BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Calculation of the spectroscopic terms derived from equivalent electrons. H. N. Russell (Physical Rev., 1927, [ii], 29, 782—789).—An extension of Breit's notation affords a simple method for the calculation of the spectroscopic terms which result from an atomic configuration containing several equivalent electrons, in which Pauli's restriction is operative. A. A. Eldridge.

Terms arising from similar and dissimilar electrons. R. C. Gibbs, D. T. Wilber, and H. E. White (Physical Rev., 1927, [ii], 29, 790—793).—Following Hund's scheme, the terms arising from similar f electrons from 1 to 14 have been worked out and tabulated. Tables are also given for one, two dissimilar, and three (two similar) electron systems. A. A. Eldridge.

Intensity of spectral lines. A. E. Brodsky (Z. Physik, 1927, 42, 899—904).—By the application of classical thermodynamic principles to an orbital electron transition considered as a "reaction," an expression $I=\alpha xe^{-x}$ has been derived for the intensity, I, of lines of frequency ν radiated by a gas or vapour, where $x=h\nu/kT$ and α is a function of $Te^{1/T}$. This expression is similar in form to Bleeker's (A., 1926, 657). It has been examined by applying it to the data of Bleeker and Bongers for I and ν (A., 1925, ii, 77) relating to the sharp and diffuse subordinate series of rubidium and cæsium. For these, when a temperature of 1700° is assigned to the radiating vapour, it is shown that $\log\alpha$ is constant within 1·4—3·5%. This agreement with theory is considered to be satisfactory. R. W. Lunt.

Intensity distribution in spectrum lines, and its application to photometric measurements. L. S. Ornstein and M. Minnaert (Z. Physik, 1927, 43, 404—412).—The intensity distribution in a spectral line has been calculated on the assumption that the true line-width is very small and that the observed width is due to the width of the slit and to refraction, and is of the form $I_x=\int_{x-\frac{1}{2}\sigma}^{x+\frac{1}{2}\sigma}x^{-2}\sin^2 x.dx$, where I_x is the intensity at a distance x from the centre of the line, and $\sigma=\pi Bs\lambda^{-1}f$, where B is the width of the refracting aperature, s the slit width, λ the wave-length, and f the focal length of the collimator. The intensity distribution computed thus from the optical constants of the apparatus for the mercury lines 5461, 4078, 3342, 3126, 3024, 2537, and 2482 Å. agrees exceedingly well with the intensity distribution measured photometrically, for which a special developer is necessary to reduce the Eberhard effect to a minimum. A number of important applications are described. R. W. Lunt.

Structure of the second order spectrum of carbon. C. Mihul (Compt. rend., 1927, 184, 1648—1649).—Three new multiplets resulting from combinations between terms of multiplicity $r=4$ are described for the C II spectrum. They consist of the triplet $^4P^4S$, and the two multiplets $^4P^4P'$ and $^4P^4D$. The corresponding electronic configurations based on Hund's theory are evaluated. J. Grant.

Spectrum of ionised neon (Ne II). T. L. de Bruin (Nature, 1927, 119, 925—926).—A number of the Ne II lines have been classified in a term scheme analogous to that of F I. A. A. Eldridge.

Reversal of neon lines. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1927, 3, 136—139).—The reversal of 18 lines of the neon spectrum in the range 7032—5852 Å. has been examined by an echelon spectroscope (resolving power 435,000 at 5000 Å.) and by a Lummer–Gehrcke plate (resolving power 400,000 at 5000 Å.). The reversals are found to be slightly asymmetric, and no definite relation with absorption can be traced. The lines of the type $1s_2-2p_m$ show diffuse reversals, $1s_3-2p_m$ are generally narrow, $1s_4-2p_m$ are sharp when m is even. Within the limits of these experiments no conclusion can be reached concerning the observed reversals with the mode of excitation, the magnetic separation, and absorption. R. W. Lunt.

Electrically excited resonance spectrum of argon. K. W. Meissner (Z. Physik, 1927, 43, 449—453).—A glass cylinder, 120×20 mm. in diameter, containing argon is provided at each end with a side-tube containing an electrode. Surrounding this tube are a number of small tubes, parallel to the axis, connected in series and ending in two electrodes. This external tube system also contains argon. An examination has been made of the spectrum of the light emitted axially from the inner cylinder, both when it is energised with 9—10 milliamp. direct current and when the external tube is energised with direct current. It is found in the latter case that the following resonance lines corresponding with the $2s_i-2p_k$ transitions are intensified: 8668, 8521, 8408, 8265, 8104, 8006, 7948, 7724, 7635, 7515, 7504, 7383, 7273, 7147, 7067, 6965, and 6677. R. W. Lunt.

Detailed explanation of spectra of metals of the second group. M. Saha (Phil. Mag., 1927, [vii], 3, 1265—1274).—The principles of non-mechanical vector addition of quantum numbers previously applied by Landé, Russell, and others to the fundamental levels of the atom have been extended to the examination of all the higher terms, and for metals of the second group all details of the spectra are satisfactorily explained. The resulting scheme of electron arrangement is in effect a modification of the scheme of Main Smith and Stoner.

A. E. Mitchell.

Relative intensities of some lines in the mercury spectrum. J. Valasek (Physical Rev., 1927, [ii], 29, 817—821).—The intensities of the most intense lines associated with transitions to and from the $2p_2$ state in mercury were measured photographically. When only transitions giving rise to radiation are considered, there appear to be more transitions to $2p_2$ than down from $2p_2$. A. A. Eldridge.

Production of the continuous spectrum of mercury by rolling it in a vacuum. M. Duffieux (Compt. rend., 1927, **184**, 1434—1436; cf. A., 1925, ii, 340).—A detailed description is given of the phenomena observed at increasing temperatures when a large drop of mercury is contained in a spherical glass vessel rotating round a horizontal diameter. At 10—40°, unstable luminous phenomena were produced depending probably on the electrical state of the glass. At about 50°, a mauve luminous discharge was produced between the tail of the drop (the positive extremity) and the glass. The green and violet mercury rays, and sometimes yellow rays, were distinguishable. At 100°, the positive extremity of the arc was separated from the glass by a dark space, and before 120° was reached, the top of the vessel lit up with a brilliant green glow of increasing intensity, which emitted only the continuous spectrum of mercury. No modification occurred at the highest temperature reached (200°). J. Grant.

Reversal of series lines of thallium. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, **3**, 140—142).—Reversal in the sharp and diffuse series of thallium has been examined in the ranges 5350·5—2315·9 Å. and 3529·4—2379·6 Å., respectively. The spectra were excited by discharging a condenser of 1·7 microfarads capacity charged to 20 kilovolts across a gap of 0·2—0·3 mm. between thallium electrodes. The amount of reversal decreases as the frequency increases; the reversal of the sharp series is asymmetric, whilst that of the diffuse series is symmetric. R. W. Lunt.

Fine structure and term constants of the bismuth spectrum. S. Goudsmit and E. Back (Z. Physik, 1927, **43**, 321—334).—The fine structure of the following bismuth lines has been determined by a grating method: 4722·5, 4308·3, 4121·8, 3888·2, 3596·1, 3510·9, 3397·2, 3076·6, 3067·7, 3024·6, 2993·3, 2989·0, 2938·3, 2898·0, 2696·7 Å. From the $\Delta\nu$ values thus obtained term constants have been assigned to the above lines. R. W. Lunt.

Direct measurement of X-ray energy. W. Rump (Z. Physik, 1927, **43**, 254—295).—An elaborate technique has been devised whereby the energy of a beam of X-rays can be measured directly by allowing the incident beam to fall into a cavity surrounded by lead or mercury, which functions as a perfect absorber. The absorber is immersed in a thermostat, and the energy received is measured by the expansion of a gas in contact with the outer surface of the absorber; the sensitivity obtained was 1×10^{-6} g.-cal. sec./cm.^{2} of cavity aperture (12·6 cm.^{2}). The apparatus was calibrated with the known energy of the α-, β-, and γ-radiation from radium, and data were reproducible within 1%. Using a Coolidge type of X-ray tube with a constant current of 10 milliamp., the total X-ray energy was found to vary as the square of the applied stationary potential in the range 43—150 kilovolts. The efficiency of the tube as a generator of X-rays increased correspondingly from 0·46 to 1·64%. Elaborate determinations have been made on the ionisation produced in air by X-rays. Data are given for the number of ions produced as a function of the energy absorbed, and of the mean energy, V, of the ions computed from $h\nu=Ve$, where ν is the mean frequency of the X-radiation. R. W. Lunt.

Absolute measurement of light quanta in an X-ray beam. W. Kossel and M. Steenbeck (Z. Physik, 1927, **42**, 832—835).—The technique of Eliger and Holthusen has been adapted to the measurement of the number of ions liberated in unit volume of a gas traversed by a beam of X-rays by using suitable precautions to ensure that the ions are liberated in a uniform field. From measurements of the number of ions liberated under these conditions, radiation at the rate of 100 X-ray quanta per minute can be observed. The method has thus a sensitivity a million times that of the thermal method. R. W. Lunt.

Intensity of X-ray spectra as a function of the exciting potential. D. Nasledov and P. Scharavski (Z. Physik, 1927, **43**, 431—441).—The intensity of the following lines of the K-series has been determined by an ionisation method as a function of the exciting potential up to five times the minimum exciting potential: Ag$K\alpha$, Ag$K\beta$, Pd$K\alpha$, Pd$K\beta$, Mo$K\alpha$, and Cu$K\alpha$. The intensity varies linearly with the square of the applied potential, and vanishes at approximately $kV^2=500$, except for copper, when it vanishes if the curve is produced backwards from $kV^2=4225$, at $kV^2=-5000$. The intensity I can therefore be expressed in the form $I=c(V-V_0)^2$, where V_0 is a constant characteristic of the metal. R. W. Lunt.

Intensity of X-ray lines as a function of the number of electrons reaching the cathode. D. Nasledov and P. Scharavski (Z. Physik, 1927, **42**, 870—882).—The authors' earlier work on copper has been extended to an examination of the lines Mo$K\alpha$, Mo$K\beta$, Pd$K\alpha$, Pd$K\alpha$, and Ag$K\alpha$. As in the case of copper, the intensities increase linearly with the current up to a certain critical value; they then increase linearly but at a diminished rate. This critical point is independent of the potential applied to the tube in the range examined, 50—83 kilovolts. For molybdenum and palladium, the critical current is 6 milliamp., and for silver between 6 and 7 milliamp. An approximately linear relationship is thus to be traced between the value of this critical current in copper (4 milliamp.), the above metals, and the corresponding atomic numbers. R. W. Lunt.

Selective displacement of 0·0153 Å in *X*-ray spectral lines. F. H. Loring (Chem. News, 1927, **134**, 385—388; **135**, 17—18, 65—67).—Theoretical. A continuation of previous work (this vol., 602).

W. E. Downey.

Effect of .chemical combination on *X*-ray absorption. W. B. Morehouse (Physical Rev., 1927, [ii], **29**, 765—774).—The *X*-ray absorption by aqueous solutions of the reactants producing reactions expressed by the equations (*a*) $KI+I_2+2Na_2S_2O_3=KI+2NaI+Na_2S_4O_6$, (*b*) $K_2Cr_2O_7+12KI+14HCl=8KCl+2CrCl_3+3I_2+6KI+7H_2O$, (*c*) $NaOH+HCl=NaCl+H_2O$, (*d*) $KOH+HCl=KCl+H_2O$, (*e*) I_2 (aqueous alcoholic)$+2Na_2S_2O_3=2NaI+Na_2S_4O_6$, and of the solutions after reaction, has been measured. The results indicate that the mass absorption coefficient for an element depends on its valency. Absorption by iodine in the free state appears to be greater than that in combination.

A. A. Eldridge.

Theory of the intensity of scattered *X*-rays. G. E. M. Jauncey (Physical Rev., 1927, [ii], **29**, 757—764).

Laboratory demonstration of the Zeeman effect. K. W. Meissner (Z. Physik, 1927, **43**, 454—455).—Plane polarised light from a neon–helium discharge tube is passed through a second discharge tube, whereby the light from the first tube is absorbed. If now a magnetic field be applied to the first tube, the frequency is slightly changed, and can therefore pass through the second tube and be focussed on a screen.

R. W. Lunt.

Zeeman effect and spherical harmonics. C. G. Darwin (Proc. Roy. Soc., 1927, *A*, **115**, 1—19).—The problem of a charged spinning spherical body moving in a central orbit in a magnetic field is solved by the method of the wave mechanics in spherical harmonics. It leads to a system of equations which are competent to determine the frequencies and intensities of the lines in the standard Zeeman effect. The model yields strictly the odd multiplicities only, but the same set of equations is also applicable in every respect to the even. Formulæ are given from which the intensity of any component in any strength of field can be obtained. A few examples are worked out. The development in spherical harmonics elucidates clearly the physical meaning of the quantum numbers k, m, r, m_k, m_r, but much more obscurely j. To elucidate the force of j, a new method of attacking the problem is outlined.

L. L. Bircumshaw.

Tentative explanation of the Zeeman effect of types D_1 and D_2. F. J. von Wiśniewski (Z. Physik, 1927, **42**, 910—914).—A theory of the Zeeman effect for weak fields and of types D_1 and D_2 has been developed by considering the two possible solutions of the equation of motion of an electron about a solid nucleus, and in a magnetic field.

R. W. Lunt.

Duration of light-emission of atoms. H. Kerschbaum (Ann. Physik, 1927, [iv], **83**, 287—295; cf. A., 1926, 652).—The earlier work has been extended to the metals calcium, strontium, and barium. The following results were obtained for the damping constant ($\times10^7$) and the mean duration of the light in seconds ($\times10^{-8}$), respectively: Calcium: spark, 15·4, 0·65; arc, 2·8, 3·4. Barium: spark I, 8·3, 1·2; spark II, 3·7, 2·7. Strontium: spark I, 8·0, 1·25; spark II, 2·78, 3·6; arc, 5·05, 1·98. Differences are observed between different spark lines in barium and strontium. The electric deflection of spectral lines has been investigated for the three elements. All the available values for the mean direction of the light for different elements are tabulated.

R. A. Morton.

Duration of the afterglow in mercury vapour. (Frl.) M. Asterblum (Z. Physik, 1927, **43**, 427—430).—The continuous afterglow of mercury vapour has two maxima, at 3300 and 4850 Å. The duration of the afterglow at these maxima is the same, and decreases in intensity logarithmically with time.

R. W. Lunt.

Light-period of the ultra-violet hydrogen series. W. Wien (Ann. Physik, 1927, [iv], **83**, 1—18).—A fine stream of hydrogen positive rays crosses the focal circle of the grating of a vacuum spectrograph so that the lines H_a 1215·68, H_b 1025·7, H_c 972·5, H_d 949·8, and H_e 937·8 Å. can be photographed on Schumann plates. The intensity of the radiation emitted by the canal-ray stream decreases along its length, so that the spectral lines exhibit a fading which is a measure of the period of line-excitation. The more usual methods for measuring the intensities of spectral lines are not applicable to vacuum spectroscopy in this region, since no material is available for the construction of wedges, and the mechanical methods for reducing the intensity are scarcely practicable. A screening arrangement was, however, devised for reducing the intensity of the positive-ray stream, which was calibrated by measurements on the heating effect of the charged particles. The decrease in intensity of H_a is given by $I=I_0e^{-\beta y}$, in which y is the distance traversed in the positive-ray stream and β is 4·3. The Döppler shift $\delta\lambda=0{\cdot}085$ mm. and $v(=\delta\lambda/\lambda c)$ is $3{\cdot}44\times10^7$ cm./sec., so that the duration constant $2\alpha(=\beta v)$ is $14{\cdot}8\times10^7$ for both H_a and H_b, a value some three times as great as that found with the Balmer series. Slack (A., 1926, 875) by excitation with electrons at 10·2 volts obtained for 2α the value $8{\cdot}3\times10^7$.

R. A. Morton.

Behaviour of Schumann plates in the vacuum spectrograph in the observation of canal-rays. W. Wien (Ann. Physik, 1927, [iv], **83**, 19—22).—The observations recorded (preceding abstract) were greatly hindered by fogging of the plates, and the effect has now been studied in detail. The fog is formed with hydrogen and oxygen positive rays, but only to a much smaller extent with nitrogen. This observation supports direct spectrographic tests, which make it improbable that the effect is due to short-wave radiation. A more likely explanation is a chemical interaction between atomic hydrogen or oxygen and the almost gelatin-free silver halide of the Schumann plate. The observations on the effect of pressure variations on the development of the fogging may be interpreted in terms of this mechanism.

R. A. Morton.

Electron emission from thoriated tungsten. S. Dushman and J. W. Ewald (Physical Rev., 1927,

[ii], 29, 857—870).—The emission for a monatomic film of thorium on tungsten is greater than that for metallic thorium. The electron emission ($I=3T^2\varepsilon^{-30,500/T}$, in amp./cm.^{2}) was measured for different states of activation of the thoriated filament.

A. A. ELDRIDGE.

Chemical activity of slow electrons. E. RABINOWITSCH (Z. Elektrochem., 1927, 33, 185—188).—Solid oxides such as lime, thoria, and ceric oxide have been submitted to bombardment by electrons under various conditions in an attempt to decompose them, and hence to determine their heats of formation from the critical electron velocity required for this purpose. With slow electrons of an energy comparable with the energy of decomposition of the oxides, traces of gas could be pumped out of the discharge tube, but oxygen could not be definitely detected in it. With electrons of about 1000 times this velocity, oxygen was obtained from rare-earth oxides, but even then the efficiency was very small, only about one impact in 400 producing decomposition. This result is not unexpected, considering that, when gas molecules are decomposed by slow electrons, the high efficiencies obtainable are due to secondary processes caused by impacts of molecules activated by the primary process, whilst in a solid these secondary effects are not possible. The small quantities of gas obtained were removed from the discharge tube by continuous pumping; otherwise most of the liberated oxygen recombines and no appreciable rise in pressure occurs. Ceric oxide blackens under the bombardment, but the amount of the decomposition product was not sufficient for analysis. Difficulties in determining the applied voltage occurred owing to the badly-conducting oxide layer becoming charged on the surface. The results of Cole (A., 1926, 1189) on the blackening of photographic emulsions by low-speed electrons are discussed in the light of similar experiments by the author. H. J. T. ELLINGHAM.

Smallest carriers of electricity in gases. H. SCHILLING (Ann. Physik, 1927, [iv], 83, 23—80).—The most important experimental result is that all attempts to obtain with the purest gases values of w greater than those normally found for the ordinary carriers of electricity in air have been unsuccessful. The largest values found are: $w^-=2{\cdot}5$ and $w^+=2{\cdot}0$ cm./sec. volt/cm., corresponding with carrier-radii of $4{\cdot}7$ and $4{\cdot}1\times10^{-8}$ cm., respectively. The radius is thus about three times that of a single molecule in air. The multiple of the molecular radius required to correspond with the radius of the negative carrier varies from 3·0 with air to 5·0 with helium and 6·0 with ethyl alcohol. The literature of this subject is critically reviewed. R. A. MORTON.

Nature of phosphorus ionisation. II. W. BUSSE (Ann. Physik, 1927, [iv], 83, 80—120; cf. this vol., 633).—The relations between temperature and ion-formation have been investigated, and the effect of increasing temperature has been shown to differ from that of decreasing temperature. The ionisation–temperature curves show maxima and minima and a noteworthy small peak at temperatures between 35° and 40°, *i.e.*, just below the flashing temperature. In dry air, ionisation occurs only at higher temperatures. The position and magnitude of the maximum are greatly influenced by the temperature of the air stream. The moisture present favours a rapid rise to maximum ionisation. The fact that moisture appears to be essential for ion-formation, in conjunction with the earlier conclusion that the negative ions take up multiple charges preferentially, leads to the view that the ionisation occurs as a result of the dissociation of an acid formed in the course of the oxidation of phosphorus. It is shown that the charge which occurs at the initial introduction of the air stream over the phosphorus is, apart from special exceptions, equal to the charge at the stage immediately preceding ignition. On the other hand, the maximum in a curve corresponds with a charge several times as great as the initial charge. The amount of dissociating acid present remains fairly constant, so that ionisation by stages must occur. This notion gives an explanation of the numerous maxima in the curves. The maximum charge appears to be eight times the initial charge, so that an acid of maximum basicity 8 may dissociate by steps. The evidence points to reaction between phosphorus pentoxide and water. The possible rôle of different oxy-acids of phosphorus is discussed; the conclusion is reached that pyrophosphoric acid must be the dissociating substance responsible for the ion-formation. R. A. MORTON.

Probability of ionisation of mercury vapour by electron impact. T. J. JONES (Physical Rev., 1927, [ii], 29, 822—829).—The curve showing the number of positive charges produced in a 1 cm. path by an electron moving through mercury vapour at 1 mm. pressure as a function of the electron energy gives a maximum value of 20·5 at 90 volts. The number of positive charges formed at an impact is maximal (0·35) at 90 volts. When, however, experimental values for the electronic mean free path are employed, the latter curve gives no indication of reaching a maximum. It is considered unlikely that only singly-charged ions are produced, since above 400 volts the number of positive charges formed at an impact appears to be greater than unity.

A. A. ELDRIDGE.

Polarisation of the light from hydrogen canal rays. K. L. HERTEL (Physical Rev., 1927, [ii], 27, 848—856).—Light from hydrogen canal rays, principally H_β, is partly (up to 10%) polarised. The half-value period of the polarisation is about one third of that of the intensity. The effect of a transverse electric field was examined. A. A. ELDRIDGE.

Ionisation of gases and stellar temperatures. G. TIERCY (Arch. Sci. phys. nat., 1927, [v], 9, 87—107).—Saha (A., 1920, ii, 659; 1921, ii, 4, 162; 1923, ii, 5) regards the ionisation of a gas as akin to dissociation of one gas into two others. The expression $\log[x^2/(1-x^2)]P=-U_0/4{\cdot}571T+2{\cdot}5\log T+C$ (x is the fraction dissociated, P the pressure in atm., U_0 the ionisation potential in volts, T the absolute temperature, C the entropy constant) serves to connect the temperature of a star with the degree of ionisation of its constituents. Nernst's expression $-1{\cdot}62+1{\cdot}5\log m$ (m being the atomic mass) was used to fix the entropy constant as $-6{\cdot}5$. On the basis of experiment, $-5{\cdot}5$ seems to be a more trustworthy value. The entropy constant may be obtained from the equation $-R\Sigma n_\lambda \log c_\lambda$, R being the gas constant, n_λ the relative minimum numbers of gaseous particles, n_0 for the original gas, n_i and n_e for the constituents, and c_λ the concentration of each, c_0, c_i, and c_e. When a g.-mol. of gas dissociates completely into two gases, or when a gas ionises completely, n_i and n_e are both unity. If simple dissociation occurs, the constant obtained corresponds with a g.-mol. of the original gas and with a g.-atom of neutral gas in the gas of ionisation. On the other hand, when ionisation occurs, the constant must be expressed in terms of a g.-mol. of original neutral gas, so that the coefficients n_λ must be doubled, *i.e.*, $C=R\Sigma 2n_\lambda \log c_\lambda$. Since $n_i=n_e=1$, and $c_i=c_e=\frac{1}{2}$, $C=1{\cdot}99(4 \log \frac{1}{2})$, *i.e.*, $-5{\cdot}52$, in agreement with the experimental value.

Nernst's expression thus fails to account for the fundamental difference between simple dissociation and ionisation. The value $-5{\cdot}52$ in conjunction with the Saha expression leads to values for the temperatures of different classes of stars which agree well with those obtained by Russell (Nature, 1914, 93, 227) on other grounds. R. A. MORTON.

Ionisation by collisions of the second kind in mixtures of hydrogen and nitrogen with the rare gases. G. P. HARNWELL (Physical Rev., 1927, [ii], 29, 830—842; cf. this vol., 604).—A study of the effect of the presence of a rare gas in ionised hydrogen and nitrogen. The evidence supports the view that a type of collision of tho second kind takes place at which an atom is ionised by colliding with an ion of an atom of higher ionising potential. The following reactions are predicted and supported by the experimental evidence: for hydrogen, $He^+ + H_2 = He + H_2^+$; $Ne^+ + H_2 = Ne + H_2^+$; $A + H_2^+ = A^+ + H_2$; for nitrogen, $He^+ + N_2 = He + N_2^+$; $Ne^+ + N_2 = Ne + {}^{17}N_2^+$; $Ne + {}^{24}N_2^+ = Ne^+ + N_2$; $A + N_2^+ = A^+ + N_2$, where ${}^{17}N_2^+$ and ${}^{24}N_2^+$ represent, respectively, the nitrogen ions produced at the expense of 17 and 24 volts. It appears that the probability of the occurrence of a transfer is an inverse function of the difference in ionising potentials. A. A. ELDRIDGE.

Ionisation by collision. H. G. L. HUXLEY (Phil. Mag., 1927, [vii], 3, 1056—1061).—A discussion of the theory of sparking potentials advanced by Taylor (Proc. Roy. Soc., 1927, A, **114**, 73). A. E. MITCHELL.

Potential gradient in the positive column. II. Oxygen, air, water vapour, helium, argon, krypton, xenon, and mercury. A. GÜNTHER-SCHULZE (Z. Physik, 1927, 42, 763—772).—The relationship observed previously for nitrogen and hydrogen (this vol., 392) relating the gradient in the positive column, G, with the mean free path, corrected for the temperature of the gas, l, and with the tube radius r, viz. $G=Cl^{-2/3}r^{-1/3}$, where C is a constant, has been found to hold for the polyatomic gases oxygen, air, and water vapour, for which gases the constant C has been evaluated. Owing to the instability of the discharge, the value for water vapour is somewhat uncertain. In the rare gases and mercury vapour, the relationship $G=Cl_0(r+\alpha i)^{-1}$ obtains, where l_0 is the mean free path at 1 mm., i the current, and α a constant. These relationships are valid, as in hydrogen, nitrogen, and neon, only when l is small compared with r, and provided that the pressure is so low that the positive column extends throughout the whole diameter of the discharge tube. R. W. LUNT.

Voltage necessary to maintain a luminous discharge in hydrogen. W. A. NOYES, jun. (Phil. Mag., 1927, [vii], 3, 1262—1265).—A discussion of some of the apparent differences between the results of Gibson and Noyes (A., 1922, ii, 812) and of McCurdy (A., 1924, ii, 808) on the voltage necessary to maintain a luminous discharge in hydrogen and mercury vapour. Some of the work of the former with hydrogen has been repeated, with results similar to those obtained previously. It is concluded that there are no real differences between the two sets of results, and that, under certain conditions, the discharge may disappear at a voltage which is approximately the ionisation potential or some multiple of it. A. E. MITCHELL.

Two magnetic moments of the atom. R. FERRIER (Compt. rend., 1927, 184, 1641—1643).—The analogy between an atom and a small magnet from the point of view of its magnetic moments is discussed with reference to the effect exercised on a particle by a magnetic field (Bohr moment), and also to the magnetic field (Weiss moment) produced by the particle itself. The apparent discordance is reconciled with the ordinary laws of electromagnetism, and an explanation of paramagnetism and diamagnetism is suggested. J. GRANT.

Attempts to separate isotopes of mercury by chemical means. H. S. KING (J. Amer. Chem. Soc., 1927, 49, 1500—1511).—Considerations of molecular structure lead to the conclusion that chemical reactions of the type $Hg_2X_2 = Hg + HgX_2$ should effect a partial separation of the isotopes of mercury. Unsuccessful experiments are described in which X=I, CN, $\frac{1}{2}O_2$, Cl, and Ph; the reaction $Hg_2Cl_2 + 2PhMgBr = Hg + Ph_2Hg + 2MgBrCl$ was also unsuccessful (cf. Richards, King, and Hall, A., 1926, 771). S. K. TWEEDY.

Nature and origin of the earth's surface structure. J. JOLY and J. H. J. POOLE (Phil. Mag., 1927, [vii], 3, 1233—1246).

Radioactivity of the earth's basaltic magma. J. H. J. POOLE (Phil. Mag., 1927, [vii], 3, 1246—1252).—Determinations of the radioactivities of specimens of authentic Oregonian plateau basalts have shown these to have the same mean thorium contents as the Hebridean and Deccan plateau basalts previously examined by Joly and Poole (A., 1924, ii, 812). It is concluded that the apparently Oregonian basalts examined previously did not belong to that series, and that all the three main series of plateau basalts are derived from the same sub-crustal basaltic magma. Examination of various eclogites shows that the radium and thorium contents of these are even less than those of the plateau basalts; this points to the conclusion that these really represent the lower layers of the earth's primary basaltic magma. The bearing of this result on the general ideas of the earth's surface structure is discussed. A. E. MITCHELL.

Radioactivity of matter exposed for a long period to solar radiation. (Mlle.) S. Maracineanu (Compt. rend., 1927, **184**, 1547—1549; cf. this vol., 605).—The radioactivity of the portion of lead roofing used in the earlier experiments could not have been due to its origin, since the unexposed parts possessed no such activity, and that of the exposed part decreased when it was removed from the roof. Nor was the radioactivity due to radioactive deposits from the atmosphere. Lead exposed to the south had a higher radioactivity than that exposed to the north. Zinc and copper roofs also possessed a radioactivity, highest on the exposed side, but less than that of the lead, whereas calcareous stone and iron had none. H. Deslandres (Compt. rend., 1927, **184**, 1549—1550) comments on the above phenomena and believes them to be of cosmic origin.
J. Grant.

Charge of α-particles emitted per sec. by 1 g. of radium. H. Jedrzejowski (Compt. rend., 1927, **184**, 1551—1553).—By means of an elaborated form of Rutherford and Geiger's method, the mean value of the total charge of the α-particles emitted in 1 sec. from 1 g. of radium has been found to be 33·4 e.s.u., corresponding with $3{\cdot}50\times10^{10}$ α-particles.
J. Grant.

Scattering of α-particles. J. R. Oppenheimer (Z. Physik, 1927, **43**, 413—415).—Rutherford's equation for the scattering of α-particles has been deduced from quantum mechanics, and its valitity has been examined.
R. W. Lunt.

Atomic disintegration by α-particles from polonium. W. Bothe and H. Franz (Z. Physik, 1927, **43**, 456—465).—Polonium has been chosen as the source of α-particles, since it produces these with practically uniform velocity and without appreciable β- and γ-radiation. The Geiger point-in-cylinder method has been used to detect the H-particles produced, and the electroscope deflexions have been photographically recorded on a moving film. All the elements from boron to calcium have been examined with the exception of neon and argon. Positive results were obtained in boron, nitrogen, magnesium, and aluminium only; for these elements, curves are given for the number of H-particles per minute as a function of their penetration in air.
R. W. Lunt.

Energy distribution in the γ-radiation of radium-*C*. D. Skobelzyn (Z. Physik, 1927, **43**, 354—378).—The earlier technique for β-rays (*ibid.*, 1924, **28**, 278) has been developed so that observations can be made of the tracks of the electrons produced by γ-rays from radium-*C* in gas subjected to a magnetic field of the order of 1000 gauss. From the observed track curvatures the energy distribution has been computed. In the range $h\nu=610$—1778 kilo-volts the intensity values obtained are considerably greater than those of Ellis; the value at $h\nu=2210$ is the same.
R. W. Lunt.

Atomic nuclei and their transformations. (Sir) E. Rutherford (Proc. Physical Soc., 1927, **39**, 359—372).—A lecture delivered on Feb. 25, 1927.

Theory of sub-electrons. T. Peczalski (Compt. rend., 1927, **185**, 49—51).

Calculation of the mean value in the electron theory of Lorentz. V. Bursian (Z. Physik, 1927, **43**, 416—426).

Number of radiating atoms in a hydrogen discharge tube. W. H. Crew and E. O. Hulburt (Physical Rev., 1927, [ii], **29**, 843—847).—About 90% of the energy radiated from a long hydrogen tube filled with moist hydrogen at 0·54 mm. pressure, and excited with 66 milliamp. at 7 kilovolts, is carried by the first three lines of the Balmer series. The number of quanta of these lines emitted per atom per sec. is calculated to be 2·84, 0·43, and 0·10, respectively.
A. A. Eldridge.

Limits of the periodic system of the elements. E. Meyer (Z. Elektrochem., 1927, **33**, 189—192).—A discussion of the probability of the existence of elements of atomic number greater than 92. It is suggested that, if the electrons are arranged around the nucleus of an atom in concentric spherical shells the radii of which are in the ratio $1^2:2^2:3^2$, etc., the number of electrons in the respective shells should be $(1+1)$, 2^2, 3^2, etc. This would give a secondary periodicity in which helium, carbon, phosphorus, gallium, barium, and uranium would be the last members of the successive periods. On this basis uranium is the element with six completed shells, and may thus be the true end member of the series of elements. Evidence supporting this arrangement is discussed. The hydrogen nucleus is regarded as an element of zero atomic number.
H. J. T. Ellingham.

Process of quantisation. G. P. Thomson and R. G. J. Fraser (Phil. Mag., 1927, [vii], **3**, 1294—1305).—Mathematical. Use is made of the probability that when the motion of an atom in a stationary state is interrupted by collision or otherwise, the subsequent adjustment of the system towards a system satisfying the quantum postulates takes a finite time, to establish a correspondence between the pressure broadening of a spectral line on both the classical and the quantum theories. Thus information is derived regarding the process of quantisation. The deductions are in agreement with the experimental results of Füchtbauer and Joos (A., 1922, ii, 242) on the pressure-broadening of spectral lines.
A. E. Mitchell.

Contribution to modern ideas on the quantum theory. H. T. Flint and J. W. Fisher (Proc. Roy. Soc., 1927, *A*, **115**, 208—214).

"Axiality" of light emission and the structure of chemical atoms. J. Stark (Physikal. Z., 1927, **28**, 421—427).—Theoretical. It is concluded that the smallest atom-ion, the positive elementary quantum of smallest mass, the hydrogen atom-ion or "archion" from which all heavier atoms are built up, is a rotatory motion with a definite axis and frequency as characteristic as the elementary electric charge. The mass for this elementary rotatory motion of the "archion" is its impulse of rotation. This elementary impulse of rotation demands the quantisation of the impulses of rotation in the stable state of the chemical atom.
W. E. Downey.

Line intensities in the hydrogen chloride fundamental band. D. G. Bourgin (Physical

Rev., 1927, [ii], 29, 794—816).—Values of the intensities of the absorption lines of the hydrogen chloride fundamental band for tube-lengths from 0·0998 to 2·97 cm. have been obtained; the results yield indirect evidence of the isotopic doubling, and confirm the predicted asymmetry in the intensities of corresponding lines in the P and R branches, the summation rule, and the new formulation of the quantum theory. The lines are narrower and "deeper" than was supposed, and the exponential law of transmission fails. Values of the Einstein probability of transition coefficients are computed to be $B_{0,1}=5·12\times10^{15}$ for the first line of the positive branch and $A_{0.1}=58$ for the first line of the negative branch. The preferred value of the variation of the molecular moment with nuclear displacement as determined for the region of the equilibrium position is $0·828\times10^{-10}$ e.s.u. A. A. Eldridge.

Index of refraction of water for short continuous waves. L. E. McCarty and L. T. Jones (Physical Rev., 1927, [ii], 29, 880—886).—The index of refraction of water for short continuous waves (300—700 cm.) is about 9, in agreement with other results, and approximately constant over the range of frequencies used. A. A. Eldridge.

Molecular spectrum of sodium. H. Schüler (Z. Physik, 1927, 43, 474—479).—From a consideration of the yellowish-red band spectrum excited in sodium vapour by the passage of a continuous current, it is concluded that the spectrum consists of the resonance series of Na_2 which is excited by the sodium D-light and of a Na-series similar to the Lyman–Wittmer H_2-series. R. W. Lunt.

Absorption bands of liquid and vapour amines. E. O. Salant (Nature, 1927, 119, 926).—The characteristic absorption band of the N–H linking around 3 μ (A., 1926, 453) is a fundamental, the band at 6 μ being weak, both for secondary and for tertiary amines (cf. also Ellis, this vol., 291). A. A. Eldridge.

Absorption of light by certain aromatic amino-acids in the ultra-violet. H. Hünecke (Ber., 1927, 60, [B], 1451—1457).—According to spectrographic measurements of *o*-aminobenzoic acid, its sodium salt, methyl ester, and hydrochloride in water, the acid exists mainly in the true acidic form, $NH_2·C_6H_4·CO_2H$. *o*-Dimethylaminobenzoic acid, on the other hand, is chiefly present in water as the "zwitter ion," $·NHMe_2·C_6H_4·CO_2^+$, probably containing appreciable amounts of the true acid. In trimethylaminobenzoic acid only the "zwitter ion" can be present. In the carboxylic acids of pyridine and quinoline, the acid form is favoured; the proportion of "zwitter ion" cannot at present be determined. H. Wren.

Influence of solvent on absorption spectrum, rate of reaction, and equilibrium. V. G. Scheibe [with E. Felger and G. Rössler] (Ber., 1927, 60, [B], 1406—1419).—The displacement of the centre of an absorption band and the change in height are two distinct processes, the first of which is immediately due to solvation. The second process can occur in different ways according to the structure of the molecule. Relationships are developed between the displacement of absorption bands and the rate and equilibrium of chemical reactions. The possibility of the experimental detection of the deformation of molecules during catalysis is thus given. H. Wren.

Relation between the absorption spectra and molecular structure of the alkali halides in the vapour state. J. Franck, H. Kuhn, and G. Rollefson (Z. Physik, 1927, 43, 155—163).—An argument is developed to show that the photochemical decomposition of a polar molecule such as sodium iodide proceeds with the formation of two normal atoms, and also of one normal and one excited atom; that therefore the quantum associated with the low-frequency limit of the first absorption band should correspond with the heat of thermal dissociation measured by thermal methods, and that the difference between the quanta associated with the low-frequency limit of the first and second bands should be equal to the quantum corresponding with the transition $2P_2-2P_1$ in the halide atom. Data obtained on the absorption of sodium, potassium, and cæsium iodides, sodium and potassium bromides, and potassium chloride have shown that the above relationships do obtain approximately. R. W. Lunt.

Absorption and fluorescence spectra of silver iodide molecules, and the nature of their molecular structure. J. Franck and H. Kuhn (Z. Physik, 1927, 43, 164—171).—The theory previously developed (preceding abstract) has been applied to the absorption of silver iodide vapour. The sum of the heat of dissociation measured thermally, 47,000 g.-cal., and the quantum associated with the transition $2P_2-2P_1$ in the iodine atom 22,000 g.-cal., is 69,000 g.-cal., which is held to be sensibly identical with the quantum corresponding with the low-frequency limit of the first absorption band of silver iodide, 76,000 g.-cal. Silver iodide therefore decomposes in the vapour state to silver and excited iodine atoms. Similarly, the sum of heat of dissociation of hydrogen iodide and the $2P_2-2P_1$ quantum is equal to 91,000 g.-cal., which is in good agreement with the quantum corresponding with the low-frequency absorption limit, 88,000 g.-cal., calculated from the spectroscopic data of Coehn and Stuckardt (A., 1917, ii, 5). It is therefore concluded that the linking of the silver iodide molecule is non-polar. R. W. Lunt.

Extinction of the fluorescence of dyes in solid and in liquid solutions. V. L. Levschin (Z. Physik, 1927, 43, 230—253).—The fluorescence of rhodulin-orange-N and of fluorescein in sugar solution has been examined for concentrations in the range 10^{-2} to 10^{-4} g. per g., and from 4900 to 5900 Å. The ratio of the fluorescence to the absorbed energy falls rapidly as the concentration increases; similar results are obtained with fluorescein in ethyl alcohol, in glycerol, and in water, and with rhodulin in water, in the range 10^{-2} to 10^{-4} g. per c.c. The results also show that for an aqueous solution of fluorescein this ratio is independent of the wave-length in the above range. The influence of temperature in the range 20—80° on this ratio has also been examined; for $c>4\times10^{-3}$ it increases, for $c=2·5\times10^{-4}$ it decreases, as the temperature increases. R. W. Lunt.

Measurement of the duration of fluorescence. E. Gaviola (Z. Physik, 1927, 42, 853—861).—An optical system has been devised for the measurement of the duration of fluorescence of the order of 10^{-9} sec. with an accuracy of 10%. The ray incident on the fluorescent material passes through crossed Nicols between which is placed a Kerr cell containing nitrobenzene; the reflected ray passes through crossed Nicols between which are placed a second Kerr cell and a plate of Iceland spar. The Kerr effect is without inertia, and it is therefore possible to interrupt rapidly the incident and reflected rays by applying to the Kerr cells a potential of frequency approximately 2×10^7 cycles per sec. The phase difference in the reflected ray, due to the persistence of the fluorescence, is measured by the rotation of the fourth Nicol necessary to produce extinction.

In this way the duration of the fluorescence has been determined for uranium glass, ruby, and for the following substances in solution in water, glycerol, and methyl alcohol: uranin, fluorescein, rhodamine-B, rhodulin-orange, erythrosin, eosin, eosin-5B, uranyl sulphate, uranyl sulphate in sulphuric acid, and quinizarin in pentane. R. W. Lunt.

Influence of temperature and concentration on the rate of decay of the fluorescence of dyes. E. Gaviola (Z. Physik, 1927, 42, 862—869).—Using the technique described in the preceding abstract, the influence of temperature and concentration on the time for which fluorescence persists has been examined for the following substances: fluorescein, rhodamine-B, and rhodulin in solution in methyl alcohol and in glycerol. The time interval diminishes with increasing concentration and with increasing temperature; correspondingly, the intensity of the fluorescence and the degree of polarisation diminish. An approximately linear relationship is observed between this time interval and the intensity of the fluorescence. The order of magnitude of the persistence of fluorescence is 5×10^{-9} sec.

R. W. Lunt.

Yield of fluorescence at the *K* level for the *K*α lines. V. Posejpal (Compt. rend., 1927, 184, 1541—1543).—A general expression for the yield of fluorescence at the *K* level, based on the author's previous assumptions (this vol., 91), is deduced, and shown to give results in good agreement with experiment. J. Grant.

Fluorescence of cadmium. W. Kapuściński (Bull. Acad. Polonaise, 1927, A, 1—26).—The fluorescence of cadmium vapour at temperatures below 1000° has been examined. It is excited by the light from the condensed spark between electrodes of cadmium, zinc, mercury, copper, aluminium, carbon, and iron, and from mercury, cadmium, and iron arcs. The fluorescence consists of a large band between 5100 and 3800 Å., with secondary maxima in the range 4200—3950 Å. At temperatures below 500° the fluorescence is excited by radiation in the neighbourhood of 2300 Å.; at 850° the effective absorbing region extends from 3100 to 2100 Å.

R. W. Lunt.

Band-types and absorption-edge series in alkaline-earth phosphors. F. Schmidt (Ann. Physik, 1927, [iv], 83, 213—246).—The spectral distribution of phosphorescence light has been to a considerable extent reduced to order. The position of maximum intensity (λ) of the *d*-excitation is connected with the dielectric constant of the phosphor by means of the relation $\lambda_0=\lambda/e^{\frac{1}{2}}$, in which λ_0 is termed the absolute wave-length and is a constant for analogous bands of the same metal in different diluents. The sulphide phosphors are divided into five groups showing the same absolute *d*-positions and λ_0 values within a group. The first group includes only Biα; the band-type is due to tervalent sulphide (oxide) linkings with the metal, and the λ_0 values of 77, 113, and 147 μμ are well separated. The second group includes Cuα, Mnα, Znα, Pbβ, Agβ, Biβ, and the λ_0 values of 78, 98, 121, 146, and 174 μμ exhibit close spacing, whilst the band-type is ascribed to bivalent sulphide (oxide)–metal linking. The third group, Pbα and Agα, shows λ_0 values of 103, 121, and 147 μμ, whilst the fourth group consists of Cuβ only; the narrow spacing 78, 94, 113, 136, 160 μμ is shown, and the band-type is regarded as due to univalent sulphide–metal linking. The fifth group, Cuγ, Pbγ, Znδ, shows 86, 99, 118, 137, 154 μμ as the λ_0 values. In order to classify the bands, the idea of absorption-edge series is used. The relations $\nu_n=K/n^2$ or $\nu_{obs.}=K/e^{\frac{1}{2}}\times n^2$ (*K* is a constant for a given band-type, ν_n and $\nu_{obs.}$ correspond with λ_0 and λ, and *n* has integral values) reproduce the observed series. The results for sulphide phosphors, oxide phosphors, and selenide phosphors are tabulated.

The SrS–Ag phosphors have been studied afresh and the *d*-positions of type III more accurately measured. Two new *d*-positions are recorded, so that there are now five of these. The distribution of excitation with time for the γ-band of silver has been measured. It is also shown that by raising the heating temperature and by increasing the duration of the heating process in the preparation of CaS–Cu and SrS–Cu phosphors, the respective dielectric constants are decreased. The occurrence of definite types of bands characteristic of a given metal does in these cases actually follow the expected lines when the dielectric constant of the same phosphor is varied in the process of preparation. The failure to obtain a constant for the type V of the sulphide bands is discussed and an explanation advanced.

R. A. Morton.

Triboluminescence. G. Renzo (Gazzetta, 1927, 57, 278—290).—A number of organic and inorganic compounds have been examined in order to investigate Karl's theory that the origin of triboluminescence is in the impurities in the substances which exhibit this phenomena. Whilst the results are not completely conclusive, it is concluded that triboluminescence occurs in pure substances; in particular, potassium bromate repeatedly recrystallised is characterised by a strong luminescence, which is diminished by the addition of the impurities to be found in the mother-liquors. R. W. Lunt.

Ionisation potential of methane. E. Pietsch and (Frl.) G. Wilcke (Z. Physik, 1927, 43, 342—353).—The ionisation potential of methane has been redetermined by investigating the current–voltage curve for platinum electrodes in methane at 10^{-2} mm.

The cathode was coated with barium oxide and calcium fluoride (10 : 1) to facilitate the electron emission, and the methane was specially purified. The following critical potentials were observed: 9·65±0·4, 11·14±0·1, 12·49±0·1, 13·59±0·1, 14·58±0·05, 15·40±0·05, 16·29±0·07, and 18·22±0·18 volts. They were identified respectively as: ionisation of mercury, first excitation of hydrogen molecule, critical potential of hydrogen molecule, ionisation of hydrogen atom, ionisation of methane, decomposition of methane, ionisation of hydrogen molecule, and the dissociation of the hydrogen molecule with the formation of one hydrogen ion. The value 15·40 volts assigned to the decomposition of methane agrees with the value of 15—16 volts obtained by the author previously for decomposition by electron collision (A., 1926, 1109), and with the value 15·7 volts obtained for the thermal decomposition. On the assumption that the critical potential observed at 18·22±0·18 volt corresponds with the dissociation of a hydrogen molecule, with the formation of one hydrogen ion (H^+), the heat of dissociation is equal to this value, less the ionisation potential of the hydrogen atom, 13·59±0·1 volt; the value thus obtained, 4·63±0·18 volt (=106·7±4×10^3 g.-cal.), is in good agreement with the recent determination of the heat of dissociation, 106·7±3×10^3 g.-cal., by Bodenstein and Jung (A., 1926, 680). R. W. Lunt.

Electron emission under the influence of chemical action at higher gas pressures, and some photo-electric experiments with liquid alloys. O. W. Richardson and M. Brotherton (Proc. Roy. Soc., 1927, A, **115**, 20—41; cf. Brotherton, A., 1924, ii, 377).—The emission of electrons when alloys of sodium and potassium react with carbonyl chloride at pressures of not less than 0·001 mm. has been examined, using a modified form of the apparatus previously described (*loc. cit.*). With an alloy of fixed composition and constant gas pressure, the electron emission increases rapidly with increase in the number of drops per sec., and when the rate and size of the drops are kept constant, the emission is independent of the gas pressure over a range of pressure from 0·005 to 0·05 mm. In the case of a drop of alloy at the centre of a large spherical electrode, if the contact *P.D.* between the two surfaces is taken into consideration and a Maxwell distribution of energy for a temperature of about 3300° Abs. is assumed, then the energy of the emitted electrons can be calculated. The photo-electric determination of the contact potential gave figures much higher than the chemical determination, but for an alloy containing 77% of potassium (NaK_2) the two are identical. In previous experiments, the average energy of the electrons expressed as an equivalent temperature was found to be 3300° Abs., whilst the temperature now found, as a mean of 44 determinations, is 2368° Abs. The results strengthen the view that the phenomenon is a direct chemical emission, and not due to secondary thermionic effects. The difference between the values obtained in the photo-electric and chemical determinations of the contact potential can be explained by the assumption that the chemical reaction does not take place uniformly over the surface of the drops, but occurs in localised patches which gradually extend to the periphery. This is in agreement with threshold frequencies determined with and without carbonyl chloride, the difficulty of obtaining saturation in certain cases, and the breaking down of the agreement with the Maxwell formula in the region of zero emission velocity. Certain hysteresis effects are also discussed. L. L. Bircumshaw.

Dielectric constants of ethyl ether and ethyl alcohol vapours. R. Sänger (Physikal. Z., 1927, 28, 455—457; cf. A., 1926, 993).—The values of the dielectric constants of ether and alcohol vapours accord with the formula $\varepsilon-1=A+B/T$ (ε the dielectric constant, T temperature Abs., A and B constants). The electric moments of the molecules are calculated from the determined values of the constant B.

W. E. Downey.

Molecular scattering of light in aqueous solutions. I. S. Venkateswaran (Indian J. Phys., 1927, 1, 235—244).—The scattering of light by aqueous solutions of nitric, hydrochloric, and sulphuric acids has been studied experimentally. The optical anisotropy of the nitric acid molecule is found to be greater than that of the sulphuric acid molecule. These aqueous solutions behave more like single liquids than like binary mixtures.

W. E. Downey.

Law of periodicity. II. Optical properties of unsaturated compounds. P. Petrenko-Kritschenko (Ber., 1927, 60, [*B*], 1324—1326; cf. A., 1926, 1121).—Well-marked periodicity is observed in the optical properties of a series of compounds so arranged that the mutual influence of double linkings in their molecules continuously increases (groupings, –C:C·C·C:C–, C:C·C:C–, C:C:C, benzene, benzene derivatives containing a double linking in α-position to ring, furan, thiophen, and pyrrole, naphthalene).

H. Wren.

Colours of chromous, vanadous, and tervalent uranium ions. K. Someya (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 411—416).—See this vol., 432.

Colour of silver chromate. (Miss) F. Bush (J. Physical Chem., 1927, 31, 931—932).—The difference in the appearance of silver chromate is caused by the rate of precipitation, and not by the action of sunlight (cf. Hunt, Mem. Chem. Soc., 1845, 2, 316). The slower the addition of potassium dichromate to the silver nitrate, the darker and more lustrous do the crystals of silver chromate become. The presence of free acid and an increase in temperature produce similar effects. L. S. Theobald.

Measurement of the ratio h/k from the anomalous dispersion of thallium vapour. E. Fernie and F. Rasetti (Z. Physik, 1927, 43, 379—383).—By applying the Boltzmann distribution law to the number of atoms of element in two different quantum states in thermal equilibrium, an expression $\log d_1/d_2=\text{constant}+h\Delta\nu/kT$ is obtained, where d_1 and d_2 are the coefficients of anomalous dispersion, corresponding with the quantum states ν_1 and ν_2, h is Planck's and k Boltzmann's constant, and T the temperature Abs. This has been applied to the temperature variation, in the range 1280—1500° Abs., of the coefficients of anomalous dispersion of thallium vapour for the lines 3776 and 5350 Å., corresponding with the quantum states 6^2P_1 and 6^2P_2. The value of h/k so obtained is $3{\cdot}9\times10^{-11}$, in satisfactory agreement with the true value, $4{\cdot}8\times10^{-11}$. Normal values have been obtained for the refractivity of thallium vapour, in contradistinction to the anomalous values reported by McLennan (Proc. Roy. Soc., 1922, A, 100, 191). R. W. Lunt.

Selective absorption, rotation, and magnetic rotation of camphorquinone in toluene. A. Krethlov (Z. Physik, 1927, 42, 840—852).—Measurements of the extinction of camphorquinone in toluene (0·17—4·7 g. per 100 c.c.) using a König–Marten spectrophotometer have been made for 33 wave-lengths between 6320 and 4400 Å. In this region, the Beer–Lambert law is obeyed within about 8%. The extinction–wave-length curve obtained corresponds with four maxima at 4840, 4690, 4540, and 4370 Å. These maxima are discussed with reference to Pfleiderer's data (Z. Physik, 1926, 39, 663) on the rotation and the magnetic rotation in the same region of wave-lengths. R. W. Lunt.

Magnetic double-refraction in paramagnetic gases. K. S. Krishnan (Indian J. Phys., 1927, 1, 245—254).—The theory of spatial quantisation is applied to the molecular magnetic moments of nitric oxide, and it is deduced that nitric oxide should exhibit double refraction. Actually no double refraction could be detected. This result is discussed, and it is concluded that paramagnetic molecules do not orientate, at least as a whole, in a magnetic field. W. E. Downey.

Chemical valency. C. D. Niven (Phil. Mag., 1927, [vii], 3, 1314—1334).—In part speculative. The Heisenberg–Hund model of the extra-nuclear electronic configurations in the atom is used to explain the properties of chemical compounds. Many properties are satisfactorily accounted for, and the general conclusions are in accordance with Werner's co-ordination theory. A. E. Mitchell.

The parachor and chemical constitution. V. Evidence for the existence of singlet linkages in the pentachlorides of phosphorus and antimony. S. Sugden [with A. Freiman] (J.C.S., 1927, 1173—1186).—The parachors of phosphorus and antimony pentachlorides are lower than the sum of the atomic constants by 26 units. Since the additive nature of the parachor has been verified for a large number of substances, this is taken to mean that the pentachlorides possess a type of linking which has not been met with in the compounds previously studied.

From a discussion of electron valency formulæ and the effect of the number of electrons in a linking on the structural constants for unsaturated linkings, it is concluded that these compounds contain two singlet linkings, each consisting of one electron held in common by two atoms. Each singlet should give a contribution of —12·4 to the parachor, so that the pentachlorides studied contain two such linkings, in agreement with the formula of Prideaux (Chem. and Ind., 1923, 42, 672).

The electronic theory of valency is extended to include linkings composed of an odd number of shared electrons, and is applied to the formulation of higher halides, co-ordination compounds, and " molecular " compounds for which, hitherto, it has not been possible to write electronic formulæ without violating the octet rule. J. S. Carter.

Constitution of boron compounds. A. Stock (Ber., 1927, 60, [B], 1039—1040).—Ullmann's formulation of the hydrides of boron and related compounds is considered unsatisfactory, since it offers no adequate explanation of the chemical properties of these compounds (cf. this vol., 399). H. Wren.

