^{20} 1·4916; N-n-*butyl*-, b. p. 100—102°/4 mm., d_4^{20} 0·9484, n_D^{20} 1·4838; and N-*allyl*-3-*piperidylcarbinol*, b. p. 110—111°/7 mm., d_4^{20} 0·9873, n_D^{20} 1·4982. These were converted into the *p*-nitrobenzoate hydrochlorides and *p*-aminobenzoate hydrochlorides by the usual methods, the m. p. of the two derivatives of each carbinol, taken in the above order, being as follows: 187—190°, 174—177°; 194—195°, 188—190°; 196—200°, 235·5—237·5°; 197—198°, 205—207°; 186—187·5°, —. The aminobenzoate hydrochlorides possess relatively low toxicity and strong local anæsthetic action. F. G. Willson.

2-Dimethylaminopyridine and its derivatives. A. E. Tschitschibabin and I. L. Knunianz (Ber., 1928, **61**, [*B*], 427—434).—2-Dimethylaminopyridine, b. p. 88°/15 mm., is obtained in 40—50% yield by the action of sodamide and methyl sulphate on 2-aminopyridine in the presence of ether. Unchanged primary and secondary amine are removed from the crude mixture by means of acetic anhydride. The compound differs from dimethylaniline in its inability to afford a nitroso-derivative or to couple with diazonium compounds. Nitration yields 5-*nitro*-2-*dimethylaminopyridine*, m. p. 154—155°, and 3 : 5-*dinitro*-2-*dimethylaminopyridine*, m. p. 125—126°. The mononitro-compound is reduced by tin and hydrochloric acid to 5-*amino*-2-*dimethylaminopyridine*, m. p. 55—56° (*dihydrochloride*, m. p. 225—226°; *chlorostannite*, m. p. 148—150°), which gives the customary diazo-reactions and yields 5-*iodo*-2-*dimethylaminopyridine*, m. p. 55°, and 5-*bromo*-2-*dimethylaminopyridine*, m. p. 42—43°. Bromination of

2-dimethylaminopyridine in dilute sulphuric acid gives the 5-bromo-derivative (*picrate*, m. p. 208°) and 3 : 5-dibromo-2-dimethylaminopyridine, isolated as the *picrate*, m. p. 185—186°. The 5-bromo-compound is also obtained by methylation of 5-bromo-2-aminopyridine with sodamide and methyl sulphate. 2-Dimethylaminopyridine is converted by sodamide at 190° into dimethylamine and 2 : 6-diaminopyridine.

H. WREN.

Constitution of vasicine. I. Synthesis of 4-hydroxy-2-propyl-(and *iso*propyl)quinazoline. A. K. DE and J. N. RAY (J. Indian Chem. Soc., 4, 541—545).—Butyranilide and *iso*butyranilide condense with ethyl carbamate in boiling xylene solution in presence of phosphoric oxide to give 4-hydroxy-2-propylquinazoline, m. p. 197° (*picrate*, m. p. 184°), and 4-hydroxy-2-*iso*propylquinazoline, m. p. 227° (decomp.) (*picrate*, m. p. 215—216°), respectively. The natural product has m. p. 196° (picrate, m. p. 199°) and depresses the m. p. of the propyl derivatives above, and thus Ghose's suggested constitution (A., 1927, 785) is incorrect. Bischler and Lang (A., 1895, i, 250) give the m. p. of the propyl and *iso*propyl derivatives as 205° and 195—196°, respectively, whilst Niementowski gives the m. p. of the latter as 224°.

C. D. LANGFORD.

Reactivity of *ortho*-diketonic groups placed between two nitrogen atoms. P. K. DE and A. C. SIRCAR (J. Indian Chem. Soc., 4, 531—534).—2-Thio-1 : 3-diphenylparabanic acid and *o*-phenylenediamine (2 mols.) react in boiling pyridine to give *o*-phenyleneoxamide, aniline, and (?) thionyl-*o*-phenylenediamine. *s*-Diphenylthiocarbamide is probably formed as an essential intermediate. *s*-Diphenylthiocarbamide and *o*-phenylenediamine under similar conditions afford aniline and thionyl-*o*-phenylenediamine. Dinitrothiophenylparabanic acid behaves like the parent acid. Diphenylparabanic acid affords *o*-phenyleneoxamide and *s*-diphenylcarbamide.

C. D. LANGFORD.

Reaction of organic halogen compounds with copper and pyridine. P. KARRER, W. WEHRLI, E. BIEDERMANN, and M. DALLA VEDOVA (Helv. Chim. Acta, 1928, **11**, 233—239).—When *p*-toluenesulphonyl chloride is treated with copper bronze and dry pyridine there are formed di-*p*-tolyl disulphoxide, di-*p*-tolyldisulphone, dipyridine copper chloride, $[(C_5H_5N)_2Cu]Cl_2$, and a compound, probably $C_6H_4Me\cdot SO_3Cu(C_5H_5N)_2$. Similar treatment of hippuryl chloride yields *NN*-dibenzoyldiketopiperazine, m. p. 137°, hydrolysed by concentrated hydrochloric acid to *N*-benzoyldiketopiperazine, m. p. 205°. Phthalyl chloride furnishes a small amount of diphthaloyl, m. p. 335°.

H. BURTON.

Formation of derivatives of dihydrobenziminazole and tetrahydroquinoxaline by the action of acetic anhydride and zinc chloride on nitro-derivatives of alkylanilines. P. VAN ROMBURGH and H. W. HUYSER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 844—849).—When dinitrodimethylanilines are boiled with zinc chloride and acetic anhydride for 4—5 hrs., acetyl derivatives of 2-keto-1 : 2-dihydrobenziminazole are obtained. Thus 3 : 6- and 2 : 4-dinitrodimethylanilines yield, respectively, 6-*nitro*- (I), m. p. 185—186°, and 5-*nitro*-, m. p. 175—176°, -2-*keto*-3-*acetyl*-1-*methyl*-1 : 2-*dihydrobenziminazoles*, which by boiling with alkali are converted into 6-*nitro*- (II), m. p. 272°, and 5-*nitro*-, m. p. 300°, -2-*keto*-1-*methyl*-1 : 2-*dihydrobenziminazoles*. The latter are readily re-acetylated to the parent substances and, by reduction with iron and hydrochloric acid, yield the *hydrochlorides* ($+H_2O$) of the corresponding 6- and 5-amino-derivatives, whilst by treatment with phosphorus pentachloride in phosphoryl chloride as a solvent they are converted into 2-*chloro*-6-*nitro*- and 2-*chloro*-5-*nitro*-1-*methylbenziminazoles*. Synthesis of (II) is effected by the interaction of carbonyl chloride and 4-nitro-2-aminomethylaniline. By a similar treatment for 72 hrs. 3 : 4 : 6-trinitrodimethylaniline yields 5 : 6-*dinitro*-2-*keto*-1-*methyl*-1 : 2-*dihydrobenziminazole*, m. p. 294°, which yields a 3-*acetyl* derivative, m. p. 191°, identical with that obtained by nitration of (I). A similar reaction applied to nitrodiethylanilines leads to the formation of derivatives of 3-keto-1 : 2 : 3 : 4-tetrahydroquinoxaline. Thus 3 : 6-dinitrodiethylaniline yields 7-*nitro*-3-*keto*-4-*acetyl*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 127°, from which, by hydrolysis, 7-*nitro*-3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 206° (*nitroso*-derivative), is obtained. Similarly, from 2 : 4-dinitrodiethylaniline, 6-*nitro*-3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 157°, is obtained.

J. W. BAKER.

Derivatives of *iso*indigotin. A. WAHL and FÉRICEAN (Compt. rend., 1928, 186, 378—380; cf. A., 1927, 470).—Treatment of 5-chloro- and 7-chloroisatin with hydrogen sulphide (A., 1925, i, 588) affords 5 : 5′-*dichloro*- and 7 : 7′-*dichloro-disulphoisatide*, which are transformed in boiling pyridine into 5 : 5′-*dichloro*- and 7 : 7′-*dichloro*-iso*indigotins*, together with small amounts of 5-*chloro*- and 7-*chloro-oxindoles* (the corresponding *benzylidene* derivatives have m. p. 204° and 185°, respectively). The formation of the oxindoles is explained thus : $2C_{16}H_{10}O_2N_2Cl_2S_2 \longrightarrow C_{16}H_8O_2N_2Cl_2+2C_8H_6ONCl+4S$. Reduction of the dichloro*iso*indigotins by zinc and acetic acid gives the corresponding *leuco*-compounds. Condensation of the chloroisatins with oxindole in presence of piperidine affords the corresponding *chloroisatans*, which are dehydrated by boiling acetic–hydrochloric acids (cf. A., 1924, i, 322) into 5-*chloro*- and 7-*chloro*-iso*indigotins*.

H. BURTON.

Syntheses in the phenazine series. H. MCCOMBIE, H. A. SCARBOROUGH, and W. A. WATERS (J.C.S., 1928, 353—359).—The method of Fischer and Heiler (A., 1893, 266) has been applied to the synthesis of various 1- and 2-substituted phenazine derivatives, the use of anhydrous sodium acetate (Kehrmann and Havas, A., 1913, i, 298) not being suitable for the preparation of substituted phenazines. The yields in all cases are only of the order of 5% of the theoretical. By heating a mixture of *o*-chloronitrobenzene, *o*-toluidine, and anhydrous sodium acetate for 20 hrs. at 220—240° a 10% yield of 2-*nitro*-2′-*methyldiphenylamine*, m. p. 76°, is obtained. This, by reduction with alcoholic stannous chloride, yields the corresponding 2-*amino*-compound, m. p. 64°, which is converted by heating with litharge at 200—240°

under reduced pressure into 1-*methylphenazine*, m. p. 108° (*chloroplatinate*, decomp. above 200°). The same compound is obtained by the action of sodium sulphate on 2 : 3-tolylenediamine and *o*-benzoquinone in anhydrous ether for 2 days. 2-*Chlorophenazine*, m. p. 139°, is similarly obtained by the litharge method from 4-chloro-2-nitrodiphenylamine, whilst 2-*bromophenazine*, m. p. 150°, is obtained from 4′-*bromo*-2-*aminodiphenylamine*, m. p. 128°, obtained by the reduction of 4′-*bromo*-2-*nitrodiphenylamine*, m. p. 167°, which is prepared by the interaction of *o*-chloronitrobenzene and *p*-bromoaniline. By similar methods, 2-*nitro*-4′-*methoxydiphenylamine*, m. p. 89° (for which crystallographic data are given), is prepared and reduced to the corresponding 2-*amino*-compound, m. p. 78°, from which 2-*methoxyphenazine*, m. p. 126° (*chloroplatinate*, decomp. above 250°), is synthesised. This compound is not identical with hemipyocyanine (Wrede and Strack, A., 1925, i, 844). A similar attempt at ring closure with 2-*amino*-2′-*methoxydiphenylamine*, m. p. 58°, obtained by reduction of the 2-*nitro*-compound, m. p. 83°, leads only to the production of phenazine, instead of the 1-methoxy-derivative. Reduction of 2-nitrodiphenylamine-2′-carboxylic acid yields the 2-*amino*-derivative, m. p. 204° (*ammonium* and *double tin* salts; *hydrochloride*, decomp. 240°), but attempts to effect ring closure in order to synthesise a substance having the seven-membered ring lactam structure, assigned by Wrede and Strack (*loc. cit.*) to hemipyocyanine, were unsuccessful. The free amino-acid by heating or by treatment with concentrated sulphuric acid yields a green *substance*, m. p. 255° (decomp.). J. W. Baker.

I. 8-Iodoxanthines. II. Preparation and properties of xanthine. III. Alkylation in the xanthine series. IV [with R. Lemberg] **Ethylation of ψ-uric acid.** H. Biltz and A. Beck (J. pr. Chem., 1928, [ii], **118**, 149—224).—In continuation of previous work (cf. A., 1922, i, 380—384) it is shown that 8-thiouric acids which have a hydrogen atom in the 7- or 9-position (8-thiolxanthines) are converted by iodine and sodium hydrogen carbonate into 8-iodo*iso*xanthines and 8-iodoxanthines, respectively. Thus, 8-thio-1 : 9-dimethyluric acid (A., 1921, i, 612) yields 8-*iodo*-1 : 9-*dimethyl*-$\Delta^{7:8}$-iso*xanthine*, decomp. 280—320°, darkening from 230°, which is reduced by hydriodic acid to 1 : 9-dimethyl*iso*xanthine; 8-thio-1 : 3 : 9-trimethyluric acid yields 8-*iodo*-1 : 3 : 9-*trimethyl*-$\Delta^{7:8}$-iso*xanthine*, m. p. 260—265°, losing iodine from 225° (*periodide*, $C_8H_9O_2N_4I_2$), which is reduced to *iso*caffeine; 8-*thio*-3 : 7-*dimethyluric acid*, m. p. 335—337° (decomp.), prepared from 8-chloro- or 8-bromo-theobromine and potassium hydrogen sulphide, yields 8-*iodotheobromine*, m. p. 330—335°, decomp. from 250°; 8-thio-1 : 3-dimethyluric acid, decomp. 320° (cf. Boehringer & Söhne, A., 1903, i, 868), prepared from 8-bromotheophylline (A., 1914, i, 586), yields 8-*iodotheophylline*, decomp. 303—305°, altering from 250°, which is reduced to theophylline; 8-thio-1 : 3 : 7-trimethyluric acid yields 8-*iodocaffeine*, m. p. 230°, and 8-thiouric acid (cf. Fischer and Tüllner, A., 1902, i, 664), prepared by an improved method, yields 8-*iodoxanthine*, decomp. from 200° (*potassium*, *sodium*, and *ammonium* salts). Unlike xanthine, this last exhibits acidic properties only. Attempts to prepare 8-iodo-9-phenyl*iso*xanthine and 2 : 6-di-iodo-7-methylpurine from the corresponding thiol derivatives by this method were unsuccessful.

A large number of experiments on the production of xanthine from uric acid and 8-thiouric acid are described. The optimum conditions, which must be closely followed, for its preparation by Sundvik's method (A., 1912, i, 321), are: a mixture at 170° of 500 c.c. of glycerol, 50 c.c. of 95% formic acid, and 20 g. of crude uric acid is warmed during 30—40 min. to 230°, maintained at this temperature until 3—10 min. after dissolution is complete, cooled rapidly, and poured into water. The xanthine (6 g.) is extracted from the unchanged uric acid by 2*N*-hydrochloric acid and completely freed from the latter by prolonged digestion with 23% nitric acid. Coloured impurities are removed by recrystallising the sodium salt. The physical properties of xanthine, its lack of reactivity, and its insolubility in all chemically indifferent solvents (except "polyglycol," from which it separates in microscopic crystals) indicate that, like cellulose, it is probably in a highly associated molecular condition. It affords a characteristic *perchlorate* ($+H_2O$), m. p. 262—264°, sintering from 250° (crystallographic data), also a *hydrobromide* ($+H_2O$), *hydriodide* ($+H_2O$), decomp. 220°; *fluoborate*; *hydrofluoride*, $C_5H_4O_2N_4,2HF$; *chlorostannite*, $(C_5H_4O_2N_4)_2,H_2SnCl_4,H_2O$, and *zincichloride*, $[Zn(C_5H_4O_2N_4)_2]Cl_2$, decomp. 310—350°. *Theobromine perchlorate* ($+H_2O$), decomp. 271—273°, sinters from 250°. Unsuccessful attempts to chlorinate, brominate, and acetylate xanthine are described.

The literature relating to the alkylation of xanthine derivatives is comprehensively reviewed. Further examples of the use of (*a*) diazomethane, (*b*) methyl sulphate and alkali, are given. Ethyl bromide may be used instead of the iodide with alkali in a sealed tube at 100° (*c*), or under reflux (*d*). The thiol group in 8-thiolxanthines may be alkylated in alkaline solution at the ordinary temperature by means of methyl iodide (*e*) or ethyl sulphate (*f*). The following compounds have been prepared by these methods: caffeine from xanthine (*a*)(*b*), or theophylline (*b*); 8-bromocaffeine from 8-bromotheophylline (*b*); 7-ethyltheophylline from theophylline (*c*); 8-bromo-7-ethyltheophylline from 8-bromotheophylline (*c*); 8-*methylthioltheobromine*, m. p. 263°, from 8-thioltheobromine (*e*); 8-*methylthioltheophylline*, m. p. 307—310°, from 8-thioltheophylline (*e*); 8-methylthiolcaffeine from 8-thiolxanthine and its lower methylation products (*a*)(*b*); 8-*ethylthiolxanthine*, m. p. 302° (decomp.), from 8-thiolxanthine (*f*); 8-*ethylthioltheobromine*, m. p. 217°, from 8-thioltheobromine (*d*)(*f*); 8-*ethylthioltheophylline*, m. p. 249°, from 8-thioltheophylline (*d*)(*f*); 8-*ethylthiolcaffeine*, m. p. 137°, from 8-thiolcaffeine (*d*)(*f*); 8-*ethylthiol*-1-*ethyltheobromine*, m. p. 136°, from 8-thioltheobromine (*c*, at 80°). 8-Bromo-7-ethyltheophylline and potassium hydrogen sulphide afford 8-*thiol*-7-*ethyltheophylline*, m. p. 264°, from which 8-*ethylthiol*-7-*ethyltheophylline*, m. p. 115°, is obtained by methods (*c*) and (*f*) and the 8-*methylthiol derivative*, m. p. 128°, by (*b*). When 8-thioltheobromine is refluxed with allyl bromide and 10% potassium hydroxide it yields a mixture of

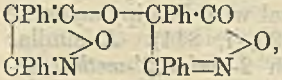
8-*allylthioltheobromine*, m. p. 212°, and 8-*allylthiol*-1-*allyltheobromine*, m. p. 118°, whilst 8-thiolcaffeine is similarly converted into 8-*allylthiolcaffeine*, m. p. 97—100°. Diallyl ether is obtained in high yield by heating allyl bromide with 50% potassium hydroxide in a sealed tube at 100°.