[Electronic interpretation of the constitution of the boron hydrides and of compounds of boron.] E. Müller (Ber., 1927, 60, [B], 1323—1324; cf. A., 1925, ii, 841).—An adverse criticism of the views of Ullmann (this vol., 399). H. Wren.

Relation between complex formation and the structure of the central atom. H. Lessheim, J. Meyer, and R. Samuel (Z. Physik, 1927, 43, 199—221).—A general classification of complex formation is described based on considerations of the orbital structure characterising the central atom of the complex. R. W. Lunt.

Molecular constitution of liquids. W. Kistiakovski (J. Chim. phys., 1927, 24, 309—324).—Liquids may be classified according to their molecular constitution into seven groups: (1) those negligibly (*e.g.*, the noble gases), (2) feebly (hydrocarbons), or (3) sensibly polymerised (liquid nitrogen and oxygen, esters and ethers); (4) strongly polymerised with unassociated vapours (water, alcohols, nitriles, amines, nitro- and sulphonic acid derivatives); (5) strongly polymerised with associated vapours (sulphur, phosphorus, etc.); (6) ionic liquids (fused salts), and (7) electronic liquids (fused metals). The Guldberg–Guye ratio T_C/T_B, where T_C is the critical temperature and T_B the normal b. p., both on the absolute scale, is of the order 1·5 for substances of the first three groups; the ratio V_C/V_B, where V_C is the critical volume and V_B the liquid volume at the b. p., is of the order 2·67, and the critical pressure 37·5 atm. ±25%; none of these quantities can be used for classification, for whereas the polymerised substances of the fourth and fifth groups usually deviate widely from the normal values, some conform to them. Similarly, the formula for the latent heat of vaporisation at the b. p. Q_B (g.-cal.)$=RT_B \log R'T_B$, where R is the gas constant in g.-cal. and R' in c.c.-atm., which usually fits substances of groups 1 and 2, occasionally fits those of group 3. The relationship $\log V_1/V_2=T_2/T_1$, where V_1 and V_2 are the volumes of vapour at T_1 and T_2, respectively, holds only for the first three groups, and thus serves to distinguish these from groups 4 and 5. S. J. Gregg.

Florentium or illinium? W. A. Noyes (Nature, 1927, 120, 14).—A question of priority. A. A. Eldridge.

***X*-Ray investigations for the identification of the element of atomic number 61 (florentium).** R. Brunetti (Gazzetta, 1927, 57, 335—346).—When a monochromatic pencil of *X*-rays traverses a material layer, it undergoes absorption, the atomic coefficient,

α, of which is a function of the frequency of the incident radiation ν and of the atomic number Z of the element, $\alpha = CZ^4/\nu^3$. The value of C remains constant until ν reaches a critical value ν_0, for which the quantum $h\nu_0$ of the incident radiation equals the energy necessary to detach an electron from one of the orbits of the absorbing atom; C then undergoes a sudden variation to another constant value. At this point, a photographic plate receiving the radiations of the continuous spectrum will exhibit a distinct discontinuity, shown by a blackening with the weaker part towards the lower wave-lengths. Investigation in this way of the discontinuity of the L-orbit shows that Brazilian monazite undoubtedly contains the element of atomic number 61. The wave-length corresponding with the limit of the absorption of the element 61 is found to be 0·2744 Å., the calculated value being 0·2746 Å. T. H. Pope.

Demonstration model for illustrating the Laue effect. G. B. Hagen (Physikal. Z., 1927, **28**, 453—455).—Small mirrors are arranged to reflect a beam of light. By a suitable arrangement of the mirrors, an effect on the beam of light similar to that obtained by interposing a crystal in the path of an X-ray beam is obtained. W. E. Downey.

Theoretical determinations of crystal parameters. J. E. Lennard-Jones and (Miss) B. M. Dent (Phil. Mag., 1927, [vii], **3**, 1204—1227).—The mathematical treatment previously adopted for the calculation of the parameters of the carbonate crystals (this vol., 96) has been extended to crystals of the rutile group, to crystals of potassium chlorostannate and of potassium chloroplatinate, and to the crystal of solid carbon dioxide. In the rutile group, it is shown that the parameters vary from crystal to crystal, the variation being in good agreement with experimental values, whereas the theoretical work of Born and Bollnov (Z. Physik, 1925, **33**, 741) leads to identical values for the parameters of all crystals of the group. For potassium chloroplatinate and potassium chlorostannate the theory indicates that the parameters are the same. The ratio of the distance between the metal and chlorine ions in these groups to the side of the unit cell is 0·17, which is identical with Scherrer and Stoll's experimental value for potassium chloroplatinate (A., 1922, ii, 514). The corresponding experimental value for potassium chlorostannate as determined by Dickinson (A., 1922, ii, 287) is 0·245. For the carbon dioxide crystal, the calculated distance between carbon and oxygen ions is in the region of 0·90 Å. This value is in fair agreement with the result of de Smedt and Keesom (A., 1925, ii, 484; Z. Krist., 1925, 62, 312), but disagrees with that of Mark and Pohland (Z. Krist., 1925, 61, 293). A confirmatory value of this parameter has been calculated from the heat of sublimation of carbon dioxide. A. E. Mitchell.

Space-group of aluminium metaphosphate. S. B. Hendricks and R. W. G. Wyckoff (Amer. J. Sci., 1927, [v], **13**, 491—496).—Laue, spectrum, and powder photographs were made from aluminium metaphosphate. Data from them fit a body-centred unit containing 16 molecules and having $a_0 = 13·63$ Å. The corresponding space-group is apparently Te_6. Since the structure is defined by at least 11 parameters, no determinations of atomic positions are possible. C. J. Smithells.

X-Ray diffraction measurements on some of the pure compounds concerned in the study of Portland cement. E. A. Harrington (Amer. J. Sci., 1927, [v], **13**, 467—479).—The crystal symmetry, axial angles, and lattice constants for a number of compounds have been determined in connexion with the constitution of Portland cement. The following values were obtained: Al_2O_3, rhombohedral, $\alpha = \beta = \gamma = 55° 17'$, 5·130 Å.; Fe_2O_3, rhombohedral, $\alpha = \beta = \gamma = 55° 17'$, 5·406 Å.; $Ca(OH)_2$, hexagonal, $\alpha = \beta = 90°$, $\gamma = 120°$, 3·580 Å.; $3CaO,Al_2O_3$, cubic, $\alpha = \beta = \gamma = 90°$, 7·623 Å.; $5CaO,3Al_2O_3$, cubic, 10·084 Å.; CaO, cubic, 4·797 Å. C. J. Smithells.

X-Ray investigations on the structure of the artificial ultramarines and the problem concerning their relations to the minerals hauyne, nosean, sodalite, lazurite, and nephelite. F. M. Jaeger, H. G. K. Westenbrink, and F. A. van Melle (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 249—267).—Powder spectrograms of ultramarines of various colours and of nosean and hauyne are found to be identical. It is found impossible to attribute any definite place in the structure to a number of components of the total mass included within each elementary cell. The colour of the solid mass seems to be connected with the presence of sulphur. W. E. Downey.

X-Ray examination of the lower ω-phenyl normal saturated fatty acids. A. L. Patterson (Phil. Mag., 1927, [vii], **3**, 1252—1262).—X-Ray examination of series of ω-phenyl derivatives of lower normal saturated fatty acids from phenylacetic acid to δ-phenylvaleric acid has given the following results. Phenylacetic acid occurs in rhombic crystals belonging to the space-group C_{2v}^{5} (b) with a, b, and c 4·2, 4·90, and 10·1 Å., respectively. β-Phenylpropionic acid occurs in monoclinic prismatic crystals of the space-group C_{2h}^{5} (a) with a, b, and c 31·6, 9·83, and 5·54 Å., respectively. γ-Phenylbutyric acid occurs in rhombic crystals of the space-group C_{2h}^{5} (b) with a, b, and c 17·8, 4·9, and 10·3 Å., respectively. A preliminary survey of δ-phenylvaleric acid has given $b = 7·13$, $c = 11·32$, and $d_{100} = 8·73$ Å. The numbers of molecules per unit cell are respectively 4, 8, 4, and possibly 4. Bragg's measurements of benzoic acid (A., 1922, ii, 128) put this in the space-group C_{2h}^{5} (a) with a, b, and c 21·6, 5·18, and 5·44 Å., respectively, with 4 molecules per unit cell. The effect of the addition of each CH_2-group is discussed.

A. E. Mitchell.

X-Ray spectrographic observations on cellulose acetate. W. Jancke (Kolloid-Z., 1927, **42**, 186—187).—X-Ray spectrographic investigations, using monochromatic radiation from a copper anticathode, reveal a difference between the fibres of artificial cellulose acetate and acetylated cotton wool. The data are not sufficient to decide whether this is due to a different grouping of the micro-crystals, or to a difference in modification. E. S. Hedges.

Variability of long diffraction spacings in paraffin waxes. G. L. Clark (Nature, 1927, **120**, 12).—Values for long spacing and side spacings are tabulated for samples of commercial paraffin waxes having m. p. 57·2°, 54·4°, 51·7°, and 48·9°. The spacings are affected by the rate of cooling of the wax and by the presence of small quantities of other substances. In particular, lead oleate impresses its own spacing on the layers. A. A. Eldridge.

Rate of growth of crystals in different directions. (Miss) M. Bentivoglio (Proc. Roy. Soc., 1927, A, 115, 59—87).—A modification of Wulff's method (Z. Krist., 1901, 34, 449) for measuring the relative rates of growth of the faces of a crystal is described. The crystal, mounted on a long fine pin, is placed at the centre of a spherical flask filled with 500 c.c. of solution, the zone of faces to be measured being horizontal, and the flask is rotated on a horizontal axis, parallel to that of the zone, at a rate of 4 or 5 revolutions per hr. The crystals investigated were the isomorphous double sulphates of magnesium–ammonium, iron–ammonium, and magnesium–potassium, of the general formula $R''R'_2(SO_4)_2,6H_2O$, belonging to the monoclinic system; and potassium tartrate, $K_2C_4H_4O_6,0{\cdot}5H_2O$, and ammonium tartrate, $(NH_4)_2C_4H_4O_6$, crystallising in the polar class of the monoclinic system. It is found that the various faces of a crystal grown under uniform conditions have characteristic relative rates of growth. The similar faces of a simple form grow at the same rate, even when of different sizes. Thus a misshapen crystal, if grown under uniform conditions, tends towards, but never attains, the ideal form with equal faces. On a combination, unlike faces grow at different rates, and like faces grow at the same rate, except when adjacent to an abnormally developed face of another, fast-growing, form which causes impoverishment of the solution in its neighbourhood and destroys the uniformity of the conditions. Except in this case there is a constant ratio, under the given conditions, between the rates of growth of any two different forms. With polar crystals, devoid of centrosymmetry, the rates of growth of parallel faces may be widely different. In the isomorphous series of double sulphates examined, the order of increasing rates of growth for different forms is widely different in the different salts. The main factors determining the form of a crystal are discussed, and for each of the sulphates investigated an " ideal form " is constructed, which is that which a crystal would possess if its faces had grown from the beginning at the observed rates. L. L. Bircumshaw.

Etch planes in metallic single crystals. H. H. Potter and W. Sucksmith (Nature, 1927, 119, 924).—Iron crystals were etched with 10% alcoholic nitric acid solution, nickel crystals with concentrated ferric chloride solution, and aluminium crystals with sodium hydroxide followed by ferric chloride. For iron, the etch planes are (100); for aluminium the planes are (100), with faint reflexions in a few cases from (110) planes. In nickel, (111) and (100) facets are formed. A. A. Eldridge.

Effect of grain-size on the hardness of pure iron. T. Ishigaki (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 285—293).—The effect of crystal size on the Brinell hardness of " Armco " iron has been measured, and also the effect on the " initial hardness," H_0, given by the relation $H_0=K/\pi D$, where K is the tangent at the origin to the load–depth curve and D the diameter of the steel ball. The Brinell hardness increases at first rapidly and then slowly, as the grain number, measured by the method of Jeffries, increases, whilst the initial hardness increases almost linearly, except with single crystals. The increase in Brinell hardness was 23%, and that of the initial hardness 51% per 1000 grain number, the amount of change being much greater than that found by other workers for copper and bronze. W. Hume-Rothery.

Determination of mol. wt. by centrifuging. II. T. Svedberg (Z. physikal. Chem., 1927, 127, 51—70; cf. A., 1926, 340).—A new method for the determination of the mol. wt. of proteins by means of the ultra-centrifuge has been developed. This method, which is more rapid and more accurate than the previous one (*loc. cit.*), is based on the measurement of the velocity of sedimentation of the molecules. It has been applied, with the aid of a special ultracentrifuge of the oil-turbine type capable of developing a centrifugal force approaching 90,000 times the gravitational force, to the determination of the mol. wt. of carbon monoxide–hæmoglobin. It was found that this protein is nearly homogeneous, comprising 80—90% of molecules of weight 66,800 with approximately equal amounts of molecules of weights 33,400 and 100,200. G. A. Elliott.

Possibility of an allotropic change at the point of transition to the superconducting state. W. H. Keesom and H. K. Onnes (Arch. Néerland., 1927, IIIa, 10, 221—223).—Bridgman's hypothesis that metals which show superconductivity undergo a polymorphic change at the transition point has been tested for lead. The *X*-ray diffraction pattern obtained at the temperature of liquid helium was found to be the same as that obtained at the ordinary temperature, and it is concluded that no change in the crystalline state occurs. C. J. Smithells.

Disturbance of superconductivity by magnetic fields and by currents. The hypothesis of Silsbee. W. Tuyn and H. K. Onnes (Arch. Néerland., 1927, IIIa, 10, 224—258).—Little data have been available with which to test Silsbee's hypothesis connecting the threshold values of the current and the magnetic field. Recent data obtained in other researches are reviewed in this connexion, and appear to support the hypothesis. C. J. Smithells.

Properties of superconducting metals in the form of thin films. G. J. Sizoo and H. K. Onnes (Arch. Néerland., 1927, IIIa, 10, 259—265).—The temperature at which the resistance of sputtered films of tin about 0·5 μ thick disappeared was determined. It varied with different specimens, and changed slightly with time, but in general was 0·1—0·2° lower than for wires. This is attributed to the granular structure of the films. The effect of the current and of a magnetic field on the conductivity was found to be the same for films and wire. Sputtered films of bismuth did not exhibit superconductivity at 1·24° Abs. C. J. Smithells.

Influence of elastic deformation on the superconductivity of tin and indium. G. J. Sizoo and H. K. Onnes (Arch. Néerland., 1927, IIIa, 10, 266—279).—The temperature at which the electrical resistance of wires of tin and indium disappears was found to be raised by tension and lowered by pressure. For indium, a pressure of 200 kg./cm.^{2} lowered the temperature 0·006°. C. J. Smithells.

Magnetic disturbance of the superconductivity of tin. G. J. Sizoo, W. J. de Haas, and H. K. Onnes (Arch. Néerland., 1927, IIIa, 10, 280—304).—Superconductivity can be disturbed by an external magnetic field, and it is found that the curve connecting field strength and resistance is in the form of a hysteresis loop. Single crystal wires of tin do not show this effect, which is attributed to the discontinuity at the crystal boundaries.

C. J. Smithells.

Electrical conductivity of solid cuprous bromide. P. Fischer (Z. Elektrochem., 1927, 33, 170—172).—The specific conductivity of solid cuprous bromide has been measured using direct current, and is shown to increase with temperature. Although this suggested that its conductivity was electrolytic, passage of a current through a cylinder of the salt between platinum electrodes did not produce any loss of weight, indicating electronic conductivity (cf. Friederich and Meyer, this vol., 114). When an anode of silver or copper was substituted for platinum, an extremely low value for the specific conductivity was obtained, and it decreased with increasing temperature. The anode remained unattacked. Mixtures of cuprous bromide and potassium bromide exhibit a maximum specific conductivity when the concentration of the latter is about 10%.

H. J. T. Ellingham.

Thermo-electric and electro-thermal properties of single crystals of bismuth. T. Terada and T. Tsutui (Proc. Imp. Acad. Tokyo, 1927, 3, 132—135).—A preliminary account of the thermoelectric effect in single crystals 15—25 cm. long and 1 mm. diameter of bismuth and cadmium. The effect in cadmium, if any, is very much smaller than in bismuth. By establishing a temperature gradient of 2000° cm.$^{-1}$ across the wire for a few cm. of its length, an *E.M.F.* of 0·003 volt was generated between the ends of the wire. It was found that this *E.M.F.* was approximately proportional to the size of the azimuth of the plane of the thermal gradient to a certain plane containing the axis of the wire. It is shown that this result is to be anticipated if it be assumed that the *E.M.F.* observed is of the form $E=e_{11}\delta T/\delta x+e_{12}\delta T/\delta y+e_{13}\delta T/\delta z$, where x, y, z are the three crystallographic axes, and z is chosen to coincide with the axis of threefold symmetry.

An inverse effect has also been observed by attaching fine insulated thermo-junctions to the opposite sides of a wire through which a current is flowing.

R. W. Lunt.

Magnetic properties of vanadyl chloride and sulphate, and the atomic moment of vanadium. N. Perrakis (Compt. rend., 1927, 184, 1430—1432).—Determinations of the variation of the coefficient of magnetisation and of the thermal behaviour of vanadyl chloride and sulphate show that in each case there is a displacement of the Curie point unaccompanied by a change of moment. Quadrivalent vanadium has therefore at least two atomic moments having the values 8 and 9 Weiss magnetons, and corresponding with the chloride and sulphate, respectively. J. Grant.

Thermal conductivity of gas carbon. R. Holm (Z. Physik, 1927, 43 466—473).—An elaborate technique is described for the measurement of the thermal conductivity of gas carbon. The value of the thermal conductivity k is found to be (gas carbon, mark *A*, Siemens & Co.) 0·039 ±0·002 watt cm.$^{-1}$ per degree, *i.e.*, 0·0093±0·0005 g.-cal. cm.$^{-1}$ sec.$^{-1}$ per degree in the range 25—45°. R. W. Lunt.

Latent heat of vaporisation of benzene at temperatures above the b. p. J. A. Sutcliffe, F. C. Lay, and W. L. Prichard (Proc. Roy. Soc., 1927, A, 115, 88—102).—A detailed description is given of an apparatus for the determinaton of the latent heat of vaporisation of liquids at temperatures above their b. p. The experimental method consists in supplying a measured quantity of electrical energy to a vacuum vessel (employed as calorimeter) containing mercury, in which the bulb of a steel bomb is immersed. The liquid under observation is allowed to evaporate slowly from the bomb, through a fine steel capillary tube, at a rate controlled by manipulation of a needle valve at the top of the capillary tube so that the mean temperature of the calorimeter during the experiment is practically identical with that of a surrounding thermostat. The weight of liquid evaporated is determined by weighing the bomb before and after each experiment, suitable corrections being applied to the loss of weight of the bomb. By the application of the method to the determination of the heat of vaporisation of benzene, consistent results in g.-cal. per g. were obtained at five different temperatures, as follows: $L=92·72$ at 86·86°, 89·20 at 105·42°, 85·53 at 125·25°, 81·74 at 143·49°, and 79·86 at 151·80°. Each value is the mean of several experiments. The results are in agreement with those obtained by Griffiths and Marshall at temperatures below the b. p. The values calculated from the empirical equation $L=106·868-1·47106+10^{-1}t-1·46582\times10^{-4}t^2-3·60266\times10^{-7}t^3$, in which L is the heat of vaporisation and t is the temperature, are in close agreement with the results obtained by direct experiment at all the temperatures at which experiments have been performed by Griffiths and Marshall and by the authors. The value at the b. p. calculated from the equation is 93·94 g.-cal. per g., in close agreement with that obtained by Nagornov and Rotinjanz (A., 1911, ii, 965), but lower than the value (94·37 g.-cal. per g) calculated on the assumption that the linear relation between the latent heat and the temperature continues to hold accurately from 50° to the b. p. L. L. Bircumshaw.

[M. p. of] monopotassium phosphate. A. R. Merz (J. Amer. Chem. Soc., 1927, 49, 1511—1512).—Pure monopotassium orthophosphate fuses with loss of water at 252·6° to 254·3°, and not at 96° as reported in the literature. S. K. Tweedy.

M. p. and heats of crystallisation of homologous series. III. Myristic acid derivatives. W. E. Garner and J. E. Rushbrooke (J.C.S., 1927, 1351—1358).—If it be assumed that the increment in the heat of crystallisation per methylene group is the same for all homologous series above C_{10}, then the empirical equation for the m. p. of the even members of the monobasic acids, previously derived (A., 1926, 1087), may be expressed in the general form $T=(x+1{\cdot}030n)/(y+0{\cdot}002652n)$, where n is the number of carbon atoms in the chain, and x and y are constants depending on the nature of the terminal group. To test this equation, the heat of crystallisation of one member of each of a number of homologous series has been determined, viz., myristamide, myristyl alcohol, and methyl and ethyl myristate. The values of x and y for each series may then be deduced (*loc. cit.*), and hence the m. p. for other members of these series. Calculated and experimental values are in fairly good agreement. The effect of the chemical constitution of the polar terminal group on the m. p. is discussed from the point of view of the theory of m. p. previously put forward (*loc. cit.*). The heat of crystallisation of the terminal group is shown to be the chief factor in determining the "equilibrium constant" of the group, and hence the m. p. of the compound.

M. S. Burr.

Course of the m.-p. line of helium at very low temperatures. J. J. van Laar (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 244—248).—Polemical against Keesom (A., 1926, 893). It is shown that if dp/dt becomes 0 at $\pm 1°$ Abs., it does not follow that dp/dt would also have to disappear at $T=0$.

W. E. Downey.

Heat of combustion of calcium cyanamide. N. Kameyama and S. Oka (Proc. Imp. Acad. Tokyo, 1927, **3**, 161—163).—The heat of combustion of calcium cyanamide ($CaCN_2$, 98·25; $CaCO_3$, 0·81; CaO, 0·94%) in oxygen has been determined in a bomb calorimeter of the Berthelot–Mahler type. Benzoic acid was mixed with the cyanamide to facilitate ignition, and the heat of combustion was obtained by allowing for the amount of benzoic acid present. The mean value of 2016±3 g.-cal. per g. of $CaCN_2$ was obtained corresponding with the equation $2CaCN_2+3O_2=2CaO+2CO_2+2N_2+322{,}340$ g.-cal.

R. W. Lunt.

Variation of the velocity of sound in gases with temperature. E. J. Irons (Phil. Mag., 1927, [vii], **3**, 1274—1285).—From the experimental results of Dixon, Campbell, and Parker (A., 1921, ii, 621) and of Partington and Shilling (A., 1923, ii, 214), formulæ to represent experimental data for the variation of the velocity of sound in gases with the absolute temperature have been developed.

A. E. Mitchell.

Chemical constant of benzene. N. de Kolosovski (Bull. Soc. chim. Belg., 1927, **36**, 358—361).—The chemical constant of benzene calculated from available data by the general method is 2·619±0·325.

L. M. Clark.

Chemical constants and absolute entropy. W. H. Rodebush (Proc. Nat. Acad. Sci., 1927, **13**, 185—188).—Disregarding the b.-p. region, the vapour-pressure data for potassium and sodium are represented satisfactorily by the equations $\log p=-4780/T-1{\cdot}40\log T+11{\cdot}670$, and $\log p=-5730/T-1{\cdot}25\log T+11{\cdot}580$, respectively. The entropies at 298° Abs. and 1 atm. of the vapours of potassium, sodium, mercury, and lead are 38·2 (36·9), 36·7 (35·4), 41·7 (41·8), and 42·9 (41·9), respectively. The numbers in parentheses are the values predicted by the Tetrode equation. Theoretical points are discussed.

J. S. Carter.

Densities of magnesium at its m. p. H. Endo (Bull. Chem. Soc. Japan, 1927, **2**, 131—134).—The mean coefficient of linear expansion of magnesium between 20° and the m. p., 650°, is 0·00003025. Taking $d_4^{20}=1{\cdot}7410$, the value of d_4^{650} calculated from the coefficient of expansion is 1·6468. Assuming the volume change on melting is 0·0255 c.c./g., the value of d_4^{650} for liquid magnesium is 1·5804.

J. S. Carter.

Density of cementite. T. Ishigaki (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 295—302).—The densities of hot-forged, annealed steels of varying carbon content were measured, and the density of cementite was determined by extrapolation of the density–composition curve to the composition of cementite. Corrections were applied for the effects of impurities, and the value attained for pure cementite was 7·662, in good agreement with the value 7·680 found by Westgren and Phragmén from X-ray crystal analysis (B., 1924, 518).

W. Hume-Rothery.

Densities of saturated vapours at corresponding temperatures. W. Herz (Arch. Pharm., 1927, **265**, 212—213).—The densities of saturated vapours of 41 compounds at two corresponding states have been calculated from published data. The densities at $9/10T_c$ and $2/3T_c$ ($s_{9/10}$ and $s_{2/3}$, respectively) have been compared with d_c and with each other. The ratio $d_c : s_{9/10}$ varies between 6·978 and 3·653, being large for alcohols and small for noble gases, whilst $d_c : s_{2/3}$ varies from 220·4 to 24·57, and $s_{9/10} : s_{2/3}$ from 34·53 to 6·30. There is no constant relationship between the densities of saturated vapours in the sense of the theory of corresponding states. S. Coffey.

Electron affinity of hydrogen and the density of the hydrides of the alkali metals. J. Kasarnovski and M. Proskurnin (Z. Physik, 1927, **43**, 512—515).—The values obtained for the densities of sodium and potassium hydrides using a pyknometer containing dry *cyclo*hexane, 1·40 and 1·47±0·03, respectively, have been used to calculate the grating energy of these substances from Born's equation. The values obtained are 211,000 and 181,000 g.-cal. respectively. The corresponding values of E_H-D_H from the Born cycle are −51,000 and −50,000 g.-cal. These are thought to be in good agreement with the mean value of −62,000 g.-cal., calculated from the available data for the hydrides of lithium, calcium, and barium, since there is an error of the order of 10,000 g.-cal. in the heats of sublimation of these metals. The most recent spectroscopic data for the heat of dissociation of hydrogen, D_H is 50,000 g.-cal.; hence the most probable value for E_H is −1000 g.-cal. This value agrees satisfactorily with that computed from Pauling's model of the hydrogen atom (this vol., 287), $E_H = -1850$ g.-cal. The low values obtained for the densities of sodium and potassium hydrides by Moissan, and by Hüttig and Brodkorb, are therefore held to be inaccurate.

R. W. LUNT.

Isometrics of gaseous methane. F. G. KEYES and H. G. BURKS (J. Amer. Chem. Soc., 1927, **49**, 1403—1410).—A previous investigation is repeated with improvements in experimental technique (Keyes, Smith, and Joubert, J. Math. Phys. Mass. Inst. Techn., 1922, **1**, 191). The temperature range was 0—200°. The isometrics of methane show curvature, which increases as smaller volumes are approached, but decreases as the temperaure rises. The Keyes equation of state for methane is $p(\text{atm.})=5{\cdot}1173T/(v-3{\cdot}64e^{-2.25/v})-9370/(v+0{\cdot}42)^2$. An equation for the degree of aggregation is deduced, it being assumed that the curvature of the isometrics is caused by aggregation.

S. K. TWEEDY.

Equation of state for easily liquefied hydrocarbons. I. Weight of a litre of *n*-butane. L. VAN BOGAERT (Bull. Soc. chim. Belg., 1927, **36**, 384—394).—The normal density of *n*-butane (prepared by a Wurtz reaction with valeronitrile) is found by the compensating-globe method to be 2·51837 g. (corr.) at 0° and 710 mm. The slight discrepancy between this value and that of Ouédinoff is attributed to a systematic error in the earlier work, either in the pressure measurements or because of an impurity in the gas. An improved manometer is described. Valeronitrile prepared by the method of Adams and Marvel (A., 1920, i, 283) may be separated into two fractions, one of which (b. p. 140·7±0·03°; d_4^0 0·81646; d_4^{15} 0·80361) has a disagreeable odour and contains only 0·06% of carbylamine.

S. K. TWEEDY.

Viscosities of methyl alcohol, acetone, and ethyl ether at low temperatures. S. MITSUKURI and T. TONOMURA (Proc. Imp. Acad. Tokyo, 1927, **3**, 155—158).—The viscosities of methyl alcohol, acetone, and ethyl ether have been determined in the range 0—120° by a modified form of Ostwald viscosimeter. An interesting device has been employed to obviate the necessity of visual observation of the motion of the liquid between two points in the apparatus. At these points, two pairs of platinum wires are sealed, which constitute two small condensers. Using a heterodyne method at a frequency of 4×10^6 per sec., the instants at which the liquid comes in contact with each pair of wires can be accurately observed by the abrupt change which takes place in the heterodyne note.

R. W. LUNT.

Surface tension of liquid metals. II. Surface tension of bismuth, cadmium, zinc, and antimony. L. L. BIRCUMSHAW (Phil. Mag., 1927, [vii], **3**, 1286—1294).—Previous work (A., 1926, 895) has been extended to molten bismuth, cadmium, zinc, and antimony. Determined values are given of the surface tensions in the ranges 300—962° for bismuth, 600—700° for zinc, 330—600° for cadmium, and 640—974° for antimony. It is shown that the surface tension of liquid cadmium passes through a maximum at 425°. Calculations of the total surface energy of the molten metals indicate that bismuth, cadmium, and antimony are all highly associated in the liquid state.

A. E. MITCHELL.

Densities of hydrocyanic acid–water mixtures. M. SHIRADO (Bull. Chem. Soc. Japan, 1927, **2**, 122—124).—Values of d_{18}^{18}, d_4^{18}, and $(d_4^{18})_{\text{vac.}}$ for the complete range of hydrocyanic acid–water mixtures are tabulated. The value of $(d_4^{18})_{\text{vac.}}$ of the pure acid is 0·6913. The following values of d_{18}^{18} at the concentrations of hydrocyanic acid indicated are illustrative of the variation of density with composition: 0·9927, 5·05%; 0·9838, 10·04%; 0·9578, 20·29%; 0·9376, 26·90%; 0·8290, 60·23%; 0·6919, 100%. Over the concentration range 27—100% of acid, d_{18}^{18} varies almost linearly with the concentration of acid. The present values of d_{18}^{18} for mixtures rich in acid are in complete agreement with those of Walker and Marvin (B., 1926, 271).

J. S. CARTER.

Densities of nicotine–water mixtures. N. SATA (Bull. Chem. Soc. Japan, 1927, **2**, 139—143).—The density–composition curves for nicotine–water mixtures at 30°, 40°, 50°, and 60° have been investigated. Both components have approximately the same density, the values of d_4^{30}, d_4^{40}, d_4^{50}, and d_4^{60} of nicotine being 1·00124, 0·99383, 0·98630, and 0·97890, respectively. The curves at the lower temperatures show a maximum value which tends to disappear as the lower temperature limit for partial miscibility (about 60°) is approached. The densities of the conjugate solutions have been determined at various temperatures between 65° and 120°. At lower temperatures, the nicotine phase is the heavier, but reversal occurs at 96°, and an 8-shaped curve is obtained on plotting densities of the conjugates against temperature.

J. S. CARTER.

Critical solution temperatures of mixtures of alcohol and some hydrocarbons. A. BOUTARIC and G. CORBET (Compt. rend., 1927, **184**, 1446—1447).—The determination of the critical solution temperatures of two liquids is often facilitated by the addition of a third substance (*e.g.*, colza oil) which renders the separation of the two layers more easily visible, and raises the temperature at which it occurs. The critical temperatures are plotted as a function of the concentration of the third substance, and the latter is extrapolated to zero to obtain the true result. The critical solution temperature of benzene and methyl alcohol is 29°. Benzene and pure ethyl alcohol are miscible in all proportions, but light petroleum and absolute alcohol are not.

J. GRANT.

General property-function of mixtures [of metals] free from mixed crystals. J. DEJMEK (Physikal. Z., 1927, **28**, 409—417).—Theoretical. An extension of Lichtenecker's work (this vol., 189) on the logarithmic rule for the properties of mixtures. It is shown that the rule correctly describes the properties of mixtures in absence of secondary phenomena.

W. E. DOWNEY.

Magnetic, electric, and thermal properties of nickel-cobalt alloys. H. MASUMOTO (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 321—341).—The intensity of magnetisation of nickel-cobalt alloys has been measured for different field strengths at the ordinary temperature. The magnetisation–composition curves have a maximum at 15% and a minimum at 6% of nickel in all fields between 50 and 600 gauss. In weak fields, two minima are shown at 30% and 70% of nickel, the former corresponding with the change from the hexagonal close-packed to the face-centred cubic structure; these minima vanish with increasing field strength. The magneto-striction effect has also been measured. Alloys with 50% to 87·5% of cobalt give complex effects showing a contraction in small and an expansion in large fields. The remaining alloys show contraction only. The 30% nickel alloy has the minimum contraction and maximum expansion. The thermal and electrical conductivities of these alloys have also been measured and vary similarly with the composition, showing maxima at about 25%, and two minima at 10% and 70% of nickel.

W. Hume-Rothery.

Coefficient of thermal expansion in nickel–cobalt and iron–cobalt alloys, and magneto-striction of iron–nickel alloys. H. Masumoto and S. Nara (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 333—343).—The coefficient of expansion of nickel–cobalt and iron–cobalt alloys has been measured. As nickel is added to cobalt, the coefficient of expansion decreases at first very slowly up to 30% of nickel, and then increases comparatively rapidly, reaching a maximum at 40% of nickel. The coefficient then decreases gradually to a minimum at 65% of nickel, and then increases uniformly up to the value of pure nickel. The comparatively rapid increase occurring at 35% of nickel nearly corresponds with the concentration at which the lattice change takes place. As iron is added to cobalt, the coefficient of expansion decreases gradually to a minimum at 47% of iron, rises to a maximum at 65%, then falls to a minimum at 73% of iron, and finally increases to the value for pure iron. There is possibly a break in the curve at 4% of iron, corresponding with the change in lattice. In the magneto-striction of iron–nickel alloys, alloys containing between 5% and 80% of nickel show expansion in all fields. The 81% nickel alloy shows no effect, whilst the alloys rich in nickel show contraction. The elongation–composition curves at all fields show maxima at 20% and 60% of nickel, and a minimum at 25%.

W. Hume-Rothery.

Magnetic determination of the solidus and solubility lines in the iron–carbon system. K. Honda and H. Endo (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 235—244).—The solidus line in the iron–carbon system has been determined by measurements of the magnetic susceptibility of slowly heated specimens of Swedish steels of varying carbon content. The susceptibility of steels diminishes linearly with rise of temperature up to the solidus point or to the solubility point of cementite, when it decreases more rapidly, the curves showing distinct breaks at these points. The solidus line thus determined lies between the lines of Carpenter and Keeling (B., 1904, 608) and of Gustowsky (Métallurgie, 1909, 731), and nearly coincides with those obtained by Asahara (A., 1924, ii, 188) and by Kaya (B., 1926, 325). The limits of solubility of cementite in austenite were similarly obtained by cooling experiments, in which the formation of graphite is avoided; the results agree with those of previous investigators. The materials used contained both silicon and manganese.

W. Hume-Rothery.

Magnetic susceptibility of some binary alloys at high temperatures, and their equilibrium diagrams. H. Endo (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 201—234).—The diamagnetic susceptibilities of bismuth, cadmium, copper, lead, antimony, tin, tellurium, thallium, and zinc have been determined at temperatures from 20° to 1100°. The results agree with those obtained by Honda (A., 1910, ii, 686). The susceptibilities of different alloys have been measured in both solid and liquid states, to find which of the solid phases correspond with compounds which retain their individuality in the liquid state. Breaks or minima in the susceptibility–composition curves show that the following compounds exist as such in the liquid state in their respective binary systems, with partial decomposition in some cases: Bi_2Te_3, PbTe, $PbTl_2$, Sb_2Te_3, ZnSb, Zn_3Sb_2, SnTe, CdSb, Cu_3Sn, Cu_2Zn_3. On the other hand, several of the solid phases in the complex copper–zinc and copper–tin systems do not correspond with any irregularity in the liquid. Thermal, magnetic, and microscopical analyses of the system antimony–tellurium have been carried out, and show that the limit of solubility of tellurium in antimony is 3% at the ordinary temperature. Alloys containing 3—55% of tellurium represent mixtures of the antimony solid solution (α) and the β solid solution, consisting of antimony dissolved in the compound Sb_2Te_3. When no intermetallic compound is present, the susceptibility–composition curve for the liquid alloys is straight or slightly curved; the systems investigated were bismuth–antimony, lead–bismuth, bismuth–tin, lead–tin, and lead–antimony. In the system antimony–tin, the β (SbSn) solid phase does not seem to correspond with any molecular compound in the liquid.

W. Hume-Rothery.

Solvent properties of liquid sulphur dioxide and liquid ammonia towards certain organic substances. F. De Carli (Gazzetta, 1927, 57, 347—355).—Liquid sulphur dioxide dissolves many aromatic hydrocarbons. When the latter are liquid at the ordinary temperature the miscibility is complete, whereas solid hydrocarbons usually form 15—30% solutions. Naphthalene is completely miscible, but anthracene and stilbene are only very slightly soluble at the ordinary temperature, whilst additive compounds such as decaline are practically insoluble. The carboxylic acids of aromatic hydrocarbons are almost insoluble in liquid sulphur dioxide, whereas the alcohols, aldehydes, ketones, phenols, ethers, amines, amides, nitriles, and nitro-derivatives dissolve readily. Instead of treating crude 30—32% anthracene oil with liquid sulphur dioxide under pressure to obtain a solid 70—80% anthracene, it seems more advantageous to use the sulphur dioxide to remove the impurities from 85—90% anthracene obtained by other means. Liquid ammonia scarcely dissolves hydrocarbons, whether of open- or closed-chain type. The most readily soluble derivatives are those of acid character, phenols and carboxylic and sulphonic acids being completely miscible to form dense solutions which yield the solvent very slowly at the ordinary temperature. Amines, amides, nitriles, nitro-derivatives, benzaldehyde, and anisaldehyde dissolve readily, but cuminaldehyde, cinnamaldehyde, and salicylaldehyde are only slightly soluble. Ketones, alcohols, and certain esters are readily soluble, but terpenes, heterocyclic compounds, and open-chain compounds, even if unsaturated, do not dissolve in liquid ammonia. T. H. Pope.

New kinds of mixed crystals. D. Balarev and G. Kandilarov (Z. anorg. Chem., 1927, **162**, 344—348).—Barium sulphate, precipitated in different ways, contains up to 3·6% of water, *i.e.*, 1 mol. of water to each mol. of barium sulphate. Part at least of the water is held mechanically, as on crushing the crystals the water content diminishes. Barium sulphate crystals, stained purple by contact with potassium permanganate solution, show no change of structure under the microscope after many days, indicating that the staining is due solely to capillary effects, and not to chemical reaction. Even large crystals of barium sulphate appear to have large internal free surfaces. The velocity of staining shows that the effect is concerned, not merely with the internal surfaces, but also with the number and size of the capillaries. The fineness of the capillaries is indicated by the fact that a porous pot in the walls of which barium sulphate has been deposited acts as a semi-permeable membrane to barium chloride solution. H. F. Gillbe.

Solvent properties of furfuraldehyde and its derivatives. J. P. Trickey (Ind. Eng. Chem., 1927, **19**, 643—644).—Furfuraldehyde and its derivatives are good solvents for cellulose nitrate, whilst their low rate of evaporation renders them particularly suitable as solvents in the lacquer industry. Measurement of the relative viscosities (expressed as times of flow from a pipette) at 25° of 8% solutions of cellulose nitrate gave the following results: in amyl acetate, 14·4; ethyl lactate, 35·4; furfuraldehyde, 25·9; methyl pyromucate, 53·6; propyl pyromucate, 64·2; *n*-butyl pyromucate, 80·8; *iso*amyl pyromucate, 79·7; furfuryl alcohol, 91·6; furfuryl acetate, 37·6; tetrahydrofurfuryl alcohol, 69·7. Qualitative data concerning the solubility of various gums and resins in the above solvents are given. W. J. Powell.

Selective solvent action. IV. Effect of temperature on the solubilities of semi-solutes in aqueous alcohol. R. Wright (J.C.S., 1927, 1334—1337).—If the formation of complexes occurs between the constituents of a mixed solvent, rise of temperature should cause the dissociation of these complexes, and hence affect the solvent power for solutes soluble in one or both of the constituents, due to the fact that more solvent becomes available at the higher temperature. The solubility of five non-hydrated inorganic salts has been determined in 50% by weight aqueous alcohol at 100° and 20°, and the ratio compared with the ratio of the solubilities in water at the same temperatures. The former ratio was considerably larger than the latter, indicating the breaking up of the alcohol–water complexes with rise of temperature. The data of other investigators, for the solubility of potassium nitrate in aqueous alcohol, of concentrations ranging from 5·5% to 90%, at 20° and 60°, when treated in the same way, give the largest deviations from the ratio for pure water in a solvent containing about 20% of alcohol. For alcohol-soluble solutes, similar results are obtained when the solubility of the substance in water, which is never negligible, is taken into consideration. The method employed for the determination of the solubilities is described. M. S. Burr.

Adsorption of vapours by ferric hydroxide gel. J. H. Perry (Ind. Eng. Chem., 1927, **19**, 746—748).—The adsorption of vapour from vapour–air mixtures by active ferric hydroxide gel containing 6·36% of water is represented by graphs which may be divided into three classes (cf. Munro and Johnson, A., 1925, ii, 191): (i) the adsorption efficiency is never 100%, and decreases continuously until the saturation value is reached (chloroform, acetone, etc.); (ii) the adsorption is 100% efficient for some time, and then proceeds to the saturation point, which is reached only after a long time (carbon tetrachloride, ethyl alcohol, benzene); (iii) the curves are almost linear up to saturation, probably indicating chemical reaction (methyl alcohol). The addition of air to sulphur dioxide or ammonia causes a marked lowering of the saturation capacity of the gel. The gel absorbs about 15% of its weight of water with 100% efficiency, after which the efficiency falls off up to saturation (18% of its weight of water). Pure commercial chloroform contains ethyl alcohol.

S. K. Tweedy.

Adsorption by metallic hydroxides. IV. Precipitated chromium hydroxide. K. C. Sen (J. Physical Chem., 1927, **31**, 922—930; cf. this vol., 617).—Adsorption by chromium hydroxide differs from that by ferric and aluminium hydroxides in that no true equilibrium can be obtained and the equilibrium is not reversible. Reproducible results are obtained, however, when the time of contact is constant, the adsorption increasing with time. Arsenious acid is adsorbed to a greater extent than sodium arsenite, whereas no difference is found in the case of aluminium hydroxide. Citric, malic, racemic, sulphuric, oxalic, succinic, benzoic, and hippuric acids are considerably adsorbed. Sodium hydroxide is adsorbed to a lesser extent, whilst the adsorption of salts is small. L. S. Theobald.

Adsorption from mixed solvents. N. A. Schilov and (Mlle.) S. M. Pevsner (J. Russ. Phys. Chem. Soc., 1927, **59**, 158—170).—See A., 1926, 238.

Electrical adsorption theory. S. G. Mokruschin and O. A. Essin (J. Russ. Phys. Chem. Soc., 1926, **58**, 737—744).—The phenomena of electrostatic adsorption are investigated from the point of view of the law of chance, the molecules being regarded as dipoles (Langmuir). Adsorption is regarded as the neutralisation of opposite electrostatic charges, on the adsorbent and adsorbed particle, without their chemical interaction. The thickness of the resulting "double layer" is of the order of 3×10^{-6} cm., *i.e.*, 300 times as great as the average molecular diameter. The surface of the adsorbent is assumed to consist of units capable of adsorbing one molecule or ion of opposite charge. An expression is developed for the number of particles adsorbed: $m=K(1-1/2n)$, where m is the number of particles adsorbed by a unit surface, n the total number of particles colliding with it, and K is a probability constant. Expressing m and n in terms of molar concentration, it is calculated that for $n = 8$ the probability is nearly equal to one, and within the limits of analysis, a formula capable of experimental verification is developed, viz., $a=S'(1-1/2\beta)$, where S' = the ratio of total surface to Avogadro's number, and β the ratio of eight times the molar concentration of the adsorbed substance to its concentration at maximum adsorption. The expression is tested by the results of Ghosh and Dhar (A., 1924, ii, 733) for the adsorption of various ions by freshly-precipitated barium sulphate, and found to give satisfactory agreement. M. ZVEGINTZOV.

Thickness of adsorbed vapour films. J. C. W. FRAZER, W. A. PATRICK, and H. E. SMITH (J. Physical Chem., 1927, **31**, 897—905).—The adsorption of toluene and water on plane surfaces of virgin glass has been studied by the method of McHaffie and Lenher (A., 1925, ii, 854). In the case of toluene, the thickness of the adsorbed film is never greater than unimolecular. Washing the glass surface with acids and water renders it no longer plane, and the silica left on the surface is sufficient to account for the multimolecular adsorption observed by previous workers (cf. McHaffie and Lenher, *loc. cit.*). Water vapour reacts with fresh glass surfaces in a similar manner. The significance of these results in relation to existing theories of adsorption is discussed.

L. S. THEOBALD.

Expansion of charcoal on sorption of carbon dioxide. F. T. MEEHAN (Proc. Roy. Soc., 1927, A, **115**, 199—207).—The expansion of yellow pine charcoal on sorption of carbon dioxide up to a pressure of 1 atm. has been measured by means of an extensometer over the range of temperature 10—36°. The process is reversible, and the expansion is of the same order of magnitude as the moisture expansion in building materials. It is suggested that this type of expansion may be characteristic of rigid gels. Measurements of the expansion in the three grain directions show that it is independent of the direction of the grain. The uniformity of expansion in different directions indicates that the æolotropy of wood is destroyed on carbonisation and that wood charcoal is isotropic. At constant temperature, the relation of expansion to pressure is represented better by the equation $\log E/p=G+HE$ (where G and H are constants) than by the usual expression $E=kp^{1/n}$. The relation of expansion to temperature at constant pressure is given by the equation $1/E=AT+B$. No discontinuity is met with at the critical temperature of carbon dioxide. L. L. BIRCUMSHAW.

Swelling of active carbon. P. N. PAVLOV (Kolloid-Z., 1927, **42**, 112—119).—The swelling of various forms of carbon in different liquids was examined and compared with the adsorption of acetic acid from these liquids. The degree of swelling depends on the liquid in question, increasing in the following series: acetic acid < water < ethyl acetate < benzene = toluene = xylene < carbon tetrachloride. The swelling in water and the adsorption of acetic acid from water by different forms of carbon increase in the following order: graphite, sugar charcoal, animal charcoal, and this is regarded as a measure of the activity of the carbon. The swelling isotherms for carbon have a maximum and a minimum value. The existence of a minimum value enables the isoelectric point to be determined. Animal charcoal and sugar charcoal were found to have two isoelectric points, one in acid solution and the other in alkaline solution. E. S. HEDGES.

Experimental test of the dipole theory of adsorption. W. G. PALMER (Proc. Roy. Soc., 1927, A, **115**, 227—236; cf. A., 1924, ii, 665; 1926, 239).—The method previously employed for the determination of the critical or cohering voltage, E, of films of gas at a metal surface has now been adapted for the study of adsorption from liquids in which the cohering junction is totally immersed. From values of E, the molecular heat of desorption can be calculated. E increases regularly in the homologous series of primary alcohols, fatty acids, and their ethyl esters according to the relation E^2/l=constant, where l is the length of the chain. The results are interpreted on the basis of views developed by Lorenz and Landé (A., 1923, ii, 13). For the substances examined, the principal doublets are $CH_2{\cdot}OH$, CO_2H, and CO_2Et, and it is shown that the molecular heat of adsorption will be proportional to the moment of the adsorbed molecules, and that this is proportional to $(K-1)$ for a fixed temperature, where K is the specific inductive capacity of the film. The heat of desorption of all the primary alcohols from a platinum surface is 7000 g.-cal. approx., but for the acids and esters the value is a little less. For pentane, E is practically the same for the vapour and the liquid. The mechanism of adsorption of non-polar molecules, such as hydrocarbons, is discussed. L. L. BIRCUMSHAW.

Thermodynamics of the adsorption isotherm. P. BERNAYS (Z. Elektrochem., 1927, **33**, 170).—It is shown that Reichinstein's relation between the partial pressures of the components of a gas mixture and their concentrations in an adsorption layer (A., 1924, ii, 22; 1926, 130) satisfies the thermodynamic condition given by Cassel (A., 1926, 127).

H. J. T. ELLINGHAM.

Interaction between iodine and starch. S. V. GORBATSCHEV and E. N. VINOGRADOVA (Z. physikal. Chem., 1927, **127**, 93—107).—The amounts of iodine taken up by starch granules in equilibrium with iodine solutions of varying concentration increase with temperature or on the addition of electrolytes. The evidence indicates that hydrogen ions are initially adsorbed and that by the removal of these by a rise of temperature or by the neutralising action of the anions of the electrolyte added the starch may adsorb further quantities of iodine. Acetates produce the greatest and sulphates the least adsorption; the position of iodides in the series is not abnormal. When the concentration of effective electrolyte is high, all the hydrogen ions become neutralised and the iodine–starch reaction reduces to a simple adsorption with a negative temperature coefficient. G. A. Elliott.

Surface tension of aqueous solutions of mono-, di-, and tri-ethylamine. A. Schnell (Z. physikal. Chem., 1927, 127, 121—126).—Measurements were made at 5° for solutions of varying concentration by the Cantor "breaking method." The results may be expressed in terms of Szyszkowski's equation, and according to Langmuir's interpretation of this equation show that the cross-sectional areas of the molecules of the three amines are proportional to the reciprocals of the molecular volumes of the pure amines. Similarly, it is shown that the lengths of the molecules are equal. Traube's rule for homologous series is also valid for these compounds.

G. A. Elliott.

Surface energy of the alkali halides and their solutions. F. De Block (Natuurwetens. Tijdsch., 1927, 9, 65—71).—The results previously obtained for the free surface energy of salt solutions (*ibid.*, 1925, 7, 73—77) are discussed in relation to those recently obtained by Rehbinder (A., 1926, 674). The relations between the surface energies of salts in the fused and crystalline conditions are also considered. S. I. Levy.

Surface tension of molten metals and alloys. II. Surface tension of tin, lead, antimony, copper, tin–bismuth, lead–bismuth, copper–antimony, and copper–tin alloys, and cast iron. G. Drath and F. Sauerwald (Z. anorg. Chem., 1927, 162, 301—320).—The surface tensions have been determined at temperatures up to 1200°. Copper differs from the other metals in that its surface tension increases with rise of temperature. The alloys fall into two main groups: alloys of bismuth and tin and of bismuth and lead show a very small negative divergence from the law of mixtures, whilst copper–antimony and copper–tin alloys exhibit a very much greater negative divergence. Certain of the copper–tin alloys resemble copper in having a positive temperature coefficient; the temperature coefficient of some of the alloys of the second group is zero. Considerable association and complex formation are suggested by the behaviour of copper and the alloys of the second group. H. F. Gillbe.

Densities of aqueous solutions of certain univalent perchlorates. II. A. Mazzucchelli and A. Rossi (Gazzetta, 1927, 57, 383—390; cf. A., 1926, 675).—In agreement with results previously obtained, lithium, silver, and guanidine perchlorates exhibit molecular coincidence pressures which increase considerably with the concentration. Tammann's assumption of the approximately additive character of such pressures would suggest that this behaviour must be regarded as characteristic of the perchlorate anion, but the physical interpretation of the effects presents difficulties.

Guanidine perchlorate, $CH_6N_3ClO_4$, forms anhydrous, non-hygroscopic crystals, and in quantities of 2—3 mg. does not explode when struck on an anvil with a hammer. The values of d^{15} in terms of p, the percentage of salt in solution, are, for lithium perchlorate solutions, $0{\cdot}99913+5{\cdot}9396\times10^{-3}p+1{\cdot}1902\times10^{-5}p^2+5{\cdot}85\times10^{-7}p^3$, and for silver perchlorate solutions, $0{\cdot}99913+7{\cdot}9183\times10^{-3}p+8{\cdot}762\times10^{-5}p^2-5{\cdot}35\times10^{-7}p^3$. T. H. Pope.

Sodium perchlorate solutions. E. Cornec and J. Dickely (Compt. rend., 1927, 184, 1555—1577).—Determinations of the solubility in water of sodium perchlorate at 0—100° are in agreement with those of Freeth (A., 1924, ii, 336). The transition temperature (anhydrous–monohydrate) is 52·75°. The density of a saturated solution of the anhydrous salt is independent of temperature, since the increase in density on cooling produced by contraction is exactly compensated by the decrease due to crystallisation. The influence of sodium chloride, sodium nitrate, and potassium perchlorate on the transition temperature was examined. J. Grant.

Rotatory power of tartaric acid in solutions of calcium chloride. E. Darmois (Compt. rend., 1927, 184, 1438—1440).—The dispersion of dilute solutions of tartaric acid in a solution of calcium chloride is feebler than that which would correspond with the two components hitherto assumed to be present. Parallel curves result when [α], and the ratio of the amounts of hydrochloric and tartaric acids required to produce the same concentration of hydrogen ions in solutions of these acids in calcium chloride solution, are plotted against the concentration of the tartaric acid. Thus variations of [α] and the p_H value are due to the same cause. The anomalies of tartaric acid may be due to the great variation of [α] from one solvent to another, and the smaller variation due to a change in concentration and the consequent production of simple and complex ions in water and other solvents, respectively. The α- and β-tartaric acids may be two isomeric weak or ψ-acids in equilibrium. J. Grant.

Rotatory dispersion, in the ultra-violet region, of aqueous solutions of tartaric acid. R. Descamps (Compt. rend., 1927, 184, 1543—1546).—The dextrorotations of aqueous solutions of tartaric acid (approximately 1, 10, 20, and 50%) increase to a maximum and then fall to zero between λ 5780 and 3650 Å. At lower wave-lengths the rotation is lævo, and increases regularly up to the limiting wave-length employed (2536). The dextrorotations decrease and the lævorotations increase with the concentration. The observed constancy of the Darmois ratio, which is characteristic of a mixture of two substances, and the high lævorotations found even with dilute solutions confirm Longchambon's theory (A., 1926, 385).

J. Grant.

Maximum absorption and the Kundt displacement. P. Vaillant (Compt. rend., 1927, 184, 1659—1660).—An attempt has been made to confirm the modified form of Kundt's rule suggested by the author (this vol., 508) according to which the displacement of the wave-length of maximum absorption λ_m towards the red is determined by the difference between two terms which are proportional respectively to the refractive index and the density of the solvent. The solutions used were obtained by diluting 5 c.c. of an alcoholic solution of eosin to 100 c.c. with each of three solutions made up from water and a glycerol–alcohol mixture having the same density as water,

and also five mixtures of alcohol and a benzene-mineral oil mixture having the same density as alcohol. The observed and calculated values of λ_m differ appreciably for three of the eight solutions.
J. GRANT.

Absorption of ultra-violet light by aqueous sugar solutions in relation to the constitution of the sugar molecules. P. NIEDERHOFF (Z. physiol. Chem., 1927, **167**, 310—311).—The amount of ultra-violet light absorbed by a dextrose solution (cf. this vol., 396) is very small compared with that absorbed by acetone. This is due to the fact that the majority of the sugar molecules in aqueous solution have the ring structure. Similar relations hold for lævulose and the other sugars examined.
A. WORMALL.

Diffusion of electrolytes. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1926, **58**, 623—629).—The solution to be investigated is allowed to diffuse through a tube fitted with pairs of electrodes at certain distances. The conductivity is measured from time to time, and results are expressed as concentrations. Applying Fick's law, and Planck's expressions for the conduction of heat and electricity in solutions of electrolytes, an expression capable of experimental verification is deduced. The results obtained with calcium chloride solutions show that Fick's law is a limiting case, applicable only to very dilute solutions, and the velocity of diffusion depends both on the concentration gradient and on the absolute value of the concentration. M. ZVEGINTZOV.

Condition of aqueous solutions of sodium urate. G. ETTISCH, L. F. LOEB, and B. LANGE (Biochem. Z., 1927, **184**, 257—272).—Observations on the dark-field illumination, ultrafiltration, and polarisation associated with the Tyndall effect suggest that solutions of sodium urate contain a sol in equilibrium with a true solution. An attempt is made to calculate the number and size of the sol particles and to derive the effect produced by temperature change and by the addition of alkali. Urate sol is considered as a "colloidal electrolyte."
R. K. CANNAN.

Preparation of colloidal lead. F. BISCHOFF and N. R. BLATHERWICK (J. Pharm. Exp. Ther., 1927, **31**, 27—34).—Using a high-frequency current of 10,000 volts, a colloidal solution of lead is prepared according to the Bredig method by arcing between lead electrodes in 400 c.c. of a solution containing 5 g. of dextrose and 4 g. of gelatin per litre, the reaction being adjusted to p_H 7·5 by the addition of potassium hydroxide. The larger particles are removed from the dark solution so obtained by centrifuging, and the resulting preparation is then stable for months if air is excluded. In particular, the toxicity does not increase with time. Besides dextrose, lævulose and glycerol also exert a marked action in preventing the rapid oxidation which occurs in the absence of any polyhydroxy-compound. The solutions of colloidal lead are precipitated with half-saturated sodium chloride solutions, and are very sensitive to acid. W. O. KERMACK.

Preparation of a stable colloidal solution of lead. M. TELKES (J. Amer. Chem. Soc., 1927, **49**, 1382—1386).—An apparatus is described by means of which a colloidal solution of lead in pure water is prepared in an atmosphere of hydrogen by passing an electric spark between lead electrodes immersed in the water. The resulting colloidal solution is black, and is stable when kept in an atmosphere of hydrogen, only the larger particles being deposited. The highest concentration of lead obtained in such a stable solution was 0·2%. When exposed to the air, the solution turns grey in a few hours, and all the lead is precipitated in a few days as a greyish-white powder, consisting chiefly of lead carbonate.
F. G. WILLSON.

Preparation and properties of colloidal molybdic acid. S. J. DIJATSCHKOVSKI and A. V. DUMANSKI (J. Russ. Phys. Chem. Soc., 1926, **58**, 630—638).—The behaviour of free molybdic acid, gradually liberated by the successive addition of small quantities of hydrochloric acid to a solution of sodium molybdate, was investigated by the electrolytic method described by Dumanski (this vol., 308). The free acid reacts in successive stages with the alkali molybdate to give complexes: $Na_2MoO_4+H_2MoO_4=Na_2O(MoO_3)_2+H_2O$ etc. A theoretical method of calculating the amount of hydrochloric acid necessary for the formation of each complex is described, and the behaviour of sodium chromate, which under the same conditions gives similar results, compared. Cryoscopic experiments corroborate the electrolytic data. Two of the theoretically possible complexes, $Na_2O(MoO_3)_4$ and $Na_2O(MoO_3)_8$, were synthesised, and their conductivities and *f.-p.* depressions found to correspond with those obtained on adding the amount of acid required by the theory. Experiments with Zsigmondy's ultramicroscope showed that colloidal particles appear only when the octamolybdate $Na_2O(MoO_3)_8$ should be formed, the presence of which is confirmed by the characteristic brown precipitate obtained with potassium ferrocyanide.

The colloid was not coagulated either by cooling or heating or addition of electrolytes, and had an apparent mol. wt. of 1139; it thus could be classed with the semi-colloids. A second modification of the colloid—a suspension of the oxide MoO_3, which has much larger particles, exhibiting Brownian movement—also exists. M. ZVEGINTZOV.

Formation of cellulose hydrate. R. O. HERZOG (Z. physikal. Chem., 1927, **127**, 108—112; cf. this vol., 342).—Further examples are given which show that the *X*-ray changes associated with the formation of cellulose hydrate (mercerisation) may be reproduced by dispersion of cellulose to a sol without chemical change. Although the swelling of cellulose during mercerisation is reversible, this is not the case for the lattice changes which occur.
G. A. ELLIOTT.

Effect of gelatin on the size and distribution of macroscopic crystals grown from aqueous solutions. T. S. ECKERT and W. G. FRANCE (J. Physical Chem., 1927, **31**, 877—881; cf. France and McBurney, A., 1924, ii, 314).—The presence of gelatin (up to 1%) in aqueous solutions of copper sulphate and of lead nitrate decreases markedly the average size of the crystals obtained by evaporation at 27°, but increases the uniformity of the size, the effect increasing with a rise in concentration of the gelatin. Two different grades of commercial material produced similar results. The influence of gelatin on microscopic crystals formed by electrical or chemical precipitation is thus similar to its influence on macroscopic crystals grown from aqueous solution by evaporation. L. S. THEOBALD.

Viscosity of some hydrophobic sols and the effect of addition of electrolytes. D. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1927, 42, 124—134).—Viscosity measurements were carried out on sols of arsenious sulphide, ferric hydroxide, sulphur, silver, potassium stearate, dicyanine, Prussian-blue, copper ferrocyanide, crystal-violet, and molybdic acid. On addition of small amounts of electrolytes, the charge of the sols is raised and the viscosity lowered; with increasing concentration of the electrolyte, the viscosity passes through a minimum and then rises; at higher concentrations of electrolyte, before flocculation occurs, the charge is reduced and the viscosity rises rapidly. The variation of the viscosity of sols of Congo-red, aluminium hydroxide, Prussian-blue, copper ferrocyanide, and stannic acid with concentration and temperature was also studied. The temperature coefficients are almost identical with those of pure water, suggesting that the particles are enveloped in a sheath of water molecules. Ferric hydroxide and aluminium hydroxide sols are more strongly hydrated than sols of arsenious sulphide of equal concentration. The viscosity of ferric hydroxide sol is lowered by potassium chloride more than by equivalent quantities of hydrochloric acid or ferric chloride. Potassium chloride has an even greater effect on the viscosity of arsenious sulphide sol, but the effect is not so great as that produced by sodium hydrogen sulphide. The viscosity of hydrolysable sols is not diminished by acids to the same extent as by other electrolytes, showing that the repression of hydrolysis raises the stability of such sols.

E. S. HEDGES.

Ageing phenomena in viscosity and conductivity of some sols and electrolytes. N. R. DHAR and D. N. CHAKRAVARTI (Kolloid-Z., 1927, 42, 120—124).—The importance of defining the age of a sol in considering its properties is emphasised. The hydrophobic sols, ferric hydroxide, Prussian-blue, copper ferrocyanide, stannic acid, arsenious sulphide, and crystal-violet, undergo a fall in viscosity and an increase in conductivity with age. On the other hand, the hydrophilic sols potassium palmitate and potassium stearate increase in viscosity with age, whilst the conductivity decreases. Sols of Congo-red and molybdic acid occupy an intermediate position, in that there is a very slight fall in viscosity and an increase in conductivity with age. Sols of ferric hydroxide and stannic acid prepared in the cold vary with their age to a much greater extent than do sols of the same substances prepared under boiling conditions; heating hastens the ageing phenomena. Solutions of cerium nitrate and of nickel sulphate show a very slight increase in conductivity with time.

E. S. HEDGES.

Dispersion of high-molecular compounds by very soluble, strongly hydrated substances. P. P. VON WEIMARN (Kolloid-Z., 1927, 42, 134—140).—The classification of disperse systems into thermodynamically stable "solutoids" and thermodynamically unstable "dispersoids" is discussed and some difficulties are pointed out (*e.g.*, a lowering of temperature may cause a change from the solutoid to the dispersoid state). Casein, fibroin, and cellulose can be dispersed by heating with concentrated solutions of polyphenols in place of the inorganic salts which have been used formerly. By adding casein in small quantities with constant stirring to an aqueous solution of pyrogallol at its b. p. (105—108°), a sol containing 10% of casein can be obtained in a few minutes. With resorcinol as the dispersing agent, the action takes place with greater difficulty. The sols are very viscous even at the b. p. Elastic coagula are obtained by addition of water or alcohol. Natural silk disperses readily in boiling aqueous solutions of pyrogallol or resorcinol (115—125°), the sols (containing about 15% of silk) being very viscous. Addition of water causes a turbidity, but a gelatinous coagulum is produced by addition of alcohol. Cellulose in the form of filter-paper disperses with great difficulty in aqueous pyrogallol solutions of b. p. 145—155°. E. S. HEDGES.

Protective action of Rochelle salt on cupric oxide sol. I. S. K. BASU and M. LAKSHMANAN (J. Indian Chem. Soc., 1927, 4, 29—36).—At low concentrations, *e.g.*, 0·003 millimol. per litre, sodium potassium tartrate coagulates cupric oxide sol; at higher concentrations, the salt causes a reversal of charge in the sol and exerts a protective action, increasing with the concentration of the salt added until at a concentration of 800 millimol. per litre the sol begins to dissolve to a bluish-green solution. The adsorption of tartrate ions by the sol, when plotted against the sodium potassium tartrate concentration, gives a curve which is convex to the concentration axis. The mechanism of protection and coagulation is discussed. B. W. ANDERSON.

Colloid chemistry of "viscose" solutions. IV. Gel-coagulation. T. MUKOYAMA (Kolloid-Z., 1927, 42, 180—183).—In the ageing of viscose solutions, two processes may occur, according to the following scheme: (1) sol $\longrightarrow$ gel $\longrightarrow$ synæresis, (2) sol $\longrightarrow$ coagulation. When processes (1) and (2) take place simultaneously, a coagel is produced. This process of gel-coagulation has been studied, and it appears to occur most readily when the viscose has an alkali content of about 5% and when the content of cellulose is low. The change is hastened by the addition of glycerol, but is prevented by adding an aged viscose sol to the fresh sol. E. S. HEDGES.

Alleged second isoelectric point of gelatin. B. N. GHOSH (J.C.S., 1927, 1250—1252).—The electric charge of gelatin, in contact with solutions of p_H ranging from 3·6 to 8·8, has been determined by an electro-endosmotic method. At p_H 4·8, the charge of the gelatin is zero, becoming negative above this value and positive below. There is no evidence of the second isoelectric point at p_H 7·7 mentioned by other investigators. The electro-endosmotic flow of water through the set gel indicates that the latter has a porous, network-like structure. M. S. Burr.

Effect of colloidal and semi-colloidal ferric oxide sols on aqueous gelatin solutions. R. Wintgen and M. Vöhl (Kolloid-Z., 1927, 42, 140—149).—Experiments were carried out in the same manner as in previous work (cf. A., 1925, ii, 524; 1926, 1204). The mutual precipitation of chromic oxide sol and gelatin sol was formerly found to differ from that of ferric oxide sol and gelatin sol. It is now found that when most of the chloride ion is removed by thorough dialysis, the behaviour of a ferric oxide sol towards gelatin is similar to that of a chromic oxide sol. From the results, the "equivalent aggregate weight" of gelatin is deduced, giving a mean value of 32,600. This result is discussed in connexion with the values obtained by other workers by different methods. E. S. Hedges.

Distribution of hydrogen ions between water and gelatin. J. J. Joukov, S. A. Tschukarev, and J. N. Bushmakin (J. Russ. Phys. Chem. Soc., 1926, 58, 639—658).—The action of acids and alkalis on gelatin was investigated by the electrometric titration of various acids by alkalis in solutions containing gelatin. The change in p_H of the acid solutions on addition of alkali was determined by a hydrogen electrode. With hydrochloric acid and sodium hydroxide, the presence of gelatin increased the value of the p_H in the acid region, but lowered it in the alkaline. For all concentrations, the isoelectric point was found to be p_H 5·6, which was higher than that usually accepted for gelatin (4·7), but depended on the nature of the gelatin. The amounts of free acid or alkali are proportional to the amount of gelatin at any fixed p_H, within the limits p_H 3 to p_H 10·5, so that a method is devised for calculating the amounts of acid or alkali necessary to obtain any value of p_H in a gelatin solution of given concentration. The amount of hydrogen ion or hydroxyl ion "bound" by 1 g. of gelatin is constant for a given p_H and independent of the concentration of the gelatin, indicating that, probably, the hypothetical, easily hydrolysed compounds between it and the electrolytes do not exist, but the phenomena are due to the adsorption of ions by the gelatin micelle. Further, although the gelatin has acid properties, it "binds" acids more readily than alkalis.

Experiments with sulphuric and acetic acids gave identical results. The isoelectric point is independent of the nature of the acid. Earlier hypotheses are discussed in the light of the above results. M. Zvegintzov.

Hydration of gelatin in solution. M. Kunitz (J. Gen. Physiol., 1927, 10, 811—836).—The volume of gelatin present in solution is calculated from the viscosity by means of the formula $\eta/\eta_0=(1+0\cdot5\varphi)/(1-\varphi)^4$ (where η is the viscosity of the solution, η_0 the viscosity of the solvent, and φ the volume occupied by the solute per unit volume of the solution). When the concentration of gelatin is corrected for the volume of water of hydration so determined, the relation between the osmotic pressure and the corrected concentration becomes linear. Calculation on this basis gives the mol. wt. of gelatin as 61,500 at 35°. Data are presented which support the view that the hydration of isoelectric gelatin is due to the osmotic pressure of quantities of a soluble substance present in the interior of the micelles (cf. Northrop and Kunitz, A., 1926, 1098). In gelatin at p_H other than that of the isoelectric point, the degree of hydration is increased by osmotic forces which appear as the result of the Donnan membrane equilibrium. W. O. Kermack.

Thermal disaggregation of gelatin. Organic natural substances of colloidal nature. M. Frankel (Z. physiol. Chem., 1927, 167, 17—36).—Experiments have been carried out to determine the effect of incubation at 36·5° on some of the properties of gelatin solution, when compared with control solutions at the ordinary temperature. Incubation increases the dialysability of the gelatin, and the amount of non-dialysable gelatin may fall to 50% or even less of the non-dialysable gelatin of the control. There is a marked fall in the power of gel-formation and in the optical rotation of the solution; after 650 hrs., the rotation was only 63% of that of the control solution. The importance of these observations lies in the fact that the phenomena occur under variations in the conditions which are biologically possible and that disaggregation takes place without the intervention of any enzyme. A. Wormall.

Determination of velocity of cataphoresis of colloidal particles. A. F. Gerasimov (J. Russ. Phys. Chem. Soc., 1926, 58, 601—609).—The velocity of cataphoresis of colloidal solutions was investigated by two varieties of the moving boundary method, to determine the effect of the nature of the electrolyte above the colloid and the influence of outside factors. The practical and theoretical limitations of the moving boundary method and the means of overcoming them are discussed. Experiments made with "collargol" in presence of sodium carbonate, sodium sulphate, and sodium hydroxide show that the velocity of cataphoresis increases at first, soon reaching a constant value. The rate of increase is proportional to the concentration, and differs for different electrolytes. It is probably due to the diffusion of ions into the colloid. The effects of the "separation potential," due to the lagging of the colloid behind the electrolyte, the diffusion of the colloid into the electrolyte, convection currents, and hydrostatic pressure are discussed and attempts at correction made, but without success. M. Zvegintzov.

Rôle of some physical factors in the electro-capillary penetration of coloured colloids. W. Kopaczewski and W. Szukiewicz (Compt. rend., 1927, 184, 1443—1445; cf. B., 1926, 353).—The effect of substances having special physical properties on the electro-capillary penetration through filter-paper of 2% aqueous colloidal solutions of direct-black *W* (negative), congorubin *FF* (amphoteric), and direct-grey *4B* (positive) has been studied. In such experiments, account must be taken of the viscosity of the medium, which tends to reduce the capillary effect. A reduction in surface tension produces an increase in the electro-capillary penetration (A., 1926, 679). The electro-capillary properties of a hydrosol of sodium oleate (1%) show periodic variations. J. Grant.

Solubility and diffusion of hydrogen in metals. G. Borelius (Ann. Physik, 1927, [iv], 83, 121—135).—The solubility c of hydrogen at pressure p in metals at high temperatures is given by the empirical equation $c=\alpha e^{-\beta/T}\sqrt{p}$, in which β is a constant characteristic of the metal under investigation and α a temperature function which is apparently the same for all metals at high temperatures. The above equation is given a theoretical interpretation. The fraction of the volume of metal which is occupied by hydrogen must be of the order 1, and experiment shows it actually to vary between 0·1 and 1·0. The speed with which hydrogen traverses a metal sheet when the pressures on the sides are p and zero, respectively, is given by $m=\text{const.}(p^{\frac{1}{2}}-p_t^{\frac{1}{2}})$ at constant temperature, when $p_t^{\frac{1}{2}}$ is dependent on temperature. On the assumption that the diffusion is analogous to the passage of hydrogen through porous materials, the form of the equation, the order of magnitude of $p_t^{\frac{1}{2}}$, and also certain experimental results all receive rational explanation. The assumption also leads to the equation $m=kcT$ (where k is a constant), a relation which is confirmed by the data on iron, platinum, and palladium–platinum at high temperatures. Deviations with nickel and palladium–platinum at lower temperatures are explained by the restricted freedom of part of the dissolved gas. R. A. Morton.

Permeability of iron and platinum to hydrogen. V. Lombard (Compt. rend., 1927, 184, 1557—1559; cf. A., 1926, 349).—The permeability of iron to hydrogen at 517° at pressures below 760 mm. of mercury is proportional to the square root of the pressure. At 760 mm. of mercury, the permeability (d) of iron or of platinum follows the rule $d=a^t$, where a is a constant and t the temperature. The permeability of iron is the greater, and its value is similar to that of nickel. J. Grant.

Permeability of membranes. II. Determination of ionic transfer numbers in membranes from concentration chains. L. Michaelis, R. McL. Ellsworth, and A. A. Weech (J. Gen. Physiol., 1927, 10, 671—683).—The transport number of an electrolyte in the pores of a narrow-pored collodion membrane (cf. Michaelis and Hayashi, A., 1926, 901) has been calculated from measurements of the *P.D.* between differently concentrated solutions of the same electrolyte on opposite sides of the membrane. The concentrations were always taken in the ratio of 2 : 1. The transport number of the chlorine ion increases rapidly as the concentration of the solution becomes greater. When associated with various cations, the transport number of the chlorine ion changes in the same way as it does in the absence of a membrane. W. O. Kermack.

Permeability of membranes. III. Electric transfer experiments with dried collodion membranes. L. Michaelis, A. A. Weech, and A. Yamatori (J. Gen. Physiol., 1927, 10, 685—701).—Direct determination of the transport numbers of various salts across a collodion membrane leads to results which, in spite of minor discrepancies, are in substantial agreement with those of the preceding paper (cf. preceding abstract). The mobility of the anions is less than that of the cations, and the transport number itself depends on the concentration of the salt. W. O. Kermack.

Collodion membranes. I. Preparation and characterisation of uniform membranes. N. Bjerrum and E. Manegold (Kolloid-Z., 1927, 42, 97—112).—Collodion membranes prepared by the usual method are not uniform as regards permeability. As criteria of uniformity, the following characteristics of the membrane may be used: (1) thickness, (2) water content per c.c. of membrane, (3) permeability to water. The permeability depends on the thickness and on the time allowed for evaporation of the solvent from the membrane before immersing in water. Uniform flat membranes may be prepared by pouring a measured quantity of collodion solution from a burette on to a surface of mercury enclosed by an iron ring floating on the surface of the mercury. The rate of evaporation of the solvent is controlled by a fan revolving at a definite rate. The membrane is removed from the iron ring by immersing in water for some hours. Uniform cylindrical membranes may be prepared by placing a known quantity of collodion solution inside a horizontal glass cylinder, which is rotated, and through which is passed a current of dry air at a definite rate. The product of permeability to water and thickness is constant for membranes of equal water content. When the film is formed in an atmosphere containing water vapour or, better, acetone vapour, the permeability to water is increased, although no alteration takes place in the thickness or the water content. E. S. Hedges.

Equation of state of a gaseous mixture. J. E. Lennard-Jones and W. R. Cook (Proc. Roy. Soc., 1927, **A**, **115**, 334—348).—It is shown that the virial coefficient B in the equation $pv=RNT(1+B/v)$ is a quadratic function of the relative concentrations. This relation reproduces satisfactorily the results obtained by Holborn and Otto (A., 1924, ii, 385) for the isotherms of a helium–neon mixture, and by Verschoyle (A., 1926, 894) for the isotherms of a hydrogen–nitrogen mixture. A method for determining the forces between the unlike molecules of a mixture is deduced. It is shown that the pressure of a gaseous mixture may be greater than that of an equal concentration of either of the constituents. This is a natural consequence of the fact that the virial coefficient passes through a maximum value.

L. L. Bircumshaw.

Chemical equilibria in non-ideal gases the isometrics of which are linear. F. G. Keyes (J. Amer. Chem. Soc., 1927, 49, 1393—1403).—The Keyes equation of state, $p=RT/(v-\beta e^{-\alpha/v})-A/(v+l)^2$, holds for a mixture of n_A mols. of A and n_B mols. of B, providing the isometrics of the mixture are linear, where $A=(n_A\sqrt{A_A}+n_B\sqrt{A_B})^2$; $\beta=n_A\beta_A+n_B\beta_B$; $\alpha=n_A\alpha_A+n_B\alpha_B$; and $l=n_Al_A+n_Bl_B$, RT being multiplied by n_A+n_B. An equation is deduced thermodynamically from this for the equilibrium constant of the reaction between two gases in a mixture, and is applied with moderate success up to 600 atm. to the ammonia equilibrium. S. K. Tweedy.

Equilibrium in a gaseous phase between acid and base: volatility product. A. Tian (Compt.

rend., 1927, **185**, 67—69).—The law of mass action suggests that the precipitation of solid salt from a mixture of the corresponding volatile acid and basic constituents will occur only when the product of the concentration of the acid and base reaches a certain value. The law has been tested experimentally for acetic acid and pyridine, and, allowing for the great experimental errors, appears to be verified.

J. Grant.

Influence of intensive drying on the physical and chemical properties of matter. A. Smits (Natuurwetens. Tijdsch., 1927, **9**, 55—65).—A *résumé* of facts and theories relating to the properties of substances intensively dried, and the supposed changes in the internal equilibria (cf. A., 1926, 1206).

S. I. Levy.

Causes of the colour changes of cobalt chloride solutions. II. J. Gróh and R. Schmid (Z. anorg. Chem., 1927, **162**, 321—332).—The molecular extinction coefficients of cobaltous chloride solutions in acetone and in propyl alcohol have been determined in presence of lithium and calcium chlorides of varying concentrations. Assumptions such that a series of complexes are formed lead to anomalies, and it is postulated therefore that the observed variations in the extinction coefficient are due to variations in the concentration of only one complex. Determination of the solubility of lithium chloride in acetone solutions of cobaltous chloride indicate that the complex formed has the formula $CoCl_4''$, a view which is confirmed by conductivity measurements of solutions of cobaltous chloride in acetone in presence of various proportions of lithium chloride. Further, *E.M.F.* measurements show that an excess of chloride ion is present in mixed acetone solutions of lithium and cobaltous chlorides when the former is present in greater quantity than is required for the formation of $CoCl_4''$. Silver chloride is soluble in acetone when lithium chloride is present, whereas cobaltous chloride does not increase its solubility. Measurements of the solubility of silver chloride in acetone solutions of cobaltous chloride of constant concentration, but of increasing lithium chloride concentration, show that a sharp increase in the solubility occurs when lithium chloride is present in excess above that required for $CoCl_4''$ formation. This view of the nature of the complex is further supported by measurements of ionic mobility.

H. F. Gillbe.

Iodine–iodine equilibrium in solvents forming brown solutions. J. Gróh [with (Frau) M. Radványi, L. Urbanek, and K. Lányi] (Z. anorg. Chem., 1927, **162**, 287—300).—By spectrophotographic measurements and by determination of the increase of solubility of iodine in carbon disulphide and carbon tetrachloride when an active solvent (*i.e.*, one which gives a brown solution) is added, it has been established that 1 mol. of iodine combines with 1 mol. of the latter to form an additive compound. The equilibrium constant of this additive reaction has been determined in carbon disulphide solution in presence of methyl, ethyl, and propyl alcohols and ethyl ether, and in carbon tetrachloride solutions containing methyl, ethyl, and propyl alcohols, ethyl ether, and acetic acid. The heat of the reaction, calculated from the equilibrium constant at various temperatures, lies between 3000 and 4000 g.-cal./mol.

H. F. Gillbe.

Existence of hexatomic iodine molecules in solutions of iodine in carbon disulphide and carbon tetrachloride. J. Gróh and J. Szelestey (Z. anorg. Chem., 1927, **162**, 333—343).—The velocity of the addition of iodine to erucic acid in carbon tetrachloride solution is proportional to the concentration of the acid, but not to that of the iodine. This is ascribed to association of the iodine molecules; only the associated molecules are capable of reacting, since the velocity of the reaction decreases with increasing dilution, *i.e.*, as the association diminishes. Further, investigation of the reaction velocity shows it to be proportional to the cube of the iodine concentration, *i.e.*, that the active molecule is I_6. The same is true of solutions in carbon disulphide. In neither solvent is the reaction complete, the equilibrium constant for the carbon disulphide solutions being 7·78, and for the carbon tetrachloride solutions 19·80.

Measurements of the reaction velocity at 35°, 15°, and 13·8° show that it diminishes rapidly with rise of temperature. It is assumed that the velocity coefficient measured is the product of the true velocity constant of the reaction and the association constant of iodine. By taking an average value for the former, viz., 2·5 for 10° rise of temperature, the heat of the reaction $3I_2 \longrightarrow I_6$ in carbon tetrachloride solution is 19,270 g.-cal./mol. of I_6 formed, and in carbon disulphide solution 17,070 g.-cal./mol.

H. F. Gillbe.

Spectrographic method for the determination of dissociation constants. R. A. Morton and A. H. Tipping (J.C.S., 1927, 1398—1399).—The dissociation constant of a weak acid obeying the dilution law is determined by measuring the maximum extinction coefficient for a mixture of the acid with violuric acid of known concentration (cf. A., 1926, ii, 9). The values are only approximate. The method can also be used for measuring the distribution of a base between violuric and another weak acid.

S. K. Tweedy.

Dissociation constants of hypophosphorous, phosphorous, and phosphoric acids. I. M. Kolthoff (Rec. trav. chim., 1927, **46**, 350—358).—The ionisation constant of hypophosphorous acid, as determined by the classical method, increases from $1·0\times10^{-2}$, in a solution of concentration 0·001*M*, to $6·2\times10^{-2}$ in 0·05*M* at 18°. Similarly, the first ionic dissociation constant of phosphorous acid increases from $1·6\times10^{-2}$ in 0·001*M* to $6·2\times10^{-2}$ in 0·1*M* solution. K_2 for phosphorous acid, determined by measurements of the p_H value of mixtures of the secondary phosphite with hydrochloric acid, by the quinhydrone electrode, is 2×10^{-7} at 18°. By measurements of the p_H values of mixtures of secondary sodium phosphate and sodium hydroxide solutions, and correction for the concentration of hydroxyl ions, K_3 for phosphoric acid is found to have a mean value of 5×10^{-13}, which is in good agreement with the value found by Abbott and Bray (A., 1909, ii, 660). Taking into consideration the activity of the ions, the conductivity data of

Abbott and Bray (*loc. cit.*) at 18° give values of K_1 for phosphoric acid varying from $8 \cdot 5 \times 10^{-3}$ to $9 \cdot 5 \times 10^{-3}$ for concentrations between $0 \cdot 01M$ and $0 \cdot 1M$. The same considerations, however, applied to the calculation of K for hypophosphorous acid, give an increase from $2 \cdot 0 \times 10^{-2}$ to $5 \cdot 3 \times 10^{-2}$ for solutions from $0 \cdot 001M$ to $0 \cdot 1M$. According to Kossel's theory, there should be a marked increase in ionisation constants in the order H_3PO_2, H_3PO_3, H_3PO_4, and no explanation of the anomalous behaviour of these acids is yet forthcoming. Hypophosphorous acid, which behaves as a strong monobasic acid, may be titrated, using methyl-orange as indicator. The first stage of phosphorous acid may also be similarly titrated, provided a comparison solution of p_H 3·85 is used. A sharp end-point may be obtained for the second stage in the titration of phosphorous acid by using thymolphthalein as indicator. In the determination of phosphorous acid by oxidation with bromine to phosphoric acid, it was found that, although this reaction goes only slowly in strongly acid solution, it goes very rapidly when the solution is buffered to p_H 4—5. M. S. BURR.

System carbonic acid–carbon dioxide–water. I. Determination of the true dissociation constant of carbonic acid. F. J. J. BUYTENDYK, R. BRINKMAN, and H. W. MOOK (Biochem. J., 1927, **21**, 576—584).—The change in hydrogen-ion concentration in a hydrogen carbonate solution to which strong acid was added was studied by continuous observations of the p_H of the system, with an accuracy of 0·005 p_H and a time lag not exceeding 0·12 sec. The true dissociation constant of carbonic acid is 4×10^{-4}. The hydration constant of carbon dioxide at p_H 7·35 is $5 \cdot 85 \times 10^{-5}$, and the dehydration constant of carbonic acid at p_H 6 is 1·73. The velocity of dehydration is proportional to the hydrogen-ion concentration. At p_H 7 the hydrogen carbonate system has practically no immediate buffering capacity. S. S. ZILVA.

Mechanism of titration with adsorbed indicators. J. HODAKOW.—See this vol., 743.

Ebullioscopic study of the complexes produced by mercuric chloride and the alkali chlorides. F. BOURION and E. ROUYER (Compt. rend., 1927, **184**, 1449—1452; cf. A., 1926, 796).—The ebullioscopic study of solutions containing mercuric chloride and the alkali chlorides affords evidence of the presence of the two complexes $M[HgCl_3]$ and $M_2[HgCl_4]$. The affinity constants for complexes of the latter type are $5 \cdot 45 \times 10^{-2}$ and $1 \cdot 31 \times 10^{-1}$ when M is K and Na, respectively. J. GRANT.

Activity coefficients of sulphuric acid in aqueous solutions with sodium sulphate at 25°. M. RANDALL and C. T. LANGFORD (J. Amer. Chem. Soc., 1927, **49**, 1445—1450).—The activity coefficients, γ, of sulphuric acid in sodium sulphate solutions are calculated from the *E.M.F.* of suitable mercurous sulphate–hydrogen cells. The relation of $\log \gamma$ to the fractional mean molality of the acid (cf. following abstract) is linear in the more dilute solutions and when the fractional average molality of the acid is large. Under these conditions, the principle of ionic strength agrees best with the facts. S. K. TWEEDY.

Activity coefficient of hydrogen chloride in aqueous solutions with barium and lanthanum chlorides at 25°. M. RANDALL and G. F. BRECKENRIDGE (J. Amer. Chem. Soc., 1927, **49**, 1435—1445).—From the *E.M.F.* of suitable calomel–hydrogen cells the activity coefficients, γ, of hydrogen chloride in pure aqueous solutions and in solutions of barium and lanthanum chlorides are calculated. For interpolation purposes the relation (M=molality or ionic strength) $M^{-\frac{1}{2}} \log \gamma = A + BM^{\frac{1}{2}}$ is more suitable than the functions usually employed. In mixtures of constant ionic strength, $\log \gamma$ is a nearly linear function of the ratio of the geometric mean of the molalities of the ionic constituents of the acid to the molality of pure acid at the same ionic strength. S. K. TWEEDY.

Vapour pressures and activities of aqueous solutions of sodium silicates. A. N. C. BENNETT (J. Physical Chem., 1927, **31**, 890—896).—The depressions of the dew-point of aqueous solutions of commercial sodium silicates and sodium hydroxide have been measured for solutions with the ratio $Na_2O : SiO_2$ varying from 1 : 0 to 1 : 3·95. The activity coefficients of the solutes calculated by the method of Lewis and Randall from these results are compared graphically with those obtained by Harned (A., 1925, ii, 397) and by Harman (this vol., 415). The introduction of an electromagnetic stirrer, which is described, increased the concordancy of the results. L. S. THEOBALD.

Activity of phenol in aqueous salt solutions. K. ENDO (Bull. Chem. Soc. Japan, 1927, **2**, 124—131).—An investigation of the influence of neutral salts on the partition of phenol between benzene and water shows that when the concentration of phenol in the benzene phase is maintained constant, the concentration C of phenol in the aqueous salt solution varies with the salt concentration S according to the equation $\log C_0/C = \beta S$, where C_0 is the corresponding concentration of phenol in the absence of salt and β a constant characteristic of the salt. The quantity β appears to be additive, *e.g.*, the differences between the β-values of corresponding sodium and potassium salts are constant within the limits of experimental error. The complete equation for the distribution of phenol between benzene and an aqueous salt solution at 25° is $B = 2 \cdot 272 \times 10^{\beta S} C + 37 \cdot 71 \times 10^{3\beta S} C^3$, where B and C are the molar concentrations of phenol in the benzene and aqueous layers, respectively. Measurements of the f. p. of aqueous solutions of sodium nitrate, with and without added phenol, furnish qualitative evidence in support of the theoretical deduction that the chemical potential X of phenol at a concentration C, in a salt solution of concentration S, is represented by the formula $X = Z_0 + \alpha S + RT \log_e C$, where Z_0 is the potential for unit concentration in the absence of salt and $\alpha = 2 \cdot 303 \beta RT$. The activity coefficient of phenol is $e^{\alpha S/RT}$. J. S. CARTER.

Relation between the activity of hydrogen and metallic cations in solutions of salts of the heavy metals. (MLLE.) M. QUINTIN (Compt. rend., 1927, **184**, 1657—1659).—Electrometric and colorimetric determinations of hydrogen-ion activities have shown that, in solutions of the sulphates and nitrates of zinc, cadmium, and copper, the activity of the metallic ion at all concentrations between *M*/2 and *M*/2048 is proportional to that of the hydrogen ion. By the choice of suitable conditions, the constant of proportionality can be made equal to unity.

J. Grant.

Vapour-composition relationships in the system bromine–water. F. H. Rhodes and C. H. Bascom (Ind. Eng. Chem., 1927, **19**, 480—481).—By the distillation method, it has been found that the percentage of bromine in the vapour given off by bromine water increases from 39·48 for a 0·2% solution to 97·7 for a 3·14% solution. The system with two liquid phases boils at 53·6° when the pressure is 748·8 mm. Under these conditions, the aqueous layer contains 3·50% of bromine and the vapour 98·85%.

C. Irwin.

Binary mixtures of volatile liquids in which the molecules of one component are partly associated. F. Michaud (Compt. rend., 1927, **184**, 1643—1645).—The partial vapour pressures of a normal component and of the free and associated molecules of a partly associated component can be calculated thermodynamically when the total vapour pressure as a function of the composition of the liquid phase and the compositions of the distillates are known. The dissociation of a volatile substance may then be studied by mixing it with a normal liquid, constructing the vapour-pressure isotherms, and determining the compositions of the distillates. In the case of mixtures of acetic acid and toluene the results are in substantial agreement with those obtained by experiment.

J. Grant.

System thallium–antimony. T. Barth (Z. physikal. Chem., 1927, **127**, 113—120).—*X*-Ray examination of alloys of these metals reveals the presence of mixed crystals of the compound TlSb with thallium, although the compound is not known in the pure state. The crystal lattice is of the space-centred cubic type (similar to that of cæsium chloride), the edge of the unit cube being approximately $3·85 \times 10^{-8}$ cm. It is shown that for crystals of this type the ratio of the intensity of reflection at the surfaces for which the sum of the indices is even, to the intensity at the surfaces for which this sum is odd, may readily be calculated from the ratio of the electron numbers for the two kinds of ions constituting the crystal.

G. A. Elliott.

Oxides. III. Oxides of antimony. A. Simon and E. Thaler (Z. anorg. Chem., 1927, **162**, 253—278).—The chief reasons for the conflicting statements in the literature concerning the oxides of antimony are the extreme slowness with which the equilibrium between antimony pentoxide and its decomposition products is attained, and the fact that many of the reactions which occur are irreversible. An oxide not previously described corresponds with the formula Sb_6O_{13}, *i.e.*, $Sb_2O_3,2Sb_2O_5$ or $2Sb_2O_4,Sb_2O_5$, and is probably an antimonyl antimonate having the structure $O{:}[Sb{:}(SbO_3)_2]_2$. This new oxide is very stable, and may be heated for a long period at 800° without decomposition commencing; when once decomposition has been initiated, however, it proceeds rapidly at lower temperatures. The tetroxide Sb_2O_4 is stable between 780° and 920°, but at 930° it decomposes very slowly but completely into antimony trioxide and oxygen. The colour changes which take place progressively as the temperature is raised indicate that the decomposition of antimony pentoxide involves the breaking down of a series of complex antimonyl antimonates, together with a change of valency from 5 to 3. The kinetics of the reactions favour this view. Quantitative investigation of the oxidation of the trioxide to the tetroxide by oxygen shows that this process takes place isothermally at 370°, with no indication of the production of intermediate oxides.

The slowness with which antimony pentoxide decomposes is the cause of great difficulty in the determination of the vapour-pressure curves. At 400°, 2 months are required for a constant oxygen pressure to be attained. Nevertheless, by employing a manometer of small volume, the vapour-pressure curves of the oxides Sb_2O_5, Sb_2O_4, Sb_6O_{13}, and Sb_2O_3 have been determined, and from the data so obtained the heats of dissociation of the various oxides have been calculated as follows (kg.-cal.): $2Sb+5O$, 210·325; Sb_2O_3+2O, 42·925; Sb_2O_4+O, 15·035; $\frac{1}{3}(Sb_6O_{13}+O_2)$, 8·49; $Sb_2O_4+\frac{1}{3}O$, 6·545; $2Sb+4O$, 195·29; Sb_2O_3+O, 27·89; $2Sb+3O$, 167·4.

H. F. Gillbe.

Solubility of potassium ferrocyanide in water at temperatures up to 25°. R. H. Vallance (J.C.S., 1927, 1328—1334).—A number of methods of determining alkali ferrocyanides are critically discussed, and a new one is described involving the conversion of the ferrocyanide into the ferric condition by concentrated sulphuric and nitric acids and subsequent determination of the iron as ferric hydroxide. This method is employed in the determination of the solubility of potassium ferrocyanide in water, at temperatures from 7·4° to 25°. A break in the curve at 18° indicates a change in the solid phase. The density–temperature curve of saturated solutions also shows a slight change in direction above 17°. By the dilatometric method, the transition point is found to be 17·7°. The transition is not between two different hydrates, since crystals above and below the transition point exhibit no apparent difference, either in degree of hydration or in crystalline form. The work of earlier investigators suggests the existence of two stereoisomeric forms of potassium ferrocyanide.

M. S. Burr.

Solubility of uric acid in carbonates; effect of carbon dioxide. S. Lang and H. Lang (Biochem. Z., 1927, **185**, 88—112).—Under conditions in which the free escape of carbon dioxide is prevented (*e.g.*, on shaking in a closed flask), the solubility of uric acid bears an exponential relationship to the concentration of carbonate or hydrogen carbonate. The actual solubility observed is much less than would be expected, owing to the fact that small amounts of free carbon dioxide have a great depressing effect on the formation of the acid urate. The possible physiological significance of these results is discussed.

C. R. Harington.

Crystallisation of saturated solutions at the b. p. Method of physico-chemical analysis. E. Cornec and P. Klug (Compt. rend., 1927, **184**, 1448—1449).—The temperature at which a salt first starts to separate from a boiling solution containing two salts depends on the ratio of the amounts of the salts present in the initial solution. It may be determined by means of time–temperature curves. The method has been applied to mixtures of the chlorides and bromides of sodium and potassium. Mixtures of ammonium sulphate with copper and with zinc sulphates give curves with three branches, corresponding in each case with two simple salts, and a double salt formed from 1 mol. of each constituent salt. J. Grant.

Setting of plaster of Paris and existence of soluble anhydrite. P. P. Budnikov (Kolloid-Z., 1927, **42**, 149—154).—Calcium sulphate was prepared in absence of water by mixing solutions of calcium chloride and sulphuric acid in methyl alcohol. The product was obtained in a colloidal form: it was dried at 38°, and when heated at 600—700° lost 7—9% of its weight. The question of the existence of a soluble anhydrite thus remains open. The velocity of dissolution in water and the velocity of rehydration, as determined by the change in electrical conductivity, are greater for the synthetic material than for the natural material which has been heated at 140°. E. S. Hedges.

Equilibrium between crystalline zinc hydroxide and aqueous solutions of ammonium hydroxide and of sodium hydroxide. H. G. Dietrich and J. Johnston (J. Amer. Chem. Soc., 1927, **49**, 1419—1431).—Orthorhombic bipyramidal crystalline zinc hydroxide is prepared by the evaporation of ammonia from a solution of pure zinc hydroxide in ammonia. The crystals exhibit no cleavage planes and form a satisfactory zinc standard for volumetric work. The preparation and properties of the crystalline *compounds*, $4ZnO,ZnSO_4,9H_2O$ and $4ZnO,ZnCl_2,8H_2O$, are described. The solubility of the hydroxide crystals in ammonium and sodium hydroxide solutions at 0°, 25°, and 35° is recorded. From the *E.M.F.* of the cell $Zn,Zn(OH)_2$(cryst.)| NaOH soln.|HgO,Hg, the thermodynamic solubility product of the hydroxide is calculated as $3{\cdot}33\times10^{-7}$ at 25° (cf. Wijs, A., 1925, ii, 889). The activity coefficients of zinc hydroxide are calculated; they are very small in alkali solutions, indicating that nearly all the zinc is present as a complex ion. The upper limit for the solubility of zinc hydroxide in water is calculated as 2×10^{-5} mol./1000 g. at 25°. The following free energy changes (25°) are also calculated: $Zn(OH)_2 \longrightarrow Zn^{\cdot\cdot}+2OH'$, $\Delta F=22{,}490$ g.-cal.; $ZnO+H_2O(\text{liq.}) \longrightarrow Zn(OH)_2$, $\Delta F=108$ g.-cal. The dissociation constant of the zincate ion is estimated to be $3{\cdot}6\times10^{-16}$. S. K. Tweedy.

Ternary system barium iodide–iodine–water and the formation of polyiodides. A. C. D. Rivett and J. Packer (J.C.S., 1927, 1342—1349).—The system has been investigated at temperatures between −15·8° and 90°, and the results have been plotted on triangular diagrams. In addition to the hydrate, $BaI_2,2H_2O$, which appears a little below 0° and disappears at 98·9°, and BaI_2,H_2O, the temperature range of which has not been accurately determined, a third hydrate, $2BaI_2,15H_2O$, has been found which exists over the range −15·8° to 25·7°. The hepta- and hexa-hydrates, commonly assumed to exist, were not observed. No solid polyiodide was obtained, but remarkably high values for the solubility of iodine were found, especially at the higher temperatures. The saturated solution at 90° corresponds approximately with $BaI_2,10I_2$. For a constant water content of the solution, the ratio of iodine to iodide increases with increase of iodide concentration, and for constant iodide concentration it increases with temperature. The results are explained by supposing that water in a hydrated iodide ion is replaced by iodine, the heat of reaction of the simple ion with water being greater than that with iodine, so that the substitution of the latter for the former is endothermic. M. S. Burr.

System lead chloride–lead iodide–water. A. L. McR. Sowerby (J.C.S., 1927, 1337—1342).—The solubility curve for lead chloride and iodide together in water at 30° consists of three sections. The solid phase in equilibrium with solutions represented by the middle portion of the curve has a composition corresponding with the formula PbICl. This confirms the conclusions of Thomas (A., 1898, ii, 585). No other compound appears to be formed at this temperature. Two methods are described for the determination of small quantities of iodide in presence of chloride. M. S. Burr.

Ternary system sodium chloride–platinum chloride–water at 25°. T. A. Henke (J. Russ. Phys. Chem. Soc., 1926, **58**, 596—600).—The solubility data for the system indicate that the chloroplatinate is hydrolysed in solution.

M. Zvegintzov.

Reciprocal pair $NaCl+KClO_3 \rightleftharpoons NaClO_3+KCl$. C. Di Capua and U. Scaletti (Gazzetta, 1927, **57**, 391—399).—Measurements of solubility have been made at 20° of the isotherms derived for the systems $NaCl–NaClO_3–H_2O$, $NaCl–KCl–H_2O$, $KCl–KClO_3–H_2O$, and $NaClO_3–KClO_3–H_2O$. The ternary solid mixtures which exist in contact with the quaternary solutions are (1) $KClO_3$, NaCl, and $NaClO_3$, and (2) $KClO_3$, NaCl, and KCl. The percentage compositions of the corresponding saturated solutions are, respectively, (1) Cl 8·50; ClO_3 22·80; K 1; Na 11·20; H_2O 56·5, and (2) Cl 16·95; ClO_3 1·41; K 5·82; Na 7·98; H_2O 67·84. The Jänecke quadratic diagram has been constructed.

T. H. Pope.

Quaternary system $K_2O–NH_3–P_2O_5–H_2O$ between 0° and 25°. Separation phenomena between 0° and 70°. E. Jänecke (Z. physikal. Chem., 1927, **127**, 71—92).—Aqueous solutions containing tripotassium phosphate and ammonia may separate into two liquid phases. Crystallisation of the liquid containing the greater proportion of phosphate gives the hydrate, $K_3PO_4,8H_2O$

G. A. Elliott.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XIX. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 282—292).—

Theoretical. The phase rule is applied to investigate the influence of pressure on osmotic systems.

W. E. DOWNEY.

Rate of dissolution. A. E. MAKOVECKI (J. Russ. Phys. Chem. Soc., 1926, 58, 726—728).—The generally accepted formula which connects the rate of dissolution with the rate of diffusion is criticised. Any solution is regarded as a two-component system consisting of the saturated portion and excess of "free" solvent, and the rate of dissolution is considered to be proportional to the surface of the solid solute and the active mass of the "free" solvent. Equations are developed for the determination of the latter, and solubility experiments with sodium chloride and copper sulphate described, which are in agreement with the hypothesis.

M. ZVEGINTZOV.

Displacement of chemical equilibrium at bounding surfaces. D. DEUTSCH (Ber., 1927, 60, [*B*], 1036—1039).—If a 0·01% aqueous solution of thymolsulphonephthalein containing $1·6 \times 10^{-3}N$-hydrochloric acid is vigorously shaken with benzene, the colour of the turbid system changes to reddish-violet, but when quiescence is again established, the aqueous layer resumes its yellow colour and the benzene layer becomes colourless. The process is reversible, and benzene may be replaced by liquid paraffin or by air. If methyl-violet at p_H about >1 is used, an apparent increase of alkalinity is observed at the bounding surface. The effect cannot be merely optical, since it is not observed when the hydrogen-ion concentration of the solution is considerably different from that producing change of colour in the indicator, and, further, all changes in colour are those produced by a change in hydrogen- or hydroxyl-ion concentration on the indicator. Probably the effect is due to an alteration of the dissociation constants of the indicator at the surface.

H. WREN.

Reaction provinces. W. P. JORISSEN (Chem. Weekblad, 1927, 24, 294—296; cf. A., 1926, 1100).—The compositions of mixtures of three substances which will react under given conditions may be expressed by means of triangular diagrams, which mark out the limits of composition for the "reaction provinces." The slowing down and final arrest of the decomposition of ammonium dichromate by addition of potassium chloride and potassium sulphate are illustrated in this manner. The extent to which carbon dioxide and carbon tetrachloride vapour, separately and together, may be added to an explosive mixture of methane and air (9% methane) in order to render the whole non-explosive is shown both by a simple curve and by a triangular diagram. The conclusions of Tanaka and Nagai (A., 1926, 1106) on the limits of composition for explosibility in mixtures of hydrogen with air and ethyl bromide are discussed and criticised.

S. I. LEVY.

Reaction regions. XIV. Closed reaction region. W. P. JORISSEN and C. GROENEVELD (Rec. trav. chim., 1927, 46, 369—372; cf. A., 1926, 246; this vol., 314).—If a mixture of aluminium turnings or powder, sulphur, and silica be packed in a tube closed at one end and above it a layer of mixed sulphur and iron powder, ignition of the latter will bring about a reaction in the first mixture if the latter is of suitable composition. By taking definite proportions of two of the three constituents, determining the upper and lower limits of the amount of the third substance necessary to produce a reaction, and plotting on a ternary diagram, a closed curve is obtained. Mixtures of a composition represented by points within this curve will react; those outside will not.

M. S. BURR.

Radiochemistry and photo-electricity. R. AUDUBERT (J. Chim. phys., 1927, 24, 357—369).—The uncertainty involved in the application of the formula $Q=H(\nu'-\nu)$, where Q is the energy change, ν and ν' the frequencies for the direct and reverse reactions, and H the product of Planck's constant and Avogadro's number, may be avoided by taking as ν and ν' the threshold frequencies. This formula has been examined by means of *E.M.F.* measurements with a cell consisting of a solution of an electrolyte into which dip two electrodes, one kept dark and the other illuminated (cf. A., 1923, ii, 827). The threshold frequencies are obtained by assuming a linear form for the *E.M.F.*-frequency curve, and extrapolating to zero *E.M.F.* With ferric salts, the *E.M.F.* due to the light is positive, *i.e.*, the illuminated electrode behaves as anode. For ferrous sulphate, the observed *E.M.F.* is positive for p_H below 1·8, and negative for higher p_H. This effect is apparently due to the action of the light on the hydrogen ions bound electrostatically on the surface of the electrode, the true *E.M.F.* for ferrous salts always being negative. In this way, the value $-30,000$ g.-cal. is obtained for the energy of the reaction $2Fe^{\cdot\cdot}+2H^{\cdot}=2Fe^{\cdot\cdot\cdot}+H_2$, in good agreement with the value obtained from *E.M.F.* determinations with the cell $Pt|$acid solution$|KCl_{sat.}|$ ferrous salt$|Pt$. Similar experiments with sodium iodide solutions give $-26,000$ g.-cal. for the heat of the reaction $3I'=I_3'+2\ominus$, whilst *E.M.F.* determinations with the cell $Pt|NaI|KCl_{sat.}|NaI_3|Pt$ give $-27,800$ g.-cal.

R. CUTHILL.

Sorption and chemical phenomena. III. New class of heterogeneous chemical reaction. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1927, 59, 112—120).—The course of the reaction between nitroalizarin and barium and copper acetates suggests that the active mass of the solid phase is proportional to the total quantity present. The author considers that this type of heterogeneous reaction should be distinguished from the type exemplified by the reaction between barium carbonate and potassium sulphate where the solid phase does not react directly. It would seem that the latter does not represent a true type of heterogeneous reaction.

E. ROTHSTEIN.

Experimental basis of the third law of thermodynamics. N. DE KOLOSOVSKI (Z. Physik, 1927, 43, 509—511).—The Clausius–Clapeyron equation $d\log p/dT=\lambda/ART^2$ is considered as representing experimental observation for all substances. Since λ is always positive, it follows that $\lim._{T=0}dp/dT=\lim._{T=0}d\log p/dT=0$, and that $\lim._{T=0}\lambda/ART^2=0$; therefore $\lim._{T=0}\lambda=\lim._{T=0}\lambda/T=\lim._{T=0}\lambda/T^2=0$. Since $\lambda/T=S_g-S_l$, where S is the entropy and g and l refer to the gaseous and liquid phases, it immediately follows that $\lim._{T=0}S_g-S_l=0$. A number of other deductions from Nernst's heat theorem are derived similarly. R. W. Lunt.

Thermodynamic theory of capillarity. J. W. Dekker (Ann. Physik, 1927, [iv], 82, 1077—1155).—Mathematical. The influence of density on available volume, entropy, and kinetic pressure is discussed. Relative values for surface tension at different temperatures are calculated. R. A. Morton.

Calorimetry at high temperatures and methods for determination of mean specific heat between high and ordinary temperatures. W. A. Roth (Z. angew. Chem., 1927, 40, 732—734).—A review of current methods and apparatus. J. S. Carter.

Heat of dilution of salts at very small concentrations. II. W. Nernst and W. Orthmann (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 136—141).—Determinations of the heats of dilution of various salts at concentrations lower than those previously examined (A., 1926, 579) have given results which, in general, do not agree with Debye's theory, the values frequently being negative. R. Cuthill.

Heats of ionisation in methyl alcohol. J. H. Wolfenden, W. Jackson, and H. B. Hartley (J. Physical Chem., 1927, **31**, 850—861).—The heats of neutralisation of hydrogen chloride, hydrogen bromide, acetic and salicylic acids by sodium methoxide, and of aniline and ammonia by hydrogen chloride have been measured in methyl alcohol as solvent in an adiabatic calorimeter at 17°. The heat of formation of methyl alcohol from its ions is 11,200 g.-cal./g.-mol., a value similar to that for ethyl alcohol. The calculated heats of ionisation of acetic and salicylic acids in methyl alcohol are —4450 and —5180 g.-cal., respectively. The heats of formation of the ammonium and anilinium ions, respectively, in methyl alcohol are 17,630 and 9900 g.-cal. The heats of neutralisation of hydrogen chloride and bromide by sodium methoxide decrease with increasing dilution, as was also observed in aqueous solution by Richards and Rowe (A., 1922, ii, 425).

The specific heat of methyl alcohol calculated from the present data is 0·632. L. S. Theobald.

Latent heat of vaporisation of pure liquids and of solutions. M. S. Vrevski (J. Russ. Phys. Chem. Soc., 1927, **59**, 69—76).—A current of air is passed through a solution immersed in a thermostat at a temperature near that required for the determination. As the liquid cools, it is heated by an electric spiral. Since the amount of current passed through the solution is known and the weight of vaporised water is measured, the latent heat can be calculated. The determinations are made either with a constant rate of increase in the temperature (the rate of increase for a solution through which air is not drawn having previously been determined), or the current is so adjusted as to keep the temperature constant. By this means, it was found that the latent heat of water at 79·3° is 552·4 g.-cal., and that of sulphuric acid (53·07%) at 96·5° is 595·1 g.-cal. E. Rothstein.