Attempts to ethylate ψ-uric acid or potassium ψ-urate using ethyl sulphate or bromide, to methylate it with diazomethane or with methyl alcohol and hydrogen chloride, and to prepare carbethoxy- and carbomethoxy-derivatives from it, were unsuccessful. H. E. F. NOTTON.

Transformation of hæmin and *meso*hæmin into isomerides. R. KUHN and C. SEYFFERT (Ber., 1928, 61, [*B*], 307—314).—Attempts to acetylate α-chlorohæmin by acetic anhydride in the presence of chloroform and pyridine result in its isomerisation to allo*hæmin*. The anhydride is the essential reagent and the same effect may be (less advantageously) produced by a large excess of boiling acetic anhydride. *allo*Hæmin differs from hæmin I in crystalline habit, free solubility in chloroform, and insolubility in cold 2*N*-sodium carbonate or boiling 0·02*M*-disodium hydrogen phosphate. The spectra of the two compounds are identical in dry or moist pyridine within the limits of experimental error. *allo*Hæmin loses the FeCl group very slowly when acted on by formic acid and iron powder under the conditions laid down for the preparation of protoporphyrin. With phosphonium iodide and hydriodic acid it gives *meso*porphyrin much more easily and in a purer form than does hæmin. When boiled with methyl alcohol containing sulphuric acid it affords tetramethylhæmatoporphyrin isolated as complex iron salt agreeing in m. p. 178—180° and crystalline form with the product obtained by Fischer and Lindner (A., 1927, 886) from hæmin. Catalytic hydrogenation in chloroform causes loss of iron. With methyl-alcoholic hydrogen chloride it affords a crystalline dimethyl ester similar to that obtained from hæmin dimethyl ester and acetic anhydride in pyridine–chloroform; it is uncertain whether the compounds are identical with one another and with Küster's hæmin dimethyl ester. If a solution of *allo*hæmin in chloroform is poured into hot, glacial acetic acid, *hæmin* II is precipitated. In solubility and spectroscopic behaviour, hæmin II is very similar to acetic acid hæmin (hæmin I), but differs from it in crystalline habit and probably is a modification of the latter substance. In pyridine–acetic anhydride, hæmins I and II yield the same *allo*-hæmin. *allo*Hæmin, unless carefully freed from enclosed acetic anhydride, is gradually isomerised if exposed to moist air, whereas the homogeneous compound is stable.

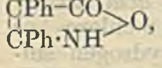
Under similar conditions, *meso*hæmin is isomerised to allomeso*hæmin*, $C_{34}H_{28}O_4N_4ClFe$, differentiated from the initial material by insolubility in 2*N*-sodium carbonate and free solubility in chloroform. It is re-converted into *meso*hæmin by crystallisation from glacial acetic acid. Manganese*meso*hæmin is isomerised by boiling acetic anhydride to allo*manganese*-meso*hæmin*, $C_{34}H_{36}O_4N_4ClMn$, readily soluble in chloroform but insoluble in cold 2*N*-sodium carbonate. H. WREN.

Diphenyl*iso*oxazolone. Tautomerism of *iso*-oxazolones. E. P. KOHLER and A. H. BLATT (J. Amer. Chem. Soc., 1928, 504—516).—When an ethereal solution of diphenyl*iso*oxazolone is shaken with aqueous copper acetate, the mixed *copper* salt, $C_{15}H_{10}O_2N{\cdot}CuO{\cdot}OAc$, deep blue or purple, is precipitated. A *magnesium bromide* salt is obtained by adding the *iso*oxazolone to excess of ethereal magnesium ethyl bromide. Treatment of diphenyl*iso*oxazolone with bromine in carbon tetrachloride affords 4-*bromo*-3 : 4-*diphenyl*iso*oxazolone*, m. p. 72°, whilst phosphorus pentachloride in chloroform yields similarly 4-*chloro*-3 : 4-*diphenyl*iso*oxazolone*, m. p. 77—78°. Diphenyl*iso*oxazolone is readily oxidised by ferric chloride, aqueous bromine, nitrous and nitric acids, potassium permanganate, and potassium ferricyanide, with formation of the *ether*



$$\begin{array}{l}\mathrm{CPh{:}C{-}O{-}CPh{\cdot}CO} \\ \mathrm{|\quad >O\quad |\qquad\quad >O} \\ \mathrm{CPh{:}N\qquad CPh{=}N}\end{array}$$

, m. p. 154—156° (decomp.), the constitution of which is established by its formation by condensation of the sodium salt of diphenyl*iso*oxazolone and the above 4-bromo-derivative in ether. Bromine titration of alcoholic solutions of diphenyl*iso*oxazolone indicates the presence, in solution, of the enolic tautomeride to the extent of about 90% after equilibrium is established, whilst the lower results obtained with fresh solutions indicate that the solid substance is not the enolic modification. Methylation of diphenyl*iso*oxazolone by a variety of methods yields always N-*methyl*-3 : 4-*diphenyl*iso*oxazolone*, m. p. 92°. The latter is unaffected by boiling concentrated hydrochloric acid, but yields deoxybenzoin and benzoic acid when boiled with methyl-alcoholic potassium hydroxide. The N-*benzyl* derivative has m. p. 123°, and behaves similarly. Treatment of the methyl derivative with ozone in carbon tetrachloride yields benzoylformic acid. Treatment of diphenyl*iso*oxazolone with benzoyl chloride yields a *benzoyl* derivative, m. p. 138—139°, whilst treatment of the sodium salt with ethereal ethyl chloroformate affords a *carbethoxy*-derivative, m. p. 109—110° after softening at 103°. Neither of these derivatives forms an ozonide, but both are readily hydrolysed with regeneration of the *iso*-oxazolone, from which it is concluded that the acyl derivatives have probably an *O*-acyl structure. Diphenyl*iso*oxazolone is very slowly attacked by 6% ozone, but does not yield an ozonide or any normal decomposition products of such a derivative, from which it appears that the possible tautomeride,



$$\begin{array}{l}\mathrm{CPh{-}CO} \\ \qquad\qquad >\mathrm{O} \\ \mathrm{CPh{\cdot}NH}\end{array}$$

, does not exist. F. G. WILLSON.

Preparation of thiolbenzthiazoles. L. B. SEBRELL and J. TEPPEMA.—See B., 1928, 152.

Heterocyclic dyes. K. FUCHS and E. GRANANG (Ber., 1928, 61, [*B*], 57—65).—Heterocyclic dyes are described analogous to pinacyanol but containing the group :CH·N:N· in place of :CH·CH:CH·. They act as powerful desensitisers towards the photographic plate whether in pre-treatment or as an addition to the developer. *as*-Phenylethylthiocarbamide is transformed by bromine in chloroform solution into

1-imino-2-ethylbenzthiazoline, $C_6H_4{<}{NEt \atop -S--}{>}C{:}NH$, m. p. 83—84° (cf. Besthorn, A., 1910, i, 507), converted by nitrous acid into the corresponding *nitroso*-derivative, decomp. 131—131·5°, passing in boiling xylene into 2-*ethylbenzthiazolone*, b. p. 170°/14 mm., and reduced by zinc dust and 50% acetic acid to 2-*ethylbenzthiazolonehydrazone*, m. p. 77·5—78·5°.

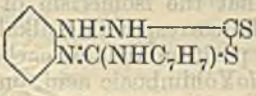
2-Iodoquinoline methiodide, prepared from 2-chloroquinoline and methyl iodide at a temperature not exceeding 80°, is transformed by methyl hydrazinecarboxylate in boiling alcohol into *methyl* 1-*methyl*-2-*quinolonehydrazonecarboxylate*, m. p. 167—168° (decomp.), converted by boiling hydrochloric acid into 1-*methyl*-2-*quinolonehydrazone*, m. p. 126—127° (decomp.) [*hydrochloride*; *hydriodide*]. Treatment of 2-quinolylhydrazine with methyl iodide does not afford a ready method for preparing the quinolone derivative. The action of a large excess of hydrazine hydrate on 2-iodoquinoline methiodide leads mainly to the production of the corresponding *ketazine*, $C_{20}H_{18}N_4$, m. p. 257—258° (*perchlorate*). 2-Iodoquinoline methiodide and 2-ethylbenzthiazolonehydrazone in boiling alcohol afford the 2-*ethylbenzthiazolonehydrazone* of 1-*methyl*-2-*quinolone*, m. p. 137—138° (*perchlorate*).

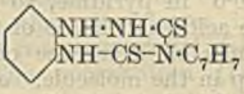
The necessary aldehydic components for the preparation of the dyes are obtained by the action of *p*-nitrosodimethylaniline in the presence of piperidine on the quaternary perchlorates or bromides of the methylquinoline or methylbenzthiazole derivatives followed by fission of the condensation products by boiling dilute acid. The dyes from 2-ethylbenzthiazolonehydrazone are derived by treating a hot aqueous solution of its hydrochloride or perchlorate with a solution of the corresponding Schiff's base in dilute perchloric acid. Those from methyl 1-methyl-2-quinolonehydrazonecarboxylate are obtained by hydrolysing the latter with boiling, fuming hydrochloric acid and adding a solution of the requisite aldehyde. The following compounds are described: 2-*ethylbenzthiazolenylhydrazone* of *pyridine-2-aldehyde methobromide*, decomp. (indef.) 234—237°, *quinoline-2-aldehyde methoperchlorate*, decomp. (indef.) 230—235°, and *benzthiazole-1-aldehyde methoperchlorate*, decomp. 260—262°; 1-*methyl-2-quinolenylhydrazone* of *quinoline-2-aldehyde methoperchlorate*, decomp. (indef.) 210—212°; 1-*methyl-2-quinolenylhydrazone* of *benzthiazole-1-aldehyde methoperchlorate*, decomp. 253—255°.

H. Wren.

o-Aminophenylhydrazine and heterocyclic compounds derived from it. III. Lengthened o-di-derivatives of benzene and their ring-closure. P. C. Guha and T. N. Ghosh (J. Indian Chem. Soc., 4, 561—572).—The following compounds are described: 1-o-*nitrophenyl*-4-p-*tolylthiosemicarbazide*, m. p. 176°; 1-o-*aminophenyl*-4-p-*tolylthiosemicarbazide*, m. p. 252—253° (decomp.); 4-p-*tolyl*-3-*thiol*-1 : 4-*dihydrobenz*-1 : 2 : 4-*triazine*, m. p. 182° (corresponding *disulphide*, m. p. 97—98°, decomp.); 1-o-*nitrophenyl*-4-(1′ : 3′ : 4′)-*xylylthiosemicarbazide*, m. p. 112°; 1-o-*aminophenyl*-4-(1′ : 3′ : 4′)-*xylylthiosemicarbazide hydrochloride*, m. p. 255—256° (decomp.); 1-*xylylthioldihydrobenztriazine*, m. p. 173—174°; 1-o-*nitrophenyl-4-allylthiosemicarbazide*, m. p. 160°; 1-o-*aminophenyl-4-allylthiosemicarbazide hydrochloride*, m. p. 247—248° (decomp.); 1-*phenylthiocarbamido-2-phenylthiosemicarbazidobenzene*, m. p. above 290°; 1-p-*tolylthiocarbamido-2-phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*xylylthiocarbamido-2-phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*allylthiocarbamido-2-phenylthiosemicarbazidobenzene*, not melting at 290°; 1-p-*tolylthiocarbamido-2-p-tolylthiosemicarbazidobenzene*, m. p. 281—282°; the *substance* (I or II), m. p. 200°; 1-*carbamido-2-phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*phenylcarbamido-2-phenylthiosemicarbazidobenzene*, m. p. above 290°; the *substance* III, m. p. 145°; the *substance* IV (R=Ph) as *hydrochloride*, m. p. 140°; the *substance* IV ($R=C_7H_7$) as *hydrochloride*, not melting at 290°; the substance V (R=Ph), m. p. 83—84°; the substance V (R=allyl), m. p. 81—82°; 1-o-*benzylideneaminophenyl-4-phenylthiosemicarbazide*, m. p. 168—169°; 1-o-(o′-*nitrobenzylideneaminophenyl-4-phenylthiosemicarbazide*, m. p. 260°; the substance VI as *hydrochloride*, m. p. 216—217°.

(I.)





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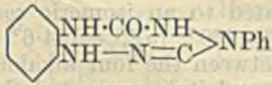

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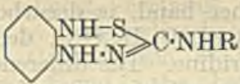

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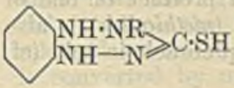

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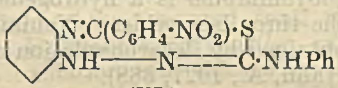
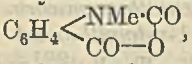


(VI.)

C. D. Langford.

Synthesis of nicotine, and Nagai's work on ephedrine. E. Späth and H. Bretschneider (Ber., 1928, **61**, [*B*], 327—334).—Pyrrolid-2-one, prepared by the reduction of succinimide at a lead cathode, is converted by methyl sulphate and sodium in presence of benzene into 1-methylpyrrolid-2-one, b. p. 82—84°/10 mm., transformed by ethyl pyridine-3-carboxylate in presence of sodium ethoxide and benzene into 3′ : 1′-*methylpyrrid-2-onyl* 3-*pyridyl ketone*, b. p. 152—154°/0·02—0·03 mm. (*picrate*, m. p. 154—155°). The ketone is converted by hydrochloric acid at 130° into 3-*pyridyl* γ-*methylamino*-n-*propyl ketone* (*chloroplatinate*, partial decomp. 180—185°), which is reduced by zinc dust in alcoholic alkaline solution to 3-*pyridyl*-γ-*amino*-n-*propylcarbinol* (*chloroplatinate*, decomp. 306—310° after darkening at 200° and shrinking at 285°). With fuming hydriodic acid at 100°, α-3-pyridyl-δ-methylamino-*n*-butyl iodide is formed from the secondary alcohol and passes in alkaline solution into *dl*-nicotine, identical with the base obtained by racemising *l*-nicotine sulphate in aqueous solution at 200°; the *picrate*, m. p. 217—218°, *picrolonate*, m. p. 238° (decomp.), and 2 : 4 : 6-*trinitro*-m-*tolyloxide*, m. p. 205—206° (decomp.), are described. The weak link in the chain is the reduction of the amino-ketone to the amino-alcohol, which is accompanied by extensive resinification. This can be obviated by using the catalytic method in aqueous suspension in the presence of palladised charcoal.

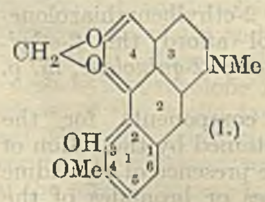
Nagai's claim to the elucidation of the constitution and to the synthesis of ephedrine (Ber., 1927, **60**, [*A*], 173) is adversely criticised. H. Wren.

Synthesis of evodiamine. Y. Asahina and T. Ohta (Ber., 1928, **61**, [*B*], 319—321; cf. A., 1924, i, 665).—*N*-Methylanthranilic acid is converted by ethyl chloroformate into N-*methylisatic anhydride*,  $C_6H_4<\begin{matrix}NMe\cdot CO\\ CO-O\end{matrix}$, m. p. 177°, which is transformed by aniline and 3-β-aminoethylindole, respectively, into o-*methylaminobenzanilide*, m. p. 126°, and 3-β-o-*methylaminobenzoylaminoethylindole*, m. p. 113°. The indole derivative and ethyl orthoformate at 175—180° afford *r*-evodiamine, m. p. 278°, converted by boiling alcoholic hydrogen chloride into *iso*evodiamine, m. p. 147°. H. Wren.