Latent heat of vaporisation of water and of aqueous solutions of sulphuric acid at 79·3°, and comparison of the thermal effect with the energy of diluting the solution with water. M. S. Vrevski and B. P. Nikolski (J. Russ. Phys. Chem. Soc., 1927, **59**, 77—88; cf. preceding abstract). The latent heats of solutions of sulphuric acid varying in concentration between 17% and 57% have been determined at 79·5°. When the concentration is above 60%, the latent heat rises too rapidly to be measured accurately. The difference between the latent heat of water and 17% sulphuric acid is 1·2 g.-cal. That between water and 57% sulphuric acid is 62·6 g.-cal. From the experimental results, the following empirical relation was deduced: if N is the number of mols. of water to 1 g. of acid, l is the latent heat of the acid, and l_0 that of water, then if $N>7·3$, $l=l_0+1268/N_2$. If $N<7·3$, $l=l_0+62/N+793/N^2$.

The experimental results are compared with the formulæ arrived at by various authors for the heat effect obtained by diluting solutions. The author reaches the conclusion that $(\partial Q/\partial N)_{N=N_2}-(\partial Q/\partial N)_{N=N_1} = RT \log_e p_1/p_2$. E. Rothstein.

Heat expenditure at the absolute zero. J. E. Verschaffelt (Z. Physik, 1927, **43**, 152—154).—Criticism of Jazyna (*ibid.*, 1927, **41**, 211). Isothermal heat exchange is possible at the absolute zero, and matter can still possess energy at this temperature. R. A. Morton.

Reaction regions. XV. Influence of mixtures of carbon dioxide and carbon tetrachloride vapour on the inflammability of a methane–air mixture. W. P. Jorissen and G. M. A. Kayser (Rec. trav. chim., 1927, **46**, 373—377).—The combined effect of two inhibitors, carbon dioxide and carbon tetrachloride, on the explosion of mixtures of air and methane has been studied. Under the conditions of the experiment, the explosive region for methane and air alone lay between 6·3% and 12·2% of methane. In order to make a 9% methane–air mixture non-explosive, 9% of carbon dioxide alone, or 6·4% of carbon tetrachloride, was necessary, but with the two together a smaller proportion was needed, *e.g.*, 4·5% of a mixture of the two containing 40% of carbon tetrachloride was sufficient. M. S. Burr.

Transference numbers of sodium and potassium in mixed chloride solution. S. A. Braley and C. W. Rippie (J. Amer. Chem. Soc., 1927, **49**, 1493—1494).—Repetition of the experiments previously described (A., 1923, ii, 456) at a total concentration of 0·2N shows that complex ions do not exist in mixed sodium and potassium chloride solution at this concentration (cf. MacInnes, A., 1925, ii, 872). The MacInnes equation for transport numbers in mixed solutions is confirmed. The erroneous nature of the results previously reported is attributed to the unsuitability of the chloroplatinate method of determining the alkali metals. S. K. Tweedy.

Conductivity of hydrofluoric acid. M. Auméras (Compt. rend., 1927, **184**, 1650—1652).—The dissociation constant derived from conductivity data affords no evidence of the existence of a complex acid. J. Grant.

Conductivity of dilute aqueous solutions of the alkali hydroxides at 25°. M. Randall and C. C. Scalione (J. Amer. Chem. Soc., 1927, **49**, 1486—1492).—The equivalent conductivities of dilute solutions (up to 0·06*M*) of the alkali hydroxides are recorded for 25°. Special precautions were taken in preparing the solutions; a special cell requiring only a small quantity of solution was used. Values of Λ_∞ are calculated by Randall's method (A., 1916, ii, 285). The conductivity ratios (Λ/Λ_∞) are practically the same as those for hydrochloric acid.

S. K. Tweedy.

Lactic acid. III. R. Dietzel and E. Rosenbaum (Z. Elektrochem., 1927, **33**, 196—200; cf. A., 1925, i, 1036; 1926, 336).—The electrical conductivity of solutions of lactic acid and of potassium lactate has been measured at concentrations from *N*/8 to *N*/1024 at 18°. Lactic acid free from anhydride was prepared from barium lactate. The equivalent conductivity at infinite dilution of potassium lactate is found to be 115·5, whence that for lactic acid is 365·9. Values of the conductivity ratio, α, for lactic acid may be expressed by the relation: $2{\cdot}1418 \log 100\alpha = 0{\cdot}198 - \log c$, where c is the concentration in g.-mol./litre. This applies accurately over the whole concentration range investigated. The constant in the Ostwald dilution law for lactic acid exhibits a drift from $1{\cdot}35 \times 10^{-4}$ at *N*/8 towards a limiting value of about $1{\cdot}26 \times 10^{-4}$ in the more dilute solutions. This variation is much greater than that to be expected from experimental errors, and it is concluded that lactic acid cannot be regarded as a weak electrolyte. This view is supported by a calculation of conductivities on the basis of Ghosh's theory: excellent agreement is obtained over the whole concentration range, and the Ghosh equilibrium constant varies only between 1·257 and $1{\cdot}260 \times 10^{-4}$ over this range (cf. Auerbach and Zeglin's results for formic acid, A., 1923, ii, 55).

H. J. T. Ellingham.

Absolute hydratation of the ions $H^{\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, Cl', and Br' in their normal solutions. J. Baborovský and J. Velišek (Chem. Listy, 1927, **6**, 227—231).—Conduction of the electric current in *N*-solutions of alkali chlorides and bromides is due almost exclusively to electrolysis, the effect of electro-osmosis being negligible. On the basis of measurements of the electrolytic transport, the number of molecules of water attached to various ions in *N*-solutions is calculated to be 5 for potassium, 9 for sodium, 14 for lithium, 4 for chlorine, 3 for bromine, and 1·06 for hydrogen ions. Discrepancies observed between those values for hydratation of ions derived from measurements of the electrolytic transport of water and from considerations of the activity of the ions in question are explained by the assumption of two types of hydratation—dynamic and static. In the latter type, the ions are surrounded by molecules of comparatively loosely-bound water, which are to a large extent removed by the motion of the ions under the influence of an electric current.

R. Truszkowski.

Transition compounds between salts and metallic alloys. II. M. Padoa (Gazzetta, 1927, **57**, 399—406).—The maximum electrical conductivities exhibited by the tin arsenides at certain temperatures (A., 1926, 226) are said to be analogous to the increments produced in the conductivities of compounds of similar type when subjected to the action of light. Pronounced maxima are shown by antimony arsenide, Sb_2As, at −10° and by antimony telluride, Sb_2Te_3, at 100°. Similar behaviour is observed with antimony selenide, Sb_2Se_3, but in this case, as in that of crystalline selenium, the effects appear to be complicated by phenomena of hysteresis.

T. H. Pope.

Electrical conductivity of the system: arsenic tribromide–ether. M. Ussanovitch (J. Russ. Phys. Chem. Soc., 1927, **59**, 14—26).—See this vol., 315.

Electrochemical resonance. V. A. Plotnikov (J. Russ. Phys. Chem. Soc., 1927, **59**, 5—13).—See this vol., 20.

Improved hydrogen electrode vessel and the *E.M.F.* of the mercury, mercurous bromide, bromide ion electrode. R. H. Gerke and J. R. Geddes (J. Physical Chem., 1927, **31**, 886—889).—The *E.M.F.* of the cell $H_2(1\ \text{atm.})|HBr,Hg_2Br_2|Hg$ is 0·2685 volt at 25°, and the potential of the electrode $Hg|Hg_2Br_2|Br'$ −0·1396 volt. An improved hydrogen electrode vessel is described.

L. S. Theobald.

Potential measurements in dilute solutions of electrolytes. A. Brester (Rec. trav. chim., 1927, **46**, 328—341).—In order to study the applicability of the theory of Debye and Hückel, the following potential measurements have been made in very dilute solutions of the electrolytes considered: Ag–$AgNO_3$, Ag–$AgClO_4$, Ag–Ag_2SO_4; Cd–$CdSO_4$, Cd—$CdCl_2$, Cd–$CdBr_2$, Cd–CdI_2. Employing the Debye formula corrected for ionic dimensions, good agreement up to a concentration of 0·1*N* is obtained between experimental and calculated values for the activity coefficients of silver salts in solution, assuming a silver ion diameter of 3×10^{-8} cm. in silver nitrate, 4×10^{-8} cm. in silver chlorate, and 1×10^{-8} cm. in silver sulphate solution. In stronger solutions, deviations increase, but this is also the region in which the influence of the dielectric constant is considered to make itself felt. In the case of cadmium sulphate, the agreement is not so good, and the ionic diameter is probably about $1{\cdot}2 \times 10^{-8}$ cm. The cadmium halides give abnormal values, which are probably due to incomplete ionisation. Values for the degree of ionisation have been deduced, and the ionisation constants calculated, using the modified mass action law for electrolytes. The results give somewhat greater constancy than the values obtained by neglecting the activity coefficients. The results show that the degree of ionisation diminishes from chloride to iodide, which is also shown by the inclination of the curves when potentials as ordinates are plotted against the square root of the corresponding concentrations as abscissæ.

M. S. Burr.

Electromotive behaviour of arsenious–arsenic acid solutions. F. Foerster and H. Pressprich (Z. Elektrochem., 1927, **33**, 176—181).—In determining the oxidation–reduction potential of arsenious–arsenic acid solutions containing a small amount of iodide as catalyst, as recommended by Loimaranta, true equilibrium values, varying normally with the concentration ratio, are obtained only if the solutions are acidified to an extent corresponding at least with

N-hydrochloric acid. For the cell Pt|0·01*M*-H_3AsO_4, 0·01*M*-H_3AsO_3, 0·001*M*-KI, *M*-HCl¦NH_4NO_3 satd. soln.¦*M*-H_2SO_4, Hg_2SO_4|Hg, $E=0{\cdot}579$ at 18°, whence, using Lewis and Randall's value for the activity of hydrochloric acid, and assuming that the activity coefficient of arsenic acid is equal to that of arsenious acid and that liquid junction potentials are negligible, substitution in the formula $\varepsilon_h={}_0\varepsilon_h+0{\cdot}029 \log ([H_3AsO_4][H^{\cdot}]^2/[H_3AsO_3])$ gives ${}_0\varepsilon_h=+0{\cdot}574$ volt, in good agreement with the value calculated by Luther from the equilibrium constant at 25°. At higher acidities, especially above 4*N*, ε_h increases more rapidly than is to be expected from the activity data for hydrochloric acid, whilst any error due to neglect of liquid junction potentials would be in the opposite direction. Acidification with perchloric acid gives potentials identical with those obtained in solutions containing hydrochloric acid at the same molar concentration. It is concluded that in strongly acid solutions the activity coefficient of arsenic acid must be greater than that of arsenious acid at the same molar concentration. H. J. T. ELLINGHAM.

Applicability of Nernst's theory to non-aqueous solutions. A. E. BRODSKY (J. Russ. Phys. Chem. Soc., 1926, **58**, 587—595).—The *E.M.F.* of concentration cells in various solvents were investigated, with the view of testing Nernst's formula. The systems used were $Hg|Hg_2Cl_2,KCl(C_1)|KBr(C_2),Hg_2Br_2|Hg$, $Hg|Hg_2Cl_2,KCl(C_2)|KCl(C_2),Hg_2Cl_2|Hg$, and $Hg|Hg_2Br_2,KBr(C_2)|KBr(C_2),Hg_2Br_2|Hg$, in water at 14·5—15°, 50% ethyl alcohol (17°), and anhydrous methyl alcohol (13—13·5°). The method has been described in an earlier paper (A., 1926, 247, 688). The results are found to show considerable discrepancies with theory unless corrected for the degree of dissociation and for the diffusion potential, according to Henderson's formula, which is found to apply well for non-aqueous solvents. The results obtained are discussed from the point of view of the theory of Debye and Hückel. M. ZVEGINTZOV.

Electrochemistry of fused salts. H. J. BLIKSLAGER (Rec. trav. chim., 1927, **46**, 305—327).—The *E.M.F.* of concentration cells, consisting of nickel electrodes in fused alkali chloride solutions of nickel chloride at 470° and 720°, respectively, have been determined, but the values found are considerably higher than those calculated from the simple formula of Nernst, assuming complete ionisation. This may be explained by supposing that complex ions, $NiCl_3^-$, with a few $NiCl_4^-$ ions, are formed, leaving very few nickel ions. The increase of *E.M.F.* with temperature is proportional to the absolute temperature. Similar concentration chains of silver in silver chloride solution and lead in lead chloride solution give values in fairly close agreement with those calculated. Cobalt in cobalt chloride solution gives values which are not reproducible and are even higher than those for nickel, probably due to the greater complexity of the ions of cobalt chloride. The concentration polarisation observed when fused nickel chloride is electrolysed has been measured, and is also discussed from the theoretical point of view. The electrolytic separation of nickel–cobalt and iron–cobalt alloys from the fused salts has been studied. In the first alloy, no concentration of cobalt higher than 15·4% was obtainable from solutions containing a very high proportion of cobalt salt. The proportion of cobalt in the alloy increases with temperature. The experimental results have been compared with a formula deduced theoretically to show the relationship between the proportions of nickel and cobalt in the fused salt and in the alloy, as well as the influence of temperature. The iron–cobalt alloys prepared electrolytically always contain a large excess of cobalt. The results show that nickel is more positive than cobalt, and the latter than iron, cobalt lying nearer to iron than to nickel. It was not possible to prepare iron–manganese alloys from solution in fused chlorides, since only iron separated. Mixtures of nickel and alkali chlorides when heated are first yellow, then dark red, and finally blue. Measurements of the change of resistance with temperature indicate that the appearance of the blue colour coincides with the beginning of melting. M. S. BURR.

Current-potential curves of passive metals, with special reference to iron. W. J. MÜLLER (Monatsh., 1927, **48**, 61—70; cf. A., 1924, ii, 743).—The different methods of expressing current–potential relations of metal anodes showing passivity are discussed. The usual methods do not show the effect of time which the author's previous work (*loc. cit.*) has shown to be important. A new method is described in which the current–potential relations are shown by two curves, one expressing the behaviour of the passive and the other of the active form of the metal, tie-lines being added to join points corresponding with the same times. The previous results for iron are expressed in this way, and show that up to quite high current densities iron at first goes into solution in the active (bivalent) form, passivation occurring after a definite time, which depends on the conditions. W. HUME-ROTHERY.

Heyrovský's theory of hydrogen over-potential and alternative suggestions. H. J. S. SAND (Rec. trav. chim., 1927, **46**, 342—349).—Heyrovský's theory of hydrogen over-voltage (A., 1925, ii, 675), according to which the latter is connected with the formation of molecular hydrogen by combination of negative and positive hydrogen ions, is criticised as leading to conclusions not in agreement with Herasymenko's experimental results (*loc. cit.*). The conditions required by these are discussed, and are shown to be fulfilled by the assumption of the formation of intermediate complex ions of the composition $H_3^{\cdot\cdot}$, as indicated by the following equations: $H+2H^{\cdot}=H_3^{\cdot\cdot}$ and $2H_3^{\cdot\cdot}=4H^{\cdot}+H_2$, the current density being proportional to the rate of formation of these ions. This is valid only for small current densities. Alternative suggestions are also made. The hypothetical ion, $H_3^{\cdot\cdot}$, is analogous to the unstable ion $H(OH)_2''$, the formation of which has been previously postulated (Sand and Weeks, A., 1924, ii, 152) to explain results obtained in alkaline solutions. M. S. BURR.

Application of the radiochemical theory to solutions of sodium iodide. R. AUDUBERT (Compt. rend., 1927, **184**, 1440—1443).—The method previously described (this vol., 429) has been applied to the determination of the heat of reaction (*Q*) by the measurement of the *E.M.F.* produced when two platinum electrodes, one of which is illuminated, are placed in a solution of sodium iodide or of sodium iodide and iodine (NaI_3). Since the *E.M.F.* is greater than that due to the normal photovoltaic effect, the following equilibrium, dependent on the photochemical action of light, is assumed between the ions I′ and I'_3: $3I'+2h\nu \rightleftharpoons I_3'+2\varepsilon+2h\nu'$. The value found for *Q* (−26,000 g.-cal.) is in close agreement with that obtained by using the data given by the cell Pt|NaI|saturated KCl|NaI+I|Pt with various concentrations of sodium iodide and iodine, in the Helmholtz equation. J. Grant.

Electrochemical behaviour of silver and copper amalgams. K. Arndt and G. Ploetz (Chem.-Ztg., 1927, **51**, 461).—The *P.D.* between copper and silver dental amalgams, the latter containing a large amount of tin, and 1% solutions of sodium chloride, lactic acid, or mixtures of the two, *i.e.*, media approximating to the fluids of the mouth, are those of copper and tin, respectively. Experiments in which the cells amalgam|1% solution of sodium chloride+lactic acid|gold were shorted show that after a week the silver and copper amalgams lost 15 and 39 mg. in weight, respectively. Corresponding amounts of tin and copper were found in the solution. J. S. Carter.

Cell with diffusion anode. Relative velocities of reaction of liquid depolarisers. C. Baillod (Helv. Chim. Acta, 1927, **10**, 487—517).—Cells were constructed which comprised a hollow carbon anode containing a liquid depolariser which was caused to flow under pressure through the pores of the electrode, so that the surface of the anode was continuously covered with a layer of fresh depolariser and a cathode of amalgamated aluminium or zinc. When the velocity of diffusion of the depolariser exceeded a certain value, the output from the cell did not vary with time, and the maximum power which it then delivered constituted a measure of the relative velocity of reaction of the depolariser. Under these conditions, the fraction of the depolariser chemically utilised was small (about 12%). The relative reaction velocity of the depolariser increased rapidly with increasing hydrogen-ion concentration, and was greatest for concentrated nitric acid. The power delivered by the cell depended also on the nature of the electrolyte, being greatest for 20% sodium hydroxide solution or for *N*-nitric acid. On the other hand, the efficiency with which the aluminium dissolved was greatest (almost 100%) for electrolytes consisting of a 10% solution of sodium carbonate saturated with sodium chloride or of *N*-sulphuric acid, and least for *N*-nitric acid. G. A. Elliott.

Burning gases in nitrous oxide. H. B. Dixon and W. F. Higgins.—See B., 1927, 513.

Theory of explosive reaction. II. H. Muraour (Bull. Soc. chim., 1927, [iv], **41**, 620—630; cf. B., 1927, 126).—The theory of explosive reactions previously outlined is discussed in greater detail. S. K. Tweedy.

Kinetics of the oxidation of hydriodic acid by free oxygen in darkness and under the action of light. A. Berthoud and G. Nicolet (Helv. Chim. Acta, 1927, **10**, 475—486).—In absence of light, the process comprises two simultaneous reactions, of which one is very slow and independent of the concentration of the iodine produced, whilst the other, more rapid reaction proceeds with a velocity proportional to the square roots of the iodine and of the hydrogen-ion concentrations. The velocity of this reaction increases at first rapidly, and then more slowly with increasing concentration of potassium iodide. Under the action of feebly-absorbed red light, the oxidation proceeds much more rapidly; nevertheless, the reaction is essentially similar to the thermal reaction catalysed by iodine. The velocity of the photochemical reaction is, however, proportional to the square root of the intensity of illumination, and it has a very small temperature coefficient. The results indicate that the action of the light consists in the dissociation of the iodine molecules to form atoms which assist the reaction, presumably by the formation of an intermediate complex with oxygen. The reaction velocity under the influence of blue light, which is strongly absorbed, is also proportional to the square root of the intensity of illumination, but it increases to a maximum and ultimately decreases as the iodine concentration is raised. G. A. Elliott.

Mutarotation. II. Relative velocities of mutarotation of α- and β-glucose: effect of acid and salt. J. C. Andrews and F. P. Worley (J. Physical Chem., 1927, **31**, 882—885; cf. Hudson and Dale, A., 1917, i, 320).—The velocity coefficients determined in aqueous hydrochloric acid solutions at 25°, for both forms of the sugar, lie on the same straight line. The addition of specially purified sodium chloride up to a concentration of 8·63 g.-mols./1000 g.-mols. of water has no effect on the rate of mutarotation of α-glucose in water. Heating the salt to 120° accelerates the rate, and after fusion of the salt an even greater effect is observed. L. S. Theobald.

Oxidisability of organic substances. G. Lejeune (J. Chim. phys., 1927, **24**, 391—426).—The experimental data leading to the conclusions already published (A., 1926, 482) are now given. The unimolecular velocity coefficient for the oxidation of primary alcohols by alkaline permanganate tends to decrease with increase in the number of carbon atoms if the solution is buffered to p_H 11·8 with carbonate, whereas with a hydrogen carbonate buffer of p_H 8·3 the reverse is true. In acid solutions, the oxidation with permanganate is much more rapid than with chromic acid. The effect of the p_H on the reactivity of secondary alcohols is similar to that observed with primary alcohols. With ketones, the magnitude of the temperature coefficient of the velocity coefficient is independent of the nature of the ketone. The rate of oxidation of acetone in alkaline solutions increases in a linear manner with the p_H. R. Cuthill.

Reactions in the solid state at high temperatures. I. Reaction velocities of endothermic decompositions. W. Jander (Z. anorg. Chem., 1927, **163**, 1—30).—The relation between time and reaction velocity in the solid state is discussed, and it is shown mathematically that if two substances capable of reacting isothermally are in contact, the square of the thickness of the layer of reaction product formed must be proportional to the time of contact; an expression is derived for testing the relationship experimentally. An equation is also obtained for the relation between reaction velocity and temperature. Measurement of the carbon dioxide pressure over a mixture of barium carbonate and silicon dioxide shows that reaction commences at about 700°, and that its velocity at constant temperatures between 800° and 890° is in agreement with the theory. The theoretical relationship between reaction velocity and temperature is also satisfied. Similar results are found for a mixture of barium carbonate and molybdenum trioxide. For the former reaction, the velocity is inversely proportional to the square of the mean particle radius, as required by the theory.

H. F. Gillbe.

Thermal decomposition of azomethane over a large pressure range. H. C. Ramsperger (J. Amer. Chem. Soc., 1927, 49, 1495—1499).—The thermal decomposition of azomethane at 290° and at 330° is homogeneous over the pressure range 0·0259—70·79 cm. It is strictly unimolecular only at the lower pressures at 290° (cf. this vol., 425). The decomposition products exert the same influence in maintaining the rate as their equivalent of azomethane.

S. K. Tweedy.

Inversion of the rôle of catalysts. P. Sabatier (Compt. rend., 1927, 185, 17—19).—A catalyst may often act on a system in two opposite senses, according to the existing conditions. Numerous examples are quoted, and the results shown to be compatible with the simpler theories of catalysis. In particular, certain metallic oxides (*e.g.*, of zinc) behave as dehydrogenation catalysts, but usually have an activity less than that of finely-divided metals. The behaviour of these oxides also as hydrogenation catalysts having less activity than metals is the basis of the Patart process for the synthesis of methyl alcohol, the high temperature required being compensated for by an increase in pressure. In presence of a more powerful catalyst (*e.g.*, nickel), this reaction passes the methyl alcohol stage, and methane is produced. J. Grant.

Acid and salt effects in catalysed reactions. IX. General kinetic method for the determination of the degree of dissociation of water. H. M. Dawson (J.C.S., 1927, 1290—1297).—The calculation of the ionisation constant of water from the results of ester hydrolysis by means of the equation $K_w=v_i^2/4k_hk_{OH}$ is described (cf. this vol., 632). The minimum velocity of reaction, v_i, must be measured in buffer solutions, preferably, for mathematical simplicity, of constant acid or constant salt concentration. The acid and salt effects associated with the use of buffer solutions for the stabilisation of p_H in reaction velocity measurements are discussed. From the results of Karlsson's experiments (A., 1925, ii, 877), the values $K_w=1{\cdot}25\times10^{-14}$ at 25° and 34×10^{-14} at 85·5° are calculated. S. K. Tweedy.

Influence of water on the combination of the halogens with hydrogen. M. Bodenstein and W. Jost (J. Amer. Chem. Soc., 1927, 49, 1416—1418).—Experiments are described indicating that the investigations of Lewis and Rideal (A., 1926, 1111) do not prove that intensive drying retards the reaction between hydrogen and bromine or iodine. The presence of phosphorus pentoxide in the heated gases is shown to vitiate the results. S. K. Tweedy.

Chain-reaction theory of negative catalysis. H. L. J. Bäckström (J. Amer. Chem. Soc., 1927, 49, 1460—1472).—The autoxidation of benzaldehyde, of heptaldehyde, and of sodium sulphite solution at 20°, both in the light and in the dark, exhibits marked negative catalysis. An inhibitor for the light reaction invariably inhibits the dark reaction, although in the case of benzaldehyde the dark reaction is the more sensitive to inhibitors. Some inhibitors suppress the light reaction in the case of sodium sulphite more strongly than the dark reaction; alcohols exert parallel effects on both reactions. Quantum efficiency measurements indicate that a large number of molecules react for every light-quantum absorbed, and, in general, it is concluded that the above photochemical reactions represent instances of thermal chain reactions (cf. Christiansen, A., 1924, ii, 242). S. K. Tweedy.

Activity of various metals and metal oxide catalysts in promoting the oxidation of methane by air. W. P. Yant and C. O. Hawk (J. Amer. Chem. Soc., 1927, 49, 1454—1460).—The catalytic oxidation of 3·75—4·1% of methane in air by various metals, metal oxides, and mixtures of oxides was investigated between 150° and 350°. Cobaltic oxide was the most efficient catalyst; excluding mixtures, it was followed by manganese dioxide and nickelic oxide. 10% of platinum-black when added to metallic nickel appears to act as a promoter. Mixtures of the oxides gave results corresponding with the proportion of each active material present. S. K. Tweedy.

Reduction of mixed oxides. Copper and zinc oxides. W. Rogers, jun. (J. Amer. Chem. Soc., 1927, 49, 1432—1435).—Zinc oxide in a mixture with copper oxide (prepared in the fused state) is completely reduced by hydrogen at 300°. It is considered that the presence of one oxide prevents the crystal units of the other oxide from arranging themselves in the normal way. The forces between the units in the lattice structure are thus altered, and the properties of each component would be expected to be different from those for the pure state. S. K. Tweedy.

Catalytic activity of lead. F. A. Madenwald, C. O. Henke, and O. W. Brown (J. Physical Chem., 1927, 31, 862—866).—The activity of various lead catalysts in the reduction of nitrobenzene by hydrogen has been compared by the method previously used (Brown and Henke, A., 1922, i, 445). Light red lead, heavy red lead, and a light and a heavy litharge, prepared from recrystallised lead nitrate by varying heat treatments, on reduction by hydrogen at 308° gave the catalysts used. The activity of the catalysts increased with use, but more slowly than is the case with copper catalysts. It also increased more rapidly in an iron than in a glass tube. The initial activity of the different samples varies, but the final activity is the same. The optimum temperature for the reduction of nitrobenzene is 308°, and one catalyst prepared from heavy litharge maintained a 97% yield of aniline for approximately 200 experiments. Grinding the catalyst had no permanent effect on its activity, but hydrogen alone destroyed the activity. The optimum rate of flow is 14 litres of hydrogen and 4 g. of nitrobenzene per hr. at 308°. Appreciable yields of azobenzene (up to 25%) were obtained only during the first few runs. L. S. THEOBALD.

Catalytic actions of silver chloride in oxidation-reduction processes. R. LANG (Ber., 1927, **60**, [*B*], 1389—1390).—A solution containing the higher chlorides of manganese in 2·5*N*-hydrochloric acid, which does not decompose appreciably at the atmospheric temperature, rapidly and quantitatively yields chlorine and manganous chloride after addition of silver nitrate. If the acid is more dilute, a higher temperature is required for the change. Ceric nitrate dissolved in hydrochloric acid becomes almost instantaneously decolorised after addition of silver nitrate. H. WREN.

New kinds of mixed crystals. III. D. BALAREV and G. KANDILAROV (Z. anorg. Chem., 1927, **163**, 141—144; cf. A., 1926, 1195).—The presence of finely-divided barium sulphate reduces the velocity of oxidation of hydrogen chloride by permanganates in dilute solution. That the barium sulphate does not behave as a chemically inert substance is demonstrated by the fact that no diminution of the reaction velocity is caused by the presence of sand. For different permanganates, the magnitude of the effect is different, being greatest for potassium permanganate. The phenomenon is ascribed to variations in the extent of the adsorption of different permanganates by barium sulphate. H. F. GILLBE.

Electrolytic oxidation of concentrated formic acid solutions. F. MÜLLER (Z. Elektrochem., 1927, **33**, 173—176).—A 95% formic acid solution (sometimes with addition of 5% of sodium formate) has been electrolysed between platinum electrodes at 0·065 amp./cm.^{2} The theoretical amount of hydrogen was obtained at the cathode, but it was accompanied by considerable amounts of carbon dioxide. At the anode, however, the carbon dioxide obtained was always less than that corresponding with the process $2HCO_2'+\oplus=H{\cdot}CO_2H+CO_2$. This deficiency is shown to be due to the considerable solubility of carbon dioxide in the electrolyte. Diffusion of carbon dioxide in solution to the cathode causes it to be carried off with the hydrogen evolved there. When the electrodes are separated by a diaphragm, no carbon dioxide is obtained at the cathode.

H. J. T. ELLINGHAM.

Action of iron as an impurity in the lead accumulator. I and II. F. M. LEA and J. T. CRENNELL.—See B., 1927, 528.

Oxidation of sodium plumbite to plumbate by alternating current. II. F. JIRSA and F. KORNALIK (Z. Elektrochem., 1927, **33**, 192—196).—The current efficiency, η, for the production of sodium plumbate by the passage of sinusoidal alternating current through sodium hydroxide solutions saturated with lead monoxide has been investigated under various conditions (cf. A., 1920, ii, 620). With electrodes of gold or cadmium, η is extremely small, with palladium it is somewhat higher, but with nickel electrodes it is about ten times as great as with palladium. With nickel electrodes, η decreases with increasing alkali concentration up to 1·5*N*, then increases up to 4·5*N*, and finally diminishes at higher concentrations: with palladium electrodes, however, these variations are reversed, the maximum being at 1·5*N*. Using alternating current at 49 cycles, the highest value of η recorded is 11·33% (calculated on current shown by an alternating-current ammeter), using 0·412 amp./cm.^{2} at nickel electrodes in 4·66*N*-sodium hydroxide saturated with lead oxide at 18°. Increasing the frequency over the range from 18 to 60 cycles decreases η considerably. With platinum electrodes, no oxidation to plumbate occurs, but the platinum is attacked, giving a brown deposit containing lead and platinum, the latter being partly in the metallic state and partly in the form of platinic oxide. It is believed that platinum dissolves essentially in the bivalent form, which subsequently changes to satisfy the equilibrium $2Pt^{\cdot\cdot}\rightleftharpoons Pt^{\cdot\cdot\cdot\cdot}+Pt$. The dissolution of platinum in pure *N*-sodium hydroxide by alternating current is also examined.

H. J. T. ELLINGHAM.

Production of ozone in air by ultra-violet rays. J. DADLEZ (Compt. rend., 1927, **185**, 89—91).—The diminution of the ozone content of the air at increasing distances from quartz lamps of various makes and candle-powers has been measured. The minimum ozone content of air producing the first symptoms of distress in adults is 1·0—1·5 mg./m.^{3}, the effects being felt after 30 min. Since only 0·05—0·3 mg./m.^{3} of ozone are produced normally, there is little chance of danger in a large, well-ventilated room. The symptoms produced in an adult after various periods in atmospheres containing various amounts of ozone are described. J. GRANT.

Glow in hydrogen at high pressure. J. KAPLAN (Nature, 1927, **120**, 48).—During attempts to obtain atomic hydrogen by means of an incandescent tungsten filament in wet hydrogen at 20—350 mm. pressure, a blue glow was observed. The glow may be caused by some material liberated from the filament; it is not due to excitation of the hydrogen by electrons from the filament. The spectrum of the glow extends from 5000 to 4400 Å., and is probably continuous. A. A. ELDRIDGE.

Photolysis of hydrogen cyanide by the total and filtered radiations of the mercury arc. A. ANDANT and E. ROUSSEAU (Compt. rend., 1927, **184**, 1553—1555).—The method previously described (this vol., 538) has been applied to the irradiation of cherry-laurel water covered with a layer of olive oil, and containing pure manganous chloride (0·126%). After 4 hrs., the phenomenon of photocatalysis follows that of photolysis. The mercury radiation 3650 Å. produces, under the same conditions, a photolytic effect of the same order as that produced by the whole of the mercury radiations up to 3130 Å. Allowing for the selective absorption of the ray 3650 Å., it appears that photolysis by ultra-violet radiation is inhibited by the presence of radiations of greater wave-length. J. GRANT.

Effect of added gases on the decomposition of ammonia sensitised by optically excited mercury

vapour. A. C. G. Mitchell and R. G. Dickinson (J. Amer. Chem. Soc., 1927, 49, 1478—1485).—Whereas argon and nitrogen at 0·3 mm. pressure have no influence on the rate of photochemical decomposition of ammonia sensitised to 2537 Å. by optically excited mercury vapour, hydrogen at the same and lower pressures has a large inhibiting effect (Stuart, A., 1925, ii, 629). This is partly due to the fact that hydrogen can be activated by collisions of the second kind with excited mercury atoms, this activated hydrogen having no effect on the ammonia decomposition. Hydrogen can also take activation from activated ammonia (cf. Kuhn, A., 1924, ii, 249). The rate of decomposition of the ammonia increases with increasing pressure. The specific rate of activation of ammonia is 4% of that of hydrogen by excited mercury atoms. S. K. Tweedy.

Light oxidation of alcohols as contribution to the knowledge of photochemical phenomena. J. Böeseken and S. L. Langedijk (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 189—196).—Certain aromatic mono- and aliphatic α-di-ketones can behave as photocatalysts in the oxidation of alcohols to the corresponding aldehyde. The photoactive region lies between 400 and 410 μμ. The theoretical bearing of these results is discussed. The reaction has been used to effect the decomposition of optical antipodes. *l*-Menthyl benzophenone-*p*-carboxylate was dissolved in methylethylcarbinol, and exposed to light in presence of oxygen. The racemic alcohol was used, and after the experiment the fractionated alcohol was found to be lævorotatory. W. E. Downey.

Photochemical reaction of bromine with fumaric and maleic esters. J. Eggert [with F. Wachholtz and R. Schmidt] (Oesterr. Chem. Ztg., 1927, 30, 110).—Measurements of the rate of photochemical conversion of ethyl maleate into fumarate in carbon tetrachloride solution, in presence of bromine, show that the quantum efficiency varies with temperature and the wave-length of the light used, but is independent of the concentrations of ester, bromine, and added ethyl fumarate. The photochemical effect is merely the initiator of the process, which is essentially chemical. The process is complicated by the fact that, under the experimental conditions, both esters take up bromine, the quantum efficiency of this reaction varying with the concentration of bromine. A reaction mechanism is suggested according to which bromine atoms are responsible for the observed effects. Bromine molecules are first dissociated into their atoms, which form an intermediate complex on collision with ester molecules. The complex is very unstable, and undergoes rearrangement and subsequent decomposition. Collisions between bromine molecules and the complex are responsible for the appearance of dibromosuccinic ester. Experiments with the methyl esters and with an aqueous solution containing maleic acid, bromic acid, and a ferrous salt furnish evidence in support of the suggested mechanism. J. S. Carter.

Addition of bromine to α-phenylcinnamonitrile under the influence of light. A. Berthoud and G. Nicolet (Helv. Chim. Acta, 1927, 10, 417—429; cf. Berthoud and Bellenot, A., 1924, ii, 327; Plotnikov, "Lehrbuch der Photochemie," p. 250).—The addition of bromine to α-phenylcinnamonitrile and the reverse reaction both take place much more slowly in the dark than Bauer and Moser allege (A., 1907, i, 307). The rate of addition, *d*[dibromide]/*dt*, for small absorption is $k_1I_0^{0·5}$[bromine]$^{1·5}$; for total absorption, $k_1I_0^{0·5}$[bromine]. The thermal coefficient is 1·4. The photochemical decomposition of the dibromide occurs only in presence of bromine, which acts as an optical sensitiser. The rate of this reaction, —*d*[dibromide]/*dt*, when the nitrile is in large excess, is for small absorption $k_2I_0^{0·5}$[dibromide][bromine]$^{0·5}$/[nitrile], for total absorption $k_2I_0^{0·5}$[dibromide]/[nitrile]; whilst in absence of large excess of nitrile the denominator must be [nitrile]+*m*[dibromide]. The thermal coefficient is 1·96. The photochemical equilibrium is independent of intensity of illumination, and is represented by the expression *K'*=([nitrile]+*m*[dibromide])[bromine]/[dibromide], *m* becoming zero when the nitrile is in large excess. A theory of these results, which are quite different from those of Plotnikov, is developed. C. Hollins.

Oxidising agents in the study of the sensitivity of photographic emulsions. W. Clark.—See B., 1927, 507.

Precipitation of metals and their oxides from salt solutions by hydrogen at high temperatures and pressures, and synthesis of minerals. I. Influence of other metals in the precipitation of copper. W. Ipatiev and N. Klinkoia. **II. Precipitation of oxides from salts of chromium, manganese, and iron.** W. Ipatiev and A. Kisselev. **III. Precipitation of metals of the iron group from solutions of their cyanides and salts with organic acids.** W. Ipatiev and I. N. Kondyrev. **IV. Precipitation of phosphorus, arsenic, and antimony from their salts at high temperatures and pressures.** W. Ipatiev and W. Nikolaiev (J. Russ. Phys. Chem. Soc., 1926, 58, 664—686, 686—692, 692—698, 698—704).—I. The effect of temperature, pressure, concentration, and duration of reaction, as well as the presence of the salts of iron, nickel, zinc, and of free acids on the precipitation of copper from solutions of its salts (mainly copper sulphate) was investigated. The experiments were performed in glass tubes, but above 200° quartz vessels were used. Increase of concentration gave a precipitate containing cuprous oxide and basic salts, owing to secondary hydrolysis reactions. The amount of copper precipitated was proportional to the time. Rise of temperature favours deposition up to 150°, but above that inhibits it. Increase of pressure always favours deposition. The significance of these results from the point of view of the dynamics of the reactions is discussed. Above 150°, the sulphuric acid liberated was reduced by the hydrogen, the deposited copper acting as a catalyst, and cuprous oxide or basic salts were formed. At higher temperatures and pressures, cupric sulphide was obtained in a crystalline form. Addition of free sulphuric acid in small quantities favoured the precipitation of metallic copper, since it inhibited the secondary hydrolytic reactions. The addition of salts of nickel, zinc, and iron had no effect on the precipitation of copper, provided some free acid was present to prevent the formation of basic salts of the metals.

II. The experiments were performed at higher temperatures (300°) and pressures (>150 atm.) in silver, gold, and platinum balls, as quartz vessels gave with the salts crystals of metal silicates. Basic salts and oxides of the metals were obtained as well-developed crystals, often identical with the naturally-occurring minerals. Chromic acid gave at 300° and 150—180 atm. a greyish-violet powder, of the formula Cr_2O_3,H_2O, whilst in a quartz tube a bright green substance of the same composition was obtained. A mixture of potassium chromate and sulphuric acid (50%) gave an insoluble crystalline substance of the formula $Cr_2(SO_4)_3,Cr_2O_3,K_2O,H_2O$, which was examined by the *X*-ray spectrograph. Potassium manganate and manganese nitrate under similar conditions gave the crystalline mineral hausmannite Mn_3O_4,H_2O. In presence of free nitric acid in a quartz tube a manganese silicate was obtained. Manganese chloride gave a hydrated oxide, MnO,H_2O, whilst manganese sulphate gave manganese sulphide.

Iron salts precipitated mixtures of iron oxide, and finally, as the pressure increased and the temperature was raised, crystalline magnetic iron oxide, Fe_3O_4. No metallic iron was obtained, even when potassium ferrocyanide was used, which on decomposition gave first formic acid and then nascent hydrogen, capable of reducing any iron oxide, owing to hydrolytic reactions. Ferric chloride gave a white, crystalline mass; ferric acetate did not react, except with water-gas, when ferrosoferric oxide was obtained; ferrous sulphate precipitated a mixture of magnetic oxide and ferrous sulphide.

III. Iron formate gave magnetic oxide; nickel formate gave metallic nickel mixed with nickel oxide, the amount of which increased with rise of temperature and pressure, owing to hydrolysis, whilst nickel cyanide gave only anhydrous, crystalline, black nickelous oxide. Ferrous cyanide, formate, and acetate gave magnetic oxide, whilst the thiocyanate gave a mixture of oxide and sulphide. With the double cyanide of potassium and manganese, crystalline manganese carbonate was obtained. In a quartz tube, manganese and zinc nitrate deposited the corresponding crystalline silicates.

IV. Free phosphoric acid and its alkali salts remained unaffected, but ferric phosphate gave a continuous series of crystalline complex phosphates of the type $Fe'''_nFe''_mPO_4,xH_2O$, depending on the conditions, identical with the naturally occurring minerals—the vivianites. Lead phosphate at 250—300 atm. and 360—400° deposited a colloidal orange oxide, Pb_2O, and hypophosphorous acid, whilst with water-gas at 400 atm., phosphine and some metallic lead were obtained. With lead hypophosphite, at high pressures, in presence of water, black, elementary phosphorus was formed. This form was also obtained by the action of water on red phosphorus at 260° and 100 atm. The salts of arsenic acid and iron oxide gave green, crystalline hydrated ferric arsenate, identical with the mineral scorodite. Further action resulted in the formation of elementary arsenic. If the action is prolonged for a few days, crystalline arsenical pyrites, Fe'''_nAs_m, is obtained. Copper arsenate gave the mineral domeite (cuprous arsenide, Cu_3As). With elementary arsenic a little arsine was evolved. Antimony sulphate formed crystals of antimony glance, Sb_2S_3, and potassium pyroantimonate formed crystalline elementary antimony. In general, antimony salts are more easily reduced than those of arsenic and phosphorus.

M. Zvegintzov.

Double sulphates of the copper–magnesium group and the sulphonium bases. I. P. C. Rây and N. Rây (J. Indian Chem. Soc., 1927, **4**, 37—42).—Double *sulphates* having the general formula $M''SO_4,(Et_3S)_2SO_4,10H_2O$, where $M''=Fe''$, Zn, Ni, Co, Cd, have been prepared by slow evaporation of triethylsulphonium sulphate (obtainable only in solution) with the appropriate metallic sulphate in the ratio 2 : 1. These compounds are hygroscopic; alcohol added to their aqueous solutions causes separation of the inorganic components. Salts of the type $2M''SO_4,(Et_3S)_2SO_4,11H_2O$ were also formed, where $M''=Mg$ or Mn, and when trimethylsulphonium sulphate was substituted for the ethyl derivative nickel formed a salt of this type.

B. W. Anderson.

Reactions of active magnesium. A. P. Terentiev (Z. anorg. Chem., 1927, **162**, 349—352).—Active magnesium may be prepared by passing the vapour of an alcoholic solution of iodine over the powdered metal; 1 g. of iodine is sufficient to activate 24 g. of magnesium, which must be dried beforehand by strong heating. The active product must be freshly prepared for use, as it is very hygroscopic and its activity is destroyed by traces of moisture. A mixture of active magnesium and ethyl alcohol does not reduce the methyl esters of the fatty acids, but yields the ethyl esters. When heated in ammonia at 350—400°, the active metal forms a grey powder, consisting of magnesium amide. Ordinary magnesium reacts with aniline vapour at about 370°, whereas the active form reacts with the vapour at about 240° and with the liquid at 130—140°.

H. F. Gillbe.

Setting of dihydrates of calcium sulphate. P. P. Budnikov.—See B., 1927, 483.

Decomposition of monocalcium phosphate by water. A. Sanfourche and B. Focet (Compt. rend., 1927, **184**, 1652—1655).—The weight of salt entering into reaction and the degree of decomposition of crystalline monocalcium phosphate in aqueous solutions at 20° may be determined by titration of the acid liberated in the reaction $2CaH_4(PO_4)_2=2H_3PO_4+Ca_2H_2(PO_4)_2$. The amount of salt decomposed increases (rapidly at first) with the amount present, 0·407 being decomposed in the case of a saturated solution (63%). The presence of calcium sulphate in the anhydrous form has no effect on the decomposition curve, but there is indirect evidence that when it is present as the hemihydrate a double salt is formed with the dicalcium phosphate produced during the reaction. Thus, up to a certain concentration of phosphate, depending on the amount of calcium sulphate present, the decomposition is characteristic of a normal salt. Beyond this point, it is characteristic of the decomposition of the pure phosphate, except that the amount decomposed increases with the concentration of calcium sulphate.

J. GRANT.

New scaly variety of aluminium hydroxide. P. NEOGI and A. K. MITRA (J.C.S., 1927, 1222—1223).—The reduction of concentrated barium nitrate (or, although less satisfactory, strontium nitrate) solution with aluminium–mercury couple at 0° yields stable scales (probably isometric crystals) of $Al_2O_3,4H_2O$, d^{31} 1·5490, soluble in mineral acids, but insoluble in methylamine. One molecule of water is lost at 100°, and the last molecule, with difficulty, at red heat. Impure products are also obtained by the similar reduction of alkali bromates and iodates.

S. K. TWEEDY.

Alkali and alkaline-earth hexabromostannates [Rb_2SnBr_6, Cs_2SnBr_6, and $BeSnBr_6,10H_2O$]. G. I. COSTEANU (Ber., 1927, 60, [*B*], 1312—1315).—The *hexabromostannates* of *rubidium*, *cæsium*, and *beryllium* are obtained from their components in aqueous solution or, in the case of cæsium, from the carbonate and hexabromostannic acid. The two former are more stable and less soluble than the other alkali hexabromostannates; the beryllium salt resembles the magnesium compound.

H. WREN.

Nitrogen sulphide. S. A. VOSNESSENSKI (J. Russ. Phys. Chem. Soc., 1927, 59, 221—232).—Pure nitrogen sulphide is obtained by passing ammonia mixed with air into an anhydrous benzene solution (20% by weight) of sulphur dichloride. After this reaction, the mixture is filtered through flannel, the nitrogen sulphide extracted in a Soxhlet apparatus with benzene, and recrystallised from benzene. The product (yield, 20%, calculated on sulphur dichloride) had m. p. 179°; the presence of sulphur has a great influence in lowering the m. p. Near the m. p., sublimation occurs, and at higher temperatures the compound explodes. The sulphide has *d* 2·2, mol. wt. 184·3, indicating the formula N_4S_4. Decomposition occurs in a damp atmosphere and in water, hot water decomposing it violently. Data are given of its solubility in carbon disulphide, benzene, and ethyl alcohol. The reactions with water, acid, and alkali, respectively, are fully investigated. General methods for preparing the series of additive *compounds* $N_4S_4,2NH_3$, $N_4S_4,2Cl_2$, $N_4S_4,2Br_2$, $3N_4S_4,2SCl_2$, N_4S_4,SCl_2, and $N_4S_4,2SCl_2$ are given. The structural formula suggested, $S{:}S({:}N{\cdot}S{:}N)_2$, agrees with (1) the equation $N_4S_4+12HCl=4NH_3+4S+12Cl$, for it may be here assumed that the sulphur and nitrogen are combined by twelve valencies, and that the atoms of nitrogen are not combined among themselves; (2) the formulation of its metallic derivatives $S{:}S{\ll}\begin{smallmatrix}N\\N\end{smallmatrix}{>}Pb$ and $S{\ll}\begin{smallmatrix}N\\N\end{smallmatrix}{>}Hg$; (3) the data obtained on hydrolysis. However, the formula does not explain the reaction $N_4S_4+Me{\cdot}COCl\longrightarrow N_3S_4Cl$ and the production of the compounds N_3S_4Br, $N_3S_4NO_3$, N_3S_4CNS, or the reaction $N_3S_4Cl+NH_3\longrightarrow N_4S_4$.

J. KAYE.

Formation of ozone by electric discharge in presence of foreign gases. A. PINKUS and A. JULIARD (J. Chim. phys., 1927, 24, 370—390).—When oxygen is subjected to the silent discharge, the fraction which is ozonised is, for a given rate of flow of the gases, nearly the same for all pressures between 300 and 600 mm., this being a maximum value. Under comparable conditions of pressure and rate of flow, hydrogen and, to a less extent, silicon tetrafluoride reduce the yield of ozone. If the rate of flow is high and the voltage is small, the presence of nitrogen may cause the yield to be better than with pure oxygen under comparable conditions. With increase in the voltage and decrease in the rate of flow, however, the optimum amount of nitrogen diminishes, probably because in these circumstances more oxides of nitrogen are formed, and these exert a greater destructive action on the ozone, according to the equations $2NO+O_3=N_2O_5$, and $2NO_2+O_3=N_2O_5+O_2$.

R. CUTHILL.

Oxidation with fluorine. VII. Action of fluorine on water and alkali hydroxide solutions. VIII. Unstable peroxide from sulphuric acid. IX. Action of fluorine on phosphoric acid, phosphates, and pyrophosphates. X. Action of fluorine on carbonates and borates. F. FICHTER and W. BLADERGROEN (Helv. Chim. Acta, 1927, 10, 549—552, 553—559, 559—565, 566—570; cf. this vol., 123).—VII. When fluorine is led into water, hydrogen peroxide is produced in amounts which at first increase rapidly and then decrease as the time of treatment is prolonged. The decrease is attributed to the decomposition of the peroxide by ozone, which is formed in the later stages. Fluorine forms with concentrated potassium hydroxide solution at −20° a brown, explosive compound which is probably potassium ozonide. This substance is decomposed by water with the formation of molecular oxygen and a small amount of hydrogen peroxide.

VIII. The unstable compound previously recorded (A., 1926, 925) is formed in greatest amount when cooled, 2·35*M*-sulphuric acid is treated with fluorine; it may also be obtained in almost equal amount (equivalent to 4·4% of the total sulphate when calculated as SO_4) from solutions of sulphates or hydrogen sulphates of medium concentration. The substance oxidises manganous sulphate rapidly to permanganate, precipitates silver peroxide immediately from silver nitrate solution, and also oxidises phenolphthalein to fluorescein and other hydroxylated derivatives. The substance originally obtained by Berthelot (Compt. rend., 1878, 86, 20) on subjecting a mixture of sulphur dioxide and oxygen to the discharge in an ozoniser, also gives these reactions when dissolved in sulphuric acid, and it is concluded that the peroxide produced by fluorine is probably a sulphur tetroxide (SO_4 or S_2O_8) identical with that present in Berthelot's substance.

IX. Solutions of phosphoric acid, after treatment with fluorine, immediately precipitate iodine from iodides. A slight additional precipitate occurs in one or two cases on keeping. The oxidising power is attributed principally to permonophosphoric acid, H_3PO_5; the solutions, and also permonophosphoric acid prepared by the action of hydrogen peroxide on phosphorus pentoxide, oxidised manganous sulphate to violet manganic phosphate, and not to permanganate (cf. Schmidlin and Massini, A., 1910, ii, 498).

The action of fluorine on di- or tri-alkali phosphates and on pyrophosphates produced salts of both permonophosphoric acid and perphosphoric acid, $H_4P_2O_8$ (iodine precipitated in two stages); the former is unstable, so that it was possible to obtain perphosphoric acid mixed with potassium fluoride from the solution. Possible mechanisms for the reactions involved are discussed.

X. Well-cooled solutions of sodium, potassium, or rubidium carbonate were treated with fluorine, alkali hydroxide being added from time to time to neutralise the acid formed. The resulting oxidising properties of the solutions were relatively feeble, and no percarbonate separated out. Addition of metaborate to the potassium carbonate solutions resulted in an increase of oxidising power to more than twice that recorded with carbonate alone, but no solid perborate was obtained. The presence of mutually antagonistic oxidation products was indicated by the fact that admixture of sodium metaborate solution with potassium hydroxide solution which had been treated with fluorine resulted in a decrease of oxidising power.

G. A. Elliott.

Mechanism of the deoxidation of potassium, lithium, and sodium permanganates in alkaline solution. A. A. Maximov (Z. anorg. Chem., 1927, **163**, 49—64).—The rates of formation of manganate at 100° from potassium, lithium, and sodium permanganates in presence of the corresponding hydroxide have been determined. The results support Bogorodsky's theory that the rate of deoxidation is related to the ease of formation of the peroxide of the alkali metal. If hydrogen peroxide or the peroxide of the alkali metal be added in excess to a solution of the hydroxide and permanganate of sodium or potassium, no manganate is formed, but a vigorous reaction, resulting in the production of manganese dioxide, takes place. The quantities of hydrogen peroxide necessary for complete deoxidation to manganate and to manganese dioxide, respectively, are in agreement with the theory that the reaction takes place in two consecutive stages, given for potassium permanganate by the equations $2KMnO_4+H_2O_2+2KOH=2K_2MnO_4+2H_2O+O_2$, and $2K_2MnO_4+2H_2O_2=4KOH+2MnO_2+2O_2$. These equations hold only when the potassium hydroxide concentration is greater than about $0{\cdot}5N$. If it is less than about $0{\cdot}05N$, hydrated manganese dioxide is formed simultaneously with potassium manganate; rise of temperature has a similar effect. The mechanism of the reactions is discussed, and it is shown that the formation of the peroxide of the alkali metal is a necessary intermediate stage. H. F. Gillbe.

Reaction between arsenite and permanganate in sulphuric acid solutions. T. Oryng (Z. anorg. Chem., 1927, 163, 195—205).—The reaction between sodium arsenite and potassium permanganate in dilute sulphuric acid solution is discussed. It has been shown experimentally that the final reaction products are compounds of tervalent and bivalent manganese, and that the hydrated manganese dioxide which appears as a precipitate during the course of the reaction is only an intermediate product, since it disappears as the reaction proceeds to completion.

H. F. Gillbe.

Composition and properties of the products of hydrolysis of ferric chloride. N. N. Petin and M. P. Golombick (J. Russ. Phys. Chem. Soc., 1927, **59**, 171—180).—Various quantities of alkali when added to equally concentrated ferric chloride solutions produce partial hydrolysis products of different composition. For each concentration of alkali, two salts are "precipitated." In the solution, two layers separate, a clear upper layer and a cloudy lower layer. The ratio of iron equivalent to that of chlorine is less than 1 in the upper clear layer, and greater than 1 in the lower layer. As the concentration of alkali increases, this ratio increases, and the easier it is to coagulate the ferric hydroxide. Light also increases the speed of coagulation. The stability of the sol depends on the concentration of alkali, being at a maximum when the amount of alkali present is 50—70% of that required for complete precipitation of the ferric hydroxide. E. Rothstein.

Action of pure carbon monoxide on iron at elevated temperatures. W. P. Fishel and J. F. Wooddell.—See B., 1927, 525.

Mode of formation of iron nonacarbonyl from iron pentacarbonyl. E. Speyer and H. Wolf (Ber., 1927, 60, [*B*], 1424—1425).—Iron pentacarbonyl dissolved in glacial acetic acid or acetic anhydride in a vacuum or an atmosphere of hydrogen gives iron nonacarbonyl when exposed to sunlight. In chloroform, acetone, ether, etc. the nonacarbonyl is accompanied by smeary by-products. H. Wren.

Thiosulphato-cobalt complexes and complex cobalt thiosulphates. I. P. R. Rây (J. Indian Chem. Soc., 1927, **4**, 64—74).—By the controlled action of ammonium or sodium thiosulphate and ammonia in varying concentration on cobalt hydroxide, chloride, or nitrate in a current of air, a number of crystalline complex thiosulphato-cobalt compounds have been prepared. They are monoacidopentammine salts in which the thiosulphate radical occupies only one co-ordination position; in solution, they hydrolyse slowly into aquo-salts. The following are described: *sulphitopentamminecobaltic thiosulphate* $[(NH_3)_5Co{\cdot}SO_3]_2S_2O_3$ (also with $1{\cdot}5H_2O$); *hydroxytetramminecobaltic sulphite*, $[(NH_3)_4Co(OH)SO_3],2H_2O$; these two compounds are brownish-yellow and thus have a sulphur atom linked direct to the cobalt atom (cf. Duff, J.C.S., 1922, **121**, 450); *thiosulphatopentamminecobaltic chloride*, $[(NH_3)_5CoS_2O_3]Cl$, and the corresponding *bromide*, *iodide*, and *nitrate*; *thiosulphatopentamminecobaltic thiosulphate*, $[(NH_3)_5CoS_2O_3]_2S_2O_3,H_2O$; *thiosulphatopentamminecobaltic dithionate*, $[(NH_3)_5CoS_2O_3],S_2O_6$, and the corresponding *chromate*; these compounds are red, the thiosulphate radical being linked to the cobalt atom through an oxygen atom; *triethylenediaminecobaltic thiosulphate*, $[Co(C_2H_8N_2)_3]_2(S_2O_3)_3$; *hexamminecobaltic chloro-thiosulphate*, $[Co(NH_3)_6]ClS_2O_3$, and *nitropentamminecobaltic thiosulphate*, $[(NH_3)_5CoNO_2]S_2O_3$. B. W. Anderson.

Osmium. Distillation of osmium tetroxide from aqueous solution, the oxidation of osmium and its relation to the regeneration of the tetroxide. I. E. Fritzmann (Z. anorg. Chem., 1927, **163**, 165—177).—A small change in the vapour pressure of the solvent in a ternary system exerts a large influence on the vapour pressure of osmium tetroxide; application of this principle affords a convenient method for the rapid removal of osmium tetroxide from aqueous solution. Osmium and its compounds are most rapidly and conveniently oxidised by methods in which free oxygen is liberated in the course of the reaction; chlorine and bromine, and the oxides of nitrogen and of chlorine, act much more slowly. By simultaneous oxidation and distillation from aqueous solution pure osmium tetroxide may be prepared.

Osmium tetroxide in aqueous solution in many ways resembles an organic substance such as phenol. It behaves as a weak acid and possesses a very small molecular conductivity; addition of inorganic salts produces salting out, and the tetroxide may be distilled in steam. Metallic osmium and to a smaller extent its sulphide may be oxidised by the usual methods employed in organic chemistry.

H. F. Gillbe.

Preparation of potassium sulphate by Hargreaves' process. K. Hepke.—See B., 1927, 478.

Preparation of potassium sulphate. K. Kölichen.—See B., 1927, 477.

Preparation of sulphuric acid from gypsum. H. Molitor.—See B., 1927, 520.

Preparation of liquid nickel carbonyl. C. F. van Duin (Rec. trav. chim., 1927, 46, 381—382).—A more active form of nickel than that used by Laird (this vol., 533) for the production of nickel carbonyl may be prepared by reducing nickelous oxalate with pure hydrogen at 290—300°, purified pumice being used as a carrier. When oxygen-free carbon monoxide is passed over this nickel at 90—100°, the concentration of the exit gases is such that the carbonyl may be separated by cooling in ice and salt only.

E. Holmes.

Smooth electrodes for p_H and conductivity measurements. I. I. Shukov (Nature, 1927, **120**, 14).—For p_H and conductivity determinations, platinum electrodes covered electrolytically with gold and with a thin, smooth layer of platinum give excellent results. Platinum foil so coated acts catalytically on a mixture of hydrogen and oxygen, whereas iridium, rhodium, and palladium have no action, or only a slight effect.

A. A. Eldridge.

Determination of end-points in potentiometric titrations. F. L. Hahn and M. Frommer (Z. physikal. Chem., 1927, **127**, 1—42).—The titrations are best carried out when the reagent is added in equal and preferably not excessively small amounts. From theoretical considerations of the potential changes to be expected in the case of a simple reaction, a method has been devised whereby the end-point may be calculated from the measured potential changes on either side, within a small fraction of the unit of reagent added. The application of this method to the results of titrations of chloride with silver and *vice versa* showed that the titration was equally accurate when carried out in amounts of 0·1 c.c. of 0·1*N* solution as with 0·025*N* solution added in drops of 0·01 c.c. The experimental data served also to determine the solubility product of silver chloride. The potential changes which occur when ferrous ammonium sulphate is titrated with permanganate solution are more complex, and would appear to be determined by unknown intermediate reactions. Nevertheless, the effective reaction is a simple one near the end-point, and accurate titration may be effected by the method described.

G. A. Elliott.

Simple apparatus for measuring hydrogen-ion concentration. F. Emslander (Woch. Brau., 1927, 44, 268—270).—A gas chain apparatus, in which a gold electrode coated with iridium replaces a platinum electrode, is described for use in cases of liquids containing colloidal material. A curve for computing the p_H from the millivolt reading on the bridge (*E.M.F.*) is given.

W. Robson.

Ionometric measurement of the acidity and alkalinity of glasses by means of the Luers quinhydrone potentiometer. A. Mauri.—See B., 1927, 523.

Effect of gelatin on the titration curves of various acids. E. Little (J. Amer. Pharm. Assoc., 1927, **16**, 414—417).—Curves are given showing the small effect of gelatin on the titration curves of sulphuric, butyric, and lactic acids against sodium hydroxide, and for the effect of *o*-aminobenzoic acid on the titration curves of pyrogallol, tannic acid, and hydrochloric acid with sodium hydroxide.

E. A. Lunt.

Mechanism of titration with adsorbed indicators. J. Hodakow (Z. physikal. Chem., 1927, **127**, 43—50).—Methyl-violet is adsorbed on the surface of finely-divided silver chloride in presence of excess of chlorine ions, and this process is accompanied by a sharp colour change from blue to pink. The amount of indicator removed in this way has been studied as a function of the charge on the silver chloride particles, and the results serve to explain the Fajans and Hassel titration method (A., 1924, ii, 60). The adsorption is reversible and is a true surface effect.

G. A. Elliott.

Standardisation of *N*- and 0·1*N*-acid and alkali solutions. G. Favrel (Ann. Chim. anal., 1927, [ii], 9, 161—162).—Potassium hydrogen tartrate is a convenient and accurate standard, since it may readily be obtained pure, does not deteriorate on keeping, and may be weighed out and dissolved for titration without difficulty.

S. I. Levy.

Preservation of standard solution of oxalic acid and reading of the burette. S. Ishimaru (Bull. Chem. Soc. Japan, 1927, 2, 134—139).—Solutions of oxalic acid undergo slow decomposition when stored in colourless bottles, and the decomposition is not prevented, but actually accelerated, in presence of sulphuric acid. Standard solutions should be kept in bottles carefully wrapped with black paper. No precautions need be taken for the exclusion of micro-organisms. A convenient device for the reading of burettes is described.

J. S. Carter.

Manganese interference in the *o*-tolidine test for available chlorine. E. S. Hopkins.—See B., 1927, 521.

Determination of available chlorine in bleaching powder. J. Hausner.—See B., 1927, 521.

Micro-reactions of the acids of chlorine, bromine, and iodine. E. M. Chamot and C. W. Mason (Mikrochem., 1927, 5, 85—101).—To detect chloride in presence of iodide and bromide, a small quantity of the solution is heated with 10% of its volume of nitric acid in a micro-crucible until brown fumes cease to be evolved, and a crystal of silver nitrate is added to a few drops of the solution on the slide; a fine-grained, apparently amorphous, precipitate indicates the presence of chloride. In the above test, iodides are recognised by the blue colour imparted to starch grains suspended in a drop of water on the underside of a cover-glass covering the crucible, and bromides by the characteristic needle crystals produced by the vapour in a drop of a solution of *m*-phenylenediamine placed next to the drop containing the starch. Other microchemical tests for iodides are based on the formation of characteristic precipitates with mercuric chloride, copper sulphate, palladous chloride, thallous nitrate, and lead nitrate. The formation of chromyl chloride may be used for detecting the presence of chloride if the reaction is conducted in a micro-crucible covered with a slide to which a drop of water adheres; if the water becomes yellow on warming the substance with sulphuric and chromic acids, a small crystal of silver nitrate is added, when, in presence of chlorides, a white precipitate of silver chloride surrounded by orange to red silver chromate appears. The oxy-acids of the halogens are tested for by reducing them with zinc dust and sulphuric acid and applying the above tests to the solution. A. R. Powell.

Argentometric titration of chlorides and iodides using adsorption indicators. III. I. M. Kolthoff (Z. anal. Chem., 1927, 71, 235—243; cf. this vol., 434, 435).—Indicators have been examined which will give sharp colour changes on addition of slight excess of silver nitrate to chloride and iodide solutions containing acetic acid, in order to permit of the application of the method to the halogen compounds of heavy metals and alkaloids. The most suitable indicator is metanil-yellow, but good results are obtained also with bromophenol-blue; the latter is specially suitable for titration of the alkaloid chlorides by this method. S. I. Levy.

Identification of iodides and bromides alone and in presence of each other. J. von Mikó (Arch. Pharm., 1927, 265, 445—450).—" Chloramine " is now officially substituted for chlorine water in the tests prescribed by the German pharmacopœia, but commoner official reagents are better adapted for detecting iodides and bromides. As little as 0·00005 g. of potassium iodide in 5 c.c. can be detected by adding 5*N*-hydrochloric acid (1—5 drops) and 3% hydrogen peroxide (1 drop) or 0·1*N*-potassium permanganate solution (1 drop) and shaking with chloroform. Bromides are similarly identified, but satisfactorily only when permanganate is used. The hydrogen peroxide method, with suitable proportions of the reagents, permits iodides to be detected in presence of bromides, whilst if concentrated hydrogen peroxide and an excess of hydrochloric acid be used, bromides can be identified in presence of iodides, for on shaking, the colour due to the iodine fades and leaves only the brown colour of the bromine. W. A. Silvester.

Determination of sulphur in pyrites by the Lunge–Berl method. Kastner.—See B., 1927, 480.

Titrimetric determination of hydrogen sulphide in producer gas. I. Ciochină.—See B., 1927, 465.

Determination of combined sulphuric and hydrochloric acids in cotton. D. A. Clibbens and A. Geake.—See B., 1927, 471.

Determination of sulphate ion as barium sulphate. V. Marjanović (Arhiv Hemiju, 1927, 1, 5—18).—The solution, which should contain not more than 0·3 g. of sulphate, is evaporated to dryness, 5 c.c. of 10% hydrochloric acid and 2 c.c. of saturated barium chloride solution are added to the residue, together with 100 c.c. of boiling water, and the whole is placed on a water-bath for 1 hr. The supernatant liquid is then decanted through a Gooch crucible and the precipitate treated with 1 c.c. of concentrated hydrochloric acid and 50 c.c. of cold water, and warmed on the water-bath for 10 min., after which the precipitate is filtered through the same Gooch crucible, washed, dried, and weighed. The average experimental error for the above method is 0·04% for solutions of pure sulphates; the presence of chlorides and nitrates, and of sodium, potassium, magnesium, iron, copper, aluminium, and ammonium ions does not affect the accuracy of this method. Phosphate ions lead to high values, whilst in presence of calcium ions low results are obtained.

R. Truszkowski.

Determination of phosphorus and silicon in ferrophosphorus. W. F. Pond.—See B., 1927, 488.

Sensitiveness of some test papers for gaseous phosphine. M. Wilmet (Compt. rend., 1927, 184, 1456—1458).—The technique previously developed (this vol., 221) has now been applied in the examination of the sensitiveness towards gaseous phosphine of copper sulphate, silver nitrate, mercuric chloride, potassium mercuri-iodide, $HgI_2,3KI$, and " sensitised " mercuric chloride (alkaline iodomercurate) impregnated on filter-paper. Copper sulphate and neutral potassium mercuri-iodide are the least sensitive. Mercuric chloride (5% solution) paper affords a means of distinguishing between phosphine and arsine, if after slight exposure to the gas the test-paper is dipped in 5% potassium iodide solution. With phosphine, the shade thus developed varies from pale yellow to reddish-orange or salmon, whereas arsine gives a reddish-brown coloration. The dynamic method allows of the approximate determination of the volume of air containing 0·5 mm.^{3} of the gas with 5% mercuric chloride papers or 0·2 mm.^{3} with silver nitrate paper (0·1*N*-solution). The odour of the gas can be recognised for concentrations above 1 : 20000; below 1 : 50000 it cannot be detected.

R. Brightman.

Determination of tervalent arsenic. L. A. Deshusses and J. Deshusses (Helv. Chim. Acta, 1927, 10, 517—530).—A critical study of the various methods of determining tervalent arsenic in commercial Schweinfurth green. The Avery–Beans method gave results which were consistently too high (0·1%), owing to the effect of the presence of copper on the end-point of the titration with iodine. A modified distillation method, in which the substance was distilled in presence of methyl alcohol saturated with hydrogen chloride, is both accurate and rapid. The removal of arsenic trichloride during the distillation was favoured equally by the addition of either powdered quartz or potassium bromide.

G. A. ELLIOTT.

Iodometric determination of arsenic acid. L. ROSENTHALER (Z. anal. Chem., 1927, 71, 190—191).—A reply to Ormont's criticism (this vol., 325) of Rosenthaler's method (A., 1926, 702). A. R. POWELL.

Determination of arsenic pentoxide as magnesium ammonium arsenate. W. M. McNABB (J. Amer. Chem. Soc., 1927, 49, 1451—1453).—The precipitation of monopotassium hydrogen arsenate by magnesia mixture is complete in ½ hr., and accurate results are obtained only when the precipitate of magnesium ammonium arsenate is converted into pyroarsenate by ignition to constant weight at 500—600°. S. K. TWEEDY.

Gas-volumetric micro-determination of carbon. C. GRÄNACHER (Helv. Chim. Acta, 1927, 10, 449—471).—A detailed description is given of a method whereby the gases issuing from the combustion tube are completely collected, and the volume change which occurs when the carbon dioxide is absorbed by potassium hydroxide is measured. The gas space within the combustion tube was made as small as possible. G. A. ELLIOTT.

Conductivity method for determination of carbon dioxide. L. E. BAYLISS (Biochem. J., 1927, 21, 662—664).—The method is based on the principle that the migration velocity of the carbonate ion is considerably smaller than that of the hydroxyl ion, and consequently the conductivity of sodium hydroxide falls as it absorbs carbon dioxide. The amount of carbonate in a sodium hydroxide–sodium carbonate mixture can thus be determined when a rapid absorption of carbon dioxide by sodium hydroxide takes place. S. S. ZILVA.

Determination of potassium in presence of iodide. F. S. HAWKINS and J. R. PARTINGTON (J.C.S., 1927, 1397—1398).—The alkali iodides are dissolved in a saturated solution of potassium perchlorate in 96% alcohol, and the potassium is precipitated by the addition of a similar saturated solution of sodium perchlorate. The mixture is boiled, cooled to 0°, and filtered; the precipitate is washed at 0° with the alcoholic potassium perchlorate and dried at 360°. The method is more accurate than the other known methods; it obviates the errors described by Smith and Ross (A., 1925, ii, 437), and is applicable to any potassium salt soluble in 96% alcohol. The result with pure potassium iodide gives a purity of 99·95%. S. K. TWEEDY.

Przibylla's tartaric acid method for the determination of potassium. E. BORSCHE.—See B., 1927, 478.

Semi-quantitative spectral analysis of calcium, strontium, barium, and lithium. K. HUKUDA (Bull. Chem. Soc. Japan, 1927, 2, 115—121).—Dilute solutions of salts fulgurated in a special fulgurator with the electrodes reversed, *i.e.*, with the anode in the solution, are observed spectroscopically. The probable limits of detection of calcium, strontium, barium, and lithium by this method are 0·013, 0·029, 0·018, and 0·0009 mg./c.c., respectively. The procedure requires only about 0·1 c.c. of solution.

J. S. CARTER.

Analysis of hydrated lime by a thermochemical method. D. F. RICHARDSON.—See B., 1927, 477.

Volumetric determination of magnesium, zinc, aluminium, and copper. F. L. HAHN and E. HARTLEB (Z. anal. Chem., 1927, 71, 225—235).—The errors arising in the titration of salts of the metals with alkali hydroxides, due to formation of basic salts and to the adsorption of the alkali by the precipitated hydroxide, are entirely eliminated by the addition of "oxine," 8-hydroxyquinoline, which forms insoluble compounds with the metals, precipitation being complete if the liberated acid is neutralised by addition of standard alkali. The compounds are yellow, but the end-points are quite sharp if phenol-red is used as indicator; in presence of nitrates or other oxidising materials, naphtholphthalein is employed, and the end-point is rendered very sharp by addition of carbon tetrachloride, in which 8-hydroxyquinoline and its metallic derivatives are very soluble. Whilst barium salts do not interfere, calcium must be removed from the solution before the titration. S. I. LEVY.

Separation and determination of metals by means of 8-hydroxyquinoline. III. Zinc. R. BERG (Z. anal. Chem., 1927, 71, 171—185; cf. this vol., 436, 639).—Addition of a 2% alcoholic solution of 8-hydroxyquinoline to an alkaline or acetic acid solution of a zinc salt produces a greenish-yellow precipitate of $Zn(C_9H_6ON)_2,2H_2O$, which loses $0{\cdot}5H_2O$ at 100°, becomes anhydrous at 120—130°, and is converted by ignition into zinc oxide. The solubilities of the precipitate in sodium acetate solutions, in ammonia, and in alkaline tartrate solutions are, respectively, 1 part in 1,000,000 parts, 1 in 277,000, and 1 in 140,000. From all metals except copper, magnesium, and cadmium, zinc may be separated by carrying out the precipitation in strongly alkaline tartrate solution, and from magnesium by precipitation in dilute acetic acid solution. The precipitate may be dried at 100° or ignited to oxide for weighing, or it may be determined bromometrically in the same way as the magnesium precipitate.

A. R. POWELL.

Determination of lead as cyanide. (MLLE.) S. GRUNDT (Compt. rend., 1927, 185, 72—73).—The so-called precipitated lead cyanide of Herz and Neukirch (A., 1923, ii, 879) is actually a mixture of lead oxycyanide and hydroxide. The latter combines with atmospheric carbon dioxide during the washing and drying processes with the production of the mixture $[Pb(CN)_2,2PbCO_3,PbO,H_2O]$. By coincidence, the percentage of lead in this is the same as in the cyanide

Attempts to produce pure lead cyanide from hydrogen cyanide and hydrated lead oxide ($3PbO,H_2O$) in absence of water were unsuccessful, and resulted in the formation of compounds the highest cyanide content of which corresponded with the formula $Pb(CN)_2,PbO$. J. GRANT.

Rapid determination of copper. G. SPAOU and J. DICK (Z. anal. Chem., 1927, 71, 185—189).—The solution of the copper salt (75—100 c.c.) is treated drop by drop with pyridine until it becomes azure-blue, 0·5 g. of solid ammonium thiocyanate is stirred in, and the precipitate collected immediately in a porcelain filtering crucible, washed with cold water containing 3 g. of ammonium thiocyanate and 3 c.c. of pyridine per litre, then with 75 vol.-% alcohol containing 8 c.c. of pyridine and 0·5 g. of ammonium thiocyanate per litre, and finally with absolute alcohol and ether containing a little pyridine, dried in a vacuum at the ordinary temperature, and weighed as $Cu(C_5H_5N)_2(SCN)_2$ which contains 18·817% Cu. A. R. POWELL.

Determination of small quantities of copper in steel. J. D. ARMOUR.—See B., 1927, 487.

Determination of cerium. R. LESSING (Z. anal. Chem., 1927, 71, 161—170).—Bunsen's method of determining cerium volumetrically in mixtures of rare-earth oxides by distillation with hydrochloric acid and potassium iodide yields high results if more than about 1% of praseodymia is present, and cannot therefore be used for determining ceria in the rare earths obtained from monazite. Fairly good results may be obtained by warming the oxide mixture with sulphuric acid and a standard ferrous sulphate solution, and titrating the excess of the latter with permanganate; part of the higher praseodymium oxide reacts with the ferrous salt, and the remainder decomposes with evolution of oxygen. With the monazite earths, the results for cerium are within 1% of those obtained by von Knorre's method. A. R. POWELL.

Determination and separation of the oxidisable constituents of aluminium alloys. G. JANDER and F. BAUR.—See B., 1927, 527.

Use of mercuri-amides in analytical chemistry. M. KRANJČEVIĆ and G. RUKONIĆ (Arhiv Hemiju, 1927, 1, 18—24).—Šolaja's method for the determination of iron and aluminium (A., 1925, ii, 602) is applied to the determination of chromium, of iron in presence of calcium, and of aluminium in presence of magnesium. R. TRUSZKOWSKI.

Detection and determination of very small quantities of iron in water. F. KRÖHNKE.—See B., 1927, 542.

Reaction between ferrous salts and dimethylglyoxime. E. J. KRAUS (Z. anal. Chem., 1927, 71, 189—190).—Under the conditions in which nickel gives a red precipitate with dimethylglyoxime, ferrous salts yield a red coloration. Filtration of the solution is therefore necessary to verify the presence of traces of nickel when the solution contains a ferrous salt. A. R. POWELL.

Use of liquid amalgams in volumetric analysis. VII. Oxidimetric determination of chromium. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 397—409).—See this vol., 333.

Gravimetric determination of chromium with mercury ammonium chloride, $HgClNH_2$. W. PUMM.—See B., 1927, 480.

Potentiometric determination of molybdenum. E. MÜLLER [with P. BRUN and G. UNGER] (Z. Elektrochem., 1927, 33, 182—185).—A method of determining molybdenum (in oxidised compounds) by reducing with zinc to the tervalent condition and titrating the resulting solution with permanganate has been developed by Reissaus (Metall und Erz, 1924). Success of the method depends on complete reduction to the tervalent state and exclusion of air during the titration. In the present work, potentiometric titration of the reduced solution with permanganate was found to give a sharp end-point corresponding with complete oxidation to the sexavalent condition in absence of air, but the accuracy still depends on the efficiency of the preliminary reduction, for the bend in the titration curve corresponding with oxidation to the quadrivalent condition is not well defined, and somewhat displaced, and no bend is found corresponding with conversion into the quinquevalent state. These results are discussed with reference to the potentiometric titration of sexavalent molybdenum with tervalent titanium in which the titration curve exhibits a bend corresponding with reduction to the quinquevalent state. Running a solution of tervalent molybdenum into excess of permanganate and titrating back with ferrous sulphate gives an unsatisfactory end-point by ordinary titration, but gives good results by the potentiometric method, and has the advantage that exclusion of air is not necessary. Fricke (Diss., Dresden, 1923) has shown that an ordinary titration method in presence of air consists in running the solution of tervalent molybdenum into excess of permanganate, adding excess of ferrous sulphate, and then titrating with permanganate. H. J. T. ELLINGHAM.

Determination of molybdenum in iron and steel. E. FÄRBER.—See B., 1927, 526.

Use of liquid amalgams in volumetric analysis. IX. Determination of vanadium and tungsten. K. SOMEYA (Z. anorg. Chem., 1927, 163, 206—212).—A new method is described for the volumetric determination of vanadium; vanadic acid is reduced by zinc amalgam to the vanadous state, and standardised iodine solution added. The excess of iodine is reduced with sodium arsenite solution, and the excess of arsenite titrated with iodine. Cupric sulphate may be employed in place of potassium permanganate for the quantitative volumetric oxidation of tungsten. In strongly acid solution, lead amalgam reduces vanadic acid to the vanadous condition; by adding an excess of cupric sulphate solution and titrating with potassium dichromate solution, using a diphenylamine indicator, vanadium may be accurately determined, provided that the correct acid concentration is maintained. H. F. GILLBE.

Crystallisation of silver beads and detection of the platinum metals by the microscope. C. O. BANNISTER (J. Roy. Micros. Soc., 1927, 47, 143—

144).—The presence of traces of the platinum metals in silver beads obtained by cupellation causes characteristics in the surface crystallisation which permit of the identification of the foreign metal. The bead is merely examined under the microscope. The effects are illustrated by means of plates. S. I. Levy.

Electric furnace for gas reactions. O. Scarpa.—See B., 1927, 529.

Platinum-wound resistance furnace. E. Orton, jun., and J. F. Krehbiel.—See B., 1927, 529.

Flames of atomic hydrogen. I. Langmuir.—See B., 1927, 529.

Carbon dioxide in a mercury interrupter. G. R. Paranjpe and H. D. Tendulkar (Nature, 1927, **120**, 117—118).—Carbon dioxide can be advantageously used instead of coal gas in mercury interrupters. When hydrogen or carbon dioxide is used, the efficiency is greater than when coal gas is used. A. A. Eldridge.

Simple automatic temperature regulator without relays. A. Simon and O. Fischer (Z. anorg. Chem., 1927, **162**, 279—286).—A device is described for maintaining a crucible in an electric oven at a constant temperature for several months. Electric contact is made and broken between a platinum wire and a small platinum sphere floating on mercury in a glass tube. The regulator is operated by the expansion and contraction of the air contained in a double-walled, crucible-shaped glass or porcelain vessel which is fitted in the oven, and into which the crucible or substance to be heated is placed. Instead of the circuit being completely broken, part of the current is allowed to pass through a shunt circuit, the actual current to be broken being thus minimised. Further, since the spark occurs between platinum electrodes, no deposit is formed on the walls of the regulator tube or on the mercury surface. H. F. Gillbe.

Weighing powdered substances in air and in a vacuum. E. Zintl and J. Goubeau (Z. anorg. Chem., 1927, **163**, 105—119).—Weighing a substance in air and reducing the value to a vacuum in the usual manner does not give consistent results for powders, on account of variable adsorption effects. For example, potassium nitrate, weighed as a powder and then melted down to a compact mass, may appear to lose up to 0·09 mg. per g. The deviation is shown not to be due to decomposition of the nitrate or to experimental error. An apparatus and a method are described for precise weighing in a vacuum. H. F. Gillbe.

Measurement of low vapour and partial pressures. H. von Halban and K. Siedentopf (Z. angew. Chem., 1927, **40**, 661—666).—The apparatus consists of a brass rod, mounted vertically in a glass tube through which the gas to be examined passes; the upper end of the rod is maintained at 0° by immersion in a bath of ice and water, the lower end at $-76°$ by immersion in a bath of ether and solid carbon dioxide. The point on the rod at which liquid or solid is deposited is a measure of the concentration of the vapour in the permanent gas. The apparatus is designed for the measurement of partial pressures of water vapour in air of less than 1 mm. (1 g./m.^{3}), and is calibrated for any particular vapour and permanent gas by the employment of known mixtures. It requires only small quantities of the mixture to be examined, readings can be made very quickly, and pressures of water vapour down to 0·001 mm. can be determined under technical conditions. S. I. Levy.

New methods of gas analysis. P. Rassfeld (Z. angew. Chem., 1927, **40**, 669—672).—An account of the methods of employment of the Haber–Löwe gas interferometer, and the principles on which the composition of gas mixtures may be determined from measurement of the refractive index. S. I. Levy.

Ferroxyl indicator in corrosion research with special reference to the problem of local corrosion. U. R. Evans.—See B., 1927, 487.

Mineralogical Chemistry.

Influence of plankton on the phosphate content of stored sea-water. R. Gill (J. Marine Biol. Assoc., 1927, [ii], **14**, 1057—1065).—The alteration in soluble phosphate content of untreated sea-water during storage is governed by the conditions of storage; strong illumination, favourable to growth, produces a decrease, whilst darkness, unfavourable to growth, produces an increase. Samples from the surface layers of the sea give greater increases of phosphate on storage in the dark than samples from deeper water, the extent of the increase being conditioned by the number and quantity of planktonic organisms included in the water sample. The phosphate content per cub. m. of North Sea water off the Northumberland coast increases from 13·5 mg. P_2O_5 at the surface to 34·6 mg. at a depth of 70 m. Surface values at northern stations are higher than those at southern stations, whilst inshore surface waters are richer in phosphate than offshore surface waters. W. Robson.

Relation of plankton to chemical and physical factors in the Clyde sea area. S. M. Marshall and A. P. Orr (J. Marine Biol. Assoc., 1927, [ii], **14**, 837—868).—Data obtained during 1924—1926 show that a close relation exists between the diatom increases and the changes in p_H, dissolved oxygen saturation, and phosphate content. Diatom cultures grow best away from direct sunlight, diatoms in the shade producing oxygen, whilst those in sunlight may even use it up. A fall in the water-temperature curve coincides with dips in those for p_H, dissolved oxygen saturation, and phosphate content. The proximity of rivers affects the silica, but not the phosphate content of the water, whilst the saline content and rainfall curves are closely related. Where animal life is rich, dissolved oxygen saturation and p_H values are low and phosphate values high. The regeneration of phosphate in the deep water of Loch Strivan is described. W. Robson.

Adsorption of ions from sea-water by sand. F. P. Stowell (J. Marine Biol. Assoc., 1927, [ii], 14, 955—966).—The adsorption of the electrolytic constituents of sea-water by sand is small. Percolation of sea-water through sand causes a slight abnormality in the concentrations of calcium and magnesium ions, due to the fact that sand is not an inert adsorbing agent, but is capable of discharging calcium ions into the water in exchange for magnesium and sodium. The extent of adsorption and exchange is insufficient to cause hydrolysis and alteration in p_H if the volume of the sea-water is large. W. Robson.

Present position of the lignin theory of [the origin of] coal. W. Fuchs (Brennstoff-Chem., 1927, 8, 187—190).—A critical review of recent work on the decomposition, under natural conditions, of cellulose and lignin. The results obtained, although complicated by the probable existence of more than one kind of lignin, support the theory that the cellulose in plants is broken down, by the action of simple organisms, to lower fatty acids, and that the lignin, which is more resistant and therefore increases in relative quantity in the decomposing vegetable matter, ultimately loses acetyl and methoxyl groups and is converted into alkali-soluble humic acids, which are further transformed into alkali-insoluble humins and finally into coal.

W. T. K. Braunholtz.

Iodine content of the salt from Rumanian rock-salt mines. D. Radulescu and V. Georgescu.—See B., 1927, 479.

Hydrated alumina of the bauxites [boehmite]. J. de Lapparent (Compt. rend., 1927, 184, 1661—1662; cf. A., 1924, ii, 269).—In certain bauxites from Cadarcet and Var in which the crystalline structure is particularly well developed, orthorhombic crystals formed by a monohydrate of alumina may be seen. Their form results from a combination of the prism *m* (110) and the base *p* (001), the acute angle of the *m* faces being 63°. The mineral has a sharp cleavage plane parallel to the direction *g′* (010), its maximum birefringence is of the order of 0·020, and the mean refractive index is a little higher than that of the surrounding hydrargillite. The author considers the mineral to be a new type of monohydrated alumina which he names *boehmite*. He discusses the possibility of its identity with Boehm's bauxite (A., 1926, 113). J. Grant.

Thorotungstite. A mineral containing tungsten and thorium from the Federated Malay States. J. B. Scrivenor and J. C. Shenton (Amer. J. Sci., 1927, [v], 13, 487—490).—A new mineral, thorotungstite, containing honey-yellow crystals was found in the Kramat Pulai mine. The crystals were transparent, apparently orthorhombic, *d* 5·55, and contained WO_3 69·69, ThO_2 16·00, Al_2O_3 4·31, Fe_2O_3 1·35, SiO_2 0·48, ZrO_2 1·96, CaO 1·02, rare earths (chiefly ceria) 1·77%, magnesia trace, loss on ignition (H_2O) 4·18, total 100·76%. The nearest molecular formula is $(ThO_2,Ce_2O_3,ZrO_2),H_2O+2WO_3,H_2O$. C. J. Smithells.

Organic Chemistry.

[Exceptional instances of stereoisomerism.] G. Hahn (Ber., 1927, 60, [*B*], 1362—1364).—A comment on the conceptions of Senior (this vol., 226), whose idea of internal compensation is considered to be too narrow. H. Wren.

Synthesis of paraffin hydrocarbons of high mol. wt. from carbon monoxide. F. Fischer and H. Tropsch [with W. Ter-Nedden] (Ber., 1927, 60, [*B*], 1330—1334).—The reaction of water gas at an iron–copper (4 : 1) contact impregnated with potassium carbonate gives rise to solid paraffin hydrocarbons the most sparingly soluble fraction of which has m. p. 104—117°, solidifying point 109°, and appears to contain on the average about 71 carbon atoms in the molecule. Formation is attributed either to the action of hydrogen on the metallic carbide or to the production and subsequent polymerisation of methylene. H. Wren.

Addition of hydrogen bromide to allene hydrocarbons. M. Bouis (Compt. rend., 1927, 184, 1563—1565).—The addition of hydrogen bromide to $\Delta^{\alpha\beta}$-pentadiene yields β-bromo-Δ^{α}-pentene (cf. Lespieau, A., 1921, i, 656), β-*bromo*-Δ^{β}-*pentene*, and ββ-dibromopentane. The two first-named compounds are not isolated in a state of purity, but as a mixture, b. p. 106—115°/760 mm. These results are discussed in relation to the analogous work on dimethylallene and on diethylallene (Mokievsky, A., 1900, i, 509; Ipatiev, A., 1899, i, 657). G. A. C. Gough.

Tautomerism of the two erythrene dibromides. C. Prévost (Compt. rend., 1927, 184, 1460—1462).—Tetramethylerythrene (βε-dimethyl-$\Delta^{\beta\delta}$-hexadiene), obtained by the action of sodium in benzene at 60° on *iso*crotyl bromide, has m. p. 14·5°, b. p. 134·6°/750 mm., $d_4^{17·8}$ 0·7646, $n_D^{19·5}$ 1·4796, and is relatively stable when pure. With 2 mols. of bromine at —20° to —10°, it affords a liquid product which slowly solidifies. The solid product, true m. p. 72°, is regarded as βε-*dibromo*-βε-*dimethyl*-Δ^{γ}-*hexene*, and when heated slowly melts at 45—50°, undergoing transformation into the liquid isomeride, βγ-*dibromo*-βε-*dimethyl*-Δ^{δ}-*hexene*. It is suggested that in general bromination of the erythrenes affords initially the βγ-dibromo-derivative which is usually in metastable equilibrium and is transformed with slight elevation of temperature into the βε-derivative. Negative substituents in positions β and ε enhance the mobility of the ε-bromine atom but decrease that of the β-bromine. Attempts to introduce 4 atoms of bromine into di*iso*crotyl failed, halogen hydride being eliminated. R. Brightman.

Reactions of the di*iso*crotyl dibromides. C. Prévost (Compt. rend., 1927, **184**, 1561—1563).—The two isomeric di*iso*crotyl dibromides (preceding abstract) lose hydrogen bromide when heated at 100°, to yield *α-bromo-βε-dimethyl-*$\Delta^{\beta\delta}$*-hexadiene*, b. p. 85—86°/12 mm., d_4^{18} 1·2230, n_D^{18} 1·5522. The latter, on treatment with sodium acetate or with silver acetate, yields *βε-dimethyl-*$\Delta^{\beta\delta}$*-hexadien-α-yl acetate*, b. p. 79°/3·5 mm., d_4^{17} 0·9597, n_D^{17} 1·4890, and a *hydrocarbon*, $C_{16}H_{28}$. *βε-Dimethyl-*$\Delta^{\beta\delta}$*-hexadien-α-ol*, b. p. 77°/3 mm., d_4^{17} 0·9197, n_D^{17} 1·5095, obtained from the acetate in the usual way, yields on hydrogenation a small amount of βε-dimethylhexan-α-ol, together with large quantities of condensation products.

G. A. C. Gough.

Stereochemistry of the tetrahedral carbon atom. V. Salt formation from the nitroparaffins. R. Kuhn and H. Albrecht (Ber., 1927, **60**, [*B*], 1297—1308).—The optically active *sec.*-butyl alcohols (cf. Pickard and Kenyon, J.C.S., 1913, **103**, 1937) are transformed into the corresponding iodides, which are then treated with silver nitrite at 0°. The mixture of active *sec.*-butyl nitrites and *β-nitrobutanes* is separated by fractional distillation, whereby the latter substances are obtained mixed with less than 0·2% of nitrite. The analytically homogeneous material has b. p. 35—36°/17 mm., 55—56°/47 mm., d_4^{17} 0·9854, n_D^{17} 1·4057; partial racemisation, however, occurs to a variable extent during the preparation, the most active specimen having $[\alpha]_D^{18}$ +9·14° in substance. Treatment of the active β-nitrobutanes with 5*N*-sodium hydroxide in methyl-alcoholic solution at the ordinary temperature causes complete racemisation, whereas at lower temperatures or in more dilute solution activity persists, but salt formation is incomplete. The action of the necessary quantity of sodium methoxide in methyl-alcoholic solution gives the sodium salt of *aci*-β-nitrobutane, the activity of which is about 60% of that of the nitro-compound. Addition of excess of methoxide tends to enhance the optical activity. The almost complete salt formation is established by the observations that the activity of the aqueous solutions is scarcely affected by extraction with ether, and that volumetric determination of the *aci*-form with bromine in presence of ferric chloride as indicator shows 80% of the calculated quantity when operations are very rapidly performed in strongly cooled solution. Precipitation of the sodium salt from its methyl-alcoholic solution by a large excess of ether gives a product retaining 25—30% of the original activity, whereas the residues from the ethereal liquor are optically inactive, so that unchanged nitro-compound, nitrite, or alcohol cannot be causative of the observed activity. This conclusion is confirmed by the formation of optically active β-bromo-β-nitrobutane, $[\alpha]_D$ +1·42° in substance, which can be derived only from the *aci*-form. The existence of the latter form in an optically active condition is not compatible with the customary formulation, and the electronic constitution,  $\begin{array}{l}\quad\;\;\mathrm{Me}\\ \mathrm{Et}:\overset{-}{\mathrm{C}}:\overset{+}{\mathrm{N}}:\mathrm{O}:\\ \qquad\quad\;\; :\mathrm{O}:^{-}\ \mathrm{Na}^{+}\end{array}$, is therefore proposed, which is shown to harmonise with the general chemical properties of the compound.

H. Wren.

Ester formation in ethylene glycol. A. Kailan and K. Melkus (Monatsh., 1927, **48**, 9—35).—The velocity of esterification (which goes to completion) of *n*-butyric, benzoic, salicylic, and *o*- and *p*-hydroxybenzoic acids in anhydrous and wet ethylene glycol with hydrogen chloride as a catalyst has been measured at 25°, and the effects of varying concentrations of acid, water, and catalyst have been determined; intrapolation formulæ expressing the velocity constant as a function of the concentrations of the water and the catalyst are given in each case. In anhydrous glycol, the velocity is proportional to the concentration of the catalyst, but in presence of water it increases more rapidly than proportionality requires. Combining these results with those obtained by Goldschmidt and Udby (A., 1907, ii, 852) for ethyl alcohol and earlier results of Melkus for glycerol, the following conclusions are reached. For a water concentration (*w*) of 0·03 mol./litre, the value of the unimolecular velocity constant (*k*) for salicylic acid in glycol is 60% greater and for the other acids 30% smaller than in alcohol. As in ethyl alcohol, the retarding influence of water is greatest with benzoic and least with butyric acid, and is slightly less in glycol than in glycerol, and much less than in alcohol. The relative values of *k* for benzoic acid and its *o*-, *m*-, and *p*-hydroxy-derivatives in acid concentrations of $\frac{1}{6}$ mol./litre, and with w=0·065, are 1 : 0·073 : 1·115 : 0·39 in glycol and 1 : 0·037 : 1·17 : 0·43 in alcohol, chlorohydrin formation affecting the figures for salicylic acid. The values of *k* for butyric and benzoic acids in glycol are, respectively, 2·5—3 and 1·25—2 times as great (depending on the concentrations of water and the catalyst) as in glycerol.

J. W. Baker.

Lactacidogen. V. G. Embden and M. Zimmermann (Z. physiol. Chem., 1927, **167**, 114—136).—A new *hexosemonophosphoric acid*, $[\alpha]_D^{20}$ +29·5°, has been isolated from fresh rabbit muscle and analysed as the crystalline *brucine* salt and the amorphous *barium* salt. The acid, like lactacidogen, leads to an increased formation of lactic and phosphoric acids by muscle juice. Although muscle juice under the influence of sodium fluoride synthesises hexosediphosphoric acid (A., 1925, i, 729), no actual proof of the presence of this acid in fresh muscle can be obtained.

A. Wormall.

Hexosediphosphoric acid. I. α- and β-Methylhexosidediphosphoric acids. W. T. J. Morgan (Biochem. J., 1927, **21**, 675—688).—The hexosides were prepared by Fischer's method. The changes in rotation in the process of methylation suggested the formation of two isomerides. The barium derivatives of the methylated compounds can be separated roughly by fractional precipitation of the aqueous solution with ethyl alcohol. A more complete separation was obtained by the preparation of the brucine salts, from which the barium salts were obtained, barium β-methylhexosidediphosphate, $C_6H_9O_3(OMe)(PO_4Ba)_2$, $[\alpha]_{\mathrm{Hg}}^{18}$ −10·4°, free acid, $[\alpha]_{\mathrm{Hg}}^{18}$ −23·2°, and barium α-methylhexosidediphosphate,

$[\alpha]_{\mathrm{Hg}}^{18}$ +8·2°, free acid, $[\alpha]_{\mathrm{Hg}}^{18}$ +19·7°. The methyl group of the α-acid is more rapidly removed by hydrolysis than that in the corresponding β-compound. Neither hexoside is hydrolysed by emulsin. Invertase causes a partial removal of the methyl group from the α-hexoside, but not from the β-compound. Bone enzyme rapidly removes the phosphoric acid groups from the β-compound, producing a strongly lævorotatory, non-reducing substance possessing the properties of a fructoside. The methylation of hexosediphosphoric acid yielded a non-reducing syrup consisting largely of the hexamethyl-methylhexosidediphosphoric acid.

S. S. Zilva.

Aliphatic and alicyclic disulphones. A. Rècsei (Ber., 1927, 60, [*B*], 1420—1423).—The action of hydrogen chloride on a mixture of ethyl mercaptan and dipropyl ketone affords *diethylthioldi*-n-*propylmethane*, which could not be distilled without decomposition. It is oxidised by aqueous permanganate to *diethylsulphonyldi*-n-*propylmethane*, m. p. 109·5°. Similarly, *n*-propyl *iso*propyl ketone gives the corresponding *dithiol*, oxidised to *diethylsulphonyl*-n-*propyl*iso*propylmethane*, m. p. 91°. *cyclo*Hexanone and ethyl mercaptan afford 1 : 1-*diethylthiol*cyclo*hexane*, b. p. 67—110°/12 mm. (partial decomp.), from which 1 : 1-*diethylsulphonyl*cyclo*hexane*, m. p. 121°, is derived. 2-*Chloro*-1 : 1-*diethylsulphonyl*cyclo*hexane*, m. p. 91°, is obtained from 2-chloro*cyclo*hexanone. Oxidation of the higher thiols is difficult. Hydrogen peroxide, chromic acid, and dilute nitric acid are ineffective; diluted Caro's acid is inferior to permanganate. The sulphones described above are much more active pharmacologically than sulphonal.

H. Wren.

Preparation of pure oleic acid. S. H. Bertram (Rec. trav. chim., 1927, 46, 397—401).—From a comparative, quantitative study of the numerous methods available for the purification of oleic acid, the author concludes that, hitherto, oleic acid has never been obtained free from appreciable quantities both of saturated and higher unsaturated acids, and suggests that the main cause of the difficulty is the isomorphism of oleic acid and its impurities. Oleic acid containing less than 0·4—0·5% of saturated acids may be prepared by adding 100 g. of crude oleic acid to a warm mixture of 175 g. of mercuric acetate, 140 c.c. of methyl alcohol, and 35 c.c. of glacial acetic acid, and heating for 2 min. on the steam-bath. After keeping for 24 hrs., the mixture is filtered and the complex mercury compound in the filtrate decomposed by boiling with 50 c.c. of hydrochloric acid (*d* 1·19). The resulting mixture of ester and acid, after extraction with light petroleum (b. p. 40—60°), is hydrolysed. It was not found practicable to remove all higher unsaturated acids by extraction of the calcium, barium, or lithium salts with ether, benzene, light petroleum, or alcohol, but this was effected by crystallising the oleic acid from an equal volume of acetone at —10° to —15°, and washing with acetone at —20°. The resulting product consisted of colourless, transparent, needles, m. p. and s. p. 13·2°, which changed to a more stable, white modification, m. p. 16°. It then had the constants, iodine value (Hübl) 89·55, n_{D}^{20} 1·45823, n_{D}^{70} 1·44179, and contained only 0·49% of saturated acids. Elaidic and erucic acids may be purified similarly.

E. Holmes.

Acid soaps: crystalline potassium hydrogen dioleate. J. W. McBain and A. Stewart (J.C.S., 1927, 1392—1394).—*Potassium hydrogen dioleate*, an anhydrous, crystalline, acid soap, has been isolated at 0° from alcoholic solutions containing oleic acid and potassium oleate in molecular proportions varying between 1 to 2 and 2 to 1, respectively. Analyses by hydrolysis with hydrochloric acid and by the determination of saponification values show good agreement, and account for 99·8% (average) of the sample taken. The compound, which may be crystallised unchanged from oleic acid, has a transition point at 43° and liquefies completely above 107°, whilst decomposition occurs when it is maintained at 55—60°.

E. Holmes.

Thermal decomposition of aryl esters of fumaric and cinnamic acids into *s*-diarylethylenes. R. Anschütz (Ber., 1927, 60, [*B*], 1320—1322; cf. Skraup and Beng, this vol., 560).—Thermal decomposition of phenyl fumarate affords phenyl cinnamate and ultimately stilbene. If a substituent is present in the phenyl group, the intermediate product cannot be isolated; the yields of *s*-diarylethylenes are lower, and the products are frequently uninviting resins. The following fumarates are described (cf. Wirtz, Diss., Bonn, 1887; Selden, Diss., Erlangen, 1888; Böringer, Diss., Bonn, 1919): o-*tolyl*, plates, m. p. 88—89°, or needles, m. p. 85°, b. p. 225°/12 mm.; m-*tolyl*, plates, m. p. 88°, or needles, m. p. 83°, b. p. 237°/12 mm.; p-*chlorophenyl*, m. p. 178° (and thence 4 : 4′-*dichlorostilbene*, m. p. 170°); p-*bromophenyl*, m. p. 174° (and thence 4 : 4′-dibromostilbene, m. p. 210—211°); p-*nitrophenyl*, m. p. 219—211° (decomp.). *Phenyl fumaranilate*, m. p. 214°. The following cinnamates are described: p-*chlorophenyl*, m. p. 105° (and thence p-*chlorostilbene*, m. p. 127°; *dibromide*, m. p. 190°); p-*bromophenyl*, m. p. 116° (and thence p-*bromostilbene*, m. p. 135°; *dibromide*, m. p. 199°); o-*nitrophenyl*, m. p. 84·5°; p-*nitrophenyl*, m. p. 146°; *phenyl* p-*nitrocinnamate*, m. p. 152°, from p-*nitrocinnamoyl chloride*, b. p. 205—210°, m. p. 124—125°, and phenol; p-*acetamidophenyl cinnamate*, m. p. 220°. The gaseous products of the thermal decomposition of the esters generally contain carbon monoxide in addition to carbon dioxide, and, frequently, the phenol employed in the preparation of the ester.

H. Wren.

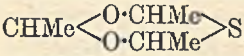
Lactones derived from simple sugars. H. D. K. Drew, E. H. Goodyear, and W. N. Haworth (J.C.S., 1927, 1237—1245).—Ten completely methylated lactones derived from normal and γ-forms of completely methylated glucose, galactose, mannose, xylose, and arabinose have been studied, with the object of establishing a comparison of the rates of hydrolysis of these lactones from the point of view of their structural relationships. Tables and comparative figures are given, together with a graph representing the percentage amount of lactone present in aqueous solution during 10 days. It is demonstrated that for each pair of lactones derived from a normal and a γ-form of the same sugar, the curve representing the rate of formation of γ-hydroxy-acid from γ-lactone is sharply distinguished from that representing the rate of formation of δ-hydroxy-acid from δ-lactone, the latter being much the steeper. Between the two extremes are found two less steep δ-lactone curves (trimethyl-δ-xylono- and tetramethyl-δ-mannono-lactones) and two less flat γ-lactone curves (trimethyl-γ-arabono- and trimethyl-γ-glucono-lactones), this phenomenon being the subject of further investigation. These results confirm the earlier findings of Charlton, Haworth, and Peat (A., 1926, 273) as to the structure of the constituent sugars. E. HOLMES.

Condensation of pyruvic acid with para-formaldehyde in presence of sulphuric acid. V. V. THEOPHILAKTOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 759—766).—The products obtained by condensing pyruvic acid with formaldehyde in presence of sulphuric acid comprise a solid *acid*, $C_9H_8O_6$ (and not $C_8H_8O_6$, as described by O. Kaltwasser), m. p. 234°, and a *lactone*, m. p. 140—144°, which loses water when slowly heated to 90°, giving a viscous liquid, which sets to a glassy mass. The alkali salts of the acid did not crystallise, whilst the silver salts lost water on keeping for 15 min., to give a viscous mass. Phenylhydrazine gave an amorphous, yellow, very unstable precipitate, whilst hydroxylamine hydrochloride gave an *oxime*, m. p. 192—194° (decomp.). On oxidation with 3% hydrogen peroxide, a *lactone-acid*, m. p. 112—113°, was obtained. Acetic anhydride gave an *acetyl* derivative, m. p. 193°, with loss of a molecule of water. On reduction of the lactone with hydrogen in presence of platinum-black, two neutral isomeric *solids*, m. p. 219° and 234—235°, differing in crystalline form, were obtained. With tin and hydrochloric acid, only the isomeride of m. p. 219° was formed. The lactone did not give a coloration with ferric chloride. M. ZVEGINTZOV.

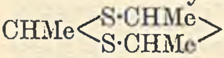
Transformation of acetaldehyde into its enolic form. S. A. SCHOȚ (Compt. rend., 1927, **184**, 1452—1454).—The absorption curves in ultra-violet light of acetaldehyde solutions show marked maxima at λ 2215 in 0·01*N*-sodium hydroxide and at λ 2205 in dilute hydrochloric acid, and minima at λ 2475 and 2465 Å., respectively. A solution of paracetaldehyde in dilute hydrochloric acid gives an absorption curve showing a maximum at λ 2205 and a minimum at λ 2465 Å. These maxima and minima indicate the presence of the enolic form of acetaldehyde, $CH_2{:}CH{\cdot}OH$, and in the proportion calculated from the curves of 1 in 335 in sodium hydroxide solution, 1 in 830 in hydrochloric acid solution, and 1 in 1045 for paracetaldehyde in hydrochloric acid solution.
R. BRIGHTMAN.

α-Bromo-aldehydes. A. KIRRMANN (Compt. rend., 1927, **184**, 1463—1465).—Addition of magnesium ethyl bromide to excess of α-bromovaleraldehyde at −10° affords the expected bromohydrin in small yield, the main product being an *olefine*, C_9H_{18}, b. p. 144°, d^{21} 0·742, n^{21} 1·4259. Similarly, α-bromoheptaldehyde and magnesium methyl bromide afford a little *γ-bromo-β-octanol*, b. p. 106—107°/12 mm., d^{16} 1·207, n^{16} 1·4751, together with methyl hexyl ketone, b. p. 64°/12 mm., 173°/760 mm., d^{16} 0·823, n^{16} 1·4196 (Moureu and Delange, A., 1903, i, 399), a tertiary *alcohol*, b. p. 79—80°/12 mm., d^{19} 0·823, n^{19} 1·4299, probably β-methyloctan-β-ol, and an *olefine*, C_9H_{18}, b. p. 146°, d^{16} 0·738, n^{16} 1·4243, resulting from dehydration of the tertiary alcohol (cf. Henry, A., 1907, i, 744). Since the action of lead hydroxide on α-bromoheptaldehyde affords heptoic acid, and not the expected aldehyde-alcohol, it is probable that the ketone is formed by molecular transposition in the action of magnesium methyl bromide, and not through the ethylene oxide, as suggested by Henry (*loc. cit.*). α-Halogeno-aldehydes thus behave in some respects as acyl halides.
R. BRIGHTMAN.

Mono- and di-thiotriacetaldehydes. S. W. LEBEDEV and M. S. PLATONOV (J. Russ. Phys. Chem. Soc., 1926, **58**, 705—711).—The products of the polymerisation of acetaldehyde by hydrogen sulphide in acid solution contain a triple *polymeride*,



$CHMe<\begin{matrix}O{\cdot}CHMe\\O{\cdot}CHMe\end{matrix}>S$, m. p. 53·5—54°, b. p. 160° (decomp.). Acid potassium permanganate gives a colourless *sulphone*, m. p. 150—152°. Further action of hydrogen sulphide gives a mixture of the monothiotriacetaldehyde with *dithiotriacetaldehyde*,



$CHMe<\begin{matrix}S{\cdot}CHMe\\S{\cdot}CHMe\end{matrix}>O$, m. p. 70—72°, which can be separated by fractionation. It does not react with phenylhydrazine or semicarbazide. Acid potassium permanganate oxidises it to a disulphone, decomp. 215°. Of the theoretically possible five optical and geometrical isomerides for each compound, only one, probably the stable racemic *trans*-form, was obtained.
M. ZVEGINTZOV.