Yohimba alkaloids. IV. G. Hahn and W. Stenner (Ber., 1928, **61**, [*B*], 278—286; cf. A., 1926, 1263; 1927, 471).—Decarboxylation of yohimbenic, *iso*yohimboaic, and yohimboaic acids affords in each case *yohimbol*, $C_{19}H_{21}ON_2$, decomp. 306—307°, $[\alpha]_D^{20}$ −100·0° in pyridine, so that the isomerism of the three acids and hence of the corresponding alkaloids depends on difference of position of the carboxy-group in the molecule. *allo*Yohimboaic acid, on the other hand, is decarboxylated to an isomeric *compound*, $C_{19}H_{24}ON_2$, decomp. 230°, $[\alpha]_D^{13}$ +144·6° in pyridine. The difference between the four alkaloids does not appear profound, and it is suggested that *allo*yohimbine is a hydrogenated product of one of the three isomerides. Yohimbol (*methiodide*) is also obtained by decarboxylation of quebrachoic acid (cf. Hahn, A., 1927, 888).

Yohimbenic acid methylbetaine is converted by ethyl alcohol and hydrogen chloride into *ethyl yohimbenate methochloride*, $C_{23}H_{31}O_3N_2Cl,4H_2O$, which is readily reconverted into the betaine by short treatment with potassium hydroxide; similarly, formation of the betaine takes place when the additive product from methyl iodide and yohimbene or ethyl yohimbenate is treated with alkali. Since a like result is obtained with yohimboaic acid methylbetaine (Spiegel's "methylyohimboaic acid"), the betaine structure of the two compounds is regarded as established. The attempted Hofmann degradation of ethyl yohimbenate methylbetaine affords ill-defined products, but, under certain conditions, isomerisation to the corresponding methyl ester takes place; this type of change has been observed previously only with *d*-betaines, so that the carboxy-group in yohimbenic acid appears to be in the α-position to the nitrogen atom. It is highly probable that a quinoline or at any rate a pyridine ring is present in the yohimbene skeleton and the assumption is made that methyl iodide or sulphate is added to this ring nitrogen atom, to which the carboxy-group stands in the α-position. The acidities of the amino-acids increase in the order yohimbenic, *allo*yohimboaic, yohimboaic, and *iso*yohimboaic, in such a manner that the differences are very marked between the pairs yohimbenic and *allo*yohimboaic acids, on the one hand, and yohimboaic and *iso*yohimboaic acids, on the other, whereas the difference between the individual members of the same pair is slight but distinct. The more strongly acidic character of the *iso*acid in comparison with yohimboaic acid is shown by the separation of the former from solutions with p_H 4·4, whereas the latter requires p_H 4·8 for separation; this behaviour, combined with the different intervals of time required for crystallisation of the acids, forms a basis for their ready separation. Comparison of the strengths of the yohimba acids with those of simple pyridinemonocarboxylic acids confirms the position 2 for the carboxy-group in yohimbenic acid and possibly in *allo*yohimboaic acid. In *iso*yohimboaic and yohimboaic acids the carboxy-group appears to occupy positions 3 and 4 respectively. These views receive support in the physiological action of the acids compared with that of the pyridinecarboxylic acids. H. Wren.

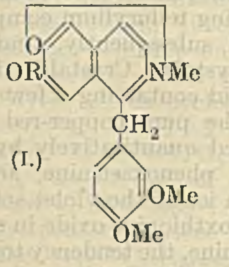
Alkaloids of *Corydalis cava*. XI. Constitution of bulbocapnine. E. Späth, H. Holter, and R. Posega (Ber., 1928, **61**, [*B*], 322—327).—Oxidative degradation of bulbocapnine under varied conditions confirms the constitution (I) assigned to the alkaloid by Gadamer (A., 1911, i, 1012 and previous abstracts). Oxidation by nitric acid of the methiodide of the methine base obtained by the Emde degradation of bulbocapnine yields benzene-1 : 2 : 3 : 4 - tetracarboxylic acid, m. p. 233—236° (decomp.), identical with the acid prepared similarly from thebenene and identified as the methyl ester, m. p. 129°. Gentle oxidation of bulbocapnine by potassium permanganate in alkaline solution affords hydroxyhydrastinine, m. p. 96—97°. Bulbocapnine methyl ether, m. p. 129—130°, is converted by permanganate into hemipinic acid (identified as the anhydride and ethylimide) and 2 : 3 - *methylenedioxy* - 2′ : 3′ - *dimethoxydiphenyl* - 5 : 6 : 6′-*tricarboxylic acid*, m. p. 258—260° (decomp.) (*anhydride*, m. p. 266—267°). *Bulbocapnine ethyl ether*, from the alkaloid and diazoethane in alcohol-ether, is oxidised to 4-methoxy-3-ethoxybenzene-1 : 2-dicarboxylic acid, thus establishing the relative position of the hydroxy- and methoxy-groups in bulbocapnine. The possibility that the groups are in the 5 : 6-position in nucleus (I) (see formula) is not excluded, but is unlikely if the constitution of analogous alkaloids is taken into account.



(I.)

H. Wren.

Opium alkaloids. IX. Constitution of protopapaverine and synthesis of *dl*-codamine. E. Späth and H. Epstein (Ber., 1928, **61**, [*B*], 334—343; cf. A., 1927, 163).—Protopapaverine, $C_{19}H_{19}O_4N$, m. p. 279—280°, is prepared by the thermal decomposition of papaverine hydrochloride at 235° and subsequently at 215—216° (cf. Hesse, A., 1903, i, 773; Pictet and Kramers, *ibid.*, 358). It is not a partly demethylated papaverine, since the alkaloid is not re-formed by treatment with diazomethane. Contrary to previous assumption, it contains only two methoxy-groups, the third methyl radical being attached to nitrogen. Reduction of protopapaverine by tin and hydrochloric acid followed by treatment of the base with diazomethane affords *dl*-laudanosine, thus establishing the close similarity of the skeletons of papaverine and protopapaverine. Its solubility in alkali hydroxide establishes the presence of at least one hydroxy-group. Oxidation of protopapaverine by permanganate affords veratric acid, whilst treatment with diazomethane gives the substance (I) (R=Me) (cf. Decker and others, A., 1908, i, 204; 1913, i, 289; Späth and Epstein, *loc. cit.*), reduced to *ψ*-laudanine. The constitution (I) (R=H) is therefore ascribed to protopapaverine.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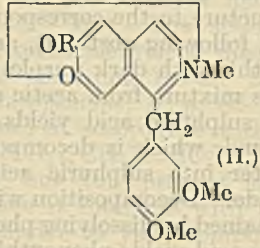
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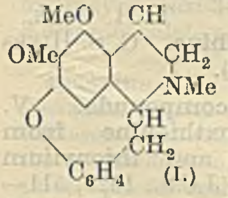
Protopapaverine is converted by methyl iodide into 7-*hydroxy*-6-*methoxy*-3′ : 4′-*dimethoxybenzylisoquinoline methiodide*, which, when converted into the corresponding *methochloride* and then reduced with tin and hydrochloric acid, gives *dl*-codamine (*picrate*, m. p. 187—188°). The identity of the base is confirmed by its methylation to *r*-laudanosine and oxidation of its ethylated product to 1-keto-6-methoxy-7-ethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline.

In addition to protopapaverine (41%), the thermal decomposition of papaverine hydrochloride affords 29% of the hydrochloride of the base (I) (R=Me), about 10% of the isomeric compound (II) (R=Me), and probably about 10% of the substance (II) (R=H). The latter compounds have not been isolated as such but as their reduction products, *dl*-codamine and 6 : 7-dihydroxy-3′ : 4′-dimethoxybenzyl-2-methyl*iso*quinoline. The latter base is oxidised to veratric acid and converted by diazomethane into *r*-laudanosine, m. p. 114—115°. Ethylation with diazoethane followed by oxidation gives 4 : 5-diethoxybenzene-1 : 2-dicarboxylic acid, identified as the ethylimide, m. p. 199—200°. For purposes of comparison, *m*-hemipinic acid is demethylated by hydriodic acid (*d* 1·7) at 100° to 4 : 5-dihydroxybenzene-1 : 2-dicarboxylic acid and then converted by diazoethane into 4 : 5-*diethoxybenzene*-1 : 2-*dicarboxylic acid*, m. p. 165—166° (decomp.), from which the corresponding *anhydride*, m. p. 157—158°, and *ethylimide*, m. p. 199—200°, are derived.

H. Wren.

Constitution of *iso*chondodendrine. F. Faltis and A. Troller (Ber., 1928, **61**, [*B*], 345—355).—Oxidation of the product, $C_{18}H_{16}O_3$, obtained from *iso*chondodendrine by a combination of the Emde and Hofmann methods of degradation has yielded an acid, $C_{12}H_5O(OMe)_2(CO_2H)_3$, derived from diphenyl ether and converted by fusion with potassium hydroxide into *p*-hydroxybenzoic acid (cf. Faltis and Neumann, A., 1922, i, 569). Direct comparison shows the acid not to be identical with 3 : 4′-carboxyphenoxy-5 : 6-dimethoxybenzene-1 : 2-dicarboxylic acid. Since the isomeric acids theoretically possible are not synthetically available, attention has been directed to the synthetic dimethoxydicarboxylic acid for purposes of comparison with the acid produced from the tricarboxylic acid and hydriodic acid (*loc. cit.*). Methyl 3-hydroxy-4 : 5-dimethoxybenzoate is converted into its sodium derivative, which is heated with methyl *p*-bromobenzoate, copper powder, and copper acetate at 180—200°, whereby, after hydrolysis, 3-p-*carboxyphenoxy*-4 : 5-*dimethoxybenzoic* [2 : 3-*dimethoxydiphenyl ether* 5 : 4′-*dicarboxylic*] *acid*, m. p. 217—218°, is produced, identical with the acid derived from *iso*chondodendrine; the non-crystalline *methyl* ester is described. Similarly, using *o*-bromobenzoic ester, the isomeric 3-o-*carboxyphenoxy*-4 : 5-*dimethoxybenzoic* [2 : 3-*dimethoxydiphenyl ether* 5 : 2′-*dicarboxylic*] *acid*, m. p. 228·5—229° (*methyl* ester, m. p. 72—73°), is obtained; fusion with potassium hydroxide gives salicylic acid unaccompanied by *p*-hydroxybenzoic acid. Since migration of the carboxy-group is not observed, the "degradation acid" cannot contain the *o*′-carboxyphenoxy-group. The reactions of the other product of the alkaline fission of the isomeric acids are identical with those of the similar product from the "degradation acid." There is therefore no reason to assume that the latter is not derived from pyrogallol (cf. *loc. cit.*). The constitution (I) can therefore almost certainly be assigned to methyl*iso*chondodendrine. Confirmation of this conception is found in the observation that the degradation product (II), obtained by reduction of the hydromethine prepared from the alkaloid by Emde and Hofmann's method (*loc. cit.*), is converted by mild oxidation into the carboxylic *acid* (III) (*barium* salt; *methyl* ester, m. p. 252—253°), which does not yield *p*-hydroxybenzoic acid when fused with potassium hydroxide. The unusually high m. p. and the value obtained for the mol. wt. of α-methyldihydro*iso*chondodendrimethine and α-methyl*iso*chondodendrimethine by Rast's method suggest a complex constitution for the parent alkaloid, but chemical evidence is adduced in favour of the simple composition $C_{18}H_{19}O_3N$; the phenomena of association appear to be characteristic of the peculiar oxygen ring system.

H. Wren.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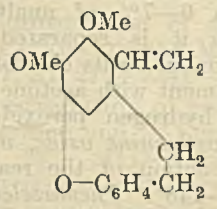
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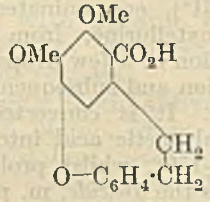

(III.)

***p*-Arsinophenoxyacetic acid.** C. S. Palmer and E. B. Kester (Org. Syntheses, 1927, 7, 4—5).—The product of interaction of sodium hydroxide, *p*-hydroxyphenylarsinic acid, and chloroacetic acid is treated with hydrochloric acid.

A. A. Eldridge.

Pure arsenobenzene and the molecular complexity of arsenobenzene and arsenomethane. C. S. Palmer and A. B. Scott (J. Amer. Chem. Soc., 1928, 50, 536—541).—Pure arsenobenzene, m. p. 195°, prepared by a modification of the method of

Binz, Bauer, and Hallstein (A., 1920, i, 401), is unimolecular in boiling carbon disulphide, but partly associated in boiling benzene (cf. Michaelis and Schäfer, A., 1913, i, 783), and probably bimolecular in molten naphthalene. Both the yellow, liquid and red, solid modifications of arsenomethane appear to exist as $(MeAs)_5$ in boiling carbon disulphide.

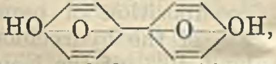
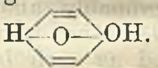
F. G. Willson.

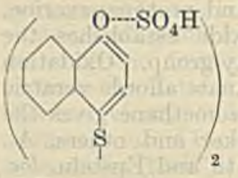
Manufacture of organic compounds of arsenic [oxazinearsinic acids]. G. Newbery, and May and Baker.—See B., 1928, 211.

Arsenical derivatives of quinoline. S. Berlingozzi (Annali Chim. Appl., 1928, **18**, 31—36).—When coupled with diazotised arsanilic acid derivatives, hydroxyquinolines yield the following red or brown hydroxyazo-compounds, which are being examined as to pharmacological properties: *2-Methyl-3-azo-4-hydroxyquinoline-*p*-phenylarsinic acid* (not melted at 300°), *5-azo-8-hydroxyquinoline-*p*-phenylarsinic acid*, *2-phenyl-4-azo-3-hydroxyquinoline-*p*-phenylarsinic acid*, and *2-methyl-4-azo-3-hydroxyquinoline-*p*-phenylarsinic acid*. All of these acids give red colorations with concentrated sulphuric acid.

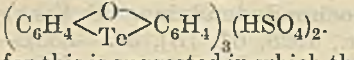
T. H. Pope.

[Preparation of] triphenylstibine. G. S. Hiers (Org. Syntheses, 1927, **7**, 80—82).

Cyclic organo-metallic compounds. V. Phenoxselenine and phenoxthionine from phenoxtellurine. Selenylium and thionylium compounds. H. D. K. Drew (J.C.S., 1928, 511—524).—When phenoxtellurine or its derivatives (with the exception of nitro-compounds) are heated with sulphur or selenium, the tellurium is replaced by these elements and the analogous phenoxthionine or phenoxselenine is obtained. These form mixed crystals and yield -ylium compounds analogous to the tellurylium salts. Thus when phenoxtellurine is boiled with sulphur it yields phenoxthionine, m. p. 58° unchanged (Mauthner, A., 1906, i, 447, gives 60—61°), contaminated with 6—7% of unaltered phenoxtellurine, from which it is separated by addition of a few drops of bromine to its chloroform solution and subsequent treatment with acetone and ether. It is converted by hydrogen peroxide in glacial acetic acid into *phenoxthionine oxide*, m. p. 158—159°, whilst prolonged action of the reagent yields the *dioxide*, m. p. 147—148°. *Phenoxselenine*, m. p. 87—88°, is obtained in a similar manner. The original complex, composed of phenoxselenine (2 mols.) and phenoxtellurine (1 mol.), is separated by boiling the mixed dibromides with acetone and treating the residue with ether, the phenoxtellurine dibromide being insoluble. When treated with the appropriate halogen in chloroform solution it yields a *dichloride*, m. p. 127° (decomp.), and *dibromide*, m. p. 147—148° (decomp.). Oxidation with hydrogen peroxide converts it into *phenoxselenine dihydroxide*, which readily loses 1 mol. of water, yielding the *oxide*, m. p. 171—172°, which is quantitatively converted into phenoxselenine by heating it above its m. p. The intensely coloured solutions of phenoxthionine in sulphuric (or phosphoric) acid are due to the presence, not, as suggested by Hilditch and Smiles (J.C.S., 1911, **99**, 408), of thionium salts, but of the *thionylium* compound (annexed formula), since by subsequent decomposition with ice, half the phenoxthionine is recovered as oxide (donor) and half unchanged (acceptor). Cautious dilution of the corresponding solution of phenoxselenine in concentrated sulphuric acid yields copper-red crystals of pure *triphenoxselenylium dibisulphate sulphuric acid dihydrate* (changing, in a sealed tube, at 155° and m. p. 168°), of analogous structure to the corresponding tellurylium compound (cf. following abstract), and, subsequently, a mixture of this with dark purple crystals. Crystallisation of this mixture from acetic acid containing a few drops of sulphuric acid yields the pure copper-red compound, which is decomposed quantitatively by cold water into sulphuric acid, phenoxselenine, and its oxide. Decomposition with ice of the violet solution obtained by dissolving phenoxthionine oxide in sulphuric acid yields phenoxthionine, the tendency towards the formation of thionylium salts being sufficiently great to cause the sulphuric acid to act either as an oxidising or a reducing agent as required. Mechanisms of the various reactions are given. It is deduced that, in their compounds, sulphur may be associated with 18 or 20 electrons, selenium with 36 or 38, and tellurium with 54 or 56, the tendency to become associated with the higher number increasing in this order. An attempt is made to interpret the quinhydrones on a carbonylium structure, quinhydrone itself being formulated as , its generator, quinol, being regarded as able to assume the carbonium structure .