New, unsaturated anhydro-sugar. K. MAURER and H. MAHN (Ber., 1927, **60**, [*B*], 1316—1320; cf. A., 1926, 602).—The action of diethylamine on acetobromoglucose in presence of benzene affords diethylammonium bromide and a *tetra-acetyl* compound, $C_{14}H_{18}O_9$, m. p. 61—62°, $[\alpha]_D^{18}$ −16·87° in ethyl alcohol. The compound reduces Fehling's solution, is readily decomposed by concentrated mineral acids, and is not converted into dextrose by 0·1*N*-hydrochloric acid. It is decomposed by hydrogen bromide in glacial acetic acid. It does not appear to react with phenylhydrazine. It takes up halogen with evolution of halogen acid; the *bromo*-derivative is very unstable, the *chloro*-compound relatively stable. Hydrolysis with methyl-alcoholic ammonia converts the tetra-acetate into an amorphous *powder*, m. p. about 94°, decomp. 134°, analyses of which do not agree well with results required for the expected anhydro-sugar, $C_6H_{10}O_5$; re-acetylation of the amorphous product does not give the original tetra-acetate.

Acetobromogalactose and diethylamine similarly yield a crystalline *tetra-acetate*, $C_{14}H_{18}O_9$, m. p. 110°, $[\alpha]_D^{21}$ +4·69° in ethyl alcohol. H. WREN.

Reactivity of the methylated sugars. I. Action of alkaline hydrogen peroxide solution on tetramethyl-*d*-glucose. E. L. GUSTUS and W. L. LEWIS (J. Amer. Chem. Soc., 1927, **49**, 1512—1521).—Oxidation of βγδζ-tetramethylglucose (100 g.) with alkaline hydrogen peroxide yields carbon dioxide (13·42 g.), formic acid (33·78 g.), *dimethyl*-d-

arabonolactone (17·24 g.), m. p. 77°, $\alpha=1{\cdot}475$, $\gamma=1{\cdot}526$, $[\alpha]^{20}_{D}$ +89° in water, falling to +71·8° in 237 hrs. (p-*bromophenylhydrazide*), demethylated hexonic and pentonic acids (3·59 g.), and methyl esters of methylated tetronic acids (6·7 g.) containing probably methyl mono- and di-methyl *d*-erythronates. These results indicate the oxidation of an αβ-enediol, together with some total destruction of the sugar molecule. This, and the known stability of the methylated sugars, are explained if enolisation is effected by keto–enol tautomerisation rather than by selective addition and loss of water.

F. G. Willson.

Sugar carbonates. III. Derivatives of γ-methylfructoside, γ-ethylfructoside, and normal methylfructoside. C. F. Allpress, W. N. Haworth, and J. J. Inkster (J.C.S., 1927, 1233—1236).—The condensation of γ-methylfructoside with methyl chloroformate in chloroform containing pyridine yields *tetracarbomethoxy-γ-methylfructoside*, b. p. 226—227°/0·1 mm., $[\alpha]_D$ +19·8° in acetone, whilst the corresponding *tetracarbethoxy-γ-methylfructoside* has b. p. 235—238°/0·07 mm., $[\alpha]_D$ +22·5°. *γ-Ethylfructoside*, $[\alpha]_D$ +28°, condenses with ethyl chloroformate to give *tetracarbethoxy-γ-ethylfructoside*, b. p. 228°/0·05 mm., $[\alpha]_D$ +27·5° in ethyl alcohol. These products retain the structure of the original methyl- and ethyl-fructosides, but the fructosidic methyl and ethyl groups lose much of their labile character. Methylation of the normal forms of tetracarbomethoxyfructose and tetracarbethoxyfructose, previously prepared by Allpress and Haworth (A., 1924, i, 943), has resulted in the preparation of *tetracarbomethoxymethylfructoside*, m. p. 107°, $[\alpha]_D$ −126·1° in chloroform, and *tetracarbethoxymethylfructoside*, $[\alpha]_D$ −90·9° in acetone, neither of which reduces Fehling's solution.

E. Holmes.

Hydrazine compounds of α-glucoheptose. E. Glaser and N. Zuckermann (Z. physiol. Chem., 1927, 167, 37—69).—The following compounds have been prepared : *α-glucoheptose*-p-*nitrophenylhydrazone*, m. p. 199°, $[\alpha]^{16}_{D}$ −39°; *α-glucoheptose*-p-*nitrophenylosazone*, m. p. 243°; *α-glucoheptose*-o-*nitrophenylhydrazone*, m. p. 172°; *α-glucoheptose*-o-*nitrophenylosazone*, m. p. 220°; *α-glucoheptose*-2 : 4-*dinitrophenylhydrazone*, m. p. 180°, $[\alpha]^{17}_{D}$ −28°; *α-glucoheptose*-2 : 4-*dinitrophenylosazone*, m. p. 231°; *α-glucoheptose*-o-*tolylosazone*, m. p. 177°, $[\alpha]^{16}_{D}$ −9°; *α-glucoheptose*-m-*tolylosazone*, m. p. 186°, $[\alpha]^{17}_{D}$ −31°; *α-glucoheptose*-p-*tolylosazone*, m. p. 215°, $[\alpha]^{17}_{D}$ ±0°; *α-glucoheptosephenylbenzylhydrazone*, m. p. 156—157°; *α-glucoheptosephenylbenzylosazone*, m. p. 216—218°, $[\alpha]^{18}_{D}$ −44°; *α-glucoheptosephenylmethylosazone*, m. p. 173°, $[\alpha]^{16}_{D}$ −204°; *α-glucoheptosephenylethylhydrazone*, m. p. 145°, $[\alpha]^{16}_{D}$ −23°, and *α-glucoheptose-β-naphthylhydrazone*, m. p. 182°, $[\alpha]^{17}_{D}$ −13°. The preparation and properties of d-*glucose*-2 : 4-*dinitrophenylhydrazone*, m. p. 118—122°, $[\alpha]^{16}_{D}$ +12°, and d-*glucose*-2 : 4-*dinitrophenylosazone*, m. p. 256—257°, $[\alpha]^{16}_{D}$ −133°, are described. All are well crystalline except the second-named above, and these compounds can be prepared easily except α-glucoheptosebenzylphenylosazone, the formation of which requires 2—3 weeks. The crystalline form, solubility, m. p., and optical rotation of these compounds and those of the corresponding compounds of *d*-glucose and *l*-xylose, where known, are tabulated. The α-glucoheptose compounds are all lævorotatory or inactive in pyridine–methyl alcohol solution; the corresponding *l*-xylose compounds behave similarly, but of the *d*-glucose compounds examined about half are dextrorotatory and about half lævorotatory

For the detection of α-glucoheptose, the preparation of the hydrazones and osazones with *p*-nitrophenylhydrazine and 2 : 4-dinitrophenylhydrazine is recommended. For micro-chemical purposes, the compounds with phenylbenzylhydrazine and phenylethylhydrazine are most suitable, on account of their characteristic crystalline forms. In the purification of α-glucoheptose, the phenylbenzylhydrazone is prepared and decomposed with formaldehyde, whilst for the separation from dextrose, the insolubility of α-glucoheptose-2 : 4-dinitrophenylhydrazone in cold ethyl alcohol compared with the corresponding glucose compound is utilised.

A. Wormall.

Degradation of reducing bioses. VI. *d*-Galacto-*d*-arabinose obtained by degradation of lactose. G. Zemplén (Ber., 1927, 60, [*B*], 1309—1312; cf. A., 1926, 1229).—After being preserved during several months, *d*-galacto-*d*-arabinose yields crystals, m. p. 166—168° (decomp.), $[\alpha]^{20}_{D}$ −50·3° to −63·1° in water after 25 hrs. The identity of the product with that derived from the oxidative degradation of calcium lactobionate is established.

H. Wren.

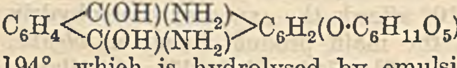
Synthesis of maltose. A. Pictet and H. Vogel (Compt. rend., 1927, 184, 1512—1514).—Maltose, in the form of the octa-acetyl derivative, is isolated from the product obtained by heating equal molecules of α- and β-glucose at 160° in a vacuum. The identity of the sugar is established by the preparation of maltose, together with its osazone and nitrate, from the synthetic acetyl compound.

G. A. C. Gough.

Third component sugar of scammonine. E. Votoček and F. Valentin (Arhiv Hemiju, 1927, 1, 3—5).—Scammonic acid yields on hydrolysis with 10% sulphuric acid not only dextrose and rhodeose, but also *l*-rhamnose.

R. Truszkowski.

Ruberythric acid. E. Glaser and O. Kahler (Ber., 1927, 60, [*B*], 1349—1356).—Alizarin is converted by acetobromoglucose in alkaline solution into the corresponding 2-*tetra-acetylgluco*-derivative, $C_{14}H_6O_2(OH){\cdot}O{\cdot}C_6H_7O_5Ac_4$, m. p. 203°, $[\alpha]^{17}_{D}$ −6·9° in acetone; the second hydroxy-group of alizarin is not attacked by a large excess of acetobromoglucose. It is converted by acetic anhydride and pyridine into the *acetyl* compound, $C_{30}H_{28}O_{14}$, m. p. 192—193°. The non-acetylated glucoside is decomposed by methyl-alcoholic ammonia into alizarin and the 1 : 2-*diglucosido*-derivative,



$C_6H_4{<}\begin{matrix}C(OH)(NH_2)\\C(OH)(NH_2)\end{matrix}{>}C_6H_2(O{\cdot}C_6H_{11}O_5)_2$, m. p. 193—194°, which is hydrolysed by emulsin to 9 : 10-*diamino*-1 : 2 : 9 : 10-*tetrahydroxy*-9 : 10-*dihydroanthracene*, m. p. 193—194°. The diglucosido-compound is converted by cold, concentrated hydrochloric acid into 1 : 2-*diglucoalizarin*, $C_{14}H_6O_2(O{\cdot}C_6H_{11}O_5)_2$, m. p.

213—214°, which is not identical with ruberythric acid. The acid is probably an alizarinmaltoside.

H. Wren.

Structure of starch. II. E. Peiser (Z. physiol. Chem., 1927, **167**, 88—90).—Acetylated starch (cf. this vol., 136), suspended in toluene and chlorinated with phosphorus pentachloride at 105°, yields a colourless substance, $C_{48}H_{56}O_{42}ClAc_{25}$. Attempts to remove the chlorine atom without the simultaneous removal of the acetyl groups have been unsuccessful. It is concluded that starch contains, in the middle of the monosaccharide chain, an aldehydic group which is not as firmly attached as the others, and that the adjacent alcohol group is not free, but is concerned in the chain formation. A. Wormall.

Cryoscopic behaviour of glycogen acetate. K. Hess and R. Stahn (Annalen, 1927, **455**, 115—122).—The cryoscopic behaviour of glycogen acetate (Pringsheim and Lassmann, A., 1922, i, 634) in acetic acid in absence of air resembles that of cellulose and inulin acetates (cf. following abstracts), although a value of the mol. wt. corresponding with a dextrose anhydride unit is not reached, the initial value in dilute solutions being midway between that of a glucosan triacetate and a biosan hexa-acetate. Hence the latter cannot be regarded as the fundamental unit. The recovered material at the end of the experiment is identical with the starting material.

J. W. Baker.

Cryoscopic behaviour of inulin acetate. K. Hess and R. Stahn (Annalen, 1927, **455**, 104—114).—Inulin triacetate, $[\alpha]_D^{19}$ $-40{\cdot}5°$ in acetic acid, prepared by the method of Bergmann and Knehe (A., 1926, 1230) from commercial inulin or chicory inulin, exhibits a similar irregular variation of its mol. wt. with time to that shown by cellulose acetates when the determination is carried out by the cryoscopic method in absence of air (cf. following abstract). In low concentrations, the value of the mol. wt. falls to that of a lævulose anhydride triacetate, before increasing slowly to infinity. In presence of air, the mol. wt. is almost a linear function of the concentration of the solution. J. W. Baker.

Cellulose. XXV. Cryoscopic behaviour of cellulose acetates. K. Hess and G. Schultze (Annalen, 1927, **455**, 81—103).—When amorphous cellulose triacetate (obtained by acetylation of cellulose with acetic anhydride and zinc chloride) is treated with acetic acid at 18—20°, only a small proportion goes into solution, and when this soluble portion is recovered and again treated with acetic acid, the same phenomenon is observed, and the process may be repeated until the whole of the sample is insoluble. The same observation is made at 45° and 60°, but at higher temperatures (90° and 100°) the sample is completely soluble. The various fractions separated in this manner have the same acetyl content and the same specific rotatory power, the varying solubility not being due to difference in chemical constitution. It may be due either to presence of impurities produced by acetolysis, or to variation in the size of the cells, the solution formed being a colloidal one. A specimen thus fractionated and completely insoluble in cold acetic acid was dissolved in warm acetic acid (90°) and reprecipitated with ether, and the variation of its mol. wt. with time determined by the cryoscopic method in 0·1—0·6% solution in acetic acid in an evacuated apparatus as previously described (Hess and Schultze, A., 1926, 715), and found to be identical with that of the crystalline triacetate, an initial decrease to the value for dextrose anhydride triacetate being followed by a continuous increase to infinity (*loc. cit.*). The substance isolated at the end of the experiment is identical with the starting material. A similar variation in the mol. wt. is exhibited by the triacetate obtained from ramie fibre and by a purified specimen of cellulose triacetate *A*, decomp. 280—285°, $[\alpha]_D^{20}$ $-19{\cdot}52°$ in chloroform (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142), and with the diacetate. These observations support the view, previously given, concerning the constitution of cellulose and its acetates.

J. W. Baker.

Lignin acetals. I. E. Hägglund and H. Urban (Cellulosechem., 1927, **8**, 69—71).—By treating finely-divided wood with amyl-alcoholic hydrogen chloride, more than half the material was dissolved. From the solution, a light brown *lignin semiacetal*, probably $C_{16}H_{10}O_5(OMe){\cdot}OC_5H_{11}$, was isolated. The residue apparently contained a lignin acetal with two amyloxy-groups in the molecule. Similar extraction with butyl-alcoholic hydrogen chloride yielded the corresponding *semiacetal* $C_{16}H_7O_2(OH)_3(OMe){\cdot}OBu$. From these experiments, it appears that lignin has M=about 315, and contains one carbonyl, one methoxyl, and three hydroxyl groups.

B. W. Anderson.

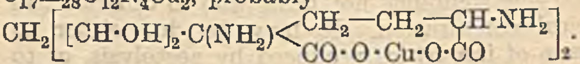
Residual affinity and co-ordination. XXIX. Cupric salts stabilised by ethylenediamine. G. T. Morgan and F. H. Burstall (J.C.S., 1927, 1259—1269).—Cupric salts of the weaker acids are known to decompose readily, and in view of the enhanced stability of these salts when they contain ethylenediamine as addenda of crystallisation exemplified by the iodide (A., 1926, 1027), further researches have been carried out to demonstrate this effect. Interaction between the requisite silver salts and bisethylenediaminocupric iodide led to the isolation of *bisaquobisethylenediaminocupric carbonate*, $[Cu,2\,en]CO_3,2H_2O$, m. p. 135° (decomp.), and *bisethylenediaminocupric nitrite*, $[Cu,2\,en](NO_2)_2$, m. p. 128° (rapid decomp.), as stable, well-defined salts. Two derivatives of cupric sulphite were obtained, depending on the method of preparation: (1) *monoaquoethylenediaminocupric sulphite*, $[Cu, en, H_2O]SO_3$, blackens at 100°, turning brown later, and (2) *bisethylenediaminocupric sulphite*, $[Cu,2\,en]SO_3$, decomp. 190—200°, this latter being the more stable. The reaction between bisethylenediaminocupric sulphate and the requisite barium salt in aqueous solution was used for the preparation of *bisethylenediaminocupric hypophosphite*, $[Cu,2\,en](H_2PO_2)_2$, decomp. 115—118°, and *thiosulphate*, $[Cu,2\,en]S_2O_3$, decomp. 150—155°. Other salts which have been prepared are *bisethylenediaminocupric dithionate*, $[Cu,2\,en]S_2O_6$, decomp. 260°; *trithionate*, $[Cu,2\,en]S_3O_6$, decomp. 170—175°; *tetrathionate*, $[Cu,2\,en]S_4O_6$, decomp. 160°; *persulphate*, $[Cu,2\,en]S_2O_8$, decomposes with explosive violence and detonates on percussion, and *seleno-*

cyanate, $[Cu,2\,en](CNSe)_2$, m. p. 159—160°, this last furnishing a noteworthy example of the stabilising effect of ethylenediamine on a cupric salt. The co-ordination numbers of bivalent copper are discussed, and it is shown that, on the evidence adduced, the value 4 gives the type most conducive to molecular stability. E. HOLMES.

Tetrachloro(triaminopropane-γ-monohydrochloride)platinum, an optically active complex salt of a new type. F. G. MANN (J.C.S., 1927, 1224—1232).—In tetrachloro(triaminopropanemonohydrochloride)platinum, previously described (A., 1926, 1234), two of the amino-groups of the triaminopropane are implicated in the co-ordination complex, the third being free for normal salt formation with acids. Such a compound might exist in two forms, depending on the inclusion of the αβ- or the αγ-diamino-groups in the ring structure, *i.e.*,
(I) $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2{\cdot}HCl]$ or
(II) $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2{\cdot}HCl){\cdot}CH_2{\cdot}NH_2]$. In (I), asymmetry is induced in the central carbon atom of the triaminopropane molecule by the disposition of the co-ordination linkings, this compound becoming capable of resolution into optically active forms, whilst (II) should not be so resolvable. The former has been proved to be correct, since fractional crystallisation of the camphorsulphonates has given the optically pure l-*tetrachloro*(*triaminopropanemono*-d-*camphor*-β-*sulphonate*)*platinum hemihydrate*, $[M]^{15}_{5461}$ —426°, m. p. 270—285° after darkening at 260°, and d-*tetrachloro*(*triaminopropanemono*-l-*camphor*-β-*sulphonate*)*platinum hemihydrate*, $[M]^{15}_{5461}$ +424°. Treatment of these compounds with calcium chloride gave, respectively, l-*tetrachloro*(*triaminopropanemonohydrochloride*)*platinum*, $[M]^{15}_{5461}$ —502°, m. p. 277—278° (decomp.) after darkening at 260—265°, and d-*tetrachloro*(*triaminopropanemonohydrochloride*)*platinum*, $[M]^{15}_{5461}$ +501°, m. p. (decomp.) 277—278° after darkening at 260—265°. This, therefore, is the first recorded case of a carbon atom owing its asymmetry to the operation of auxiliary valencies. The following compounds are also described: *tetrachloro*(*triaminopropanemono*-d-α-*bromocamphor*-π-*sulphonate*)*platinum*, $[M]^{15}_{5461}$ +346°, m. p. 271—273° (decomp.); *trichlorotriaminopropaneplatinic chloride*, m. p. 242—243° (decomp.) after darkening at 210°; *tetrachloro*(*triaminopropanehydrogenoxalate*)*platinum*, m. p. 248—251° (decomp.), and *monochloromono-oxalatotriaminopropaneplatinic chloride*, decomp. 200—210°. E. HOLMES.

Substituted *o*-alkylhydroxylamines chemically related to medicinally valuable amines. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1927, 49, 1527—1540).—Treatment of *ON*-dimethylhydroxylamine with ethylene oxide yields ON-*dimethyl*-N-*hydroxyethylhydroxylamine*, b. p. 57—58°/23 mm. (*hydrochloride*, m. p. 71—72°; *chloroplatinate*, m. p. 112—113°). When treated with methyl iodide, this affords *methoxydimethylhydroxyethylammonium iodide*, m. p. 57—58°, deliquescent, darkening on exposure to light, from which the corresponding *hydroxide* is obtained in solution by treatment with silver oxide. The corresponding *hydrochloride*, liquid, and *chloroplatinate*, m. p. 183° (decomp.), were prepared. Treatment of diethylaminoethanol in benzene with acetyl or benzoyl chloride yields, respectively, the *acetate*, b. p. 80°/20 mm. (*chloroplatinate*, m. p. 147°), or *benzoate*, b. p. 156—158°/19 mm. (*chloroplatinate*, m. p. 161°), and these, on treatment with ethyl iodide, afford, respectively, *triethylacetoxyethylammonium iodide*, m. p. 113°, and *triethylbenzoxyethylammonium iodide*, m. p. 134°. Treatment of diethylaminoethanol with aqueous 3% hydrogen peroxide affords *diethylhydroxyethylamine oxide*, liquid [*chloroplatinate*, m. p. 191° (decomp.)]. *Ethylethoxyaminoethyl* p-*aminobenzoate*, b. p. 217°/11 mm., is obtained by heating *ON*-diethylhydroxylamine with chloroethyl *p*-aminobenzoate in a sealed tube for 24 hrs. at 100°. *Ethylethoxyaminoethyl benzoate*, b. p. 152—153°/10 mm., is obtained by heating benzoyl chloride with *ON*-diethyl-*N*-hydroxyethylhydroxylamine, but could not be prepared from β-*chloroethyl benzoate*, b. p. 256—257°/752 mm., and *ON*-diethylhydroxylamine. *Ethylethoxyaminoethyl* p-*nitrobenzoate*, m. p. 180—190°, is obtained analogously. β-*Iodoethyl* p-*nitrobenzoate*, m. p. 68—69°, and β-*hydroxyethyl* p-*nitrobenzoate*, m. p. 77—78°, are described. *p*-Nitrobenzoyl chloride and *ON*-dimethyl-*N*-hydroxyethylhydroxylamine in benzene afford *methylmethoxyaminoethyl* p-*nitrobenzoate*, m. p. 51·4°. *Methoxycarbamide*, m. p. 84·5°, and *ethoxycarbamide*, m. p. 91·5°, are obtained by treating the appropriate *O*-alkylhydroxylamine hydrochlorides with aqueous potassium cyanate. When heated with diethylmalonyl chloride in benzene at 110° for 30 hrs., ethoxycarbamide yields N-*ethoxy*-CC-*diethylbarbituric acid*, m. p. 70°. NN′-*Dimethoxydiethylmalonamide*, m. p. 130°, and NN′-*diethoxydiethylmalonamide*, m. p. 117—118°, are obtained by treating the respective *O*-alkylhydroxylamines with diethylmalonyl chloride in ether, in presence of potassium carbonate. Condensation of phenylcarbimide in benzene with *O*-methyl- and *O*-ethylhydroxylamines yields, respectively, β-*methoxy*-α-*phenyl*-, m. p. 115°, and β-*ethoxy*-α-*phenyl*-*carbamide*, m. p. 106—108°, whilst β′-*methoxy*-α-*phenyl*-β-*methylcarbamide*, m. p. 61°, and β′-*ethoxy*-α-*phenyl*-β-*ethylcarbamide*, m. p. 63°, are obtained similarly from the corresponding *ON*-dialkylhydroxylamines. β-*Methoxy*-α-*propylthiocarbamide*, m. p. 37°, is obtained by treating *O*-methylhydroxylamine with propylthiocarbimide in benzene. The pharmacological action of the substituted *O*-alkylhydroxylamines appears to differ only in degree from that of the corresponding amines. F. G. WILLSON.

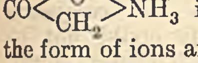
New compound obtained by the catalytic decomposition of collagen. W. S. SADIKOV (J. Russ. Phys. Chem. Soc., 1926, 58, 775—778).—The products of the decomposition of collagen by 1% hydrochloric acid were extracted with non-aqueous solvents. The amyl alcohol extract gave, on treatment with copper carbonate, a green solution, from which acetone precipitated a green *powder*, $C_{17}H_{28}O_{12}N_4Cu_2$, probably



$$CH_2\left[[CH{\cdot}OH]_2{\cdot}C(NH_2){<}\begin{matrix}CH_2{-}CH_2{-}CH{\cdot}NH_2\\ CO{\cdot}O{\cdot}Cu{\cdot}O{\cdot}CO\end{matrix}\right]_2.$$

Such a type of compound occurs also in the amyl alcohol fraction of the decomposition products of goose feathers, and in bilirubin. M. ZVEGINTZOV.

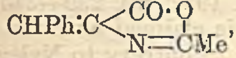
Kinetics of the reaction of formation of glycine from monochloroacetic acid and the influence of neutral salts. I. V. Sapojnikova (J. Russ. Phys. Chem. Soc., 1927, 59, 125—136).—Ammonium chloroacetate reacts slowly with ammonia at 25°, the reaction being bimolecular. Increase in concentration, or the presence of ammonium salts, increases the speed of reaction, unlike that between ethyl chloroacetate or ethyl acetate and ammonia. Barium and potassium salts also increase the speed of reaction. Alcohol, on the other hand, reduces the speed of reaction by about 59%, probably due to the sparing solubility of glycine in alcohol. It follows, then, that the usual ring formula for the substance



$CO{<}\begin{smallmatrix}-O-\\CH_2\end{smallmatrix}{>}NH_3$

is incorrect, and that it exists in the form of ions and consists of complexes of the type $^+NH_3{\cdot}CH_2{\cdot}CO-{}^+NH_3{\cdot}CH_2{\cdot}CO_2-$ $-CO_2{\cdot}CH_2{\cdot}NH_3{}^+-CO_2{\cdot}CH_2{\cdot}NH_3{}^+$. E. Rothstein.

Synthesis of dipeptides containing arginine. Isomeric phenylalanylarginines and their conversion into phenylalanylornithine. M. Bergmann and H. Köster (Z. physiol. Chem., 1927, **167**, 91—113).—The azlactone of α-acetamidocinnamic acid,



$CHPh{:}C{<}\begin{smallmatrix}CO\cdot O\\ | \\ N{=\!=}CMe\end{smallmatrix}$

, reacts with free *d*-arginine in a water–acetone solution to form an acetylated unsaturated peptide. This compound takes up 2 atoms of hydrogen in presence of palladium-black to form the saturated acetyldipeptide, from which the free dipeptide is obtained by treatment with cold acetic anhydride followed by heating with *N*-hydrochloric acid. The following compounds have been prepared : 2-*acetamidocinnamoyl*-d-*arginine*, m. p. 192—193° (corr.), $[\alpha]_D^{23}$ —18·0°; N-*acetylphenylalanyl*-d-*arginine*, m. p. about 178°; optically inactive N-*acetylphenylalanylarginine*, m. p. 216° (corr.), and its *dihydrate*, m. p. 216° (corr.); d-*phenylalanyl*-d-*arginine* and its o-*hydroxybenzylidene* compound, m. p. 199° (corr.), *picrate*, m. p. 95—97°, and *dihydrochloride*, m. p. 192—193° (corr.); inactive *phenylalanylarginine*, m. p. 236° (corr.), and its o-*hydroxybenzylidene* compound, m. p. 162—163° (corr.), and a second *modification*, m. p. 237° (corr.), and *dihydrochloride*, m. p. 130° (corr.); *acetylphenylalanyldiacetylanhydroarginine*, m. p. 201° (corr.); *acetylphenylalanylanhydro-ornithine*, m. p. 245° (corr.), and in a second modification with similar properties but lower m. p.; and *phenylalanylornithine*, m. p. 149° (corr.). A. Wormall.

Ethyl cyanoacetate [W. A. Noyes' method of preparation]. Y. Urushibara (Bull. Chem. Soc. Japan, 1927, 2, 143—145).—The product of the interaction of ethyl chloroacetate and potassium cyanide in methyl-alcoholic solution, according to the method of Noyes, is shown by chemical and physical means to be a mixture of about equal parts of the methyl and ethyl esters. Methyl cyanoacetate has d_4^{17} 1·133, as compared with d_4^{17} 1·114 for the ester prepared by Noyes' method, whilst pure ethyl cyanoacetate, prepared in ethyl-alcoholic solution, has d_4^{20} 1·063, against d_4^{20} 1·110 for the mixed esters. When the mixed esters react in ethyl-alcoholic solution they do so as the ethyl ester only. E. Holmes.

Selective action of organo-magnesium compounds and ethyl diethyloxamate. A. McKenzie and G. K. Duff (Ber., 1927, 60, [*B*], 1335—1341; cf. Barré, this vol., 447).—The action of an excess of hot Grignard's reagent on ethyl diethyloxamate affects only the carbethoxy-group, leaving the diethylcarboxylamide group unattacked. A general method of preparing the diethylamides of α-hydroxy-acids is thus afforded, but the compounds are remarkably stable towards hydrolytic agents, so that their transformation into α-hydroxy-acids is difficult. *Benzildiethylamide*, m. p. 95—96°, prepared from ethyl diethyloxamate and magnesium phenyl bromide (but not from methyl benzilate and diethylamine), is reduced by stannous chloride to *diphenylacetdiethylamide*, prisms, m. p. 67—68°, or needles, m. p. 64—65°, which is readily obtained from diphenylacetyl chloride and diethylamine in presence of light petroleum. *Di-α-naphthylglycolldiethylamide*, m. p. 196—197° (and thence *di-α-naphthylacetdiethylamide*, m. p. 204—205°), *di*-p-*tolylglycolldiethylamide*, m. p. 118—119°, *di*-o-*tolylglycolldiethylamide*, m. p. 140—141°, diethylglycolldiethylamide, m. p. 122—123°, and *dibenzylglycolldiethylamide*, m. p. 120·5—121·5°, are similarly obtained. Oxalic acid and magnesium phenyl bromide yield benzoylformic acid in traces, whereas oxamide is very stable towards the reagent. Triphenylcarbinol is obtained by the action of magnesium phenyl bromide on oxamethane or ethyl cyanoformate. H. Wren.

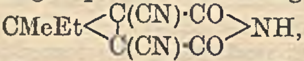
Additive compounds of allylthiocarbamide with silver halides. S. E. Sheppard and H. Hudson (Phot. J., 1927, 67, 331—335, and J. Amer. Chem. Soc., 1927, 49, 1814—1819).—By the action of dilute aqueous allylthiocarbamide on fused silver bromide, crystals of *allylthiocarbamide silver bromide*, $AgBr,C_4H_8N_2S$, were obtained. Silver nitrate added to a solution of allylthiocarbamide and potassium iodide precipitated a non-crystallisable mass of *allylthiocarbamide silver iodide* (?). The corresponding silver chloride compound was similarly prepared. These compounds with their low solubilities (the silver iodide compound being the least soluble) are of interest in their bearing on photographic sensitisation. Their constitution according to co-ordination theories is discussed. B. W. Anderson.

Mechanism of hydrolysis of guanidines. H. Lecher and G. Demmler (Z. physiol. Chem., 1927, **167**, 163—176).—Earlier results and conclusions (Lecher and Graf, A., 1924, i, 1051) are discussed in the light of more recent publications. It is considered impossible to apply Werner's scheme for the hydrolysis of carbamide to guanidines. The scheme of hydrolysis of "kreatinol" suggested by Schotte (Z. angew. Chem., 1926, 39, 677), in which is postulated the formation of a diguanidide as an intermediate compound, is not valid for *as*-diethylguanidine, which is used as a typical compound. Quantitative examination of the products of hydrolysis gives inconclusive results, but the scheme is impossible, since *as*-diethylguanidine and diethylcyanamide do not react. Schenck's preparation of *s*-tetramethylguanidine from cyanogen iodide and dimethylamine has been repeated with diethylamine.

Tetraethylguanidine is formed, but, in addition, some diethylcyanamide was isolated from the reaction mixture, and is regarded as a secondary and not as an intermediate product. This opposes Schenck's scheme for the reaction, which postulates the intermediate formation of dimethylcyanamide. An alternative scheme for this reaction is given. The following compounds are prepared: the *anhydro-base*, m. p. 88—89°, the *hydrochloride*, m. p. 148—149° (corr.), and the *picrate*, m. p. 221—224°, of as-*diethylguanidine*; *s*-tetraethylguanidine, b. p. 83·5° (corr.)/10 mm., and 92° (corr.)/13 mm., and its *picrate* and *chloroplatinate*, m. p. 203—207° (corr.). A. WORMALL.

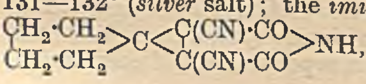
Influence of groups and associated rings on the stability of heterocyclic systems. II. Substituted succinimides. III. Substituted paraconic acids. S. S. G. SIRCAR (J.C.S., 1927, 1252—1256, 1257—1259; cf. this vol., 451).—II. The rates of hydrolysis of various substituted succinimides show that, in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane and *cyclo*hexane, the steady increase in stability anticipated in accordance with Thorpe and Ingold's modified strain theory is found in all but the first two members. The methyl group produces an abnormal increase in the stability of the ring, and the unsubstituted succinimide is also unusually stable. The velocities of hydrolysis of a number of imide systems in which the hetero-ring is attached to a carbocyclic ring by two carbon atoms show much-decreased stability compared with the corresponding *spiro*-systems. A possible explanation is offered. The following are described: as-*methylethylsuccinimide*, m. p. 64—65°; as-*diethylsuccinimide*, m. p. 85—86°; cyclo*pentane*spiro*succinimide*, m. p. 124°; cyclo*hexane*spiro*succinimide*, m. p. 145°; trans-*hexahydrophthalimide*, m. p. 163—164°; trans-*hexahydrohomophthalimide*, m. p. 185°. *Ethyl* Δ^1-cyclo*pentenecarboxylate*, b. p. 92°/25 mm., prepared by treating ethyl *cyclo*pentan-1-ol-1-carboxylate with phosphorus pentachloride and heating the product with diethylaniline, condenses with ethyl cyanoacetate in presence of sodium ethoxide to give an additive *compound*, b. p. 185—186°/17 mm. Hydrolysis with concentrated hydrochloric acid gives trans-cyclo*pentane*-1-*carboxy*-2-*acetic acid*, m. p. 158°, yielding an *imide*, m. p. 184—185°.

III. The rates of hydrolysis of various substituted paraconic acids show that, in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane and *cyclo*hexane, there is a steady increase in stability, in accordance with Thorpe and Ingold's modified strain theory. The influence of two ethyl groups is, however, greater than that of the *cyclo*pentane or *cyclo*hexane group. The following are described: the *imide*,



$\mathrm{CMeEt}{<}\begin{matrix}\mathrm{C(CN)\cdot CO}\\ \mathrm{C(CN)\cdot CO}\end{matrix}{>}\mathrm{NH}$,

m. p. 225—227° (cf. Birch, Gough, and Kon, J.C.S., 1921, **119**, 1320); 2 : 3-*dicyano*-1-*methyl*-1-*ethyl*cyclo*propane-2-carboxylamide*, m. p. 127—128°; γ-*lactone* of β-*hydroxy*-β-*ethylbutane*-γδδ-*tricarboxylic acid*, m. p. 157—158° (decomp.); *methylethylparaconic acid*, m. p. 131—132° (*silver* salt); the *imide*,



$\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{C(CN)\cdot CO}\\ \mathrm{C(CN)\cdot CO}\end{matrix}{>}\mathrm{NH}$,

m. p. 202—203°; cyclo*pentane*spiro-2 : 3-*dicyano*cyclo*propane*-2-*carboxylamide*, m. p. 126°; γ-*lactone* of 1-*hydroxy*cyclo*pentylethane*-αββ-*tricarboxylic acid*, m. p. 175—177° (decomp.); cyclo*pentane*spiro*paraconic acid*, m. p. 127° (*silver* salt). M. CLARK.

Behaviour of cyanogen bromide towards metallic salts. F. OBERHAUSER (Ber., 1927, 60, [*B*], 1434—1439).—Antimony tribromide, when heated with cyanogen bromide at 180° and subsequently at 120°, gives the additive *compound*, $2SbBr_3,3BrCN$; the *compounds* $SbCl_3,2BrCN$, $AsBr_3,2BrCN$, and $AsCl_3,2BrCN$ are analogously prepared. Antimony pentachloride and cyanogen bromide in carbon disulphide afford sulphur monochloride. Tin tetrabromide yields the *compound* $SnBr_4,2BrCN$. Additive compounds could not be obtained from aluminium halides. Titanium tetrachloride readily yields the *product* $3TiCl_4,2BrCN$. Cuprous and ferrous bromides yield the corresponding cupric and ferric salts. Compounds of metallic halides or hydrogen cyanide with cyanogen chloride have been prepared. H. WREN.

Phosphinocarboxylic acids. A. E. ARBUSOV (J. Russ. Phys. Chem. Soc., 1927, 59, 239—245; cf. A., 1914, i, 653).—Priority is claimed over the work of Nylén (A., 1925, i, 1134). Contrary to Nylén, the action of halogen-substituted esters on triethyl phosphite appears the most general method for the preparation of phosphinocarboxylic esters, and is applicable to α-bromo- and β-iodo-propionic and α-bromobutyric esters. Results of hydrolyses of ethyl phosphinoacetate, α- and β-phosphinopropionates, and phosphinoformate agree, in general, with those of Nylén. J. KAYE.

Cacodylic acid from trimethylarsine. A. VALEUR and P. GAILLIOT (Compt. rend., 1927, 184, 1559—1561).—*Trimethylarsine dichloride*, prepared by the passage of chlorine over the surface of a benzene solution of trimethylarsine, decomposes into chloroform and cacodyl chloride (90% yield) when heated at 180°. From the latter, cacodylic acid is obtained by oxidation. The two additive *compounds*, $AsMe_3,AsCl_3$ and $AsMe_3,AsMeCl_2$, are also described. G. A. C. GOUGH.

Electrolysis of Grignard solutions. L. W. GADDUM and H. E. FRENCH (J. Amer. Chem. Soc., 1927, 49, 1295—1299).—Electrolysis of ethereal magnesium benzyl chloride (110—130 volts, 0·02 amp.) yields metallic magnesium, magnesium chloride, and dibenzyl in approximately equimolecular amounts. Results obtained analogously with magnesium phenyl bromide were indefinite, possibly owing to side reactions brought about by the solubility of magnesium bromide in ether. During the electrolysis of magnesium phenyl bromide, marked anodic luminescence was observed. The deposited magnesium reacted with cold water with evolution of heat, and violently with halogen compounds under Grignard conditions. F. G. WILLSON.

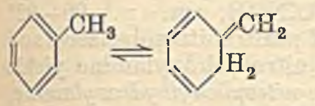
Substitution in the benzene nucleus. M. V. IONESCU (Bul. Soc. Chim. România, 1926, 8, 25—28).—An account of Wieland's work on the reaction between ethylene and nitric acid (A., 1919, i, 307;

1920, i, 280) and the application of the results to the problem of substitution in the benzene nucleus (cf. Holleman, Chem. Reviews, 1925, 1, 192).

The experiments of Datta (A., 1917, i, 15, 332; 1919, i, 153) on the halogenation of benzene hydrocarbons in presence of nitric acid are criticised.

H. BURTON.

Tautomeric forms of toluene. P. P. SCHORIGIN (J. Russ. Phys. Chem. Soc., 1926, 58, 767—774).—Theoretical. The physical and chemical properties of toluene and its derivatives are reviewed and the existence of an "active" form (annexed formula) is suggested. The amount of "active" modification is assumed to increase by addition of external energy, hence the side-chain reactions of toluene in strong light and on heating. The mechanisms of halogenation, oxidation with potassium permanganate, nitration, and some migration reactions are explained on this hypothesis. The "active" form should, theoretically, give an exaltation of molecular refractivity, and it is shown that for toluene and benzyl alcohol the refractivity increases rapidly with rise of temperature, owing to the increase of the "active" constituent.



M. ZVEGINTZOV.

Nitration of mixed dihalogen derivatives of benzene. I and II. T. VAN HOVE (Bull. Acad. roy. Belg., 1926, [v], 12, 801—823, 823—835).—I. In contrast to *p*-chlorofluorobenzene, the nitration of *p*-bromofluorobenzene yields a preponderance of the compound nitrated *ortho* to the fluorine (cf. A., 1916, i, 133). The constitutions of the two possible isomerides are determined by synthesis, and the relative proportions produced in the nitration estimated. 5-*Bromo*-o-*fluoronitrobenzene*, b. p. 145—147°/13 mm., m. p. 19°, obtained from 4-fluoro-*m*-nitroaniline, is easily attacked by alkalis (including sodium carbonate) to give 4-bromo-*o*-nitrophenol. With sodium methoxide, it yields 4-bromo-*o*-nitroanisole, and with ammonia 4-bromo-*o*-nitroaniline. 6-*Bromo*-m-*fluoronitrobenzene*, b. p. 140°/30 mm., m. p. 38·5°, prepared similarly from 4-fluoro-*m*-nitroaniline, is only slowly attacked by alkalis (bromine eliminated).

Nitration of *p*-bromofluorobenzene with a mixture of nitric and sulphuric acids, and with a mixture of nitric and fuming sulphuric acids (30% SO_3), yields 43·5% and 40·6% of 5-bromo-*o*-fluoronitrobenzene, respectively. The percentages are calculated on the total mononitrated product from the proportion attacked by sodium methoxide; small amounts of 4-bromo-*o*-nitrophenol and of 2 : 4-dinitrophenol are formed at the same time. By a study of the m. p. of mixtures of the two isomerides, similar results are obtained.

II. Nitration of *p*-iodofluorobenzene with potassium nitrate and sulphuric acid at −10° yields *p*-fluoronitrobenzene, together with a tri-iodofluorobenzene and iodofluoronitrobenzenes in small amounts. Similarly, *p*-chloroiodobenzene yields *p*-chloronitrobenzene, a chlorodi-iodonitrobenzene, and small amounts of chloroiodonitrobenzenes. 6-*Iodo*-m-*fluoronitrobenzene*, b. p. 162—163°/35 mm., m. p. 22·5°, and 5-*iodo*-o-*fluoronitrobenzene*, b. p. 174—176°/45 mm., m. p. 35°, are obtained from the corresponding fluoronitroanilines. The latter is easily attacked by sodium methoxide and by ammonia to give 4-iodo-*o*-nitroanisole and 4-iodo-*o*-nitroaniline, respectively.

G. A. C. GOUGH.

Aromatic sulphonyl disulphides. L. G. S. BROOKER, R. CHILD, and S. SMILES (J.C.S., 1927, 1384—1388).—The following sulphonyl disulphides, having the general formula $R·SO_2·S·S·R'$, have been prepared by the interaction of the appropriate aryl thiosulphonates with the aryl sulphur chlorides: 4-*toluenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 141°; 4-*acetamidobenzenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 171° (decomp.); 4-*toluenesulphonyl* 4-*chloro*-2-*nitrophenyl disulphide*, m. p. 114°; 4-*toluenesulphonyl* 2 : 5-*dichlorophenyl disulphide*, m. p. 95—96°; 4-*methoxytoluene*-3-*sulphonyl* 2-*nitrophenyl disulphide*, m. p. 115—116°; 4-*chlorobenzenesulphonyl* 2-*nitrophenyl disulphide*, m. p. 147° after softening at 130°. The behaviour of these compounds with such reagents as sodium 2-naphthoxide, sodium acetylacetone, and mercaptans has been studied, and the following products are described: 2 : 5-*dibromophenyl trisulphide*, m. p. 167—168°; 2 : 5-*dibromophenyl* 2-*nitrophenyl disulphide*, m. p. 138°; 2 : 5-*dichlorophenyl* 2-*nitrophenyl disulphide*, m. p. 138°, and 2 : 5-*dichlorophenyl trisulphide*, m. p. 140°. Alternative methods of synthesis have been devised and used in the identification of these products.

E. HOLMES.

Constitution of mixed magnesium organic compounds. A. P. TERENTIEV (J. Russ. Phys. Chem. Soc., 1927, 58, 1252—1264).—See A., 1926, 1130.

Action of *m*- and *p*-nitroaniline on 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine. C. F. VAN DUIN and D. R. KOOLHAAS (Rec. trav. chim., 1927, 46, 378—380).—In continuation of earlier work (van Duin and Roeters van Lennep, A., 1920, i, 155), it is shown that besides 2 : 4 : 6 : 4′-tetranitro-5-methylnitroaminodiphenylamine, the main product of the interaction of *p*-nitroaniline and 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine in saturated benzene solution, there is also formed in smaller amount 4 : 4′-dinitrodiazoaminobenzene. In the case of *m*-nitroaniline no such secondary product is obtained.

E. HOLMES.

Reduction of aromatic nitro-derivatives by hydrogen in presence of platinum-black. V. VESELY and E. REIN (Arhiv Hemiju, 1927, 1, 55—61).—Hydrogen in presence of platinum-black acts selectively on one of the nitro-groups of dinitroaryl compounds. Thus *m*-dinitrobenzene yields *m*-nitroaniline, 1 : 2-, 1 : 3-, and 1 : 8-dinitronaphthalenes yield 2-, 3-, and 8-nitronaphthylamines, whilst 5 : 6-dinitrotetralin yields mainly 5-nitro-6-aminotetralin, together with a small quantity of 6-nitro-5-aminotetralin. Similarly are obtained *o*-nitro-*p*-toluidine, 6-nitro-*o*-toluidine, and 1-*nitro*-2-*methyl*-8-*naphthylamine*, m. p. 106—107° (*acetyl* derivative, m. p. 191—193°), the position of the amino-group of which was determined by conversion through the diazo-derivative into 1-nitro-2-methylnaphthalene, or into

8-bromo-1-nitro-2-methylnaphthalene, m. p. 113°, yielding on reduction *8-bromo-2-methyl-1-naphthylamine*, m. p. 84—85°. A mixture of 1 : 5- and 1 : 8-dinitro-2-methylnaphthalenes yields on catalytic reduction only the 8-amino-derivative, thus affording a method for the separation of these isomerides.

R. TRUSZKOWSKI.

Condensation of nitriles with thioamides. III. Nitriles with thioanilides and thionaphthalides. S. ISHIKAWA (Mem. Coll. Sci. Kyoto, 1927, **10**, 191—198).—From a study of the condensation of acetonitrile and benzonitrile with thioformanilide, thioacetanilide, and thiobenzanilide, and of benzonitrile with α- and β-thioacetonaphthalides and α- and β-thiobenzonaphthalides, in ethereal hydrogen chloride solution, it is concluded that iminosulphides are produced thus: $\mathrm{NR'{:}CR{\cdot}SH+NCR'' \longrightarrow NR'{:}CR{\cdot}S{\cdot}CR''{:}NH}$. When isolated, the iminosulphides are unstable, yellow substances, which become red in moist air, and then decompose. When no iminosulphide was isolated, its hydrolytic decomposition products (thioamide+anilide), or other condensation products (imino*iso*thioamide, cf. A., 1921, i, 728), were obtained. H. BURTON.

Interaction of sulphuryl chloride with substances containing the reactive methylene group. K. G. NAIK and M. L. SHAH (J. Indian Chem. Soc., 1927, **4**, 11—21).—In the reaction of sulphuryl chloride with various mono- and di-substituted amides of malonic and methylmalonic acids, the methylene group is completely chlorinated in the compounds malondiphenylamide, malondibenzylamide, malondi-*o*-tolylamide, malondi-*p*-tolylamide, malondipropylamide, and malon-*p*-tolylamide, which are converted, respectively, into *dichloromalondiphenylamide*, m. p. 127°; *dichloromalondibenzylamide*, m. p. 170—171°; *dichloromalondi-*o*-tolylamide*, m. p. 140—141°; *dichloromalondi-*p*-tolylamide*, m. p. 145—146°; *dichloromalondipropylamide*, m. p. 108—109°, and *dichloromalon-*p*-tolylamide*, m. p. 145—146°. In the case of *malondi-*m*-tolylamide*, m. p. 152°, malonanilide, and malondi-β-naphthylamide, chlorination of the nucleus takes place in addition, with formation of *dichloromalondi-*m*-tolylamide dichloride*, m. p. 164°; *dichloromalonchlorophenylamide*, m. p. 136°; and *dichloromalondi-β-naphthylamide dichloride*, m. p. 183°, respectively. Malondimethylphenylamide is converted into *chloromalondimethylphenylamide*, m. p. 187°, and malondi-α-naphthylamide into *chloromalondi-α-naphthylamide dichloride*, m. p. 182°. Methylmalondiphenylamide, methylmalondi-*o*-tolylamide, and methylmalondi-*p*-tolylamide after chlorination form *chloromethylchloromalondiphenylamide*, m. p. 128°, *chloromethylchloromalondi-*o*-tolylamide*, m. p. 130°, and *chloromethylchloromalondi-*p*-tolylamide*, m. p. 138°, respectively, the course of the latter reactions apparently being due to the enolisation of the terminal methyl groups. B. W. ANDERSON.

Phenyl-*o*-nitrobenzyldimethylammonium chloride. H. BAW (J.C.S., 1927, 1398).—*o*-Nitrobenzyl chloride and dimethylaniline, when mixed in equivalent proportions, combine slowly to form yellow rhombs of *phenyl-*o*-nitrobenzyldimethylammonium chloride*, m. p. 99·5°. G. A. C. GOUGH.

Formation of nitrosoarylhydroxylamines. D. BIGIAVI and F. FRANCESCHI (Gazzetta, 1927, **57**, 362—383).—The action of hydroxylamine on *p*-nitro-β-azoxybenzene, $\mathrm{NPh{:}NO{\cdot}C_6H_4{\cdot}NO_2}$, in presence of sodium ethoxide yields *p*-nitroazobenzene, and the *nitrosohydroxylamine*, $\mathrm{NPh{:}NO{\cdot}C_6H_4{\cdot}NO{:}NOH}$, orange scales, m. p. 97—98° (decomp.), which forms salts with *phenylhydrazine*, $\mathrm{C_{12}H_{10}O_3N_4,NHPh{\cdot}NH_2}$, m. p. 117° (decomp.), *hydroxylamine*, m. p. 200—204° (decomp.), various metals, and ammonium. Similarly, hydroxylamine and *p*-nitro-α-azoxybenzene, $\mathrm{O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NO_2}$, give the orange *nitrosohydroxylamine*, $\mathrm{O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NO{:}NOH}$, m. p. 90—92° (decomp.). Interaction of *p*-nitronitrosobenzene and the sodium derivative of nitrohydroxylamine yields the *sodium* salt of *nitroso-*p*-nitrophenylhydroxylamine*, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}NO{:}NONa,5H_2O}$; free *nitroso-*p*-nitrophenylhydroxylamine*, m. p. 75° (decomp.), readily decomposes with formation of *p*-nitronitrosobenzene, and forms a sparingly soluble *phenylhydrazine* salt, m. p. 140°; an *ammonium* salt (p-*nitrocupferron*), m. p. 145° (decomp.); a *silver* salt; a *barium* salt ($+3H_2O$); a *ferric* salt, m. p. 202° (decomp.); a *copper* salt, m. p. 250° (decomp.); a *nickel* salt, m. p. 249° (decomp.), and a *cobalt* salt, m. p. 222° (decomp.).

As regards the analogy between the reactions of nitrohydroxylaminic acid (nitroxyl) with nitroso-derivatives and with aldehydes, the nitrosoarylhydroxylamines and the hydroxamic acids formed in the two cases both yield complex metallic salts. In the latter reaction, the formation of the hydroxamic acid is preceded by the appearance of a greenish-blue coloration owing to the formation of the nitroso-alcohol, $\mathrm{OH{\cdot}CHR{\cdot}NO}$; similarly, the transitory deep red coloration sometimes observed on mixing solutions of *p*-nitronitrosobenzene and the sodium salt of nitrohydroxylamine may appertain to a labile form represented by the old formula, $\mathrm{OH{\cdot}NR{\cdot}NO}$, ascribed to the nitrosoarylhydroxylamines by Bamberger.

Not only the nitroso-group, but also the nitro-group of aromatic derivatives is transformed by nitroxyl into the grouping of the nitrosoarylhydroxylamines $\mathrm{R{\cdot}NO_2 \longrightarrow O{:}NR{:}NOH}$. In this way nitrosohydroxylamines have been obtained from nitrobenzene, *p*-nitrotoluene, *m*- and *p*-dinitrobenzenes, and *pp'*-dinitroazobenzene. Thus, *m*-dinitrobenzene gives, as *sodium* salt, *nitroso-*m*-nitrophenylhydroxylamine*, $\mathrm{C_6H_5O_4N_3}$, m. p. 75—76°, and *p*-dinitrobenzene gives, first, the sodium salt of nitroso-*p*-nitrophenylhydroxylamine (see above), and then the *sodium* salt ($+1H_2O$) of p-*dinitrosophenylenedihydroxylamine*, $\mathrm{NOH{:}NO{\cdot}C_6H_4{\cdot}NO{:}NOH}$, which begins to blacken at 85°, yields *p*-dinitrosobenzene, possibly identical with that obtained by Nietzki and Kehrmann (A., 1887, 575), when heated with dilute mineral acid, and forms complex metallic salts.

Various azoxy-derivatives are reduced by nitrohydroxylaminic acid. Thus, azoxybenzene is converted into azobenzene and an orange sodium salt, possibly $\mathrm{NONa{:}NPh{:}NPh}$; *pp'*-dinitroazoxybenzene gives *pp'*-dinitroazobenzene and a sodium salt of a nitrosohydroxylamine (?); *p*-nitroazoxybenzene gives *p*-nitroazobenzene.

The reduction of nitro- to azoxy-derivatives by alcoholic potassium hydroxide sometimes proceeds further. Thus, trisazoxybenzene and monoazoxybisazobenzene are reduced to *trisazobenzene*, m. p. 235°. T. H. Pope.

Nitration of aromatic compounds with metallic nitrates. G. Bacharach (J. Amer. Chem. Soc., 1927, 49, 1522—1527).—Treatment of *p*-toluidine with cupric, ferric, manganese, nickel, or cobalt nitrate in a mixture of acetic anhydride and glacial acetic acid, or with mercurous nitrate in glacial acetic acid, or with lithium nitrate in boiling acetic anhydride, affords *m*-nitroaceto-*p*-toluidide. Aniline and lithium nitrate yield, similarly, *p*-nitroacetanilide. In acetic anhydride at 100°, cupric nitrate is without action on benzoic acid, benzaldehyde, and nitrobenzene. The nitrating action of metallic nitrates is thus selective, and the structure of the nitro-derivative produced depends on the particular nitrate applied (cf. Menke, A., 1925, i, 655; Spiegel and Haymann, A., 1926, 390). F. G. Willson.

Preparation of pharmacologically valuable amines. K. Kindler [with F. Burghard, P. Körding, O. Giese, F. Hesse, F. Finndorf, and H. Christlieb] (Arch. Pharm., 1927, 265, 389—415).—The author's recent work (A., 1923, i, 568; 1924, i, 731 etc.) is reviewed and amplified, the practical value of the electrolytic reduction processes being emphasised. In general, the electrolyte is alcoholic hydrochloric or sulphuric acid; a specially prepared lead cathode is used and the current density is high. The yields (given below in parentheses in % of theory) are much higher than those obtainable by other methods. In the following list of results obtained, m. p. or b. p. are given only when they differ from those recorded by earlier workers, and in all cases the figures are corrected. β-Arylethylamines are easily prepared from aldehydes (cf. Kindler, *loc. cit.*, 1923); thus, benzaldehyde, through acetylthiomandeloylamide (Albert, A., 1915, i, 8), yields β-phenylethylamine, and piperonal is similarly converted into homopiperonylamine. The following are obtained by the reduction of the corresponding acid amide: benzylamine (74%) and benzyl alcohol (23%); *o*-tolylmethylamine (83%) and *o*-methylbenzyl alcohol (11%); *m*-tolylmethylamine (53%) and *m*-methylbenzyl alcohol (35%); *p*-tolylmethylamine (79%) and *p*-methylbenzyl alcohol (18%); *p*-anisylmethylamine (73%) and *p*-methoxybenzyl alcohol (22%); m-*bromobenzylamine*, b. p. 244—245° (*hydrochloride*, m. p. 218·5°; *chloroplatinate*, m. p. 250·5—251·5°, decomp.) (64%), and *m*-bromobenzyl alcohol (19%); *p*-bromobenzylamine, b. p. 249·5—251·5° (67%)—some bromine is split off during this reduction; *p*-chlorobenzylamine, b. p. 229—230·5° (carbonate, m. p. 121—121·5°; hydrochloride, m. p. 261·5°; benzoyl derivative, m. p. 142·5°) (65%); ω-α-naphthylmethylamine (55%). Benzomethylamide and phenylacetmethylamide are also reduced to benzylmethylamine and β-phenylethylmethylamine, respectively, but, in general, secondary amines are more readily obtained from the thioamides as described below. p-*Anisoyldimethylamide* (from the chloride), b. p. 196°/16 mm., yields on reduction *p*-methoxybenzyldimethylamine, b. p. 108°/11 mm. *N*-Benzoylpiperidine similarly gives *N*-benzylpiperidine (57%); phenylacetdimethylamide gives β-phenylethyldimethylamine (76%); phenylacetdiethylamide gives β-phenylethyldiethylamine, b. p. 97—99°/8 mm. (80%); *phenylacetdipropylamide*, b. p. 183—184°/16 mm., prepared from the chloride, gives β-*phenylethyldipropylamine*, b. p. 268—269° (89%); *phenylacetpiperidide*, b. p. 201—202°/18 mm., gives N-β-*phenylethylpiperidine*, b. p. 272°, *hydrochloride*, m. p. 223° (63%); hydrocinnamodimethylamide gives γ-phenylpropyldimethylamine (70%); p-*methoxyhydrocinnamodimethylamide*, b. p. 200°/17 mm., obtained by heating the dimethylammonium salt of the acid at 200°, gives on reduction γ-p-*methoxyphenylpropyldimethylamine*, b. p. 260° (*picrate*, m. p. 92°), which affords homohordenine, m. p. 111—111·5° (von Braun and Deutsch, A., 1912, i, 845), quantitatively on demethylation. Details, which were omitted in earlier papers, are now given for the preparation of *N*-alkylthioamides: the aldehyde or ketone is mixed with sulphur and the amine (in 10% excess); the mixture is heated in a closed tube fitted with an inner vessel containing potassium hydroxide to take up the water as fast as it is formed. The interaction is complete, at 140—150° and 3—4 atm. pressure, in about 4 hrs. In this way, benzaldehyde yields thiobenzdimethylamide (80%); acetophenone yields phenylthioacetdimethylamide (70%); *p*-tolyl methyl ketone yields p-*tolylthioacetdimethylamide*, m. p. 72° (80%); *p*-ethylphenyl methyl ketone yields p-*ethylphenylthioacetdimethylamide*, b. p. 224—225°/20 mm. (40%); *p*-anisyl methyl ketone gives *p*-methoxyphenylthioacetdimethylamide (75%); 3 : 4-dimethoxyphenyl methyl ketone gives 3 : 4-*dimethoxyphenylthioacetdimethylamide*, m. p. 118° (68%), and phenyl ethyl ketone gives β-*phenylthiopropiondimethylamide*, m. p. 55—56° (58%). When aldehydes or ketones are heated with sulphur and a monoalkylamine, poor yields are obtained, but *N*-methylaldimines and *N*-methylketimines are smoothly converted into thioamides. *N*-Methylbenzaldimine thus affords, when heated with sulphur, thiobenzmethylamide (80%); N-*methyl*-p-*methoxybenzaldimine*, b. p. 129—130°/18 mm., gives *p*-methoxythiobenzmethylamide (40%); *N*-methylacetophenoneimine gives phenylthioacetmethylamide (30%), and its 3 : 4-dimethoxy-analogue gives 3 : 4-dimethoxyphenylthioacetmethylamide (45%). All these compounds are smoothly reduced by the electrolytic method in alcoholic hydrochloric or sulphuric acid; thus, thiobenzmethylamide gives benzylmethylamine (79%); similarly are obtained *p*-methoxybenzylmethylamine (84%), β-phenylethylmethylamine (83%), benzyldimethylamine (100%), β-phenylethyldimethylamine (100%), β-p-*tolylethyldimethylamine*, b. p. 226·5° (88%), β-*p*-ethylphenylethyldimethylamine (74%), and γ-phenylpropyldimethylamine (73%). The production of *N*-methylhomopiperonylamine, available for the synthesis of hydrastinine, by similar methods is described (cf. also *loc. cit.*, 1923), and further details are given for preparing hordenine and certain analogues. Thus, *p*-nitrophenylacetdimethylamide (*loc. cit.*, 1923) is smoothly reduced electrolytically to β-p-*aminophenylethyldimethylamine*, m. p. 41—42°, b. p. 150°/18 mm., which is easily converted into hordenine by decomposition of its diazonium derivative. Hordenine is also obtained from anisole as follows: anisole is converted into *p*-methoxyacetophenone, and the *p*-methoxyphenylthioacetdimethylamide obtained thence is electrolytically reduced (yield 92%) to β-p-*methoxyphenylethyldimethylamine*, b. p. 253—254°, readily demethylated by hydrobromic acid and red phosphorus to hordenine. Similarly, 3 : 4-dimethoxyphenylthioacetdimethylamide, described above, yields (80%) β-3 : 4-*dimethoxyphenylethyldimethylamine*, b. p. 168—170°/19 mm. (*picrate*, m. p. 126°, *methiodide*, m. p. 232°), which on demethylation affords (90%) β-3 : 4-*dihydroxyphenylethyldimethylamine*, m. p. 156° (*picrate*, m. p. 169°; *methiodide*, m. p. 205°). *p*-Methoxyacetophenone, sulphur, and piperidine at 165° yield N-p-*methoxyphenylthioacetopiperidide*, m. p. 65°, which is successively converted into N-β-p-*methoxyphenylethylpiperidine*, b. p. 175—176°, and N-β-p-*hydroxyphenylethylpiperidine*, m. p. 163°. W. A. Silvester.

Influence of the sulphonic group on the isomeric naphthylaminesulphonic acids. G. G. Vendelstein (J. Russ. Phys. Chem. Soc., 1927, **59**, 146—157).—The relative speeds of diazotisation of α-naphthylamine and the seven isomeric monosulphonic acids derived from it, and the relative rates of coupling and of decomposition of the diazo-compounds have been measured. The reactions in the first two instances were bimolecular, and in the last case unimolecular. The presence of a sulphonic acid group in α-naphthylamine decreases the stability of the amino-group towards nitrous acid. The isomeric naphthylaminesulphonic acids divide themselves into three groups, the 1 : 3-, 1 : 6-, and 1 : 7-naphthylaminesulphonic acids have much the same speeds of diazotisation; the 1 : 5- and 1 : 8-acids are much more stable than these, and their diazo-compounds form derivatives much less readily. The remaining two, the 1 : 4- and 1 : 2-acids, show the greatest tendency to form diazo-derivatives. The speeds of decomposition of the isomeric diazo-compounds are of much the same order in every case.

E. Rothstein.

Preparation of *o*-chloro-*p*-aminoacetanilide. S. C. Niyogy (J. Indian Chem. Soc., 1927, **4**, 80—83).—Cain's method (J.C.S., 1909, **95**, 716) having proved unsatisfactory, the following preparation of *o*-chloro-*p*-aminoacetanilide was devised. *p*-Nitroaniline is dissolved in water containing hydrochloric and acetic acids and a slow current of chlorine passed at 10—15°; after boiling, adding alcohol, and filtering rapidly, a good yield of *o*-chloro-*p*-nitroaniline separates from the diluted filtrate. This is dissolved in acetic acid, acetylated in presence of sulphuric acid, and reduced with iron dust and acetic acid. *o*-Chloro-*p*-aminoacetanilide has m. p. 134—135° (Cain, *loc. cit.*, gave m. p. 111°). B. W. Anderson.

Action of nitrous acid on substituted *p*-phenylenediamines. I. *as*-Benzyl-*n*-butyl-*p*-phenylenediamine. J. Reilly and P. J. Drumm (J.C.S., 1927, 1395—1397).—The study of the influence of substitution on the diazo-reaction is extended, and it is found that *benzyl*-n-*butyl*-p-*phenylenediamine*, $NH_2\cdot C_6H_4\cdot NBu\cdot CH_2Ph$, like *n*-butyl-*p*-phenylenediamine (J.C.S., 1917, **111**, 1034), yields a stable diazo-solution. Whilst methyl-*p*-phenylenediamine cannot be diazotised in hydrochloric acid solution, it yields a stable diazo-solution in dilute sulphuric acid.

Benzyl-*n*-butylaniline (see this vol., 553; *picrate*, m. p. 129°; *chloroplatinate*, m. p. 185—186°), also obtained by the interaction of *n*-butyl iodide and benzylaniline in alcohol at 100°, yields with nitrous acid, followed by treatment of the product with hydrogen chloride in benzene, p-*nitrosobenzyl*-n-*butylaniline hydrochloride*, m. p. 138° (with previous darkening). The corresponding *base*, m. p. 48—49°, on reduction with zinc dust and sulphuric acid, gives *benzyl*-n-*butyl*-p-*phenylenediamine*, b. p. 220—224°/12 mm. (*sulphate*, *hydrochloride*, and *benzoyl* compound, m. p. 131°, described).

4-p-*Sulphobenzeneazobenzyl*-n-*butylaniline*, obtained by the action of *p*-diazobenzenesulphonic acid on an acetic acid solution of benzyl-*n*-butylaniline, yields, on reduction with ammonium sulphide, benzyl-*n*-butyl-*p*-phenylenediamine identical with that described above. The last-named base, when diazotised and coupled with β-naphthol, gives p-*benzyl*-n-*butylaminobenzeneazo*-β-*naphthol*, m. p. 133—134°.

G. A. C. Gough.

Diacyl derivatives of benzidine and *p*-phenylenediamine. F. J. A. Brogan (J.C.S., 1927, 1381—1384).—The ascending homologous series of normal diacyl derivatives of benzidine and of *p*-phenylenediamine show no alternation in m. p. such as that existing in the corresponding series of normal fatty acids (cf. Robertson, J.C.S., 1908, **93**, 1033; 1919, **115**, 1210). Both m.-p. curves fall sharply at first, and then more slowly with increasing mol. wt., without attaining a minimum at either eighteenth member. In connexion with these results, an explanation of the alternation of the m. p. of the dibasic acids, founded on considerations of polarity, is suggested.

The diacyl derivatives were prepared by Cain's method (J.C.S., 1909, **95**, 714), and of them the following are new. Benzidine derivatives: *dipropionyl*, m. p. 317°; *dibutyryl*, m. p. 310°; *divaleryl*, m. p. 301°; *dihexoyl*, m. p. 283°; *diheptoyl*, m. p. 274°; *dioctoyl*, m. p. 268°; *didecoyl*, m. p. 256°; *diundecoyl*, m. p. 250°; *dilauryl*, m. p. 247°; *ditridecoyl*, m. p. 243°; *dimyristyl*, m. p. 241°; *dipalmityl*, m. p. 233°; *distearyl*, m. p. 231°. *p*-Phenylenediamine derivatives: *divaleryl*, m. p. 225°; *dihexoyl*, m. p. 215°; *diheptoyl*, m. p. 211°; *dioctoyl*, m. p. 208°; *dinonoyl*, m. p. 205°; *didecoyl*, m. p. 202°; *diundecoyl*, m. p. 199°; *dilauryl*, m. p. 194°; *ditridecoyl*, m. p. 190°; *dimyristyl*, m. p. 187°; *dipalmityl*, m. p. 182°; *distearyl*, m. p. 178°. G. A. C. Gough.

Benzidine. H. H. Hodgson (J. Soc. Dyers Col., 1927, **43**, 185—189).—Mainly a discussion of work already published (A., 1926, 945, 1133). In addition to Cain's 4'' : 4'''-dichlorotetranitro-*pp'*-diphenyldiphenyl, m. p. 203° (J.C.S., 1912, **101**, 2298; 1913, **103**, 2074), treatment of tetrazotised 3 : 5'-dinitrobenzidine with cuprous chloride affords an *isomeride*, orange-red, m. p. 300°, probably 4'' : 4'''-*dichloro*-2 : 2' : 3'' : 3'''-*tetranitro*-pp'-*diphenyldiphenyl*, together with a crystalline substance, m. p. 170—180°, containing chlorine. If the tetrazo-solution is saturated with sodium chloride before treating with cuprous chloride, orange-red products soluble in alcohol are obtained, of lower m. p. and higher chlorine content, probably formed by displacement of nitro-groups by chlorine. In the preparation of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl from 4-chloro-3-nitroaniline, a yellowish-white substance, $C_{12}H_6O_4N_2Cl$, m. p. 160—170°, is also obtained, which is probably a mixture of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl with either 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl or 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl. R. BRIGHTMAN.

Derivatives of benzeneazopyrogallol. D. BIGIAVI and G. GRECHI (Gazzetta, 1927, **57**, 355—361).—For benzeneazopyrogallol (cf. Stebbins, A., 1880, 880), m. p. 198° (decomp.), the structure indicated by Ghosh and Watson (J.C.S., 1917, **111**, 816) is preferred, as the triacetyl and tribenzoyl derivatives of this compound are only slowly oxidised to the corresponding azoxy-compounds by peracetic acid. Benzeneazopyrogallol forms the following derivatives: *diacetyl*, m. p. 126—128°; *triacetyl*, m. p. 108—110°; *tribenzoyl*, m. p. 125°. *Benzeneazoxypyrogallol*-A, $O:NPh:N\cdot C_6H_2(OH)_3$, m. p. 146—147°, forms a *tribenzoyl* compound, m. p. 161—163°. *Benzeneazoxypyrogallol*-B, $NPh:NO\cdot C_6H_2(OH)_3$, has m. p. 109—112°. T. H. POPE.

Addition of amino- and hydrazino-bases to nitrostyrene. D. E. WORRALL (J. Amer. Chem. Soc., 1927, 49, 1598—1605).—β-Nitrostyrene reacts with certain amines and hydrazines, with formation of the corresponding derivatives of α-nitro-β-amino-β-phenylethane. The applicability of the reaction is limited on account of the ease with which the nitrostyrene polymerises and hydrolyses, so that the additive reaction is prevented in many cases by steric hindrance under the mild conditions which have to be employed. The products are amphoteric. The following derivatives of α-nitroethane are described: β-*anilino*-, m. p. 86—87° (*hydrochloride*, m. p. 126—127°; *hydrobromide*, m. p. 113—114°; *nitrate*, m. p. 113—114°; *sodium* salt, unstable, m. p. indefinite); β-p-*toluidino*-, m. p. 82—84° (*hydrochloride*, m. p. 132°; *sodium* and *potassium* salts); β-p-*aminodiphenylamino*-, m. p. 113° (decomp.); β-*phenylhydrazino*-, m. p. 75° (*hydrochloride*, m. p. 135—136°; *nitrate*, m. p. 77°); β-*diphenylhydrazino*-, m. p. 81—82°; β-(β-*naphthyl*)*hydrazino*-, m. p. 117—118°; β-p-*tolylhydrazino*-, yellow, m. p. 86—87°; β-*semicarbazido*-, m. p. 131—132°; β-*thiosemicarbazido*-, m. p. 128—129°; and α-*nitro*-β-*piperidino*-β-*phenylethane*, m. p. 71—72°. ββ′-*Dinitro*-αα′-*diphenyldiethylamine*, m. p. 122—123°, is obtained by passing ammonia into a benzene solution of β-nitrostyrene. *p*-Phenylenediamine in alcohol affords similarly ββ′-*dinitro*-αα′-*diphenyl*-s-*diethyl*-p-*phenylenediamine*, yellow, m. p. 146—149° (*hydrochloride*, m. p. indefinite; *sodium* salt), whilst benzidine yields ββ′-*dinitro*-αα′-*diphenyldiethylbenzidine*, yellow, m. p. 162°. F. G. WILLSON.

Action of *cyclo*hexyl bromide on arylhydrazines. II. Decomposition of phenylhydrazine in presence of its salts. M. BUSCH [with A. BECKER] (J. pr. Chem., 1927, [ii], **116**, 34—42).—In correction of previous work (this vol., 455) it is now found that *cyclo*hexyl bromide and *o*-tolylhydrazine give only *cyclo*hexene and *o*-tolylhydrazine hydrobromide. The compound described as *cyclo*hexyl-*o*-tolylhydrazine was *o*-toluidine formed by catalytic decomposition (see below) of the hydrazine, and the supposed hydrazones were Schiff's bases, $C_7H_7\cdot N:CHR$. Attempts to prepare *cyclo*hexyltolylhydrazine from sodium *o*-tolylhydrazine and *cyclo*hexyl bromide were also unsuccessful. Other *o*-substituted phenylhydrazines, viz., 2 : 4-dimethyl-, *o*-methoxy-, *o*-chloro-, and *o*-bromo-phenylhydrazine, and also *p*-bromophenylhydrazine, react similarly, yielding in each case the corresponding amine and *cyclo*hexene, whilst α-naphthylhydrazine gives resinous products. With *p*-chlorophenylhydrazine, however, at 120—135°, *cyclo*hexyl bromide gives the *hydrobromide* of as-cyclo*hexyl*-p-*chlorophenylhydrazine*, m. p. 57—58° [*hydrochloride*, m. p. 185° (decomp.); *benzoyl* derivative, m. p. 221°], and with β-naphthylhydrazine, the *hydrobromide* of as-cyclo*hexyl*-β-*naphthylhydrazine*, m. p. 106° (*hydrochloride*, m. p. 184—185°, softening at 180°), from which *benzaldehyde*cyclo*hexyl*-β-*naphthylhydrazone*, m. p. 102°, is obtained.

When phenylhydrazine is heated in contact with its hydrochloride, it is catalytically decomposed (cf. Arbusov and Tichwinsky, A., 1910, i, 776) as follows: (*a*) $3NHPh\cdot NH_2+HCl \longrightarrow 3NH_2Ph+N_2+NH_4Cl$; (*b*) $2NHPh\cdot NH_2+HCl \longrightarrow NH_2Ph+C_6H_6+N_2+NH_4Cl$. At 100—135° the reaction proceeds slowly, and only according to (*a*), but above 160° the secondary reaction, (*b*), sets in, with vigorous decomposition, the proportion of benzene formed increasing with rising temperature. H. E. F. NOTTON.

Dehydration of *cyclo*hexanols to ethers. A. LACOURT (Bull. Soc. chim. Belg., 1927, 36, 346—358).—Di*cyclo*hexyl ether, b. p. 115·8°/15 mm., 242·2°/758·9 mm., d_4^{20} 0·9227, is obtained in 7·6% yield by heating *cyclo*hexanol in an autoclave with toluene-*p*-sulphonic acid at 170°. Lower yields are obtained by heating the alcohol with other catalysts at atmospheric pressure, the main product being *cyclo*hexene. By heating mixtures of *cyclo*hexanol and *cyclo*hexene in presence of toluene-*p*-sulphonic acid, up to 20% of the ether is obtained. Refractive indices and dispersions of the ether for several wave-lengths are given. Hydrolysis of di*cyclo*hexyl ether by hydriodic acid and red phosphorus yields mainly iodo*cyclo*hexane. Treatment of the mixtures of geometrical isomerides of the methyl*cyclo*hexanols with toluene-*p*-sulphonic acid gives, in addition to the corresponding hexenes, *di-4-methyl*cyclo*hexyl ether*, b. p. 135·3—141·6°/16 mm., *di-3-methyl*cyclo*hexyl ether*, b. p. 131·8—138°/16 mm., and *di-2-methyl*cyclo*hexyl ether*, b. p. 116—123°/13 mm. A mixture of *cis-* and *trans*-3-methyl*cyclo*hexanols was separated by distillation with the addition of phenetole into isomerides, b. p. 171—171·4°/760 mm., $d_4^{19\cdot4}$ 0·920 and b. p. 173·6—174·6°/760 mm., $d_4^{19\cdot4}$ 0·9139. The corresponding *allophanates* have m. p. 141·6° and 178·8° (cf. Gough, Hunter, and Kenyon, A., 1926, 1032). L. M. CLARK.

***cis-trans*-Isomerism and steric hindrance. V. (I). 4-*iso*Propyl*cyclo*hexanols.** G. VAVON and A. CALLIER (Bull. Soc. chim., 1927, [iv], 41, 677—687; cf. this vol., 455).—The influence of the *iso*-

propyl group is less marked in the *para-* than in the *ortho*-position, and the difference in reaction velocities between the *cis-* and *trans*-forms of *p-iso*propyl*cyclo*hexanol is considerably smaller than between the *cis-* and *trans*-forms of 2-*iso*propyl*cyclo*hexanol (*loc. cit.*). *p*-Nitro*iso*propylbenzene is reduced by hydrogen more rapidly than the *o*-isomeride, affording an 80% yield of *p-iso*propylaniline, b. p. 100—101°/10 mm., 226—227°/745 mm., converted by the diazo-reaction into *p-iso*propylphenol, b. p. 109—111°/10 mm., m. p. 61° (yield 65%). Hydrogenation of the phenol in acetic acid in presence of platinum-black is also more rapid than with the *o*-isomeride, and affords a mixture consisting of 1 part of *iso*propyl*cyclo*hexane and 2 parts of a mixture of the *cis-* and *trans*-forms of 4-*iso*propyl*cyclo*hexanol in approximately equal proportions. The same mixture of alcohols (b. p. 100—102°/12 mm., d^{18} 0·919, n_D^{18} 1·4665) is obtained by hydrogenation of 4-*iso*propyl*cyclo*hexanone, b. p. 85—86°/10 mm., d^{23} 0·915, n_D^{23} 1·4563 [*oxime*, b. p. 129—130°/12 mm., m. p. 33—35° (affording, on hydrogenation in dilute hydrochloric acid in presence of platinum-black, β-4-iso*propyl*cyclo*hexylhydroxylamine*, m. p. 61°); the semicarbazone, m. p. 187—188°, similarly affords 4-iso*propyl*cyclo*hexylsemicarbazide*, m. p. 159—160°], in ether or acetic acid in presence of platinum-black. Hydrogenation of the ketone in acetic acid containing hydrochloric acid affords a mixture in which the cis-4-iso*propyl*cyclo*hexanol*, m. p. 36—37°, b. p. 89°/8 mm., $n^{11·5}$ 1·4690, $d^{11·5}$ 0·926 (*hydrogen phthalate*, m. p. 129—130°; *hydrogen succinate*, m. p. 32—33°; *phenylurethane*, m. p. 88—89°), preponderates, the influence of the medium being thus manifested when steric hindrance is less marked. Reduction of 4-*iso*propyl*cyclo*hexanone with sodium and absolute alcohol affords mainly trans-4-iso*propyl*cyclo*hexanol*, m. p. 5—6°, b. p. 94°/10 mm., $d^{11·5}$ 0·920, $n^{11·5}$ 1·4696 (*hydrogen phthalate*, m. p. 114—115°; *hydrogen succinate*, m. p. 66—67°; *phenylurethane*, m. p. 112—113°), the *trans*-alcohol also being obtained by heating the sodium derivative of the *cis*-form at 160° for 2 hrs. *trans*-4-*iso*Propyl*cyclo*hexanol is esterified more rapidly than the *cis*-isomeride, the difference being more marked at a low temperature and in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed more rapidly than the *cis*-phthalate, the ratio of the velocity constants in 75% alcohol being 2·6 : 1 at 68° and 2·5 : 1 at 39°. With the hydrogen succinates, the ratio of the velocity constants for the *trans-* and *cis*-forms is 4 : 1 in water at 0°. The hydrogen phthalate of *cis*-4-*iso*propyl*cyclo*hexanol is hydrolysed fifty times as fast in 75% alcohol at 68° as that of the corresponding *cis*-2-isomeride; the corresponding ratio for the hydrogen succinates in water at 0° is 175 : 1.

R. BRIGHTMAN.

Action of *cyclo*hexene oxide on alkali and ammonium halides. H. K. SEN and C. BARAT (J. Indian Chem. Soc., 1927, 4, 22).—Neutral solutions of potassium halides treated with a few drops of *cyclo*hexene oxide quickly developed alkalinity in the order: iodide, bromide, chloride. Ammonium chloride behaves similarly. An explanation is tentatively suggested.

B. W. ANDERSON.

Interaction of phenol and methyl alcohol at high temperatures and pressures. V. IPATIEV, N. ORLOV, and A. PETROV (J. Russ. Phys. Chem. Soc., 1927, 59, 181—186).—The reaction of phenol with methyl alcohol has already been described (A., 1926, 281). When anisole and aluminium oxide were heated for 36 hrs. at 440° in an atmosphere of hydrogen at a maximum pressure of 200 atm., ethylene and *o*-cresol were formed. Phenol and *o*-cresol with aluminium oxide at 440—450° under 125 atm. gave a 2% yield of xanthen in 10 hrs. Phenol with aluminium oxide at 480—500° and a maximum pressure of 200 atm. yielded hydrogen, diphenylene oxide, and diphenyl ether. In addition to the above products, in every case a small quantity of a solid of low m. p. was obtained which dissolved in sodium hydroxide, giving a deep blue colour, and in alcohol with a deep green fluorescence.

E. ROTHSTEIN.

Nature of the alternating effect in carbon chains. XIX. Mechanism of certain aromatic migrations. C. K. INGOLD, E. W. SMITH, and C. C. N. VASS (J.C.S., 1927, 1245—1250).—The hypothesis that the migration reactions of aryl iodide dichlorides are really substitutions in one molecule of chlorine derived from another, is tested by investigation of the apparent exception of *o*-iodoanisole dichloride (Jannasch and Hinterskirch, A., 1898, i, 575). The main product of the migration reaction of the latter is shown to be, not 5-chloro-2-iodoanisole (as stated by the previous workers), but 4-chloro-2-iodoanisole. The hypothesis is further confirmed by the chlorination of acetanilide to *p*-chloroacetanilide by means of 4-*chloro-2-iodoanisole dichloride*.

4-Chloro-2-iodoanisole, m. p. 48°, is synthesised from *p*-chloroanisole by nitration to 4-chloro-2-nitroanisole, followed by reduction to the amine and replacement of the amino-group by iodine. This product is found to be identical with that obtained by the rearrangement of *o*-iodoanisole dichloride. During the preparation of the latter, a *dichloroiodoanisole*, m. p. 37°, is also obtained.

4-*Chloro-2-iodoanisole dichloride*, m. p. 76° (decomp.), spontaneously decomposes in chloroform solution to give the *dichloroiodoanisole*, m. p. 37°, and 4-*chloro-2-iodoanisole*. The 5-chloro-2-iodophenetole described by Jannasch and Naphtali (A., 1898, i, 576) is really 4-*chloro-2-iodophenetole*.

G. A. C. GOUGH.

***p*-Methylaminophenyl acetate.** L. GALATIS (Ber., 1927, 60, [*B*], 1399—1402).—*p*-Benzylideneaminophenyl acetate is converted by methyl sulphate at 80—85° into the corresponding *methosulphate*, which, at a higher temperature and with excess of the reagent, evolves methyl acetate and forms the *compound*, $SO_3Me\cdot C_6H_4\cdot NMe(\colon CHPh)\cdot O\cdot SO_3Me$. An analogous reaction is observed with the diacetyl derivative of *p*-aminophenol and methyl sulphate, ethyl sulphate, or sodium ethyl sulphate. The methosulphate of *p*-benzylideneaminophenyl acetate is converted by water into benzaldehyde and p-*methylaminophenyl acetate*, b. p. 168·5° (corr.)/9 mm., m. p. 43°; the corresponding *hydrochloride*, m. p. 200°, *oxalate*, and *picrate*, m. p. 157·5° (corr.), are described. p-*Aminophenyl acetate picrate* has m. p. 189° (corr.). *p*-Benzylideneaminophenol is transformed by ethyl sulphate at 100—105° and treatment of the product with water into benzaldehyde and p-*ethylaminophenol*, m. p. 103—104° (*monoacetyl* derivative, m. p. 187°). *p*-Benzylideneaminophenyl-acetate gives only small yields of the corresponding quaternary compound with ethyl sulphate or ethyl iodide. H. Wren.

New derivatives of phenacetin. M. T. Bogert and W. H. Taylor (J. Amer. Chem. Soc., 1927, 49, 1578—1583).—When heated with alcoholic ammonia for 10—12 hrs. at 110—120°, 2 : 3-dinitrophenacetin affords 3-*nitro*-2-*amino*-4-*acetamidophenetole*, (I), golden-orange, m. p. 160° (*acetyl* derivative, yellow, m. p. 258°), which, on hydrolysis with concentrated sulphuric acid yields 3-*nitro*-2 : 4-*diaminophenetole*, dark purple, m. p. 95°, whilst elimination of the amino-group yields 3-nitro-4-acetamidophenetole. The formation of this nitroamine is contrary to the conclusions of Reverdin and Roethlisberger (A., 1922, i, 537). Reduction of (I) affords 4-*amino*-5-*ethoxy*-2-*methylbenziminazole*, m. p. 147°, whilst treatment according to the method of Bogert and Hand (A., 1903, i, 292) yields 2-*nitro*-3-*acetamido*-6-*ethoxybenzonitrile*, (II), m. p. 219°, and this, on treatment with concentrated sulphuric acid at 100°, affords 2-*nitro*-3-*amino*-6-*ethoxybenzamide*, yellow, m. p. 199°. Treatment of the latter with acetic anhydride yields 2-*nitro*-3-*amino*-6-*ethoxybenzonitrile*, m. p. 201°. Reduction of (II) with tin and glacial acetic acid affords 2-*amino*-3-*acetamido*-6-*ethoxybenzonitrile*, m. p. 250°. F. G. Willson.

Chloro- and bromo-derivatives of *o*- and *m*-cresol. E. Bureš (Chem. Listy, 1927, 21, 221—227, 261—265; cf. this vol., 554).—The following substances were prepared: 3 : 5-*dibromo*-2-*methoxytoluene*, m. p. 33·5°, b. p. 265°; 3 : 5-dibromo-2-ethoxytoluene; *bismuth* and *mercuric* 3 : 5-*dibromo*-*o*-*tolyloxide*; *basic mercuric* 3 : 5-*dibromo*-o-*tolyloxide*; 2 : 4 : 6-*trichloro*-3-*methoxytoluene*, m. p. 46°, b. p. 258°, and the corresponding *ethoxy*- and *phenoxy*-derivatives, m. p. 35·5° and 103°, b. p. 266° and 234°, respectively; *antimony*, *bismuth*, and *mercuric* 2 : 4 : 6-*trichloro*-m-*tolyloxides*; *basic mercuric* 2 : 4 : 6-*trichloro*-m-*tolyloxide*; *di*- and *tri*-2 : 4 : 6-*trichloro*-m-*tolyl phosphates*, m. p. 94·5° and 230°, respectively; 2 : 4 : 6-*tribromo*-m-*cresol*, m. p. 81·6—81·9°, the corresponding *methoxy*- and *ethoxy*-derivatives, m. p. 67° and 47·5°, respectively, and *bismuth*, *mercuric*, and *basic mercuric* 2 : 4 : 6-*tribromo*-m-*tolyloxides*; 2 : 4 : 6-tribromo-*m*-toluidine, m. p. 101° (*acetyl* derivative, m. p. 155°), and 2 : 4 : 5 : 6-*tetrabromo*-3-*ethoxytoluene*, m. p. 108°. Bromination of *m*-cresol in sunlight yields, not 2 : 4 : 6-tribromocresol, but a tetrabromo-derivative, m. p. 115—125° (decomp.), which appears to be either 2 : 4 : 6 : 6-tetrabromo-1-methyl-$\Delta^{1:3}$-*cyclo*hexadien-5-one, 2 : 4 : 6 : 6-tetrabromo-1-methyl-$\Delta^{1:4}$-*cyclo*hexadien-3-one, or 2 : 4 : 4 : 6-tetrabromo-1-methyl-$\Delta^{1:5}$-*cyclo*hexadien-3-one. Chloro- or bromo-substitution of *o*- or *m*-cresol follows the same rules as for amino- or hydroxy-derivatives of benzene. In halogen derivatives of *o*-cresol, the halogen atom in the *ortho*-position to the hydroxyl group and in *m*-cresol derivatives those in the positions 4 and 6 to the hydroxyl group are the most labile. Bromine is more easily displaced by other substituents from the benzene nucleus than chlorine. R. Truszkowski.

Reduction products of some nitrodi-*p*-tolyl ethers. J. Reilly and H. S. B. Barrett (J.C.S., 1927, 1399—1400; cf. this vol., 239).—3-*Nitrodi*-p-*tolyl ether*, b. p. 206°/11 mm., prepared from potassium *p*-tolyloxide and 4-bromo-2-nitrotoluene in presence of copper bronze and *p*-cresol, yields, on reduction with stannous chloride, 3-*aminodi*-p-*tolyl ether*, m. p. 76° (*hydrochloride*, m. p. 190—195°, *chloroaurate*, *benzoyl* compound, m. p. 107°, and *azo*-β-*naphthol* compound, m. p. 149°, described).

2-*Aminodi*-p-*tolyl ether*, prepared similarly from the corresponding nitro-compound, has b. p. 196—198°/13 mm. (*hydrochloride*, m. p. 180—184°; *sulphate*, m. p. 160—162°). Addition of the 2-diazonium chloride solution to boiling sulphuric acid (50%) yields di-*p*-tolylene ether, m. p. 165°, and (?) 2-chlorodi-*p*-tolyl ether, m. p. 70°. Partial reduction of 2 : 6-dinitrodi-*p*-tolyl ether at 50—60° with stannous chloride gives 6-*nitro*-2-*aminodi*-p-*tolyl ether*, m. p. 120—122° (*hydrochloride*, m. p. 206—210°; *azo*-β-*naphthol* compound, m. p. 190—200°). The diazonium solutions of this nitroamine are less stable than those described above. Nitration of 2-nitrodi-*p*-tolyl ether gives mainly 3 : 5-dinitro-*p*-cresol, together with 2 : 2′-dinitrodi-*p*-tolyl ether, m. p. 126°. G. A. C. Gough.

Development of chromogenic properties in cholesterol by the action of heat. T. Moore and S. G. Willimott (Biochem. J., 1927, 21, 585—588).—Brown, resinous substances are produced if cholesterol is melted or heated in aqueous colloidal solution. At the same time, chromogenic properties similar to those of " oxycholesterol " are acquired. Robertson's observation (A. 1925, i, 1119) on the stability of cholesterol towards " oxidation " when aërated as an aqueous colloidal solution at the b. p. in absence of brain extract as a catalyst, *i.e.*, without the production of chromogenic substances, is not confirmed. S. S. Zilva.

Preparation of aromatic carboxylic esters of alkoxy- and dialkoxy-aryldialkylaminopropyl alcohols. C. Mannich.—See B., 1927, 507.

Photo-oxidation of adrenaline. T. Vacek (Biochem. J., 1927, 21, 457—459).—Pure adrenaline dissolved in distilled water takes up only minute quantities of oxygen in the dark. On the other hand, when exposed to visible light, and much more so when exposed to ultra-violet radiation, it takes up oxygen freely. The compound turns pink in the process of oxidation, the intensity of the colour being commensurate with the amount of oxygen taken up Different preparations of adrenaline show different tendencies to oxidation, pure adrenaline in distilled water being more oxidisable than adrenaline hydrochloride. S. S. Zilva.

Relation between *as*-phenylmethylethylene glycol and its corresponding anhydrous derivatives. S. Danilov and (Mme.) E. Venus-Danilova (J. Russ. Phys. Chem. Soc., 1927, 59, 187—216).—See this vol., 661.

Absorption spectra of di- and tri-phenylmethane, their carbinols, and triphenylmethyl

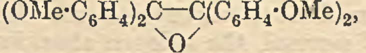
chloride. W. R. ORNDORFF, R. C. GIBBS, (Miss) S. A. MCNULTY, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1927, 49, 1541—1545; cf. A., 1926, 733).—The absorption spectra of diphenylmethane, diphenylcarbinol, triphenylmethane, triphenylcarbinol, and triphenylmethyl chloride were measured in neutral, absolute-alcoholic solution. The absorption spectrum of diphenylmethane is similar to that of benzene, but the intensity of absorption is much greater. Diphenylcarbinol shows a similar absorption spectrum, but the bands are displaced slightly towards the ultra-violet. The absorption spectrum of triphenylmethane is again similar, the intensity being greater than in the case of diphenylmethane. Triphenylcarbinol shows absorption similar to that of triphenylmethane, but the intensity is less except in the extreme ultra-violet, and the bands are shifted towards the shorter wave-lengths. The absorption of triphenylmethyl chloride is again similar, and the bands, intermediate in intensity between those of triphenylmethane and triphenylcarbinol, are shifted in the normal manner towards lower frequencies.

F. G. WILLSON.

Absorption spectra of fuchsone, benzaurin, and aurin. W. R. ORNDORFF, R. C. GIBBS, (Miss) S. A. MCNULTY, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1927, 49, 1545—1556; cf. preceding abstract).—The absorption spectra of fuchsone, benzaurin, aurin, and *p*-hydroxytriphenylcarbinol have been determined in freshly-prepared, neutral alcoholic solution. The first three compounds appear to be present initially in quinonoid form, subsequently changing to an equilibrium mixture of quinonoid hydrate and carbinol, a conclusion supported by the changes in the absorption spectra of solutions of the two forms of *p*-hydroxytriphenylcarbinol. When hydrogen chloride is added to alcoholic solutions of fuchsone and aurin, salt formation takes place first, and is followed, in more concentrated acid solutions, by more or less complete reduction. In concentrated sulphuric acid solution, the absorption spectra confirm the carbonium salt formation in the case of triphenylcarbinol (Baeyer, A., 1905, i, 281, 358) as distinct from the oxonium salts of fuchsone and aurin. The addition of successive hydroxyl groups results in the appearance of more absorption bands; thus, fuchsone has four, benzaurin five, and aurin six. In presence of potassium hydroxide, fuchsone changes in alcoholic solution to the carbinol form, with formation of the potassium salt. The type of absorption spectrum obtained from aurin in alcohol in presence of potassium hydroxide depends on whether the latter is added to a solution of aurin of the required concentration, or whether this concentration is reached by dilution of a more concentrated solution to which the alkali has been added previously. In the first case, the spectrum is similar to that which is consistently obtained in presence of higher concentrations of potassium hydroxide, whilst in the second case other bands appear. In concentrated aqueous potassium hydroxide, aurin is present as a tripotassium salt of the carbinol form.

F. G. WILLSON.

Auxochromes and antiauxochromes. I. Tetraphenylethane dyes. R. WIZINGER [with J. FONTAINE] (Ber., 1927, 60, [*B*], 1377—1389).—In extension of Dilthey's chromophore theory, it is proposed to subdivide auxochromes in the following manner: (i) positive auxochromes, including those groups previously considered auxochromic and alkyls, which favour the electro-positive condition, facilitate oxidation and analogous reactions, and deepen the colour in positive ions; (ii) negative auxochromes (groups, $\cdot NO$, $\cdot NO_2$, quinoid systems, $:CO$, $\cdot N:N-$, $\cdot C:N\cdot$, etc.) which favour the electro-negative condition and the addition of positive residues and analogous reactions, and deepen the colour in negative ions; (iii) amphoteric auxochromes (aryls and the group $>C:C<$) which favour ionisation in the positive and negative sense, facilitate the substitution of hydrogen by metals or negative groups, and deepen the colour in positive and negative ions. From this point of view, it is shown that the introduction of positive auxochromes into tetraphenylethylene, in itself possessing limited additive ability and yielding the colourless, homopolar dichlorotetraphenylethane only under peculiar conditions, gives compounds with negative residues which are heteropolar and coloured. Thus octamethyltetra-aminotetraphenylethylene, m. p. 295—300°, is converted by cautious treatment with chlorine in carbon tetrachloride solution into the coloured *chloride*, $[(NMe_2\cdot C_6H_4)_2\dot{C}\cdot\dot{C}(C_6H_4\cdot NMe_2)_2]^{++}Cl_2^{-}$, and by bromine and iodine under similar conditions into the *perhalides*, $C_{34}H_{40}N_4Br_6$ and $C_{34}H_{40}N_4I_6$. Salts are also prepared by treatment of the ethylenic compound with acids and various oxidising agents (air, hydrogen peroxide, lead tetra-acetate) and by double decomposition from the halides; the *nitrate*, *sulphate*, *phosphate*, *oxalate*, *acetate*, *perchlorate*, *chloroaurate*, *chloroplatinate*, and *iodide* are described. Substitution of other auxochromes for the dimethylamino-group shows that the stability of the salts is increased by the number and strength of such groups. Thus tetramethyldiaminotetraphenylethylene yields the *chloride*, $C_{30}H_{30}N_2Cl_2$, *iodide*, $C_{30}H_{30}N_2I_6$, *perchlorate*, $C_{30}H_{30}O_8N_2Cl_2$, *chloroaurate*, $C_{30}H_{30}N_2Cl_8Au_2$, *sulphate*, and *nitrate*. *Tetra-p-aminophenylethylene*, m. p. 250°, prepared by reduction of diaminobenzophenone or tetra-*p*-nitrophenylethylene, affords the *periodide*, $C_{26}H_{24}N_4I_6$, and *chloroaurate*, $C_{26}H_{24}N_4Cl_8Au_2$. The coloured halide salts are converted into the ethylenes by treatment with copper powder. Tetrahydroxyphenylethylene gives a bluish-black *perchlorate*, $[(OH\cdot C_6H_4)_2\dot{C}\cdot\dot{C}(C_6H_4\cdot OH)_2]^{++}(ClO_4)_2^{-}$ converted by water into the anhydro-glycol, $OH\cdot C_6H_4\cdot C(:C_6H_4:O)\cdot C(:C_6H_4:O)\cdot C_6H_4\cdot OH$. Tetramethoxyphenylethylene yields still more unstable salts, among which the *perchlorate* is described. The carbinol bases corresponding with the dyes are the substituted benzpinacols. Octamethyltetra-aminotetraphenylethylene glycol and tetramethyldiaminotetraphenylethylene glycol yield the corresponding violet and red dyes; in the tetrahydroxy- and tetramethoxy-series, however, the anhydro-compounds, $OH\cdot C_6H_4\cdot C(:C_6H_4:O)\cdot C(:C_6H_4:O)\cdot C_6H_4\cdot OH$ and



$(OMe\cdot C_6H_4)_2C—C(C_6H_4\cdot OMe)_2$ (bridged by O), are obtained.

Evidence in favour of the predicted behaviour of antiauxochromes is derived from the literature. Thus, tetraphenylethylene yields an unstable, yellowish-red sodium salt, whereas dianthrone, derived from tetraphenylethylene by introduction of the antiauxochrome, $C{:}O$, gives a corresponding, completely stable compound.

In the stilbene series a new group of dye salts, $[OMe\cdot C_{10}H_6\cdot \dot{C}H\cdot \dot{C}H\cdot C_{10}H_6\cdot OMe]^{++}X_2$ and $[NH_2\cdot C_6H_4\cdot \dot{C}H\cdot \dot{C}H\cdot C_6H_4\cdot NH_2{}^{++}X_2$, has been isolated.

H. Wren.

Reactions of 1-anilino*cyclo*hexane-1-carboxylic acid. Synthesis of ψ-indoxyl*spirocyclo*hexane. R. L. Betts, R. Muspratt, and S. G. P. Plant (J.C.S., 1927, 1310—1314).—The similarity of the properties of 1-*anilino*cyclo*hexane*-1-*carboxylic acid* to those of 1-anilino*cyclo*pentane-1-carboxylic acid (A., 1925, i, 1271) confirms the constitution assigned to the latter. 1-Anilino-1-cyano*cyclo*hexane (Walther and Hübner, A., 1916, i, 560), on keeping with concentrated sulphuric acid, gives 1-*anilino*cyclo*hexane*-1-*carboxylamide*, m. p. 148° (*hydrochloride* and *nitrosoamine*, m. p. 172°, described), which in turn yields 1-*anilino*cyclo*hexane*-1-*carboxylic acid*, m. p. 142° (*nitrosoamine*, m. p. 70°). This acid decomposes when heated to give Δ^1-*cyclo*hexene-1-carboxylic acid, which combines additively with bromine to produce 1 : 2-dibromo*cyclo*hexane-1-carboxylic acid.

ψ-*Indoxyl*spirocyclo*hexane*, m. p. 124°, is prepared by the fusion of 1-anilino*cyclo*hexane-1-carboxylic acid with potassium hydroxide at 340—350° for ½ hr. The crude product is acetylated and the purified 7-*acetyl*-ψ-*indoxyl*spirocyclo*hexane*, m. p. 105°, hydrolysed to give pure ψ-*indoxyl*spirocyclo*hexane*. This compound is unaffected by boiling dilute hydrochloric acid or dilute sodium hydroxide solution, but when heated with an excess of the latter at 200°, it gives a *sodium* derivative. Attempts to prepare the nitrosoamine and the semicarbazone were unsuccessful. With boiling dilute nitric acid, it gives 10-*nitro*-ψ-*indoxyl*spirocyclo*hexane*, pink, m. p. 177—178°, which yields a yellow *sodium* derivative and a 7-*methyl* derivative, m. p. 129°, by methylation with methyl sulphate. That the methyl group is attached to nitrogen is shown by the fact that no methyl iodide is produced under the conditions of the Zeisel experiment.

G. A. C. Gough.

α-Imino- and α-amino-acids from amines and carbonyl compounds. A. Skita and C. Wulff (Annalen, 1927, 455, 17—40; cf. this vol., 559).—Condensation of pyruvic acid with Schiff's bases of the type $CHAr{:}NR$ (Ar=aryl, R=aliphatic radical) yields, intermediately, α-imino-acids of the type $NR{:}CHMe\cdot CO_2H$, with liberation of the aryl aldehyde, and these further condense to yield α-imino-unsaturated acids of the type $CHAr{:}CH\cdot C({:}NR)\cdot CO_2H$, which are the first isolated products. The latter, on catalytic reduction with colloidal platinum in acetic acid, yield the corresponding substituted α-aminobutyric acids, $CH_2Ar\cdot CH_2\cdot CH(NHR)\cdot CO_2H$, which on decarboxylation yield the corresponding secondary amines, $CH_2Ar\cdot[CH_2]_2\cdot NHR$. Thus the compound $C_{16}H_{19}O_2N$, obtained by the action of benzylidene*cyclo*hexylamine on pyruvic acid (this vol., 157), is α-cyclo*hexylimino*-β-*benzylidenepropionic acid* (Ar=Ph, R=C_6H_{11}), which on reduction yields α-*cyclo*hexylamino-γ-phenylbutyric acid (*loc. cit.*; *methyl ester*, b. p. 215—217°/12 mm.; *hydrochloride* of methyl ester, m. p. 148°; *nitroso*-derivative of methyl ester, m. p. 63°), which is synthesised by heating *cyclo*hexylamine and α-bromo-γ-phenylbutyric acid in alcohol at 130° for 6 hrs. On decarboxylation by heating in quinoline, this amino-acid yields cyclo*hexyl-γ-phenylpropylamine*, b. p. 169—171°/12 mm. (*hydrochloride*, m. p. 217—218°; *nitrobenzoyl* derivative, m. p. 106—107°; *picrolonate*, m. p. 217—218°), which is also obtained by the reduction, with colloidal platinum in acetic acid, of *cinnamylidene*cyclo*hexylamine*, b. p. 180—185°/12 mm. (obtained by the condensation of cinnamaldehyde with *cyclo*hexylamine). On reduction in acetic acid suspension with hydrogen at 45°/3 at. in presence of colloidal platinum, α-*cyclo*hexylamino-γ-phenylbutyric acid yields α-cyclo*hexylamino-γ-*cyclo*hexylbutyric acid*, m. p. 265° (*ethyl* ester, b. p. 198—199°/11 mm.). The action of benzaldehyde on the condensation product of pyruvic acid with propylidene*cyclo*hexylamine also yields the same parent compound, $C_{16}H_{19}O_2N$. Benzylidene-ethylamine and pyruvic acid similarly yield α-*ethylimino*-β-*benzylidenepropionic acid*, m. p. 133—134°, which when heated in glycerol suspension at 140° for 1 hr. yields cinnamaldehyde, and on hydrolysis with dilute hydrochloric acid yields benzylidenepyruvic acid and ethylamine. On similar treatment in glycerol, the corresponding β-anisylidene-acid yields *p*-methoxycinnamaldehyde, and on hydrolysis with dilute hydrochloric acid, α-*cyclo*hexylimino- and α-amylimino-β-benzylidenepropionic acids yield benzylidenepyruvic acid, α-ethylimino-β-anisylidenepropionic acid yields anisylidenepyruvic acid, and α-amylimino-β-piperonylidenepropionic acid yields piperonylidenepyruvic acid. On reduction, α-ethylimino-β-benzylidenepropionic acid yields α-*ethylamino-γ-phenylbutyric acid*, m. p. 250° (*hydrochloride*, m. p. 198—199°), which on decarboxylation yields γ-phenylpropylethylamine, which is also obtained by the reduction of cinnamylidene-ethylamine. Condensation of benzylidenepyruvic acid with *cyclo*hexylamine, however, yields a *substance*, m. p. 122°, to which the constitution $NH\cdot C_6H_{11}\cdot CHPh\cdot CH_2\cdot CO\cdot CO_2H$ is assigned, whilst with aniline it yields 2 : 3-*diketo*-1 : 5-*diphenylpyrrolidine*, m. p. 163°. Phenylpyruvic acid and benzylidene*cyclo*hexylamine condense to yield *γ-hydroxy-α-keto-βγ-diphenylbutyro*cyclo*hexylamide*, $CHPh(OH)\cdot CHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_{11}$, m. p. 114—115°, which when heated with dilute hydrochloric acid yields 2 : 3-*diketo*-4 : 5-*diphenyl*-1-cyclo*hexylpyrrolidine*, m. p. 234—235°, the *dipotassium* salt of which with ethyl iodide yields 2 : 3-*diethoxy*-4 : 5-*diphenyl*-1-cyclo*hexylpyrrole*, m. p. 155—156°. By similar condensations with pyruvic acid and the appropriate Schiff's bases and subsequent treatment as above are obtained: α-*amylimino*-β-*benzylidenepropionic acid*, m. p. 136°; α-*amylamino-γ-phenylbutyric acid*, m. p. 216—218°; γ-*phenylpropylamylamine hydrochloride*, m. p. 215°; p-*tolylideneamylamine*, b. p. 134°/12 mm.; α-*amylimino*-β-p-*tolylidenepropionic acid*, m. p. 130°; α-*amylamino-γ*-p-*tolylbutyric acid*, m. p. 232°; γ-p-*tolylpropylamylamine*, b. p. 153—154°/13 mm. (*hydrochloride*, m. p. 213°; *nitrobenzoyl* derivative, m. p. 225°); p-*tolylidenepyruvic acid*, m. p. 123°; α-*ethylimino*-β-*anisylidenepropionic acid*, m. p. 122° (decomp.); α-*ethylamino-γ*-

anisylbutyric acid, m. p. 225°; *piperonylideneamylamine*, m. p. 36°, b. p. 210—215°/25 mm.; α-*amylimino-β-piperonylidenepropionic acid*, m. p. 135° (decomp.); α-*amylamino-γ-piperonylbutyric acid*, m. p. 230—231°; γ-piperonylpropylamylamine, b. p. 196°/12 mm. (*hydrochloride*, m. p. 203°; *picrate*, m. p. 128°). Similar compounds are obtained from the Schiff's bases derived from cinnamaldehyde, and thus are obtained: α-*amylimino*-, m. p. 136—138°; α-*ethylimino*-, m. p. 151—152°; and α-cyclo*hexylimino*-, m. p. 145°, -β-*cinnamylidenepropionic acids*. Partial reduction of the α-amylimino-acid yields α-*amylamino-ε-phenylhexenoic acid*, m. p. 213°, which on further reduction yields α-*amylamino-ε-phenylhexoic acid*, m. p. 214—216°; α-*ethylamino*-, m. p. 222—223°, and α-cyclo*hexylamino*-, m. p. 242°, -ε-*phenylhexoic acids* are obtained similarly. Decarboxylation yields, respectively, ε-*phenylamyleneamylamine hydrochloride*, m. p. 215°; ε-*phenyldiamylamine*, b. p. 310° (*hydrochloride*, m. p. 184—186°); ε-*phenylamylethylamine*, b. p. 295° (*hydrochloride*, m. p. 144°), and cyclo*hexyl-ε-phenylamylamine*, b. p. 315° (*hydrochloride*, m. p. 246°). J. W. Baker.

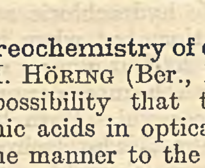
New way of utilising carbon monoxide. H. Dieterle and W. Eschenbach (Arch. Pharm., 1927, **265**, 187—195).—That carbon monoxide yields carbonyl compounds with many elements has been shown particularly by Manchot (A., 1925, ii, 232 and earlier papers), whilst that, *e.g.*, acid amides are "decarbonylated" by certain catalysts has been demonstrated by Mailhe (A., 1926, 54). Details of an apparatus, but none of the particular catalysts employed, are given for carrying out on the laboratory scale processes based on the above facts. These processes, covered by patent applications, are outlined as follows. Chlorobenzene and carbon monoxide yield benzoic acid; *p*-chlorotoluene similarly gives *p*-toluic acid. *o*-Dichlorobenzene also yields benzoic acid, and phthalic acid as an intermediate stage has not yet been detected. Chlorobenzene with carbon monoxide and ammonia yields aniline, presumably by carbonylation followed by decarbonylation, and *p*-chlorotoluene similarly gives *p*-toluidine. W. A. Silvester.