J. W. Baker.

Cyclic organometallic compounds. IV. Tellurylium compounds. H. D. K. Drew (J.C.S., 1928, 506—510).—The author's method of ascertaining the relative proportions of donor and acceptor in the molecule of a tellurylium compound (A., 1927, 164) has been improved to give quantitative results, and its application to the compounds previously described (*loc. cit.*) proves the correctness of the formulæ assigned except in the case of the compound previously described as diphenoxtellurylium hydroxybisulphate monohydrate, obtained by crystallising diphenoxtellurylium dibisulphate or its complex with 2 mols. of sulphuric acid from glacial acetic acid. This is really *triphenoxtellurylium dibisulphate*,  $\left(C_6H_4{<}{}^{O}_{Te}{>}C_6H_4\right)_3(HSO_4)_2$. An expanded formula for this is suggested in which the three tellurium atoms are held together by four electrons. There exists, therefore, a series of compounds of the type $[R_x](HSO_4)_2$ in which x may be 1, 2, or 3, some of which have addenda of water or sulphuric acid molecules. The compound of m. p. 59° described by Thomason and Drew (A., 1927, 267) as a complex of phenoxtellurine and chloromethylphenoxtellurine has been separated into these components by fractional precipitation of its chloroform solution with bromine. Phenoxtellurine dibromide separates first and then the *dibromide*, m. p. 315° (decomp.), of *chloromethylphenoxtellurine*, m. p. 46—47° [*dichloride*, m. p. 300° (decomp.); *diacetate*, m. p. 230—232° (decomp.); *disulphate*; di-α-bromocamphor-π-sulphonate which could not be purified owing to its tendency to hydrolyse], which is obtained from the dibromide by reduction with potassium metabisulphite, and from which a *tellurylium* compound was obtained. J. W. Baker.

***cyclo*Telluropentane.** G. T. Morgan and H. Burgess (J.C.S., 1928, 321—329).—The action of aluminium telluride on αε-pentamethylene dihalides under varying conditions according to the halide employed, yields cyclo*telluropentane*, b. p. 82—83°/12 mm., 44—45°/1—2 mm., in accordance with the equation $Al_2Te_3+3CH_2X\cdot[CH_2]_3\cdot CH_2X=3C_5H_{10}{:}Te+2AlX_3$ (X=Cl, Br, or I), but this product is not isolated at this stage, since it interacts with more of the pentamethylene dihalide to yield compounds of the type $C_5H_{10}{:}TeX\cdot CH_2\cdot[CH_2]_3\cdot CH_2X$ (I) and $C_5H_{10}{:}TeX\cdot CH_2\cdot[CH_2]_3\cdot CH_2\cdot TeX{:}C_5H_{10}$ (II). A small amount of the *cyclo*telluripentane dihalide, $C_5H_{10}{:}TeX_2$, is also obtained in the case of the bromine and iodine compounds, but this is best prepared by the addition of halogen to the compounds (I) or (II) or their products of thermal decomposition (below). Thus are obtained: 1-ε-*chloroamyl*-cyclo*telluripentane*-1-*chloride*, m. p. 149—151°, -1-*bromide*, m. p. 143—145°, and -1-*iodide*, m. p. 135—136°, resolidifying almost immediately and then having m. p. 197—198°; *pentamethylene*-αε-*bis*cyclo-*telluripentane*-1 : 1′-*dichloride*, decomp. 224—225°, -1 : 1′-*dibromide*, exploding on rapid heating, and -1 : 1′-di-iodide, m. p. 216—217° (decomp.). cyclo-*Telluripentane*-1 : 1-*dichloride*, m. p. 106—107° (*dichromate*), is prepared either by thermal dissociation, or by the action of a slight excess of chlorine, from (I). The corresponding -1 : 1-*dibromide*, m. p. 105—107°, is best prepared by heating either (I) or (II) to 160—190°/25—30 mm. and the action of excess of bromine on the *cyclo*telluropentane thus liberated, or by the direct action of bromine on (I) in carbon tetrachloride solution. By treatment with bromine in carbon tetrachloride it yields the corresponding -1 : 1-*bisperbromide*, m. p. 102—104°. The -1 : 1-*di-iodide*, m. p. 135—136°, which is obtained in two forms, one deep red with purplish-blue reflex (stable) and the other orange, transformation of the latter into the former occurring slowly at the ordinary temperature, and at 105° on heating, is obtained by addition of iodine to *cyclo*telluropentane in carbon tetrachloride. By reduction with potassium metabisulphite in aqueous solution, *cyclo*telluripentane-1 : 1-dibromide is converted into *cyclo*telluropentane (above), which must be distilled in an inert atmosphere, since it is rapidly oxidised either by air or hydrogen peroxide to cyclo*telluripentane*-1 : 1-*dioxide*, $+H_2O$, a white, amorphous powder which explodes on rapid heating. J. W. Baker.

Valency problem of boron. III. Valency phenomena of boron in boron tri*cyclo*hexyl and boron tri-*p*-tolyl. E. Krause and H. Polack (Ber., 1928, 61, [*B*], 271—276; cf. A., 1922, i, 694; 1924, i, 436; 1926, 628).—*Boron tri*-p-*tolyl*, m. p. above 175°, resembles boron triphenyl in that it is sensitive towards air but forms stable additive compounds with nitrogenous bases which are indifferent towards oxygen; the *substances* $B(C_7H_7)_3,NH_3$, m. p. 225—226° in a sealed capillary; $B(C_7H_7)_3,C_5H_5N$, m. p. 201—202°, and $B(C_7H_7)_3,C_5H_{11}N$, m. p. 202° after softening, are described. Like the phenyl derivative, boron tri-*p*-tolyl reacts with sodium and potassium, but the products crystallise with difficulty. *Boron tri*cyclo*hexyl*, m. p. 98—100°, is much more sensitive to air than the phenyl compound. Its additive *compounds* with ammonia, $B(C_6H_{11}),NH_3$, m. p. 105—106°, and pyridine, $B(C_6H_{11})_3,C_5H_5N$, are readily affected by atmospheric oxygen, whereas the *compound* $B(C_6H_{11})_3,C_5H_{11}N$, m. p. 135—136°, is stable when solid, but rapidly oxidised when dissolved. Like boron tri-*n*-propyl, m. p. −56°, it does not react with the alkali metals. H. Wren.

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid. F. C. Whitmore, P. J. Culhane, and H. T. Neher (Org. Syntheses, 1927, 7, 1—3).—Experimental details for the preparation of anhydro-2-hydroxymercuri-3-nitrobenzoic acid from sodium 3-nitrophthalate and mercuric acetate are recorded. A. A. Eldridge.

Proteins. V. Glutamic acid. C. Okinaka (Sexagint [Osaka celebration], Kyoto, 1927, 27—59). Glutamic acid probably plays an important part in the metabolism of proteins in plants. Ethyl glutamate passes readily into ethyl pyrrolidine-1-carboxylate and the free acid gives the corresponding acid; this reaction is accelerated by heat or dilute alkali but retarded by excess of strong acid or alkalis. The reaction does not go to completion but attains an equilibrium. The optical properties of its solutions of various p_H values indicate that the acid exists normally to some extent in the form of an internal salt and this is probably the first step in the formation of the pyrrolidinecarboxylic acid. C. D. Langford.

Combination of gelatin with organic bases. A. Petrunkin and M. Petrunkin (Arch. Sci. biol., 1927, 27, 219—234).—See this vol., 190.

Degradation of gelatin with acetic anhydride. A. Fodor and C. Epstein (Z. physiol. Chem., 1927, 171, 222—241).—Various crystalline *products*, very hygroscopic and varying in solubility in alcohol, have been obtained from the syrupy product of the degradation of gelatin with boiling acetic anhydride. Investigations were confined to the more soluble portions over the range $[\alpha]_D^{20}$ −76·92° to −101·4°. These are identified by their chemical behaviour, mol. wt., and analysis as: hydroxyprolylalanine, $C_8H_{14}N_2O_4$, $[\alpha]_D^{20}$ −76·92°; $(C_8H_{14}N_2O_4)_4$ (polymerised hydroxyprolylalanine, ?), $[\alpha]_D^{20}$ −78·2°; $4(C_8H_{14}N_2O_4),3H_2O$, $[\alpha]_D^{20}$ −78·2°; $4(C_8H_{14}N_2O_4),H_2O$, $[\alpha]_D^{20}$ −88·8°; and (hydroxyprolylalanine +3-hydroxyprolylglycine $-3H_2O$), $[\alpha]_D^{20}$ −101·4°. Depolymerisation of these by barium hydroxide or by sodium hydroxide to dipeptide and amino-acid furnishes evidence on which suggested structural formulæ for the polymerides are based. J. Stewart.

Decomposition of soya-bean protein. V. Decomposition of soya-bean protein by sulphuric acid. VI. Decomposition of soya-bean pro-

tein by organic acids. VII. Decomposition by Japanese acid clay. M. MASHINO and T. SHISHIDO (J. Soc. Chem. Ind. Japan, 1927, **30**, 552—560, 561—564, 565—568; cf. A., 1927, 474).—V. Soya bean from which oil had previously been extracted with light petroleum was treated for 6 hrs. with dilute sulphuric acid (1—20%) at 4·7 atm. The action of the acid was much more rapid and the amounts of ammonia and amino-nitrogen formed were much larger than at atmospheric pressure. The amount of nitrogen appearing as ammonia increased with increasing time of treatment, reaching 11·63—20·05% of the total nitrogen at the end of 6 hrs. With 20% sulphuric acid the amount of amino-nitrogen formed increased rapidly at first, reached a maximum (about 80% of the total nitrogen), and then decreased gradually to about 60% at the end of 6 hrs. With more dilute acid no maximum was found.

VI. When soya-bean protein was treated with acetic, lactic, citric, tartaric, or oxalic acid for several hours at 2·66—5·8 atm., the ammonia-nitrogen liberated was nearly the same in every case (10—13% of the total nitrogen). The amino-nitrogen liberated varied from 3·1 to 25·1% of the total nitrogen, according to the acid used, and increased in the order: acetic, lactic, citric, tartaric, oxalic acid.

VII. When soya-bean protein was heated under pressure with acid clay and water, or with acid clay and sodium chloride solution, the ammonia-nitrogen and amino-nitrogen liberated was about 8·5% and about 5% of the total nitrogen, respectively. With acid clay and hydrochloric acid the amount of amino-nitrogen liberated was somewhat less than with the acid alone. Y. NAGAI.

Nitrogen distribution of soya-bean protein. M. MASHINO and S. NISHIMURA (J. Soc. Chem. Ind. Japan, 1927, **30**, 607—610).—The nitrogen distribution of several varieties of soya-bean protein has been determined by the Van Slyke method. Y. NAGAI.

Purification of soya-bean protein. M. MASHINO (J. Soc. Chem. Ind. Japan, 1927, **30**, 610—617).—Soya bean, from which oil had previously been extracted with light petroleum, was treated with various solvents to remove constituents other than the protein. Methyl alcohol proved best. The amount of extraction increased with temperature. Extraction by methyl or ethyl alcohol at 67—68° or at 82—83° was almost complete in 1 hr. Soya-bean protein purified with methyl alcohol is no longer hygroscopic, is odourless, and has only a light colour. Y. NAGAI.

Behaviour of proteins with alkali with some conclusions in regard to their structure. J. TILLMANS and P. HIRSCH (Biochem. Z., 1928, **193**, 216—236).—The changes of "molecular binding power, δ" of egg-albumin and gliadin solutions on addition of acids and alkalis is investigated. These proteins, especially gliadin, have very low δ values, but the latter increases considerably on adding sodium hydroxide (especially in the case of albumin), due to the liberation of new acid and basic groups, the strengths of which correspond with those of peptides. Peptides, however, are only difficultly attacked by sodium hydroxide and the results favour, therefore, the ring (diketopiperazine) rather than the peptide structure of the proteins. Although the δ values for albumin increase much more quickly than for gliadin, the final values, after more prolonged digestion with alkali, are bigger for gliadin than for albumin.

P. W. CLUTTERBUCK.

Rapid determination of carbon, nitrogen, and hydrogen in organic compounds. R. VANDONI and M. ALGRAIN (Bull. Soc. chim., 1928, [iv], **43**, 255—260).—A modified Dumas apparatus is described for the volumetric determination of carbon and nitrogen at the same time. The combustion is carried out using oxygen in slight excess of the calculated amount, and the apparatus is arranged so that the gaseous products can be passed over heated copper oxide as many times as are necessary for complete burning. A similar apparatus is described for the gravimetric determination of hydrogen. The methods are quick and give trustworthy results. H. BURTON.

Determination of halogens in organic compounds. M. PRONER (Rocz. Farm., 1926, **4**, 99—106; Chem. Zentr., 1927, ii, 1596).—The method is specially suitable for naphthalene derivatives, terpenes, and heterocyclic compounds. The substance (0·1—0·2 g.) is slowly warmed with 95% alcohol, and small pieces of sodium (1 g.) are added; the mixture is warmed with 30% hydrogen peroxide solution (5 c.c.) until evolution of oxygen ceases, acidified with nitric acid, reduced with sodium sulphite, warmed, and the chloride precipitated with silver nitrate.

A. A. ELDRIDGE.

Determination of selenium in organic compounds. W. E. BRADT and R. E. LYONS (Proc. Indiana Acad. Sci., 1926, **36**, 195—201).—The (halogen-free) substance is heated with nitric acid in a sealed tube, the solution being made alkaline with potassium hydroxide (free from halide), slightly acid with nitric acid, and then neutral with excess of zinc oxide, and finally titrated with siver nitrate in presence of sodium chromate. CHEMICAL ABSTRACTS.

Thalleioquinine reaction. B. OLSZEWSKI (Rocz. Farm., 1926, **4**, 119—130; Chem. Zentr., 1927, ii, 1598).—Optimally, 1 mol. of quinine is treated with 4—8 atoms of bromine for 15 sec. In the micro-reaction, the precipitate is dissolved in 30% acetic acid, the acid removed by evaporation, and the residue, after dissolution in water, treated with 1 drop of dilute bromine water. A. A. ELDRIDGE.

Determination of the isoelectric point of amino-acids, asparagine, or glycine. M. D. BACH (Bull. Soc. Chim. biol., 1928, **9**, 1233—1243).—The compound to be examined is added in equal amounts to each of a series of tubes containing suitable buffer solutions chosen so as to extend over a range of p_H including the isoelectric point required. An identical set of buffer tubes is also prepared to which none of the compound is added. By electrometric methods or by the addition of a suitable indicator to each of the two sets of tubes the particular p_H is found which is such that the addition of the compound causes no change in hydrogen-ion concentration. By this method it has been found that the isoelectric points of glycine and of asparagine are at p_H 4·3 and 5·8, respectively. W. O. KERMACK.

Biochemistry.

Glycerol and potassium hydroxide in the microscopical detection of blood. K. Meixner (Deuts. Z. ges. gericht. Med., 1927, **10**, 253—254; Chem. Zentr., 1927, ii, 1742).—A mixture of concentrated aqueous potassium hydroxide and glycerol, or a glycerol solution of potassium hydroxide is preferred to aqueous potassium hydroxide; the formation of hæmatin and hæmochromogen takes place completely, but more slowly. The use of reducing agents for this purpose is objectionable.

A. A. Eldridge.

Value of benzidine reaction and the clinical significance of the hæmatoporphyrin test in fæces. D. E. Schouten (Ned. maandschr. geneesk., 1926, **13**, 651—668; Chem. Zentr., 1927, ii, 963).—The pigment of the blood is partly or completely converted in the intestinal canal into hæmatoporphyrin; spectroscopic detection of the porphyrin is preferred. The test is not less sensitive than the benzidine reaction.

A. A. Eldridge.

Effect of posture on the composition and volume of blood in man. W. O. Thompson, P. K. Thompson, and M. E. Dailey (Proc. Nat. Acad. Sci., 1928, **14**, 94—98).—In the standing-still position there occurs a net loss of approximately protein-free fluid from the blood. This seems to be due to an increase in capillary pressure. The loss amounts to about 11% of the total plasma volume, and is probably greatest in the lower extremities.

W. E. Downey.

Origin of the pigment of *Chironomus* larvæ. M. Comas (Compt. rend. Soc. Biol., 1927, **96**, 866—868; Chem. Zentr., 1927, ii, 100).—Hæmoglobin in *Chironomus* larvæ does not arise from ingestion of chlorophyll, but is hereditary. It is associated with a green pigment similar in its properties to biliverdin.

A. A. Eldridge.

Coagulation of hæmoglobin in presence of organic substances. B. Jirgensons (Biochem. Z., 1928, **193**, 109—121).—The coagulation of hæmoglobin with potassium chloride and magnesium chloride is sensitised by the presence of small amounts of capillary-active substances having small dielectric constants (ether, chloroform, amyl and *iso*butyl alcohols, acetone, methylurethane), whilst in larger concentrations these substances may act either as sensitisers if the salt concentration is small, or as stabilisers if it is large. Some capillary-inactive substances (mannitol and dextrose) have a slight stabilising action (cf. A., 1927, 512, 624).

P. W. Clutterbuck.

Amino-acids in blood of insects. M. Duval, P. Portier, and A. Courtois (Compt. rend., 1928, **186**, 652—653).—Amino-acids have been determined by the Sørensen titration method in the blood of insects, in the chrysalid, larval, and fully-grown states. The value is high in each case, and particularly in the chrysalis.

W. K. Slater.

Blood-creatinine. O. H. Gaebler and A. K. Keltch (J. Biol. Chem., 1928, **76**, 337—359).—Addition of a 10% solution of phosphotungstic acid, saturated with picric acid, to a saturated picric acid solution containing creatinine causes precipitation of the latter; the precipitate can be decomposed with a mixture of alcohol and ether and the creatinine re-precipitated by addition of picric acid to the filtrate. Picric acid is removed by shaking the precipitate with dilute sulphuric acid and ether, the creatinine is re-precipitated with basic lead acetate, recovered with hydrogen sulphide in the usual manner, and finally isolated as potassium creatinine picrate; in order to obtain the maximum yield of the latter it is important to have the correct concentration of potassium in the solution. The above method has been applied to the isolation of creatinine from blood which has been freed from protein by treatment with picric acid. Treatment of such protein-free blood-filtrates with kaolin removes the creatinine but leaves in solution other substances which give the Jaffé reaction and also accumulate in those pathological conditions which lead to retention of creatinine. Creatinine may also be separated from blood-filtrates by treatment with Lloyd's reagent, and decomposition of the precipitate by means of lead hydroxide.

C. R. Harington.

Determination of cholesterol in small amounts of blood. S. M. Ling (J. Biol. Chem., 1928, **76**, 361—365).—Blood is dried on filter-paper and extracted for 40 min. with chloroform in a special apparatus; cholesterol in the extract is determined colorimetrically.

C. R. Harington.

Determination of dihydroxyacetone in blood and urine. W. S. McClellan (J. Biol. Chem., 1928, **76**, 481—486).—The utility of the method of Campbell (A., 1926, 443) for the determination of dihydroxyacetone in blood is confirmed; the method can be applied to urine, after preliminary removal of phosphates.

C. R. Harington.

Methylglyoxal as intermediate product in glycolysis in blood. H. K. Barrenscheen (Biochem. Z., 1928, **193**, 105—108).—The formation of methylglyoxal during glycolysis in blood is detected by addition of semicarbazide with isolation and identification of methylglyoxal disemicarbazone.

P. W. Clutterbuck.

Glycolysis of dextrose and lævulose in the blood of normal and diabetic dogs. E. Turgatti (Rev. Soc. Argentina Biol., 1927, **3**, 716—720).—Venous blood from dogs was incubated for 6 hrs., alone, and with the addition of dextrose or lævulose. The greatest amount of glycolysis occurred in blood of low blood-sugar level, and *vice versa.* Glycolysis was retarded considerably by the addition of dextrose and moderately by the addition of lævulose. Glycolysis was slower in the blood of dogs from which the pancreas had been removed, and was retarded or even inhibited by addition of dextrose, but the addition of lævulose had, on the whole, little effect. It is suggested that hyperglycæmia can be considered not only as a symptom, but also as itself a cause of disturbance.

R. K. Callow.

"Protein"-blood-sugar. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, **97**, 186—187; Chem. Zentr., 1927, ii, 1162).—Hydrolysis of plasma-protein yields a small fraction of a reducible and fermentable substance, having a reducing power about 6% of that of the sugar-free hydrolysate; the ratio of protein to the substance is about 1 : 0·0044.
A. A. Eldridge.

Reducing and fermentable substances in combination with proteins of the blood-plasma. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, **97**, 187—191; Chem. Zentr., 1927, ii, 1162—1163; cf. preceding abstract).—Pure constituents of the blood-serum were submitted to hydrolysis. Proteins give by acid hydrolysis 7·4% of reducing substance expressed as dextrose and calculated on the original quantity of sheep blood-proteins; the fermentable fraction is only 0·8—1·2%, and is ascribed to traces of nucleoproteins.
A. A. Eldridge.

Presence of two reducing carbohydrates in blood. G. Fontès and L. Thivolle (Compt. rend. Soc. Biol., 1927, **96**, 994—996; Chem. Zentr., 1927, ii, 449).—The use of mercuric nitrate and of tungstic acid (the former, but not the latter, precipitating creatinine and uric acid) indicates the presence in blood, in addition to that of "glucose," of an ethereal component the reducing power of which is unchanged by hydrolysis. The amount is not increased by muscular work or insulin. A. A. Eldridge.

Distribution of the carbohydrate reducing substances between plasma and blood-corpuscles. G. Fontès and L. Thivolle (Compt. rend. Soc. Biol., 1927, **96**, 997—998; Chem. Zentr., 1927, ii, 449).—Hirudin does not affect the natural distribution of reducing carbohydrates in the corpuscles; other anticoagulants affect the plasma and corpuscles in the same sense. A. A. Eldridge.

Determination of blood-sugar. II. S. R. Benedict (J. Biol. Chem., 1928, **76**, 457—470).—Evidence was obtained of the presence in protein-free blood filtrates of substances which affect the dissociation of the complex copper salt, in the solutions usually employed for the determination of blood-sugar, rendering it more easily reduced by dextrose; this effect has been overcome by the addition of alanine to a new reagent of the Fehling type. The new reagent gives results for the blood-sugar about 22 mg.% lower than the reagent of Folin and Svedberg (A., 1926, 1282); further, dextrose added to protein-free filtrates of blood which have been subjected to yeast fermentation can be quantitatively determined by the new reagent, which therefore appears not to be affected by the non-dextrose reducing substances present in such filtrates. The work of Somogyi (A., 1927, 1214) is criticised on the ground that insufficient time was allowed for fermentation; good results are obtained by diluting blood with a suspension of washed yeast and keeping the mixture for 15 min. before precipitation with tungstic acid. C. R. Harington.

Micro-determination of blood-sugar. H. Citron (Deutsch. med. Woch., 1927, **53**, 1216—1217; Chem. Zentr., 1927, ii, 1598).—The Hagedorn–Jensen method is improved. A. A. Eldridge.

Serum-calcium. I. Oral administration. J. C. Hoyle (J. Pharm. Exp. Ther., 1928, **32**, 309—320).—No definite differences in the normal serum-calcium content of male and female rabbits have been detected, but a seasonal variation occurs. Loss of blood equivalent to about one fifth of the body-weight causes a fall in the serum-calcium of approximately 14%. Administration by mouth of single or repeated doses of 1 g. of calcium carbonate per kg. body-weight causes an increase of serum-calcium up to 16% which, when allowance is made for effect of hæmorrhage, is equal to an increase of 20—25%. By administration of 2 g. of calcium carbonate per day a permanent increase of serum-calcium of 5—15% has been obtained. Single doses of calcium lactate (3 g. per kg. body-weight) cause an increase in serum-calcium of 15—22%, whilst repeated daily doses of 6 g. of the salt cause a maximum increase of only 5%, or 12% if allowance be made for the effects of repeated bleeding. W. O. Kermack.

Replacement of the serum-calcium and thyroid gland in rabbits after intravenous injections of oxalate. H. W. C. Vines (Endocrinol., 1927, **11**, 290—296).—The speed of replacement of calcium, which has been removed from the blood following the intravenous injection of ammonium oxalate, was determined. Chemical Abstracts.

Blood-phosphorus in health and disease. I. Distribution of phosphorus in human blood in health. H. D. Kay and F. B. Byrom (Brit. J. Exp. Path., 1927, **8**, 240—253).—The distribution of phosphorus in venous blood is fairly constant; the ester phosphorus is greater, and the portion thereof hydrolysable by phosphatase is less, in men than in women. After a meal there is a slight diminution in inorganic phosphorus, a diminution in phosphoric ester hydrolysable by phosphatase, and a corresponding increase in the ester fraction resistant to enzyme hydrolysis; there is also possibly a slight rise in lipin-phosphorus. The phosphorus index (mg. of ester phosphorus in 100 c.c. of red cells) is a more stable constant than the p_H of the blood.
Chemical Abstracts.

Use of the quinhydrone electrode for the determination of the p_H of whole blood and serum. J. Gewecke (Biochem. Z., 1928, **193**, 181—186).—The experiments of F. Schmidt (Z. Immun. exp. Ther., 1926, **46**, 386) were repeated using rabbit's in place of guinea-pig's blood, but the results were not consistent and often very different from those obtained by the hydrogen electrode. With inactivated human serum the initial potential was highest and quickly fell, and the results again differed from those obtained by the hydrogen electrode.
P. W. Clutterbuck.

Determination of p_H of blood. I. Accuracy of quinhydrone electrode for determining p_H of blood-plasma or serum. G. E. Cullen and I. P. Earle. **II. Comparison of colorimetric method with hydrogen and quinhydrone electrodes.** I. P. Earle and G. E. Cullen (J. Biol. Chem., 1928, **76**, 565—581, 583—590).—I. A modified technique for the use of the quinhydrone electrode (cf. Cullen and Biilmann, A., 1925, i, 1201) is described, by the employment of which reproducible results for the p_H of normal blood-plasma or -serum may be obtained, these results being always 0·06 p_H more acid than the corresponding figures obtained with the hydrogen electrode.

II. Figures obtained for the p_H of normal diluted human blood-serum by the colorimetric method of Cullen (A., 1922, ii, 672) were 7·41—7·50, and were 0·14 p_H more alkaline than those obtained with the quinhydrone electrode. C. R. Harington.

Calculation of cell volume changes as a function of p_H. D. B. Dill (J. Biol. Chem., 1928, **76**, 543—545).—By mathematical extension of the calculations of Van Slyke, Wu, and McLean (A., 1923, i, 1249) a relationship is developed between the relative volume of the red blood-corpuscles and the p_H of the serum. C. R. Harington.

Effect of carbon dioxide equilibration on surface tension of blood-serum. J. M. Johlin (J. Biol. Chem., 1928, **76**, 559—564).—Neither the absolute magnitude of the surface tension of blood-serum nor the change in surface tension with time is significantly affected by equilibration with varying tensions of carbon dioxide. C. R. Harington.

Hæmoclastic changes *in vitro* from agents causing anaphylactoid reactions. P. J. Hanzlik, F. De Eds, L. W. Empey, and W. H. Farr (J. Pharm. Exp. Ther., 1928, **32**, 273—294).—Various anaphylactoid reagents, copper sulphate, arsphenamine, peptone, acacia, agar, and toxified serum added *in vitro* to oxalated blood-plasma or serum cause a decrease in surface tension and an increase in the albumin–globulin ratio. Albumin, peptone, and agar increase the viscosity of blood-serum, acacia and gelatin increase the rate of sedimentation of blood-corpuscles suspended in plasma. The fragility of the corpuscles is decreased by acacia and gelatin and increased by arsphenamine and copper sulphate. The results are considered to support the view that anaphylactoid changes are of the nature of a disturbance in the equilibrium of the body colloids. W. O. Kermack.

Variations in the coagulability of the blood normally and after ingestion of food. C. A. Mills and H. Necheles. **Relation of blood coagulability to body metabolism and to the specific dynamic action of food.** H. Necheles and C. A. Mills (Chinese J. Physiol., 1928, **2**, 19—23, 25—32).—The coagulation time of blood is decreased after a meal containing protein, but not after one containing only carbohydrate or fat. It is decreased also after administration of glycine, which, like proteins, has a marked specific dynamic action. The decrease in coagulation time appears to be related, not directly to the increase of metabolism which occurs after a meal, but rather to the presence in the blood-stream of substances which exert specific dynamic action. W. O. Kermack.

Action of soluble iron salts on coagulation of blood. P. Bordet (Compt. rend. Soc. Biol., 1927, **96**, 1061—1063; Chem. Zentr., 1927, ii, 450).—Ferrous sulphate and chloride, aluminium sulphate, and chrome alum hinder the coagulation of blood owing to interaction with the blood constituents. A. A. Eldridge.

Chemistry of specific hæmagglutination. A. Konikov (Žurn. eksp. biol. med., 1926, 128—145; Chem. Zentr., 1927, ii, 1046).—The erythrocytes can be regarded as an amphoteric protein of isoelectric point p_H 5. Probably only between p_H 6 and 9 are the stroma and agglutinin oppositely charged. The presence of electrolyte is necessary in the first phase of hæmagglutination; the action of the salt is expressed by the scheme stroma—Na—Cl—agglutinin, in which auxiliary valencies function. The subject is discussed from this point of view. A. A. Eldridge.

Rapid preparation of crystalline egg-albumin. W. La Rosa (Chemist-Analyst, 1927, **16**, No. 2, 3).—The whites of fresh eggs are beaten well and mixed with an equal volume of saturated ammonium sulphate solution. After 15 hrs. the liquid is centrifuged and the clear supernatant liquid is siphoned off. Acetic acid (10%) is then added, with stirring, until a permanent turbidity appears, an additional 1 c.c. for each 100 c.c. of liquid being finally added. Chemical Abstracts.

Physiology of the fœtus. T. Sugano (Kinki Fuji. Gak. Zassi, 1926, **9**, 97—100; Chem. Zentr., 1927, ii, 945).—Pepsin appears in the fœtus at the fifth or sixth month. A. A. Eldridge.

Oxidising substances in animal cells. W. Loele (Arch. path. Anat. Physiol., 1926, **261**, 484—502; Chem. Zentr., 1927, ii, 943).

Microchemistry of the cell. I. Chromatin content of normal and malignant cells. R. J. Ludford (Proc. Roy. Soc., 1927, B, **102**, 397—406).—The chromatin content of various normal and abnormal animal cells has been investigated by means of Feulgen's "nucleal" reaction" During oögenesis in the rat and in the mouse there is no increase in the chromatin content of the nuclei, and when formation of the chromosomes takes place no chromatin is extruded into the cytoplasm; the heads of the spermatozoa of the rat and the mouse contain chromatin. Experiments on the nuclei of gland cells before and after secretory activity indicate no appreciable diminution in chromatin content. There is no correlation between the amount of chromatin in the nuclei of tumour-cells and the rate of growth of the tumour; the nuclear extrusions occurring in certain tumours do not consist of chromatin. E. A. Lunt.

Oxidising and reducing powers of mitochondria. P. Joyet-Lavergne (Compt. rend., 1928, **186**, 471—473).—Histological studies have been made on the effect of certain comparatively non-toxic substances which become coloured on oxidation, *e.g.*, quinol, "metol," pyrogallol, and of aqueous solutions of gold chloride and of silver nitrate on fresh liver cells, and are held to indicate the oxidising and reducing properties of the chondriosome system. E. A. Lunt.

Spectrophotometric studies of the two components of trypan-blue. (**Adsorption theory of**

vital staining.) N. Okuneff (Biochem. Z., 1928, **193**, 70—84).—Aqueous solutions of trypan-blue possess a definite absorption constant (max. 0·911) and a definite absorption maximum (580—590 μμ). The absorption constant is independent of the concentration within certain limits (1/5000—1/100,000), but differs with the different commercial samples of the dye. When strips of filter-paper are dipped in dilute solutions of the dye, the solution gradually becomes red and the paper blue, the absorption constant then showing a progressive decrease and the absorption maximum a displacement to the left. The blue component is adsorbed much more firmly than the red. Addition of gelatin, protein, or plasma-colloids increases the adsorption constant and displaces the absorption maximum to the right. The fate of the two components in the organism is therefore conditioned, not only by their different diffusibilities, but also by their different adsorbabilities.
P. W. Clutterbuck.

Microchemical detection of potassium and calcium in histological sections. W. Jacobi and W. Keuscher (Arch. Psych. Nerv., 1927, **79**, 323—326; Chem. Zentr., 1927, ii, 1985—1986).—The tests depend, respectively, on the formation of potassium chloroplatinate and calcium sulphate.
A. A. Eldridge.

Chemical composition and histological structure of normal and atrophied muscle. T. Cahn (Ann. physiol. physicochim. biol., 1926, **2**, 646—681; Chem. Zentr., 1927, ii, 846—847).—A critical review.

Composition of human epidermis. Y. Jono (J. Biophys., 1927, **2**, xlviii).—Human epidermis contained water 20%, ash 1·5% (the silica content being high; sulphur content of ash 0·78%), fat 2%. Hydrolysis of the protein yielded tyrosine, leucine, alanine, valine, *iso*leucine, proline, glutamic acid, arginine, and lysine. Chemical Abstracts.

Ferments of human skin. N. Melczer (Dermatol. Z., 1926, **49**, 252—261; Chem. Zentr., 1927, ii, 945).—Diastase, phenolase, catalase, peroxidase, and glycolytic ferment are present in human skin; lipase is produced by the epidermal cells. In fatal pulmonary or peritoneal tuberculosis the skin lipase is practically or completely absent.
A. A. Eldridge.

Organic content of human enamel. C. Sprawson and F. W. Bury (Proc. Roy. Soc., 1927, B, **102**, 419—426).—The protein content of human enamel calculated from the nitrogen and the carbon contents of enamel is, respectively, 0·15% and 0·21%; it is suggested that the discrepancy in these results is due to the contamination of the enamel with carbon from the steel used in filing the enamel from the tooth. The organic content of enamel is independent of the dentition or the age of the tooth.
E. A. Lunt.

Determination of glutathione. A. Blanchetière and L. Mélon (Compt. rend. Soc. Biol., 1927, **97**, 242—244; Chem. Zentr., 1927, ii, 1495).—Tunnicliffe's method is preferred to that of Thompson and Voegtlin. The lower limits of sensitiveness are for cysteine, 200 mg. per litre, and for reduced glutathione 125 mg. per litre. A. A. Eldridge.

Osmotic concentration of secretions. J. Straub and L. Soep (Arch. Néerland. Physiol., 1928. **12**, 346—367).—A series of analyses of secretions and sera before and after dialysis, with an interpretation of the results in the light of modern theories.
W. Robson.

Bacterial growth as a factor in the deposition of calcium from saliva. W. A. Peabody, I. C. Hall, and R. C. Lewis (Dental Cosmos, 1927, **69**, 1087).—Direct precipitation of calcium in centrifuged saliva determines at least 93% of the total calcium. Incubation of raw saliva with or without excess of fermentable carbohydrate produces, respectively, an acid reaction with an increase of soluble calcium, or an alkaline reaction with a decrease of soluble calcium. Chemical Abstracts.

Composition of synovial fluid. F. A. Cajori and R. Pemberton (J. Biol. Chem., 1928, **76**, 471—480).—The concentrations of the non-protein nitrogenous compounds of synovial fluid and of blood-plasma are similar; synovial fluid has a variable content of globulin, and usually a higher albumin : globulin ratio than plasma. Glycolysis is rapid in synovial fluid containing many leucocytes, and probably accounts for the high acidity and low sugar content of such fluid; glycolysis does not occur in the absence of leucocytes. C. R. Harington.

Differences in the behaviour of raw, pasteurised, boiled, evaporated, and dried milk at the hydrogen-ion concentration of the stomach. A. M. Courtney (J. Can. Med. Assoc., 1927, **17**, 919—922).—The characters of the casein precipitated by acid, but not the soluble calcium and protein contents, differed. Chemical Abstracts.

Detection of lactic acid in stomach contents. B. Bisbini (Rinasc. med., 1926, **3**, 514—516; Chem. Zentr., 1927, ii, 964).—The stomach liquor (20 c.c.) is evaporated at 70° to 2 c.c., thoroughly extracted with ether (40—50 c.c.), the residue after removal of the ether is dissolved in lukewarm distilled water (30—40 c.c.), made alkaline with calcium oxide, filtered, and the filtrate evaporated to dryness. The residue is treated with a little water, the solution filtered, evaporated on the water-bath to 0·5 c.c., and the solution placed on an object slide in a desiccator. The formation of calcium lactate crystals is observed with a microscope; 0·05% of lactic acid can be detected. A. A. Eldridge.

Detection of reducing sugars in urine by Castellani's mycological method. P. Pietra (Giorn. batteriol. immunol., 1927, **2**, 1—10; Chem. Zentr., 1927, ii, 963).—Characteristic organisms suitable for symbiotic fermentation with yeast of dextrose, lævulose, maltose, galactose, lactose, pentoses, sucrose, and inositol by Castellani's method are described. Within limits, several sugars present together in urine can be detected. A. A. Eldridge.

Determination of bismuth in urine. H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou (Biochem. Z., 1928, **193**, 53—61).—See A., 1927, 788.

Pigment obtained from fæces. L. F. Hewitt (Brit. J. Exp. Path., 1927, **8**, 333—335).—The rose-red pigment obtained when fæces are subjected to prolonged heating with alcoholic hydrogen chloride is believed to be a dye of the diphenylmethane type, derived by oxidation of the product of condensation of a pyrrole derivative, *e.g.*, skatole, with aldehyde present in the alcohol. CHEMICAL ABSTRACTS.

Chemical changes of the blood in asphyxia. I. R. RITTMANN (Z. ges. exp. Med., 1927, **56**, 262—270; Chem. Zentr., 1927, ii, 951).—The blood-calcium rises, and -potassium falls; the residual nitrogen is not increased. Fibrinogen, globulin, and albumin are scarcely affected. A. A. ELDRIDGE.

Carbon dioxide tension in tissues in relation to cancerous cells. J. C. MOTTRAM (Nature, 1928, **121**, 420—421).—A mechanism whereby localised increase of the carbon dioxide tension in the tissues may induce abnormal cell division is indicated.

A. A. ELDRIDGE.

Fractionation of the Rous chicken sarcoma. K. SUGIURA and S. R. BENEDICT (J. Cancer Res., 1927, **11**, 164—186).—The nitrogen content of the Rous chicken sarcoma (dried) was 11·0—12·2% and the ash 5·69—8·01%. The tumour-producing substance is carried down with the globulin fraction of the tumour proteins on addition of ammonium sulphate.

CHEMICAL ABSTRACTS.

Lipin metabolism in the transplanted tumour. J. HOMMA and T. ISSIKI (Gann, 1927, **31**, 38—40).—The blood-lipin and -lipase of tumour chickens is subnormal; the blood-lipin and serum-lipase in the tumour wing are also less than that in the normal wing. CHEMICAL ABSTRACTS.

Effect of radiation on blood-cholesterol in malignant disease. W. L. MATTICK and K. BUCHWALD (J. Cancer Res., 1927, **11**, 86—100).—A solution of cholesterol in chloroform is affected by radiation of short wave-length, the amount of change depending on the condition of the solute.

CHEMICAL ABSTRACTS.

Hyperallantoinuria in experimental polyuria and diabetes insipidus in man. A. E. Y COSTA (Compt. rend., 1928, **186**, 650—652).—Allantoin is determined by a variation of Wiechowski's method. The precipitate with mercury is decomposed by hydrogen sulphide and half the solution used for the determination of carbamide by xanthydrol. The other half is hydrolysed with hydrochloric acid in an autoclave and the ammonia determined. The difference between total and carbamide ammonia represents 92% of the nitrogen of the allantoin. Polyuria produced by the ingestion of water, injection of "novasurol," and in diabetes insipidus is always accompanied by a high allantoin excretion.

W. K. SLATER.

Acetates in normal and diabetic blood. A. A. BRUNO (Rev. Soc. Argentina Biol., 1927, **3**, 617—620).—The blood of normal dogs contained 1·0—1·5 mg.-% of acetic acid. Higher proportions were found in diabetic dogs and lower proportions in dogs after the injection of insulin. It is concluded that acetic acid is not formed directly from carbohydrates.

R. K. CALLOW.

Reaction of tissues. I. Hydrogen-ion concentration of tissues during fever. J. OGAWA (Proc. Imp. Acad. Tokyo, 1927, **3**, 699—701).—Injection of *Leptospira icterohæmorrhagiæ*, *icteroides*, and *hebdomadis*, coli and typhus vaccines, and tetrahydro-β-naphthylamine in aqueous emulsion, into the rabbit, guinea-pig, rat, and mouse, or overheating the animal at 40—41°, and subsequent determination of the p_H values of the tissues of various organs, shows that there is a decrease in the normal value of 7·0—7·3 to 6·7—6·9. H. BURTON.

Iodine metabolism. I. Urinary excretion of iodine by the inhabitants of a Norwegian goiterous district. G. LUNDE (Biochem. Z., 1928, **193**, 94—104).—The urinary iodine excretions of a large number of men are tabulated and the high values correlated with the type of diet.

P. W. CLUTTERBUCK.

Excretion of hippuric acid in renal disease. I. SNAPPER and A. GRÜNBAUM (Presse med., 1926, **34**, 1524—1526; Chem. Zentr., 1927, ii, 1977).—Oral administration of 5 g. of sodium benzoate to healthy men results in 12 hrs. in its quantitative excretion as hippuric acid. In renal disease with nitrogen retention the excretion (but not the formation) is incomplete. A. A. ELDRIDGE.

Metabolic changes in rickets. H. HENTSCHEL and E. ZÖLLER (Monatsschr. Kinderheilk., 1926, **34**, 248—253; Chem. Zentr., 1927, ii, 952).—In rachitic rats the total phosphoric acid was unchanged; the ability to synthesise a lactacidogenic substance from inorganic phosphoric acid and hexose was diminished.

A. A. ELDRIDGE.

Rôle of calcium in the nutrition and biological processes of the animal organism. A. W. POPOVA (Arch. Sci. Biol., 1927, **27**, 377—392).—The variations in blood-calcium have been determined in the guinea-pig as an index of the progress of the diseases of scurvy and tuberculosis, and it is concluded in the latter case that these variations give results which can be correlated with the corresponding variations in temperature and body-weight; the author regards hypercalcæmia as an index of serious pathological catabolism. E. A. LUNT.

Blood-sugar level in pulmonary tuberculosis. G. SAYAGO, T. DE V. LASTRA, and C. M. VOCOS (Rev. Soc. Argentina Biol., 1927, **3**, 585—595).—It was found that the mean blood-sugar level was lower in acute cases of pulmonary tuberculosis than in mild cases, but the range of variation was much greater in acute cases. Administration of dextrose *per os* caused a prolonged subnormal reaction in acute cases and a subnormal or normal reaction of normal duration in mild cases. Both rise and fall of blood-sugar level were observed following pneumothorax of different origin, but no definite conclusion could be reached as to the cause of variation. R. K. CALLOW.

Buffering power of serum and immunity. W. KOPACZEWSKI (Compt. rend., 1928, **186**, 635—637).—The physico-chemical properties of the medium in which pathogenic organisms are grown begin to change only when the number of organisms has increased to such an extent that the regulating mechanisms of the medium are exhausted. It is suggested that the periods of incubation in, and immunity from, certain diseases are to be attributed to this effect. W. K. Slater.

Respiration of the frog's heart. I. Oxygen consumption of the surviving frog's heart perfused with Ringer, Tyrode, and Locke solutions. T. Hiraoka. **II. Influence of acid and alkali on the oxygen consumption of the surviving frog's heart.** W. Arnoldi and T. Hiraoka (Biochem. Z., 1928, **193**, 197—202, 203—206).—I. The oxygen consumption of the frog's heart is much more constant with Tyrode than with Ringer solution. No difference in oxygen utilisation was obtained on perfusing with Tyrode solution (p_H 7·7) with or without dextrose, the oxygen usage being 0·1 c.c. per g. per hr. more than during perfusion with Ringer solution (p_H 6·7).

II. The oxygen consumption of the surviving frog's heart perfused with 121 c.c. of Tyrode solution (without dextrose), on addition of 0·001*N*-hydrochloric acid, at first rapidly decreases (with 0·5 c.c.), then rises to the original value (0·5—3 c.c.), then again decreases (3—8 c.c.), and finally increases again (8—11 c.c.). Similar addition of 0·001*N*-sodium hydroxide causes with the first 0·5 c.c. a rapid fall, followed by a more gentle fall (0·5—7 c.c.) of oxygen utilisation. P. W. Clutterbuck.

Gas and sugar metabolism of the vivi-perfused stomach. T. G. Ni and R. K. S. Lim (Chinese J. Physiol., 1928, **2**, 45—86).—In the vivi-perfused stomach there is an increase in oxygen consumption during secretion from 3- to 9-fold as compared with the quiescent oxygen consumption of 0·007 c.c. per g. per min. (corresponding with a basal coefficient of the gastric mucosa of 0·013 c.c. of oxygen). The respiratory quotient of the stomach may vary from 0·6 during motility to 1·31 during secretion. After a meal the metabolism of the stomach may account for an increase of 10—12% of the basal metabolism.
W. O. Kermack.

Relation between glutathione and the intracellular oxidation–reduction potential. P. Joyet-Lavergne (Compt. rend. Soc. Biol., 1927, **97**, 140—142; Chem. Zentr., 1927, ii, 1168).—Glutathione is an important factor in the r_H value, and therefore influences intracellular respiration. In organs the regions rich in glutathione appear to be those of the most intensive carbohydrate metabolism.
A. A. Eldridge.

Urinary excretion of ketonic substances by the fasting dog. F. Maignon and E. Knithakis (Compt. rend., 1928, **186**, 463—465).—The daily average urinary excretion of β-hydroxybutyric acid falls from 0·077 to 0·023 g. during 8—16 days' starvation, during which water only was administered, whilst that of acetone rises from 0·001 to 0·005 g.
E. W. Wignall.

Variations of the p_H and the alkaline reserve of the blood of the fasting dog. [F.] Maignon and E. Knithakis (Compt. rend., 1928, **186**, 600—602).—In dogs given nothing but water the acidosis leads generally to a fall in the p_H and to only slight variations in the alkaline reserve and the total carbon dioxide content of the blood; in a few cases rapid adjustment is observed. In prolonged fasting, when water only was administered, diminishing alternations of the rise and fall of the two first-named variables were observed. G. A. C. Gough.

Metabolism with regard to calcium supply. W. Krane (Pflüger's Archiv, 1927, **217**, 24—35; Chem. Zentr., 1927, ii, 1166).—The requirement for calcium equilibrium is 1·2—1·5 g. of calcium per day. The value is higher for a diet rich in meat. Calcium administration has no influence on the nitrogen metabolism. Fæcal nitrogen diminishes during administration of calcium. Deposition of calcium in the body causes loss of chlorine and removal of sodium and potassium from the body.
A. A. Eldridge.

Effect of variations in calcium, magnesium, and phosphorus of the diet. J. R. Haag and L. S. Palmer (J. Biol. Chem., 1928, **76**, 367—389).—Normal growth in rats could be obtained only so long as a balance was preserved between the above-mentioned elements in the diet; in particular, it was found that a high concentration of magnesium, in combination with low concentrations of calcium and phosphorus, retarded growth and calcification.
C. R. Harington.

Action of sugar in the organism. IV. Behaviour of blood-sugar after intravenous injections of methylglyoxal, dihydroxyacetone, and dextrose. F. Fischler and O. Hirsch (Arch. exp. Path. Pharm., 1928, **127**, 287—307).—The authors advance a scheme of the mechanism of sugar regulation in the body. Methylglyoxal is considered to be an intermediate in the decomposition of sugar. It is produced whenever there is a large and rapid breakdown of sugar, and then it acts as a central nervous stimulant whereby the store of glycogen is mobilised and sugar produced. Dihydroxyacetone is able to prevent the excessive action of methylglyoxal in this direction. W. Robson.

Relation between vegetable and animal carbohydrate degradation. A. Gottschalk (Ergebn. Physiol., 1926, **25**, 643—663; Chem. Zentr., 1927, ii, 953).—A discussion. Three types of carbohydrate degradation are differentiated. A. A. Eldridge.

Is there a proportionality between the performance of work and the lactic acid, phosphorus, and sugar contents of blood? N. P. Riabouschinsky (Biochem. Z., 1928, **193**, 161—175).—By increasing the performance of work, the percentage content of lactic acid which reaches the blood from the muscles increases in direct proportion. The lactic acid is not distributed throughout the body uniformly immediately after the work or in the resting period. After lifting weights, the lactic acid content of the blood of the active arm is increased, the increase being conditioned by congestion and insufficient oxygen supply. During this static work, the lactic acid content of the blood of the inactive arm remained almost unchanged. Immediately after the work, a considerable increase of inorganic phosphorus is found which is proportional to the amount of work done. In the resting period, the inorganic phosphorus of the blood in the working arm decreases below the original level, the decrease being the greater the larger the amount of work done. Immediately after work, a slight increase of blood-sugar is usually observed, and in the resting phase, a decrease, but these changes are not in proportion to the amount of work done.

P. W. Clutterbuck.

Metabolism after extirpation of [dog's] liver. V. M. Vesselkina (Z. ges. exp. Med., 1927, **55**, 198—213; Chem. Zentr., 1927, ii, 453).—After extirpation of the livers of fasting dogs (after which death occurred in 3—16 hrs.), the urine was free from albumin and was strongly acid. The ammonia, amino-nitrogen, uric acid, and purine- and allantoin-nitrogen were increased. A. A. Eldridge.

Growth on diets practically devoid of arginine. Relation of glutamic and aspartic acids to nutrition. W. E. Bunney and W. C. Rose (J. Biol. Chem., 1928, **76**, 521—534).—Good growth was obtained in rats on a diet in which the source of nitrogen was hydrolysed caseinogen from which practically all the arginine had been removed by precipitation with flavianic acid; in some experiments, in which a large proportion of the dicarboxylic amino-acids had also been removed, growth continued to be satisfactory. C. R. Harington.

Nitrogen minimum. Effect of protein-free diet on urinary nitrogen and on heat production. Effect of thyroxine following protein-free diet. H. J. Deuel, jun., I. Sandiford, K. Sandiford, and W. M. Boothby (J. Biol. Chem., 1928, **76**, 391—406, 407—414).—After 30 days on a protein-free diet the urinary nitrogen excretion of a normal man was 2·1 g. per day; the basal metabolic rate fell about 20%; at this stage thyroxine was administered, and exerted its characteristic effect in increasing the basal metabolic rate and the excretion of carbamide. Continuance of the protein-free diet after treatment with thyroxine finally reduced the daily excretion of nitrogen to 1·75 g. Practically all variations in nitrogen excretion were due to variations in carbamide. The total excretion of nitrogen throughout the whole protein-free period was 291 g. and indicates that the reserve protein of the body is greater than has been previously supposed. C. R. Harington.

Limit of acid taste and hydrogen-ion concentration. A. Berlatzky and T. Guevara (Rev. Soc. Argentina Biol., 1927, **3**, 721—724).—The values of p_H at the limiting concentrations for perception of acid taste were: sulphuric acid, 2·9; nitric, 3·2; citric, 3·9; tartaric, hydrochloric, and lactic, 4·3; acetic, 4·5; phosphoric, 4·7. If acid taste is due to hydrogen ions, this series is explicable if the anion has an antagonistic cation, which is probably dependent on the ionic mobility. Thus sulphate ions depress the sensitivity of the nerves more than chloride ions, magnesium sulphate having a higher concentration limit of bitter taste (due to magnesium ions) than the chloride. Similar results were obtained with sodium and potassium nitrates and chlorides.

R. K. Callow.

Effect of β-indolethylamine on blood-sugar. S. Hasegawa (J. Biophys., 1927, **2**, xlvi—xlvii).—With small, but not large, injections, hyperglycæmia occurred. Chemical Abstracts.

Influence of climatic factors on the cholesterol of the blood and suprarenal capsule. I—III. A. Rabbeno (Arch. sci. biol., 1926, **9**, 161—167, 168—177, 178—183; Chem. Zentr., 1927, ii, 1163).—The effect of life at a high altitude, and that of maintenance at a constant temperature throughout the year, on the cholesterol and neutral fat content are investigated. A. A. Eldridge.

Biological activity of the porphyrins. K. Reitlinger and P. Klee (Arch. exp. Path. Pharm., 1928, **127**, 277—286).—Hæmato-, copro-, and uroporphyrin increase the tonus of the surviving small intestine of the guinea-pig, cat, and rabbit. The action is strongest in the case of the dibasic hæmatoporphyrin and the tetrabasic coproporphyrin, weakest in the case of the octabasic uroporphyrin. Atropine is unable to inhibit the action of porphyrin. No relationship between the actions of porphyrin and choline has been found. The porphyrins are unable to sensitise the intestine to light rays.

W. Robson.

Alcohol. III. Variations in the alcohol content of human blood. H. Kionka. **IV. Determination of ethyl alcohol in urine.** P. Hirsch. **V. Excretion of alcohol by the kidneys.** H. Kionka and M. Haufe (Arch. exp. Path. Pharm., 1928, **128**, 133—145, 146—149, 150—164; cf. A., 1924, i, 1366).—III. The concentration of alcohol in the blood has been determined in individuals fasting and after the administration by mouth of various quantities of alcohol. The maximum concentration found in the blood increases with the quantity of alcohol taken from a mean fasting value of 0·0031% to a mean value of 0·0452% after administration of 114 c.c. of alcohol. The effect of various factors on the blood-alcohol curve has been investigated, and in particular the previous consumption of a meal and also the induction of marked diuresis causes the maximal values attained to be lower.

IV. The interferometer method previously devised by Kionka and Hirsch (A., 1924, i, 1366) for the determination of alcohol in blood has been developed so as to be applicable to the determination of alcohol in urine.

V. The quantity of alcohol excreted in the urine, always a small percentage of that administered, increases relatively when the quantity administered is very small. The major part of the alcohol excreted in the urine is eliminated during the 3—4 hrs. following consumption. Relatively more appears in the urine when it is administered in a concentrated form. The maximum urine concentration never exceeds about 0·1%. With increased diuresis the quantity of alcohol excreted is increased. The concentration of alcohol in the urine depends on the concentration in the blood, but no simple relationship appears to exist. W. O. Kermack.

Higher toxicity of methyl alcohol in presence of ethyl alcohol. M. Pantaleoni (Ann. Igiene, 1927, **37**, 537—540; Chem. Zentr., 1927, ii, 1980—1981).—A mixture of equal parts of methyl and ethyl alcohols is much more toxic to cats than either alcohol alone. A. A. Eldridge.

Effect of chloralose on blood-sugar level. M. A. Magenta (Rev. Soc. Argentina Biol., 1927, **3**, 681—686).—The blood-sugar level of dogs injected with chloralose, after slight irregular variation, fell to a minimum after 5—7 hrs. and then regained the normal value. The variation from normal is small, and chloralose is therefore a good anæsthetic for use in the study of hyperglycæmia. R. K. Callow.

Elimination of morphine. F. de Camelis (Arch. Farm. sperim., 1927, **44**, 77—92).—Only a very small proportion of a dose of morphine is eliminated in the fæces. The urine contains morphine 24 or 48 hrs., but not on the third day, after the administration. Repeated administration of morphine results in the appearance of reducing substances, probably owing to the presence of morphine-glycuronic acid. T. H. Pope.

Pharmacological assay of ergot. I. B. von Issekutz and M. von Leinzinger. II. M. von Leinzinger and J. von Kelemen (Arch. exp. Path. Pharm., 1928, **128**, 165—172, 173—178).—I. The antagonistic action of ergotamine and adrenaline on the isolated rabbit intestine may be used to determine the activity of the alkaloids of ergot.

II. Determination of the alkaloid content of ergot by the Keller–Fromme method (cf. Z. anal. Chem., 1894, **34**, 115; 1907, **46**, 743) gives a very good indication of its biological activity. W. O. Kermack.

Comparative behaviour of animal charcoal and activated aluminium in toxicology. G. Sensi and C. De Rosa (Annali Chim. Appl., 1928, **18**, 3—18).—Aqueous alcoholic extracts of alkaloids obtained from animal organs in toxicological investigations may be conveniently purified by means of activated aluminium, prepared by immersion of sheet metal or turnings in 10% mercuric chloride solution for 3 min., washing with much water, then with alcohol, and finally with ether, and storing the dried metal under light petroleum; the latter is removed and the metal weighed immediately before use. Activated aluminium is easier to prepare, and more convenient to use, than animal charcoal. From none of the alkaloid solutions tested is more alkaloid removed by the aluminium than by animal charcoal, and in some cases considerably less is removed. T. H. Pope.

Effect of sodium fluoride on blood-sugar level. M. A. Magenta (Rev. Soc. Argentina Biol., 1927, **3**, 691—693).—Injection of sodium fluoride into dogs had little effect on the blood-sugar level, increasing it only when the toxic dose (50 mg. per kg.) was reached. R. K. Callow.

Degree of dispersity and pharmacological action of colloidal sulphur. M. Messini (Arch. exp. Path. Pharm., 1928, **127**, 366—382).—The toxicity of colloidal sulphur depends on the mode of its preparation, its age, its concentration, and on the rate of its injection. With these factors the degree of dispersity of the colloidal sulphur varies, and with the latter in turn its surface of contact with the body fluids which reduce it to hydrogen sulphide. The pharmacological and toxic actions of colloidal sulphur depend on its conversion into hydrogen sulphide, and hence its therapeutic action must be assigned chiefly to the hydrogen sulphide and in general its application limited to those cases in which hydrogen sulphide is of use. W. Robson.

Detoxication of hydrogen cyanide. A. W. Forst (Arch. exp. Path. Pharm., 1928, **128**, 1—66).—The toxic action of hydrogen cyanide is inhibited (except in the case of white rats) by previous administration of sodium thiosulphate or, even more effectively, of colloidal sulphur. These compounds are quite ineffective against poisoning by aromatic nitriles. Administration of dextrose protects against four times the lethal dose of hydrogen cyanide. Insulin alone has very little action, whilst insulin and dextrose are practically no more effective than is dextrose alone. Dihydroxyacetone effectively protects against nine times the lethal dose of the poison. If dihydroxyacetone is administered after the symptoms have developed, the symptoms disappear but death is not averted. When, however, dihydroxyacetone and sulphur are administered together (after poisoning by 9—10 times the lethal dose of hydrogen cyanide), recovery is effected even after the symptoms of poisoning have developed. W. O. Kermack.

Barium and sulphate as antidotes. L. Scremin (Arch. int. pharmacodyn. ther., 1926, **32**, 207—215; Chem. Zentr., 1927, ii, 954).—When injected slowly, but not when injected rapidly, colloidal barium carbonate is somewhat less toxic than barium chloride. The toxicity is not reduced by simultaneous injection of equimolecular sodium sulphate; a solution five times as concentrated is required. Barium hydrogen carbonate is apparently formed in the blood. On slow injection elimination of sulphate runs parallel with injection, and in dilute solutions the conditions do not favour the formation of complex salts containing anionic barium. A. A. Eldridge.

Chemical changes in blood in mercuric chloride poisoning. H. M. Trusler, W. S. Fisher, and C. L. Richardson (Arch. Int. Med., 1928, **41**, 234—243).—Mercuric chloride poisoning by intravenous injection causes a lowering of the blood-chlorides in dogs, but not in rabbits. The dogs suffer from violent vomiting, whilst the rabbits do not. Other symptoms are similar, hence it is concluded that the chlorides are lost by vomiting. Hypochloræmia was found to cause gastric tetany associated with acidosis. Intravenous injection of 2% sodium chloride solution prevents tetany but does not influence the other symptoms. The clinical aspect is discussed. W. K. Slater.

Preventive action of metals against syphilis. C. Levaditi, V. S. Bayarri, R. Schoen, and Y. Manin (Ann. Inst. Pasteur, 1928, **42**, 105—169; cf. A., 1927, 587).—Administration of finely-divided tellurium and bismuth and of certain derivatives of these metals to rabbits renders them resistant to subsequent experimental infection with syphilis. The protection given by bismuth may exceed that conferred by arsenobenzene and other arsenicals. The degree and duration of immunity depend both on the dose and on the nature of the metal derivative administered. W. O. Kermack.

Azo-dyes containing antimony in the treatment of trypanosomiasis. F. Dunning and

D. I. Macht (J. Pharm. Exp. Ther., 1928, **32**, 205—213).—Azo-dyes of the general formulæ $Na_2O_3Sb\cdot C_6H_4\cdot N{:}N\cdot C_6H_3R\cdot OH$ or $Na_2O_3Sb\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NR_2$ do not cure rats infected with *Trypanosoma equiperdum*. Of the dyes formed by coupling diazotised stibanilic acid with α-naphthol-4-sulphonic acid, β-naphthol-3 : 6-disulphonic acid, 1 : 8-dihydroxynaphthalene-2 : 6-disulphonic acid, 8-amino-α-naphthol-3 : 6-disulphonic acid, 6-amino-α-naphthol-3-sulphonic acid, and β-naphthylamine-3 : 6-disulphonic acid, respectively, the sodium salts of the last three possess marked curative action, the ratio of the maximum tolerated dose to the minimum curative dose being 6—7, 4—5, and 4—5, respectively. W. O. Kermack.

Effect of catalase injected into the circulating blood. Catalase and anticatalase content of various tissues. L. Belkine, R. Falk, and L. Kremlev (Compt. rend. Soc. Biol., 1927, **97**, 525—526; Chem. Zentr., 1927, ii, 1480).—Catalase, when injected into the blood, disappears in 3 hrs. The catalase content of tissue is at first increased, particularly in the kidneys and muscles, and then gradually falls to the normal value. Anticatalase changes show no such regularity. A. A. Eldridge.

Action of light on the decolorisation process in a dehydrogenase–methylene-blue system. A. Krestovnikov (Skand. Arch. Physiol., 1927, **52**, 199—208; Chem. Zentr., 1927, ii, 1478).—The decolorisation of methylene-blue in the presence of dehydrogenase and a hydrogen donator is accelerated by light; hence in Thunberg's method the illumination must be weak and uniform. A. A. Eldridge.

Preparation of succinodehydrogenase. N. Andersson (Skand. Arch. Physiol., 1927, **52**, 187—198; Chem. Zentr., 1927, ii, 1479).—Chopped muscle (100 g.) is washed with 100 c.c. quantities of 0·25% sodium chloride solution until the mass is colourless; it is then ground with $M/15$-disodium hydrogen phosphate solution, shaken for 1 hr., and the ferment solution separated by centrifuging. A. A. Eldridge.

Purification of the lactic acid-forming enzyme. K. Meyer (Biochem. Z., 1928, **193**, 139—160).—Purification of the lactic acid-forming enzyme of muscle from protein may be effected either by repeated acetate precipitation at p_H 5 with subsequent elution by dilute phosphate at p_H 7·5—8, or by adsorption of the enzyme on alumina followed by phosphate elution. The first method occasionally gives an enzyme of high degree of activity (50 times the original), but the result is difficult to reproduce. The second method gives much more consistent results, the activity being increased 20 times. The amount of the increased activity depends on various factors, especially on the dilution of the alumina adsorbate and on the distribution of enzyme between precipitate and solution. To elute the enzyme, short, gentle shaking with phosphate is used, since vigorous shaking inactivates it. In this case only the heat-sensitive part of the enzyme is freed from protein. Addition of the heat-stable co-enzyme (boiled muscle extract) is always necessary for the formation of lactic acid. The purified enzyme is relatively more stable than the extract. Whereas the latter becomes inactive on keeping for a few hours, the purified enzyme solution loses only about half its activity in 24—48 hrs. Sodium fluoride acts on the purified enzyme much less than on the extract, attacking probably the protein substances accompanying the enzyme. The action of arsenate is, however, the same for both. P. W. Clutterbuck.

Lipase. I. Optimum action of gastric lipase. II. Lipase of organs and its resistance to acids and alkalis. III. Action of quinine on lipase of organs. K. Gyotoku (Biochem. Z., 1928, **193**, 18—26, 27—38, 39—52).—I. The optimal p_H for the action of rabbit's and human gastric lipase is 6·0, and after purification 7·6—7·8. When pig's gastric lipase, the optimal p_H of which lies on the alkaline side, is kept in the dry condition, its optimal p_H is displaced to 6·0—6·5, the change not being obtained with the gastric lipase of rabbit, dog, and man. When the enzyme is kept in solution, the optimum is displaced to the alkaline side. Normal gastric lipase is probably combined with substances which activate the lipolytic action in acid, and inhibit in alkaline medium.

II. Gastric lipase is more resistant to acids than alkalis and pancreatic and liver lipases are more resistant to alkalis, but gastric lipase is much more stable than other organ lipases to such reagents. Purification of gastric lipases of man, dog, and pig causes decrease of resistance to acids, the enzyme becoming no more stable than pancreatic lipase. Pancreatic and liver lipases also lose their resistance to alkalis on purification. Unpurified gastric lipase retains its resistance to acids for a long time on keeping. Strong acids and alkalis cause great injury to lipases, the degree of injury being directly related to the concentration of hydrogen or hydroxyl ions; addition of proteins or peptones protects the enzyme to some extent.

III. Pancreatic, liver, and gastric lipases are often sensitive to quinine and may be either activated or inhibited. Refractory lipases, on purification, become considerably inhibited by quinine. When dried lipases of organs are kept for several months, the extent of the quinine inhibition decreases. With pig's liver lipase an 80—90% activation is obtained. The action of quinine on the lipase is the sum of two opposed effects, that on the enzyme itself and that on the substances accompanying it which are lost on purification. The organ lipases of man and dog are much more sensitive to quinine than those of rabbit, pig, cat, sheep, and guinea-pig, and serum-lipases of man and dog are much more sensitive than pancreatic lipase. P. W. Clutterbuck.

Influence of cations on the action of lipase. S. Ueno (J. Biophys., 1927, **2**, xxxiv).—Potassium and (to a smaller extent) sodium retard, whilst manganese and cobalt accelerate, the action of pancreatic lipase on cream. Strontium, calcium, barium, magnesium, nickel, uranyl, copper, and mercury depress the action in that order. The depressing action of sodium is neutralised by strontium, barium, calcium, and magnesium.

Chemical Abstracts.

Melibiase. II. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1928, 99—110; cf. *ibid.*, 1927, 699).—Purified yeast melibiase has a maximum activity at p_H 4·8, but it does not vary much between p_H 3·5 and 5·5. With varying concentrations of enzyme the same percentage of melibiose is hydrolysed in times inversely proportional to the concentration of the enzyme provided the other conditions are kept constant. The activity of melibiase in certain preparations is within limits approximately represented by the formula for a unimolecular reaction. Suitable units in which to measure the activity of melibiase and the concentration of it in any particular material are suggested, following the principles used by Willstätter (A., 1920, 1, 795) in relation to maltase. Methods are described for the preparation of melibiase solutions and for the determination of melibiase in yeast.

W. O. Kermack.

Decomposition of urea by urease. S. Mori (J. Biophys., 1927, 2, xxiii).—When the solution is sufficiently buffered against the ammonia formed, the reaction is shown to be unimolecular.

Chemical Abstracts.

Decomposition of caseinogen by trypsin. S. Mori (J. Biophys., 1927, 2, xxiii).—The velocity is proportional to the amount of enzyme. The optimal reaction takes place at 55° with p_H 7·76—7·78.

Chemical Abstracts.

Denaturation of proteins. VI. Effect of denaturation on the digestibility of ovalbumin by pepsin and trypsin. K. H. Lin, H. Wu, and T. T. Chen (Chinese J. Physiol., 1928, 2, 107—130).—Natural and denatured egg-albumins are digested by pepsin or trypsin at different rates. The optimal p_H varies according to the method of denaturation. The results are considered to support the view that the fundamental change in denaturation is similar in nature to some of the early stages of tryptic digestion.

W. O. Kermack.

Digestibility of racemised caseinogen and egg-albumin. K. H. Lin, H. Wu, and T. T. Chen (Chinese J. Physiol., 1928, 2, 131—137).—Racemised egg-albumin and racemised caseinogen are subject to putrefaction, and are hydrolysed by enzymes provided the hydrogen-ion concentration of the medium is suitable, but the rates of hydrolysis are less than those of the natural proteins. These results do not agree with those of Dakin and Dudley (cf. A., 1913, i, 1249), who claim that racemised protein undergoes neither hydrolysis by enzymes nor putrefaction. The racemised egg-albumin is purified by utilising its low solubility at the isoelectric point, p_H 4·45.

W. O. Kermack.

Specificity of animal proteases. XII. Specificity of pancreatic trypsin and intestinal erepsin. E. Waldschmidt-Leitz, A Schäffner, H. Schlatter, and W. Klein (Ber., 1928, 61, [*B*], 299—306; cf. A., 1927, 1112).—Investigation has been made of the hydrolytic action of intestinal erepsin, trypsin kinase, and, in some cases, of trypsin towards glycylglycine, leucylglycine, leucyl-leucine, glycylserine, alanylserine, leucylmethyl*iso*serine, glycylcystine, dileucylcystine, leucylglutamic acid, phenylalanylglutamic acid, glycyltyrosine, diarginine trinitrate, alanyl- and leucyl-β-amino-*n*-butyric acids, glycyl- and alanyl-α-amino-*n*-hexoic acids, leucyl-ε-amino-*n*-hexoic acid, glycyl anhydride, glycylalanine anhydride, alanylphenylalanyl anhydride, glycylserine anhydride, phenyldiketopiperazine, leucyltriglycyl-leucine, leucylheptoglycine, leucylnonaglycine, α-bromo*iso*hexoylnonaglycine, α-bromo*iso*hexoyltriglycyl-leucylnonaglycine, leucyltriglycyl-leucyltriglycyl-leucylnonaglycine, leucylglycyltyrosine, glycylalanyltyrosine, glycyltyrosylglycine, glycylalanylglycyltyrosine, and β-naphthalenesulphonylglycyltyrosine. The dipeptides occupy an exceptional position, since, independently of the nature of the amino-acids from which they are derived, they act as specific substrates for erepsin; a possible exception is diarginine trinitrate, which may not have the constitution ascribed to it by Fischer and Suzuki (A., 1906, i, 73). Fission of higher peptides by pancreas trypsin, which is inactive towards all dipeptides, depends on the presence of certain amino-acids, of which tyrosine is an example. An indication of the cause of the specific differences in the actions of trypsin and erepsin is found in the alteration of the behaviour of glycyltyrosine consequent on the introduction of the β-naphthalenesulphonyl group; glycyltyrosine is hydrolysed only by erepsin, β-naphthalenesulphonylglycyltyrosine only by trypsin. Erepsin appears to require the presence of a free amino-group, which is unnecessary for trypsin.

H. Wren.

Growth of the yeast *Saccharomyces cerevisiæ*. I. The growth curve and the effect of temperature on the yeast growth. O. W. Richards (Ann. Bot., 1928, 42, 271—283).—The growth curve is an asymmetrical S-shaped curve in which, in the medium employed, maximum growth is attained within 100 hrs. following seeding. Cell-volume increase exceeds cell-number increase for the first 15 hrs. and then decreases; both have the same value after 90 hrs. Analyses of the curve indicate that the limiting master reaction is quinquemolecular.

E. A. Lunt.

Acetylmethylcarbinol formation in the alcoholic fermentation of sugar. L. Elion (Ned. tijdschr. hyg. microbiol., 1926, 1, 171—179; Chem. Zentr., 1927, ii, 1042).—The appearance of acetylmethylcarbinol as a product of the fermentation of sugar fixes the acetaldehyde, which can no longer act as hydrogen-acceptor. Free hydrogen, however, is not evolved, but a complex reduction process takes place, the nature of which is under investigation.

A. A. Eldridge.

Comparison of the actions of arsenate and organic derivatives of arsenic acid on alcoholic fermentation of sugar. P. Mayer (Biochem. Z., 1928, 193, 176—180).—A number of aromatic derivatives of arsenic acid can accelerate fermentation of hexosediphosphate, especially phenylarsinic and arsanilic acids, but none of these substances has as great an effect as potassium arsenate.

P. W. Clutterbuck.

Thermophilic and thermoduric micro-organisms, with special reference to species isolated from milk. I. Review of literature. III. Description of non-spore-forming, thermoduric

organisms isolated. A. H. Robertson (New York Agric. Exp. Sta., Tech. Bulls. 130 and 131, Aug. 1927, 56 and 62 pp.).

Thermophilic fermentation processes. C. Coolhaas (Ned. tijdschr. hyg. microbiol., 1926, **1**, 338—350; Chem. Zentr., 1927, ii, 1159).—A rapid thermophilic fermentation of formate, acetate, oxalate, gluconate, and lactate, and a slower fermentation of butyrate and propionate to carbon dioxide and methane took place with spore-forming rod-bacteria of very different lengths. In a fermentation of peptone to carbon dioxide and methane, most of the nitrogen was converted into ammonia. A motile, spore-forming, aërobic bacterium caused the extraordinarily rapid conversion of starch into maltose and dextrin; another bacterium fermented various carbohydrates to carbon dioxide, hydrogen, butyric acid, and active lactic acid. A. A. Eldridge.

Action of digestive juices on lactic organisms. C. A. Sagastume and A. Solari (Rev. Soc. Argentina Biol., 1927, **3**, 573—580).—When a mixture of *B. acidi lacti*, a lactic streptococcus, and a torula from milk was incubated in acid and alkaline media (p_H 1·2—1·9 and 10·4—10·8), the first two alone were affected, being killed at $p_H < 1{\cdot}4$. *B. acidophilus* and *B. bulgaricus* were tested in the same media and in hypochlorhydric, normal, and hyperchlorhydric gastric juice, and in duodenal juice. Whilst *B. acidophilus* was practically unaffected, *B. bulgaricus* was killed in the acid media and in hyperchlorhydric gastric juice.

Since the nutritive requirements of *B. acidophilus* and *B. bulgaricus* are similar, the difficulty of adaptation of the latter to the human intestine which is generally recorded can be attributed to its lower resistance to the digestive juices, combined with the bacterial antagonism of the intestinal medium.

R. K. Callow.

Fermentation of dextrose by *Bacillus coli*. Rosnatovsky (Zentr. Bakt. Par., 1927, I, **102**, 145—148; Chem. Zentr., 1927, ii, 1481).—When *B. coli* is grown on acid or neutral bouillon in presence of 0·5—2·0% of dextrose, the amount of gas produced (hydrogen : carbon dioxide = 6 : 1 to 10 : 1 in acid, always 2 : 1 in neutral bouillon) is variable, and independent of the sugar content. Intermediate products therefore appear to be concerned.

A. A. Eldridge.

Biochemical preparation of a disaccharidemonophosphoric ester. C. Neuberg and J. Leibowitz (Biochem. Z., 1928, **193**, 237—244).—Dephosphorylation of sodium hexosediphosphate by the action of *B. coli* and *B. lactis aërogenes* gave poor results, the action being slow and incomplete. With the lactic acid bacterium, *B. Delbrücki*, however, a disaccharidemonophosphoric ester was obtained, determinations of carbon, hydrogen, barium (of barium salt), and phosphorus agreeing with the formula for the barium salt of $C_{12}H_{21}O_{14}PBa$, α_D +55·2°. P. W. Clutterbuck.

Influence of sodium chloride on the formation of volutin in the cells of spore-forming bacteria. P. Smirnov (Zentr. Bakt. Par., 1927, II, **70**, 29—36; Chem. Zentr., 1927, ii, 1480—1481).—The formation of volutin by *Bacillus alvei* depends on the size of the cell, and hence on the sodium chloride content.

A. A. Eldridge.

Fat metabolism of *Hyphomycetæ*. I. A. von Mallinckrodt-Haupt (Zentr. Bakt. Par., 1927, I, **103**, 73—87; Chem. Zentr., 1927, ii, 1041).—*Trichophyton gypseum* grows on Uschinsky's medium with butter or lard, but not cod-liver oil; growth was poor on beef- or mutton-fat. Olive and castor oils were suitable, as well as pure triacetin and triolein. The optimum p_H for tributyrin hydrolysis is 6·0, and for peptone 7·0. A. A. Eldridge.

Oxidation of waxes by micro-organisms. W. O. Tausson (Biochem. Z., 1928, **193**, 85—93).—*Aspergillus flavus* can utilise as a source of carbon the esters of higher fatty acids with glycerol and with the higher alcohols. There is a close correspondence between the power of the mould to use these substances and to oxidise paraffin. The absolute amount of wax oxidised by the mould is proportional to the age of the culture and is smaller than the amounts of paraffin oxidised under the same conditions. The results support the view that such esters are formed as an intermediate stage in the oxidation of paraffin.

P. W. Clutterbuck.

Formation of citric acid by *Aspergillus niger*. F. Challenger, L. Klein, V. Subramaniam, and T. K. Walker (Nature, 1928, **121**, 244).—Potassium citrate has been isolated from cultures of *A. niger* on potassium hydrogen adipate and on potassium muconate. A. A. Eldridge.

Formation of an *o*-diphenol at the expense of sugars by certain microbes of the soil. Lemoigne (Compt. rend., 1928, **186**, 473—475).—*B. subtilis* and other soil bacteria which give a butyleneglycol fermentation are cultivated on an acid medium containing sugar as the sole organic constituent; the product gives with ferric chloride, after precipitation and re-dissolution of ferric phosphate, a green coloration attributed to the presence of an *o*-diphenol. The product on concentration shows all the reactions of *o*-diphenols, but no chemical individual is isolated.

E. W. Wignall.

Nitrate reduction by *Azotobacter*. S. Kostytschev and O. Schvezova (Z. wiss. Biol., Abt. 3. Planta, Arch. wiss. Bot., 1926, **2**, 527—529; Chem. Zentr., 1927, ii, 1159).—A discussion.

A. A. Eldridge.

Biological reduction of mineral phosphate. K. I. Rudakov (Zentr. Bakt. Par., 1927, II, **70**, 202—214; Chem. Zentr., 1927, ii, 947).—Reduction of phosphoric acid in soil to phosphorous and hypophosphorous acids and phosphine by micro-organisms in soil has been observed. The reduction process is diminished by addition of potassium nitrate and magnesium sulphate. A pure culture of the reducing organism was obtained. A. A. Eldridge.

Decomposition of fats by the tubercle bacillus. A. Sédych and G. Seliber (Compt. rend. Soc. Biol., 1927, **97**, 57—58; Chem. Zentr., 1927, ii, 1158).—Fats are hydrolysed by the tubercle bacillus.

A. A. Eldridge.

Electrodialysis of tuberculin. VIII. F. B. Seibert and M. T. Hanke (J. Biol. Chem., 1928, 76, 535—541).—Electrodialysis causes a more efficient removal of the last traces of electrolytes from tuberculin than does ordinary dialysis, although the initial stages of the process are no quicker; no loss of activity is brought about by the electric current, but under its influence small amounts of the protein diffuse through parchment; in the absence of the electric current such diffusion takes place only through collodion membranes prepared from a solution of collodion in a mixture of ether and 95% (not absolute) alcohol. C. R. Harington.

Antigens. F. Przesmycki (Z. Immunitätsforsch., 1927, 51, 408—420; Chem. Zentr., 1927, ii, 1717—1718).—For the preparation of the residual antigens of bacteria, an aqueous extract is boiled with 10% acetic acid for 5 min., and the precipitate is separated in a centrifuge; 10 vols. of 95% alcohol are added, the precipitate is dissolved in water and reprecipitated with alcohol. The process is repeated 6 times in alternately alkaline and acid medium. The aqueous dialysate is then precipitated with acetone. A. A. Eldridge.

Does adrenaline act through calcium? L. Jendrassik and A. Czike (Klin. Woch., 1927, 6, 1521; cf. Jendrassik and Antal, *ibid.*, 1338; Chem. Zentr., 1927, ii, 1722—1723).—Zondeck's theory of parallelism between the action of adrenaline and calcium ions is unsupported by experiment. A. A. Eldridge.

Influence of amino-acids and their derivatives on adrenaline hyperglycæmia. M. Chikano (J. Biophys., 1927, 3, xlv—xlvi).—Dihydroxyphenylalanine and pyrocatechol cause considerable, and tryptophan slight, hyperglycæmia. Tyrosine, hydroxyphenylpyruvic acid, and tryptophan augment adrenaline hyperglycæmia; leucine and histidine counteract it, and phenylalanine exerts no action. Glycine and glutamic acid have no influence on blood-sugar. Chemical Abstracts.

Influence of some protein derivatives on the regulation of blood-sugar. I. Effect on the blood-sugar curve and the hyperglycæmic reaction after adrenaline. F. Nord (Acta med. scand., 1926, 65, 1—115; Chem. Zentr., 1927, ii, 1717).—Glycine, glutamic acid, and Witte's peptone exercise a sugar-mobilising effect, but do not increase the action of adrenaline on the blood-sugar. Glycine and glutamic acid can completely suppress insulin hypoglycæmia; the action of Witte's peptone is irregular. A. A. Eldridge.

Inner secretion of the pancreas. VI. Substance in human urine which diminishes the blood-sugar. K. Kozuka (Tohoku J. Exp. Med., 1927, 9, 130—147).—Human urine contains a very variable quantity of a hypoglycæmic substance. The substance cannot be isolated in diabetes unless sugar is eliminated from the urine by treatment with the pancreatic hormone, with which the substance is probably identical. Chemical Abstracts.

Mode of action of insulin. C. Lundsgaard (Acta med. scand., Suppl. Bd., 1926, 16, 473—484; Chem. Zentr., 1927, ii, 1974).—The action of insulin depends on an intramolecular rearrangement of the sugar, with formation of neoglucose; sufficient insulin for the purpose is normally present. The effect of insulin depends on the presence of some substance present in fresh muscle; if this is provided, the action can be reproduced *in vitro*. A. A. Eldridge.

Hormonal processes after administration of dextrose. IV. Detection of insulin in human blood after peroral administration of dextrose. H. Häusler and R. Weeber (Klin. Woch., 1927, 6, 1521—1522; Chem. Zentr., 1927, ii, 1974).—Insulin was detected. A. A. Eldridge.

Colorimetric determination of iodine in homœopathic and biochemical preparations. C. A. Rojahn (Apoth.-Ztg., 1927, 42, 551; Chem. Zentr., 1927, ii, 149).—An aqueous extract (5 c.c.) is filtered, and the filtrate is treated with sulphuric acid, potassium iodate, and chloroform; after shaking, the colour of the chloroform layer is compared with that of a standard solution. A. A. Eldridge.

Determination of uric acid [in body fluids]. C. Currado (Pediatria, 1926, 2, 216; Chem. Zentr., 1927, ii, 306).—Benedict's method is preferred. A. A. Eldridge.

Rapid volumetric determination of amino-acids, organic acids, and bases. I. Determination of ammonia and volatile amines in biological fluids and determination of the different classes of acid radicals represented in the total alcohol titration value. II. Quantitative removal and determination of the carbonic acid radical especially in bacterial cultures. F. W. Foreman (Biochem. J., 1928, 22, 208—221, 222—229).—I. A detailed description of the methods which are an extension of the author's original method (cf. A., 1920, ii, 564).

II. The method is based on the observation that concentrated alcohol in which carbonic acid and small quantities of "free" volatile acids are dissolved very readily parts with the whole of the carbon dioxide, but completely retains the volatile acids on aëration. Hydrogen carbonates of "weak" nitrogenous bases lose their carbon dioxide by this treatment. S. S. Zilva.

Stain solubilities. III. W. C. Holmes (Stain Tech., 1928, 3, 12—13).—The solubilities in water and 95% alcohol of 45 dyes are tabulated. H. W. Dudley.

Fast-green, a substitute for light-green S. F. yellowish. R. Haynes (Stain Tech., 1928, 3, 40).—Fast-green, a triphenylmethane dye (see Johnson and Staub, B., 1927, 404), is slightly greener, stains more intensely in a shorter time, destains safranine more slowly (making differentiation easier), and is much more permanent than light-green. H. W. Dudley.