Aminobenzoate of thiodiglycol [ββ'-dihydroxydiethyl sulphide] and its sulphone. New higher homologue of ββ'-dihydroxydiethyl sulphide. R. T. Major (Bull. Soc. chim., 1927, [iv], **41**, 634—637).—To obtain anæsthetics for external application, the author has prepared ββ'-*di*-p-*aminobenzoyloxydiethyl sulphide*, m. p. 184·5° (yield 70%), by reduction of ββ'-*di*-p-*nitrobenzoyloxydiethyl sulphide*, m. p. 107·7° (obtained by Fromm and Kohn's method, A., 1921, i, 242). Neither the sulphide nor the corresponding sulphone possesses any anæsthetic action by external application, probably in consequence of their slight solubility in most solvents. ββ'-*Di*-p-*nitrobenzoyloxydiethyl sulphone*, m. p. 153°, obtained by oxidation of the sulphide in acetic acid with potassium permanganate and sulphuric acid, on reduction by Einhorn's method (A., 1910, i, 170) affords ββ'-*di*-p-*aminobenzoyloxydiethyl sulphone*, m. p. 149—150°. Hydrolysis of ββ'-di-*p*-aminobenzoyloxydiethyl sulphide with alcoholic potassium hydroxide affords ethyl *p*-aminobenzoate and sulphur dioxide. ββ'-*Dihydroxy*-ββ'-*dimethyl di*-n-*butyl sulphide*, b. p. 148·5—149°/11 mm., obtained in 45% yield by the action of sodium sulphide on β-chloromethyl-*n*-butan-β-ol in alcoholic solution, has an intense soporific action on mice, and slight toxicity. R. Brightman.

Union of benzoylacetonitrile with organic bases in presence of salicylaldehyde. I. P. Krishnamurti and B. B. Dey (J.C.S., 1927, 1349—1351).—Benzoylacetonitrile combines with piperidine in presence of traces of salicylaldehyde to yield a mono-acid *base*, $C_{10}H_{18}ON_2$, m. p. 173° [*hydrochloride*, m. p. 235—242°, *picrate*, m. p. 138° (losing alcohol of crystallisation at 98°), and *chloroplatinate* described]. When the base is oxidised with alkaline potassium permanganate, benzoic acid and piperidine are produced. Piperidine and benzoylacetonitrile are formed when the base is heated above its m. p. The action of nitrous acid on the hydrochloride of the base yields a *nitroso-hydrochloride*, m. p. 258° (decomp.), which in turn yields an iso*nitroso*-compound, $C_{14}H_{17}O_2N_3$, m. p. 183° (decomp.) [*diacetyl* derivative, m. p. 180—181° (decomp.), and *dibenzoyl* derivative, m. p. 148°]. *N*-Alkylpiperidines do not give this reaction. The alternative constitutions $CH_2Bz\cdot C⁝NH\cdot NC_5H_{10}$ and $CH_2Bz\cdot C(⁝NH)\cdot NC_5H_{10}$ are proposed for the base, and in consideration of its stability to alkalis and its instability to acids, the former is favoured. The *iso*nitroso-derivative is represented $OH\cdot N⁝CBz\cdot C⁝NH\cdot NC_5H_{10}$. G. A. C. Gough.

Stereochemistry of diphenyl. J. Meisenheimer and M. Höring (Ber., 1927, **60**, [*B*], 1425—1433).—The possibility that the existence of substituted diphenic acids in optically active forms may be due in some manner to the carboxy-groups is discounted by the impossibility of resolving *o*-nitrobenzoic, 8-nitronaphthoic, or 5-nitronaphthoic acid into optical isomerides. 6 : 6'-Dinitrodi-*o*-tolyl, obtained by the action of copper powder on 2-iodo-3-nitrotoluene, is reduced by stannous chloride to 6 : 6'-diaminodi-*o*-tolyl, which is resolved into its optically active forms by the alternate use of *d*- and *l*-tartaric acids in absolute alcoholic solution. l-6 : 6'-*Diamino-di*-o-*tolyl* has m. p. 156°, $[\alpha]_D$ −34·8° in *N*-hydrochloric acid; the properties of the d-*base* are similar. The compounds are not prone to racemisation. The only possible explanation of the stereoisomerism appears to lie in the assumption that with a particular type of substitution (I) free rotation of the two rings is impossible (cf. Christie and Kenner, J.C.S., 1922, **121**, 615). Consideration of the distances between the groups as shown by Röntgen spectrography indicates that the proximity of the methyl and amino-groups to one another may easily be such as to inhibit free rotation of the benzene nuclei around the

(I.)



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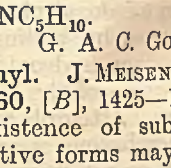


common axis and to permit only vibratory motion. If this explanation be accepted, isomerism must disappear when the substituting groups are mutually attractive or actually react chemically with one another. The active 6 : 6′-*diaminodi*-o-*tolyls* are therefore transformed (without considerable racemisation) into the corresponding *diacetyl* derivatives, m. p. 229°, $[\alpha]_D$ −131° (+133°), which are oxidised by boiling, neutral potassium permanganate solution to largely racemised 6 : 6′-diacetamidodiphenic acids. [The *quinine* salt of *d*-diacetamidodiphenic acid has m. p. 187°, $[\alpha]_D$ −92·2° in methyl-alcoholic solution (c = 2·489); the rotation of optically homogeneous *sodium* d-*diacetamidodiphenate* is calculated to be $[\alpha]_D$ −211·6°.] If the active diacetamido-acids are hydrolysed under as mild conditions as possible (contact with dilute sulphuric acid at the atmospheric temperature), the acetyl groups are removed and the completely racemised *dilactam* (II), m. p. above 330°, is produced.

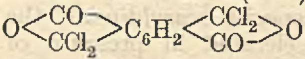
The resolution of 6 : 6′-diaminodi-*o*-tolyl cannot readily be effected by π-bromocamphorsulphonic acid. The following salts are described incidentally: *brucine* o-*nitrobenzoate*, m. p. about 120° (decomp.); *brucine* 8-*nitronaphthoate*, decomp. 155—165°, m. p. 242° (decomp.); *brucine* 5-*nitronaphthoates*, m. p. 212° and decomp. about 170°, which probably differ from one another in their content of solvent of crystallisation.

H. WREN.

Hydrocaffeic acid a constituent of spores of *Lycopodium clavatum*. F. ZETZSCHE and K. HUGGLER (Helv. Chim. Acta, 1927, **10**, 472—474).—The acidified alkali extract of spores of *Lycopodium clavatum* is extracted with ether and the oil so obtained is freed from lycopodium oil with chloroform or light petroleum, giving a 5% yield of crude hydrocaffeic acid (β-3 : 4-dihydroxyphenylpropionic acid), from which the pure acid, m. p. 139° (dimethyl ether, m. p. 97°), is obtained by crystallisation from xylene. The dimethyl ether is oxidised by alkaline permanganate to veratric acid, m. p. 179—180°.

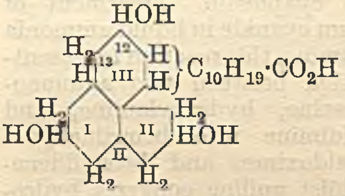
C. HOLLINS.

Derivatives of cumidic and pyromellitic acids. H. DE DIESBACH and M. GUHL (Helv. Chim. Acta, 1927, **10**, 442—449; cf. de Diesbach and Zurbriggen, A., 1925, i, 1427).—By the action of chlorine on β-cumidyl chloride at 150° and finally at 180—190°, there is obtained 1 : 4-*bisdichloromethylbenzene*-2 : 5-*dicarboxyl chloride*, m. p. 110—111°. The corresponding *acid*, m. p. 270°, and *ethyl* ester, m. p. 127·5°, are described. The ethyl ester is converted at 190°, with elimination of 2 mols. of ethyl chloride, into *dichloro*-p-*pyromellitide* [*dilactone* of 1 : 4-*bis*(*chlorohydroxymethyl*)*benzene*-2 : 5-*dicarboxylic acid*], m. p. 263°. If the temperature of chlorination does not exceed 150°, the product is impure 1 : 4-*bischloromethylbenzene*-2 : 5-*dicarboxyl chloride* [free *acid* decomp. 325° without melting; *ethyl* ester, m. p. 132° (decomp.)]. By continuing chlorination at 265°, there is obtained the symmetrical octachloride of pyromellitic acid, *dianhydro*-1 : 2 : 4 : 5-*tetrakis*(*dichlorohydroxy*)*benzene*, m. p. 267—268°, which is not hydrolysed by formic or acetic acid, but gives pyromellitic acid when boiled with concentrated alkali. Chlorination above 265° gives decarboxylated products. The octachloride is formed directly at 150° (better 200°) when α-cumidic acid is used, and also from *m*- or *p*-pyromellitide, pyromellitic acid, its chloride or anhydride, by action of phosphorus pentachloride in a sealed tube at 200—210°. The normal chloride of pyromellitic acid is converted by aluminium chloride at all temperatures between 80° and 180° into the as(2 : 5)-*chloride*,


$O<\substack{CO-\\CCl_2}>C_6H_2<\substack{CCl_2\\CO-}>O$, m. p. 225—227° (with regeneration of the normal chloride), reducible by zinc and acetic acid to *p*-pyromellitide without any trace of *m*-pyromellitide. Of the three di-imides of pyromellitic acid described by Meyer and Steiner (A., 1914, i, 841), the so-called *as*-di-imide, prepared by sublimation in a vacuum, could not be obtained. A benzene solution of the *as*-acid chloride gives with dry ammonia the *p*-diamide, $C_6H_2(CO_2H)_2(CO{\cdot}NH_2)_2$, which is converted at 200° into the normal di-imide.

C. HOLLINS.

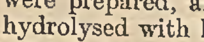
Bile acids. XXVII. Constitution of acids resulting from the breakdown of cholic acid. H. WIELAND (Z. physiol. Chem., 1927, **167**, 70—75).—The results of Windaus and van Schoor (A., 1926, 169; this vol., 56) and Borsche and Frank (A., 1926, 1140) are regarded as establishing definitely the position of the hydroxyl group in ring III in cholic acid, this group being attached to the carbon atom 12 instead of 13. The statement of the latter authors, that the liberation of carbon monoxide when choloidanic acid is heated with concentrated sulphuric acid proves the presence in this acid of a tertiary-bound carboxyl group, is regarded as erroneous. The production of carbon monoxide from choloidanic acid under such stringent conditions, resulting in the production of a black fused mass and the evolution of appreciable amounts of sulphur dioxide, is not satisfactory evidence of this fact. Similarly, Borsche's formula for solanellic acid, where this acid is regarded as a derivative of malonic acid, is incorrect, since this substance loses only one third of the theoretical amount of carbon dioxide at 210—215°.



A. WORMALL.

Application of the Perkin reaction to phenolic aldehydes. S. OGAWA (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 383—396).—See this vol., 359.

Hydrobenzamide and benzaldimine as ammono-aldehydes. H. H. STRAIN (J. Amer. Chem. Soc., 1927, **49**, 1558—1571).—In extension of Franklin's conception of nitrogen compounds (A., 1924, ii, 850) as acids, bases, or salts of ammonia, analogy is drawn between certain organic oxygen and nitrogen derivatives. Thus primary and secondary amines are the nitrogen analogues of the alcohols, and tertiary amines those of the ethers. Similarly, the acid amidines (carbazylic acids) are the ammonia analogues of the carboxylic acids, and as the latter lose water with formation of the acid anhydrides, so the acid amidines lose ammonia with formation of the corresponding acid anammonides, the nitriles, whilst the pyrogenic decomposition of an acid salt of an amidine, with formation of a hydrocarbon and cyanamide, is analogous to the decomposition of the sodium salts of the carboxylic acids with formation of hydrocarbons and carbon dioxide. Certain more complex analogies are similarly formulated.

Hydrobenzamide dissolves slowly in liquid ammonia, and the solution deposits *benzaldimine*, the formation of which is accelerated in presence of ammonium chloride. Benzaldimine loses ammonia when kept or heated, with formation of hydrobenzamide. On reduction with sodium and liquid ammonia, it yields benzylamine. It dissolves sodium and potassium amides in liquid ammonia solution, with formation of *sodium* and *potassium* salts. When heated at 210° with potassamide and liquid ammonia, it yields potassium benzamidine and benzylamine, a reaction analogous to the Cannizzaro reaction with benzaldehyde and potassium hydroxide. At the same time, about 60% of the benzaldimine is converted into amarine, which in turn is converted into lophine by the action of the potassamide. Treatment of benzaldimine with iodine in liquid ammonia at −39° affords cyaphenin (20%) and benzamidine (40%), together, probably, with a trace of benzonitrile, whilst amarine yields similarly lophine, and this, on further treatment with iodine in boiling liquid ammonia, yields cyaphenin. Treatment of cyaphenin with ammonium cyanide in liquid ammonia affords benzylidenecyanamine, this reaction representing an aldol condensation between two ammonoaldehydes. Phenylhydrazine, hydroxylamine, and aniline convert benzaldimine into benzaldehydephenylhydrazone, benzaldoxime, and benzylideneaniline, respectively, whilst aniline converts hydrobenzamide into benzylideneaniline and ammonia. Hydrobenzamide does not combine with dry sulphur dioxide in absolute alcohol, Otto's product (Annalen, 1859, **112**, 305) being precipitated on addition of the necessary proportion of water. Treatment of hydrobenzamide in benzene with sulphurous acid affords the *compound* $[CHPh(SO_2{\cdot}OH){\cdot}NH]_2CHPh$, and this is hydrolysed by water with formation of benzaldehyde and Otto's compound, to which the formula  $CHPh{<}{}^{NH_3}_{SO_2}{>}O$ is ascribed. F. G. Willson.

Influence of substituents on the stability of Schiff's bases. I. Hydrolysis of nitro- and methoxy-benzylideneanilines. (Miss) E. M. Langman, W. Healy, and P. K. Dutt (J. Indian Chem. Soc., 1927, **4**, 75—79).—The *o*-, *m*-, and *p*-nitro- and *o*-, *m*-, and *p*-methoxy-benzylideneanilines were prepared, and equivalent quantities separately hydrolysed with hydrochloric acid. The percentages of anils hydrolysed were determined at intervals in each case until equilibrium was reached. In the light of the results thus obtained, the influence of general polar effect, induced polar effect, mass, steric effects, conjugation, and constitutional changes on the equilibrium points and initial velocities of reaction in the hydrolysis of the anils is discussed.

B. W. Anderson.

Bromination of anisaldehydephenylhydrazone. I. M. Vanghelovitch (Bul. Soc. Chim. Rômania, 1926, **8**, 20—25; cf. Chattaway and Walker, A., 1925, i, 929).—Bromination of anisaldehydephenylhydrazone in cold glacial acetic acid in absence of light yields ω-*bromoanisaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 129—130°, which is converted by alcoholic potassium cyanide into ω-*cyanoanisaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 182°. Bromination in sunlight gives 1 : 4-*di*-p-*bromophenyl*-3 : 6-*di*-p-*methoxyphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*, m. p. 150°, formed by elimination of 2 mols. of hydrogen bromide from 2 mols. of ω-bromoanisaldehyde-*p*-bromophenylhydrazone. H. Burton.

Constitution and derivatives of 4 : 6- and 2 : 6-dinitro-3-methoxybenzaldehyde. J. Tröger and C. Eicker (J. pr. Chem., 1927, [ii], **116**, 17—33). —The two isomeric dinitromethoxybenzaldehydes obtained by direct nitration of *m*-methoxybenzaldehyde (Tiemann and Ludwig, A., 1883, 188) are both converted by boiling 5% sodium hydroxide into a mixture of 2 : 4-dinitroanisole and 2 : 4-dinitrophenol [*sodium* (+H_2O) and other salts are described]. Of the two possible compounds from which these substances could be derived, that of m. p. 110° must be 4 : 6-*dinitro*-3-*methoxybenzaldehyde* (*phenylhydrazone*, m. p. 210°; *semicarbazone*, m. p. 247°; *oxime*, m. p. 117°), since it is oxidised by hot aqueous permanganate to 4 : 6-dinitro-3-methoxybenzoic acid (*potassium* and *silver* salts; *acid chloride*, m. p. 85°; *amide*, m. p. 215°; *anilide*, m. p. 215°). The aldehyde condenses with acetone in alkaline solution to amorphous 6 : 6′-*dinitro*-5 : 5′-*dimethoxyindigotin*, and with sodium phenylacetate in presence of acetic anhydride to 4 : 6-*dinitro*-3-*methoxy*-α-*phenylcinnamic acid*, m. p. 160° (*barium* salt); with aqueous ammonia, it gives 2 : 4-dinitroanisole. The second isomeride, m. p. 156°, must be 2 : 6-*dinitro*-3-*methoxybenzaldehyde* (*phenylhydrazone*, m. p. 185°; *semicarbazone*, m. p. 225°; *oxime*, m. p. 165°); this is confirmed by the formation with acetone and alkali of amorphous 4 : 4′-*dinitro*-5 : 5′(? 7 : 7′)-*dimethoxyindigotin*. It condenses with sodium phenylacetate, giving 2 : 6-*dinitro*-3-*methoxy*-α-*phenylcinnamic acid*, m. p. 255° (*silver* salt), and is oxidised by permanganate to 2 : 6-*dinitro*-3-*methoxybenzoic acid*, m. p. 195° (*potassium* and *silver* salts; *acid chloride*, m. p. 85°; *amide*, m. p. 222°; *anilide*, m. p. 243°), which yields 2 : 4-dinitroanisole when heated with soda-lime at 185—190°. Attempts to obtain amino-derivatives from the aldehydes by reduction or heating with alcoholic ammonia, or from the dinitromethoxyphenylcinnamic acids by reduction, were unsuccessful. H. E. F. Notton.

New derivatives of vanillin and some of their reactions. L. C. Raiford and G. C. Hilman (J. Amer. Chem. Soc., 1927, **49**, 1571—1577; cf. this vol., 564).—The following derivatives of 5-bromovanillin are described: *phenylhydrazone*, m. p. 117°; p-*bromophenylhydrazone*, m. p. 153°; *semicarbazone*, m. p. 185—186°; 5-*bromovanillylidene-aniline*, m. p. 124°; -p-*toluidine*, m. p. 159—160°, and -*tolidine*, m. p. 184—185°. 5 : 6-*Dibromovanillylideneaniline*, m. p. 147°, is obtained by boiling the aldehyde and aniline together in pyridine; *p*-toluidine yields similarly 5 : 6-*dibromovanillylidene*-p-*toluidine*, purple, becoming yellow below 100°, m. p. 150°. *Di*-5 : 6-*dibromovanillylidenebenzidine*, m. p. not below 350°, is described, as well as the aldehyde *phenylhydrazone*, m. p. 102° after softening at 94°, *semicarbazone* ($+C_5H_5N$), m. p. (solvent-free) 224°, and *oxime*, m. p. 187°. No stereoisomeride of the latter could be obtained, the oxime of dibromoprotocatechualdehyde being obtained when the dibromovanillin was heated with alcohol, hydroxylamine hydrochloride, and hydrochloric acid at 160—170°. When boiled with acetic anhydride, the oxime yields 5 : 6-*dibromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 169°, which, on hydrolysis with alkali, yields 5 : 6-*dibromo*-4-*hydroxy*-3-*methoxybenzonitrile*, m. p. 179° (*benzoyl* derivative, m. p. 215° after softening at 212°). The cyano-group of this nitrile is particularly resistant to hydrolysis. F. G. Willson.

Mechanism of the formation of ketones during the dry distillation of salts of organic acids. C. Dosios and G. Leucaditis (Compt. rend., 1927, 184, 1458—1460).—The formation of mixed ketones by dry distillation of a mixture of the salts of different organic acids is explained on the assumption that anhydrides are primarily formed, $(R\cdot CO_2)_2Ca \longrightarrow (R\cdot CO)_2O+CaO$, and that interchange of groups occurs between the anhydrides prior to the decomposition, $(R\cdot CO)_2O+CaO \longrightarrow R\cdot CO\cdot R+CaCO_3$. This assumption is supported by the presence of traces of anhydrides among the reaction products, *e.g.* calcium benzoate affords a little benzoic anhydride, and crude acetone from calcium acetate always contains a little acetic acid. Further support is found in the observations that under 1 mm., calcium benzoate affords benzophenone at 420° in place of at 550° under 760 mm.; that mixed ketones are obtained by passing the vapours of anhydrides over heated calcium carbonate (Sabatier and Mailhe, A., 1914, i, 168), and that, whilst benzoic acid vapour passed over calcium carbonate at 550° affords only decomposition products, ketones containing the benzoyl group are obtained at much lower temperatures by the use of a suitable vapour mixture. The decomposition temperature of the intermediate mixed anhydride is evidently lower than that of benzoic anhydride. R. Brightman.

Relative affinity of the *p*-tolyl radical. M. Tiffeneau and (Mlle.) J. Lévy (Compt. rend., 1927, 184, 1465—1467).—In the addition of hypoiodous acid to α-*p*-tolyl-β-methyl-Δ^a-propylene, the *p*-tolyl group behaves as the anisyl radical, and not as the phenyl group, affording β-*iodo*-α-p-*tolyl*-β-*methyl*-n-*propyl alcohol*, converted by dry potassium hydroxide into α-*p*-tolyl-α-methylpropaldehyde, b. p. 129°/24 mm. (*semicarbazone*, m. p. 172°). Similarly, the isomerisation of α-p-*tolyl*-β-*methylpropylene oxide*, b. p. 120—125°/27 mm., obtained by oxidation of the olefine with perbenzoic acid, affords α-*p*-tolylethyl methyl ketone, showing that the affinity of the *p*-tolyl radical, like that of the anisyl group, is greater than that of the phenyl radical. On the other hand, dehydration of α-*p*-tolyl-β-methylpropane-αβ-diol with dilute sulphuric acid affords α-*p*-tolyl-α-methylpropaldehyde, the *p*-tolyl group, like the phenyl group, migrating to the carbon atom carrying the methyl groups. β-*Phenyl*-α-p-*tolylethylene oxide*, m. p. 59—60°, obtained by oxidising *p*-methylstilbene with perbenzoic acid, when heated in presence of zinc chloride, affords phenyl-*p*-tolylacetaldehyde, b. p. 190—192°/22 mm. (semicarbazone, m. p. 153—154°), isomerisation of α-*p*-tolyl-α-phenylethylene oxide affording the same product. R. Brightman.

Thiosemicarbazone series. P. K. Bose and D. R. Chaudhury (J. Indian Chem. Soc., 1927, 4, 84—88).—Since cinnamylidenephenylhydrazone and some similar compounds are known to undergo ring-closure readily, forming pyrazolines, it was thought that the thiosemicarbazones of unsaturated aldehydes or ketones which contain the same system, $-C\colon CH\cdot CH\colon N\cdot NH-$, might also undergo conversion into pyrazolines. Several cinnamylidene- and styryl methyl ketone thiosemicarbazones were prepared, but did not undergo conversion, the compounds probably existing in the form $CHPh\colon CH\cdot CH\colon N\cdot N\colon C(SH)\cdot NHR$, where the necessary imino-hydrogen atom has migrated to the sulphur atom. The following are described: *cinnamylidenethiosemicarbazone*, m. p. 134—135°; *cinnamylidene*-4-*methyl*-, -4-*ethyl*-, -4-p-*tolyl*-, -4-o-*tolyl*-, -4-m-*tolyl*-, and -4-β-*naphthyl-thiosemicarbazones*, m. p. 170°, 166—167°, 194°, 207°, 146°, and 213°, respectively; *styryl methyl ketone thiosemicarbazone*, m. p. 147—148°, and the corresponding 4-*methyl*-, 4-o-*tolyl*-, 4-α-*naphthyl*-, and 4-*phenyl-thiosemicarbazones*, m. p. 149°, 185°, 189°, and 163—164°, respectively; *cinnamylidenebenzyldithiocarbazinate*, m. p. 183°, and *styryl methyl ketone benzyldithiocarbazinate*, m. p. 130—131°. Cinnamylidene-4-phenylthiosemicarbazone has m. p. 182—183°. B. W. Anderson.

Interaction of ketones and alcohols under the influence of light. J. Böeseken, W. D. Cohen, and S. L. Langedijk. **II. Explanation of some photochemical discrepancies by the theory of the interior filter.** S. L. Langedijk (Rec. trav. chim., 1927, 46, 383—396).—By using various aromatic ketones in alcoholic solution as exterior light filters for the transformation of benzophenone into benzpinacone, under the influence of light, it has been found possible to measure their relative "extinction coefficients." The various ketones examined have values of the same order as that of benzophenone, which was taken as the standard, with the exception of fluorenone and phenyl α-naphthyl ketone, which gave abnormally high figures, whilst the maximum effect is noticeable, not at 4050—4080 Å., corresponding with the maximum absorption, but nearer the ultra-violet end of the spectrum, at approximately 3850 Å. The theory of the interior light filter (A., 1925, i, 408), applied to the mutual action of mixed organic liquids on their photochemical reactions, is now shown to explain the discrepancies noticed by Cohen (A., 1920, i, 393) in the photochemical behaviour of mixtures of aromatic ketones in alcoholic solution. This theory accounts satisfactorily also for the observed phenomena when oxygen is bubbled into alcoholic solutions of these ketones subjected to photochemical action, except in the two cases already mentioned, to explain which an ingenious theory is advanced. E. Holmes.

Transformation of phenyl acetate into *p*-hydroxyacetophenone. W. J. Minaev (J. Russ. Phys. Chem. Soc., 1926, **58**, 729—736).—The preparation of *p*-hydroxyacetophenone from phenol and acetyl chloride by Friedel and Crafts' method was investigated, with a view of elucidating the mechanism of the reaction, which always gives low yields. The hypothesis that the *p*-hydroxyacetophenone is a product of the migration of the acetyl group of the previously formed phenyl acetate under the influence of the metallic chloride to the nucleus was tested by adding dry aluminium chloride to phenyl acetate saturated with dry hydrogen chloride: a 28·8% yield of *p*-hydroxyacetophenone was obtained, indicating that the migration to the nucleus was probably a stage in the Friedel and Crafts reaction. M. Zvegintzov.

Reactivity of positive hydrogen atoms. I. Diphenacyl sulphide. W. Dilthey [with A. Lachs] (Ber., 1927, **60**, [*B*], 1403—1405).—The methylene hydrogen atoms of diphenacyl sulphide can be proved to react readily with aldehyde if piperidine is used as condensing agent, since the products are stabilised by the production of additive compounds with the base, in which the latter is so firmly attached that it is not removed when the adduct is crystallised from indifferent media. Presumably, the piperidine molecule is attached to the sulphur atom. Condensation occurs also in presence of ammonia, methylamine, sodium methoxide, aniline, dimethylaniline, or pyridine, but crystalline products could not be isolated. The following derivatives of diphenacyl sulphide are described: *dibenzylidene*- $[\mathrm{COPh{\cdot}C(\!:\!CHPh)}]_2\mathrm{S}$, m. p. 139—140° (also $+2\mathrm{C_5H_{11}N}$, m. p. 167—169°); *di*-p-*anisylidene*- ($+\mathrm{C_5H_{11}N}$), m. p. 157—159°; *disalicylidene*- ($+\mathrm{C_5H_{11}N}$), m. p. 167—169° (decomp.); *di*-p-*dimethylaminobenzylidene*- ($+\mathrm{C_5H_{11}N}$), m. p. about 153—154°. H. Wren.

Pungent principles of ginger. IV. H. Nomura and S. Tsurumi (Proc. Imp. Acad. Tokyo, 1927, **3**, 159—161).—Assuming that shogaol is β-4-hydroxy-3-methoxyphenylethyl *n*-heptenyl ketone, the authors have synthesised this substance by the condensation of zingerone with *n*-hexaldehyde. An oil with a pungent taste similar to natural shogaol was obtained, b. p. 201—203°/2—2·5 mm., n_{D}^{25} 1·52518, d_4^{25} 1·0419 (shogaol, n_{D}^{25} 1·52467, d_4^{25} 1·0448). E. A. Lunt.

Preparation of fisetol. P. Karrer and H. Biedermann (Helv. Chim. Acta, 1927, **10**, 441).—Condensation of hydroxyacetonitrile with resorcinol in presence of zinc chloride gave fisetol, m. p. 189° (phenylhydrazone, m. p. 107—109°), instead of the 5-hydroxycumaran-2-one obtained by Slater and Stephen (J.C.S., 1920, **117**, 314). The formation of one or the other compound may be due to traces of catalytic substances. C. Hollins.

Diarylquinones. II. Yellow and red varieties of diarylquinones. R. Pummerer and H. Fiedler (Ber., 1927, **60**, [*B*], 1439—1442).—Yellowish-red dimorphism is a comparatively infrequent phenomenon among diarylquinones. 2 : 5-*Di*-p-*xylyl*-p-*benzoquinone*, m. p. 159—160°, prepared by the action of aluminium chloride on *p*-xylene and *p*-benzoquinone followed by oxidation of the quinhydrone by ferric chloride, exists only in golden-yellow needles. 2 : 5-*Di*-p-*phenetyl*-p-*benzoquinone*, prepared in a similar manner, forms a stable yellow variety, m. p. 186—187°, and a labile red form obtained by slow crystallisation from ethyl acetate, acetone, or benzene. Above 150°, the red passes into the yellow variety. Crystallographic investigation proves physical dimorphism. Solutions of the two forms appear identical or become so with immeasurable rapidity. Differences in solubility are not observable; Beer's law is obeyed. The mol. wt. in a series of solvents is normal. Differences appear confined to the solid state. Chemical differences are, however, established, since the finely-powdered, yellow variety is reduced by phenylhydrazine in acetic acid at the ordinary temperature to the quinhydrone and ultimately to diphenetylquinol, whereas the red form remains unchanged. With phenol, the yellow variety yields a red phenoquinone obtained also from the red form, but related to the former, since it is reduced by phenylhydrazine and loses phenol in a high vacuum at 110°, leaving the yellow compound. H. Wren.

Diarylquinones. III. Condensation of quinones with phenols. R. Pummerer and G. Huppmann (Ber., 1927, **60**, [*B*], 1442—1451).—Contrary to the views of Friedländer and Blumenfeld, condensation between phenols and quinones, when irreversible, invariably occurs in such a manner that the nucleus of the phenol becomes attached to the quinone nucleus; entry of the phenoxy-group has not been observed. Resorcinol and *p*-benzoquinone, heated at 250°/vac., afford 2 : 5 : 2′ : 4′-*tetrahydroxydiphenyl*, m. p. 131° (Friedländer's 2 : 5 : 3′-trihydroxydiphenyl ether), the constitution of which is established by the isolation of a *tetra-acetate*, m. p. 120°, and by oxidation through the *quinhydrone* to 2-2′ : 4′-*dihydroxyphenyl*-p-*benzoquinone*, decomp. 280°, which contains two hydroxyl groups. In presence of 10% sulphuric acid, resorcinol and *p*-benzoquinone very readily yield *diresorcylquinhydrone*, oxidised by *p*-benzoquinone in boiling water to *diresorcylquinone* (2 : 5-*di*-2′ : 4′-*dihydroxyphenyl*-p-*benzoquinone*), m. p. 345°. Reduction of the quinone with stannous chloride in glacial acetic acid gives the corresponding *quinol*, m. p. 193—195° (decomp.). *p*-Benzoquinone and pyrogallol, under the influence of aluminium chloride in carbon disulphide, give the expected quinhydrone, converted by reductive acetylation into 2 : 5-*di*-3′ : 4′ : 5′-*trihydroxyphenylquinol octa-acetate*, m. p. 158°. α-Naphthaquinone and resorcinol are converted by dilute sulphuric acid in glacial acetic acid into 2-2′ : 4′-*dihydroxyphenyl*-α-*naphthaquinol*, m. p. 167°, which gives a tetra-acetyl compound and is oxidised by ferric chloride to 2-2′ : 4′-*dihydroxyphenyl*-α-*naphthaquinone*, m. p. 218°, in which the presence of two hydroxyl groups is established. Similarly, 2-3′ : 4′ : 5′-*trihydroxyphenyl*-α-*naphthaquinol*, m. p. 245° (Friedländer's dihydroxyphenyl dihydroxynaphthyl ether), is obtained from pyrogallol and α-naphthaquinone; the constitution follows from the production of a *penta-acetate*, m. p. 167°, and of 2-3′ : 4′ : 5′-*trihydroxyphenyl*-α-*naphthaquinone*, m. p. 270°, yielding a *triacetate*, m. p. 194° (decomp.); α-naphthaquinone and α-naphthol afford

2-4′-*hydroxynaphthyl*-α-*naphthaquinol*, m. p. 243° (decomp.) [*triacetate*, m. p. 336° (decomp.)], oxidised by *p*-benzoquinone to 2-4′-*hydroxynaphthyl*-α-*naphthaquinone*, m. p. 175° (decomp.), in which the presence of one hydroxyl group is established by the isolation of a *monoacetate*, m. p. 221°. H. Wren.

Anthraquinonesulphonic acids. H. E. Fierz-David (Helv. Chim. Acta, 1927, 10, 429; cf. this vol., 463).—Priority against Coppens (cf. Wibaut, this vol., 566) is claimed. C. Hollins.

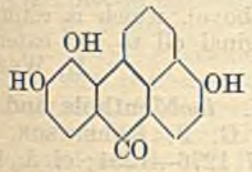
Manufacture of anthraquinone derivatives [meso-*pp*′-diaminodiarylanthracenes and 9 : 9-bis-*p*-aminoarylanthrones]. I. G. Farbenind. A.-G.—See B., 1927, 518.

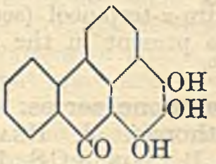
Reduction products of the hydroxyanthraquinones. VIII. E. J. Cross and A. G. Perkin (J.C.S., 1927, 1297—1306).—The positions of the hydroxyl groups in the anthranols derived from anthragallol and anthra- and flavo-purpurins are investigated by the benzanthrone process (Miller and Perkin, A., 1926, 174), and it is shown that they are oriented in the 3 : 4 : 6-, 1 : 2 : 3-, and 1 : 2 : 6-positions, respectively.

Anthrapurpurin-anthranol, when heated with glycerol and sulphuric acid at 125—130° for 1 hr., followed by treatment of the product with acetic anhydride and pyridine, yields *triacetylbenzanthrapurpurin*, m. p. 245—246°. This on treatment with cold sulphuric acid gives *benzanthrapurpurin sulphate*, which in turn yields benzanthrapurpurin (I), unmelted at 340° (*benzanthrapurpurin trimethyl ether*, m. p. 185—185·5°).

Anthragallol-anthranol when heated with potassium hydrogen sulphate and glycerol, followed by acetylation of the product, gives *diacetyl*iso*benzanthragallol*, m. p. 232—233°. The latter when hydrolysed with hydrochloric and acetic acids yields iso*benzanthragallol*, m. p. 319—321° (II), converted by ethereal diazomethane into iso*benzanthragallol dimethyl ether*, m. p. 152—153°. The methylation cannot be effected by the use of methyl iodide or by methyl sulphate. Attempts to acetylate the dimethyl ether or to prepare the trimethyl ether were unsuccessful.

(I.)





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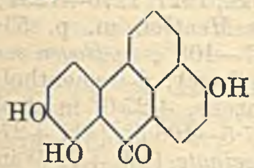
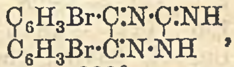


(III.)

Diacetylflavopurpurin-anthranol, m. p. 209—212°, obtained by the reduction of flavopurpurin with stannous chloride, yields *tetra-acetylflavopurpurin-anthranol*, m. p. 181—182°, on further acetylation, and *flavopurpurin-anthranol*, m. p. 231—233° (heated slowly), on hydrolysis. When heated suddenly at 235°, the latter melts at 243—245° (cf. Graebe and Thode, A., 1906, i, 863). Attempts to prepare the benzanthrone derivative by the methods already indicated were unsuccessful, but on treatment with a solution of acraldehyde in acetic acid containing hydrogen chloride, it yielded finally *diacetyl*iso*benzflavopurpurin*, m. p. 236°. iso*Benzflavopurpurin*, m. p. 293—295°, yields on methylation with methyl iodide the *dimethyl ether*, m. p. 199—200°. G. A. C. Gough.

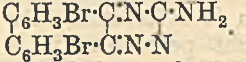
Reduction products of the hydroxyanthraquinones. IX. A. Macmaster and A. G. Perkin (J.C.S., 1927, 1306—1309).—3 : 4 : 6 : 9-*Tetramethoxyanthranol*, m. p. 107°, is obtained by acetylating 3 : 4 : 6-trihydroxyanthranol and methylating the product in absence of air. When oxidised with an acetic acid solution of chromic acid, it yields anthrapurpurin trimethyl ether, m. p. 198° (Graebe and Bernhard, A., 1906, i, 865, give 201°), which on reduction with aluminium–mercury couple in ammonia gives 1 : 2 : 7-*trimethoxyanthracene*, m. p. 95°. 3 : 4 : 6-*Trimethoxyanthranol*, m. p. 149°, is obtained by reduction of anthrapurpurin trimethyl ether with stannous chloride. 9-*Acetyl*-3 : 4 : 6-*trimethoxyanthranol*, m. p. 127°, is obtained in the usual way. 3 : 4 : 6 : 3′ : 4′ : 6′-*Hexamethoxydianthrone*, m. p. 224°, is obtained by oxidation of 3 : 4 : 6-trimethoxyanthranol with an acetic acid solution of ferric chloride. G. A. C. Gough.

Phenanthrene series. XXXVI. 2 : 7-Dibromophenanthraquinone and its derivatives. J. Schmidt and H. Bürkert (Ber., 1927, 60, [*B*], 1356—1362; cf. Schmidt and Junghaus, A., 1904, i, 1034).—Phenanthraquinone is converted by phenylhydrazine-*p*-sulphonic acid in boiling, aqueous acid suspension into 9-hydroxyphenanthrene-10-azobenzenesulphonic acid, which, when treated with an excess of bromine in sunlight, affords 2 : 7-dibromophenanthraquinone, m. p. 322—323°, in good yield, a dibromide of the bromo-derivative being probably formed intermediately. When a greater excess of bromine is employed, (?)2 : 4 : 5 : 7-*tetrabromophenanthraquinone*, m. p. 285—287° (characterised by conversion into 2 : 4 : 5 : 7-*tetrabromophenanthraphenazine*, m. p. 262°), appears to be formed. The 2 : 7-dibromo-compound is converted by phenylhydrazine into 2 : 7-*dibromo*-9-*hydroxyphenanthrene*-10-*azobenzene*, m. p. 272—273°, the mother-liquors from which contain 2 : 7-dibromophenanthraquinol, isolated as the *diacetate*, m. p. 242—244°. 2 : 7-*Dibromophenanthraquinonemonosemicarbazone*, m. p. about 300°, is described. Successive treatment of 2 : 7-dibromophenanthraquinone with semicarbazide hydrochloride and hydrochloric acid gives 6 : 11-*dibromo*-3-*hydroxyphenantriazine*, m. p. 295°. Aminoguanidine and 2 : 7-dibromophenanthraquinone yield 6 : 11-*dibromo*-3-*aminophenantriazine hydrochloride*, m. p. 238° (cf. Schmidt, Schairer, and Glatz, A., 1911, i, 239), from which ammonia liberates the *base* which is isolated in the labile, red imino-form,



$$\begin{array}{l}\mathrm{C_6H_3Br\cdot C{:}N\cdot C{:}NH}\\ \mathrm{C_6H_3Br\cdot C{:}N\cdot NH}\end{array},$$

and the stable, yellow variety, m. p. 333°,



$$\begin{array}{l}\mathrm{C_6H_3Br\cdot C{:}N\cdot C\cdot NH_2}\\ \mathrm{C_6H_3Br\cdot C{:}N\cdot N}\end{array}.$$

The following derivatives are regarded as derived from the amino-form: *perchlorate*, m. p. 258° (decomp.); *picrate*, m. p. 293°;

acetyl derivative, m. p. 309°; *benzoyl* derivative, m. p. 240° (decomp.). Phosphorus pentachloride converts 2 : 7-dibromophenanthraquinone suspended in boiling benzene into 9 : 9-*dichloro*-2 : 7-*dibromophenanthrene*, m. p. 229°, which is reduced by phenylhydrazine to 9-*chloro*-2 : 7-*dibromo*-10-*hydroxyphenanthrene*, m. p. 226° (*benzoyl* derivative, m. p. 193°). H. Wren.

Constitution of the bile acids. XI. Ciloxanic acid. W. Borsche and R. Frank (Ber., 1927, 60, [*B*], 1216—1220).—*Ciloxanic acid*, m. p. 216—217°, $[\alpha]_D^{15}$ +142·5° in alcohol, is obtained by the oxidation of cilianic acid by potassium permanganate in acid solution, and is conveniently isolated as the *dioxime*, $C_{22}H_{34}O_6N_2$, m. p. 239—240°; the *methyl* ester, m. p. 105°, and its *dioxime*, m. p. 241—242° (decomp.), and, apparently, *ethyl hydrogen ciloxanate dioxime*, m. p. 221—222° (decomp.), are described. The production of ciloxanic acid by the action of concentrated sulphuric acid on cilianic acid is established (cf. this vol., 459). Oxidation of ciloxanic acid by nitric acid (*d* 1·4) affords biloidanic acid, m. p. 229—230° (decomp.), whereas reduction with amalgamated zinc and hydrochloric acid gives *deoxyciloxanic acid*, m. p. 187—188° (*methyl* ester, m. p. 85—87°). H. Wren.

Paprika dyes. II. L. Zechmeister and L. von Cholnoky (Annalen, 1927, **455**, 70—81).—Carotin (0·5—0·6 g.), identical in all respects with that obtained from leaves, is isolated from the light-petroleum extract of the dried fruit rind of *Capsicum annuum* (1 kg.) after removal of the capsanthin (4·0 g.) by means of alkali (this vol., 669). The amounts of the two colouring matters isolated represent, respectively, 50% and 54% of the total quantity determined colorimetrically. In agreement with the results of Kylin (this vol., 669), no lycopin or xanthophyll could be detected. J. W. Baker.

Lupeol. H. D. Nöjd (Arch. Pharm., 1927, **265**, 381—389).—Two empirical formulæ, viz., Cohen's $C_{31}H_{50}O$ (A., 1907, i, 211) and Vesterberg's $C_{30}H_{50}O$ (A., 1922, i, 825), have been attributed to lupeol. The following investigation of lupeol, isolated from East Indian "bresk" in the way described by Cohen, and separated from amyrin by fractional precipitation of the benzoates from benzene by addition of acetone, has proved that Vesterberg's formula is correct. The physical properties of the lupeol obtained, and those of its acetate and benzoate, agreed with the description given by Cohen. The formate is not homogeneous, but consists of a mixture of α-*allolupeol formate*, m. p. 229°, $[\alpha]_D^{15}$ +50·01° (in chloroform), insoluble in alcohol and forming about 60% of the whole, and β-*allolupeol formate*, m. p. 180—183°, $[\alpha]_D^{15}$ +48·8°, soluble in alcohol. α-*Allolupeol*, $C_{30}H_{49}\cdot OH$, has m. p. 191°, $[\alpha]_D^{15}$ +28·79°; the *acetate*, m. p. 199°, $[\alpha]_D^{15}$ +45·46°, and *benzoate*, m. p. 256°, $[\alpha]_D^{15}$ +42·82°, are also described. β-*Allolupeol*, m. p. 151°, $[\alpha]_D^{15}$ +48·08°, similarly yields an *acetate*, m. p. 196°, $[\alpha]_D^{15}$ +28·57°, and a *benzoate*, m. p. 228°. Lupeol, having the composition $C_{30}H_{50}O$, is thus isomeric with amyrin. It does not suffer dehydration when heated at 220°, but when it is treated with phosphorus pentachloride in light petroleum it is converted into a *hydrocarbon*, $C_{30}H_{48}$, m. p. 173—174°, b. p. 287°/10 mm., $[\alpha]_D^{15}$ +27·5°, to which the name *lupeylene*, already given by Jungfleisch and Leroux (A., 1906, i, 525, 783) to a similar compound, has been applied. In suffering dehydration when treated with phosphorus pentachloride, lupeol resembles amyrin (cf. Vesterberg and Nöjd, A., 1926, 619). Attempts to dehydrogenate lupeol by heating it with sulphur and to break it down by oxidation gave unsatisfactory results. W. A. Silvester.

The two stereoisomeric dihydro-α-terpineols; occurrence of the *trans*-variety in American pine oil. O. Zeitschel and H. Schmidt (Ber., 1927, 60, [*B*], 1372—1377).—α-Terpineol, m. p. 35°, d^{15} 0·939, α^{100} +8·90°, is hydrogenated at the atmospheric pressure in presence of a nickel catalyst, and the product, after removal of unsaturated compounds and not inconsiderable amounts of hydrocarbons, is fractionally distilled under diminished pressure, whereby trans-*dihydro-α-terpineol*, m. p. 35°, s. p. 34·7°, b. p. 209—209·5°/750 mm., d_{20}^{20} 0·901, n_D^{20} 1·46310, $[\alpha]_D$ ±0°, is obtained (phenylurethane, m. p. 117—118°). The liquid portions of the distillates are transformed into the corresponding phenylurethanes, m. p. 117—118° and 90—92°, respectively, the latter of which when hydrolysed affords cis-*dihydro-α-terpineol*, b. p. 210—210·5°/750 mm., d_{15}^{15} 0·9164, d_{20}^{20} 0·9124, n_D^{20} 1·46550, $[\alpha]_D$ ±0°.

The fraction of b. p. 205—220° obtained as by-product of the preparation of terpineol from American pine oil, is treated with boric acid, and the difficultly volatile borates are separated from the indifferent components by distillation. Hydrolysis of the esters followed by fractional treatment of the recovered alcohols by boric acid permits the separation of borneol and fenchyl alcohol, leaving terpineol and dihydroterpineol. Oxidation of the mixed tertiary alcohols with permanganate destroys the terpineol, thus permitting the isolation of homogeneous *trans*-dihydro-α-terpineol (see above), which is estimated to be present in the original oil to the extent of 3—5%. H. Wren.

Menthone series. IV. *iso*Menthols and *iso*menthones. J. Read, G. J. Robertson, and A. M. R. Cook (J.C.S., 1927, 1276—1284; cf. A., 1926, 1147, 1250).—dl-iso*Menthol*, m. p. 53·5° (*hydrogen phthalate*, m. p. 107—108°; *hydrogen succinate*, m. p. 72—73°; *phenylurethane*); d-*iso*menthol, m. p. 81·5°, $[\alpha]_D^{15}$ +24·0° in benzene, +27·0° in alcohol (*hydrogen phthalate*, m. p. 107·5—108·5°, $[\alpha]_D^{15}$ +27·5° in chloroform; *hydrogen succinate*, $[\alpha]_D^{15}$ +22·5° in chloroform), and *l*-*iso*menthol, m. p. 80·5°, $[\alpha]_D^{15}$ −24·1° in alcohol, have been prepared by the action of nitrous acid on *dl*-, *d*-, and *l*-*iso*menthylamine, respectively. An equimolecular mixture of *d*- and *l*-*iso*menthol forms a conglomerate. Both *dl*-menthol and *dl*-*iso*menthol are produced in the reduction of *dl*-piperitone with sodium and alcohol. Pure *d*-*iso*menthone, prepared by chromic acid oxidation of *d*-*iso*menthol, has $[\alpha]_D^{15}$ +91·7°, n_D^{16} 1·4545 [*oxime*, viscid oil, n_D^{14} 1·4865, $[\alpha]_D^{15}$ +46·0° in alcohol (p-*nitrobenzoyl* derivative)], and is best characterised by conversion into the *oxime hydrochloride*, m. p. 132°, $[\alpha]_D^{15}$ +38·6° in chloroform. The following are described: dl-iso*menthoneoxime hydrochloride*, m. p. 127—128° (decomp.); dl-*menthoneoxime hydrochloride*, m. p. 94°; l-*menthone*-

oxime hydrochloride, m. p. 118—119°, $[\alpha]_D^{15}$ −89·1° in chloroform; p-*nitrobenzoyl*-l-*menthoneoxime*, m. p. 102·5°; *salicylidene*-derivative of the hitherto unknown l-neoiso*menthylamine*, m. p. 99—100°, $[\alpha]_D^{15}$ −17·9° in chloroform. The claim of Bedos (A., 1926, 729) to have demonstrated the existence of the four racemic menthols and the two corresponding racemic menthones through a study of the interaction of magnesium *iso*propyl bromide and the two isomeric 2-chloro-5-methyl*cyclo*hexanols is criticised adversely.

M. CLARK.

Recovery of pinene from its nitrosochloride. J. C. EARL and J. KENNER (J.C.S., 1927, 1269—1276).—Regeneration of a hydrocarbon from its nitrosochloride by treatment with aniline, hitherto observed only in the case of pinene, is shown to occur under similar conditions, although less readily, with the derivatives of tetramethylethylene and γ-terpinyl acetate. The reaction in the case of pinene nitrosochloride is due to the hydrogen chloride which this compound liberates with remarkable ease. Suppression of hydrogen chloride by the presence of sodium acetate or pyridine leads to the formation of *pinene nitrolanilide*, m. p. 122°, provided that these reagents are employed in a homogeneous solution. Reaction in chloroform solution in presence of either anhydrous sodium acetate or crystalline lead acetate leads to the formation of diazoaminobenzene. In explanation of these results, it is suggested that pinene nitrosochloride may undergo isomeric change under the influence of hydrogen chloride, yielding a product formally analogous with the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate.

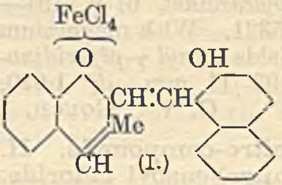
M. CLARK.

Camphor series. XI. Synthesis of camphor. II. Preparation of liquid and solid camphenes from pinene hydrochloride by the catalytic elimination of hydrogen chloride with copper oxide. B. MASUMOTO (Mem. Coll. Sci. Kyoto, 1927, 10, 175—181).—Alcoholic solutions of pinene hydrochloride were passed over eight specimens of copper oxide (details of preparations and densities given) at 220°, with uniform velocity. The resulting products were fractionated, and fractions of b. p. 150—165° assumed to be camphene. These fractions do not possess the same physical data. H. BURTON.

Stereochemistry of dicyclic ring systems. III. [Correction.] Strain in camphor and *trans*-hexahydrohydrindene. W. HÜCKEL (Annalen, 1927, 455, 123—126).—The comparison made by Hückel and Friedrich (this vol., 238) between *trans*-hexahydrohydrindene and camphor is invalid, since the angle subtended by the bridge in the camphor model was erroneously given as 43° instead of 71° 12′. A redetermination of the heat of combustion of *trans*-β-hexahydrohydrindone by Roth gives a value only 2 kg.-cal./mol. less than that of the *cis*-form, a difference comparable with that between *trans*- and *cis*-decalone. These facts are therefore in agreement with Baeyer's strain theory. J. W. BAKER.

Isomerisation of hydrocarbons by phenols. S. KONDAKOV.—See B., 1927, 504.

Pyrylium salts and *spiro*dipyrans. I. Condensation products from *o*-hydroxyaldehydes and α-alkylated β-ketonic esters. S. C. DE (J. Indian Chem. Soc., 1927, 4, 23—28).—When dry hydrogen chloride was passed into an ethereal solution of salicylaldehyde and ethyl α-methylacetoacetate, 2-(o-*hydroxystyryl*)-3-*methylbenzopyrylium chloride*, m. p. 200°, was formed, and from this the corresponding *ferrichloride*, m. p. 180°, and *perchlorate*, m. p. 240°, were obtained. Decomposition of the above ferric salt by ammonia solution in presence of sodium acetate yielded 3-*methyl*spiro*dibenzopyran*, m. p. 80°. Similarly were obtained: 3-*benzyl*-2-(o-*hydroxystyryl*)*benzopyrylium chloride*, m. p. 129° (corresponding *ferrichloride*, m. p. 194°, and *perchlorate*, m. p. 234°); 3-*benzyl*spiro*dibenzopyran*, m. p. 120°; 2-(β-2′-*hydroxy*-1′-*naphthylethenyl*)-3-*methyl*-β-*naphthapyrylium ferrichloride* (I) (corresponding *perchlorate*, m. p. >308°); 3-*methyl*spiro-2 : 2′-*di*-(5 : 6-β-*naphthyl*-1 : 2-*pyran*), m. p. 200°; 3-*benzyl*-2-(β-2′-*hydroxy*-1′-*naphthylethenyl*)-β-*naphthapyrylium ferrichloride* (corresponding *perchlorate*, m. p. 204°); 3-*benzyl*spiro-2 : 2′-*di*-(5 : 6-β-*naphtha*-1 : 2-*pyran*), m. p. 205°, and 2-*phenyl*-3-*methylbenzopyrylium perchlorate*, m. p. 179°. The colourless *spiro*dipyrans were converted by strong acids into the deeply-coloured benzopyrylium salts. B. W. ANDERSON.



(I.)

Constitution of erythrosin and related dyes. W. C. HOLMES and J. T. SCANLAN (J. Amer. Chem. Soc., 1927, 49, 1594—1598).—The *monosodium* salt of erythrosin contains 1 mol. of water of constitution, similarly to the disodium salt (cf. Wales and Nelson, A., 1923, i, 936). Spectrophotometric investigation of the salt formation of erythrosin, together with the above result, are regarded as supporting the hemiquinonoid structure of the dye suggested by Gomberg and Tabern (A., 1923, i, 112), and an analogous structure is indicated generally for the halogen derivatives of fluorescein. F. G. WILLSON.

Absorption spectra of *o*-cresolbenzein. W. R. ORNDORFF and (MISS) S. A. MCNULTY (J. Amer. Chem. Soc., 1927, 49, 1588—1593).—A study of absorption spectra indicates that *o*-cresolbenzein exists in absolute alcoholic solution as an equilibrium mixture of the quinonoid hydrate and carbinol forms. Addition of hydrogen chloride completely changes the absorption spectrum, probably owing to the formation of the hydrochloride (this vol., 557). Addition of alkali produces a similar change, the similarity being due to the formation, in both cases, of the quinonoid hydrate, which then combines with the acid or the base. In aqueous 33% potassium hydroxide, *o*-cresolbenzein is present as the dipotassium salt of the carbinol form, the resemblance of the absorption curve for this solution to that of the absolute alcoholic solution supporting the view that some carbinol is present in the latter solution. In 93% sulphuric acid solution, *o*-cresolbenzein is present as the sulphate. F. G. WILLSON.

Action of organo-magnesium compounds on nitriles. γ-Aminonitriles. F. PETIT (Bull. Acad. roy. Belg., 1926, [v], 12, 775—784; cf. A., 1926, 826, 1044).—γ-Piperidinobutyronitrile, b. p. 110—112°/11 mm., d_4^{20} 0·931, n_D^{20} 1·4672, reacts abnormally with magnesium methyl and ethyl bromides to give, in each case, a dimeride of the nitrile as the principal product, *αη-dipiperidino-δ-imino-ε-cyanoheptane*, m. p. 75—76°, b. p. 265°/12 mm. On hydrolysis with alcoholic picric acid, the latter yields *αη-dipiperidino-ε-cyanoheptan-δ-one dipicrate*, m. p. 205—206°, and with concentrated hydrochloric acid, *αη-dipiperidinoheptan-δ-one*, b. p. 203—204°/13 mm., d_4^{20} 0·9555, n_D^{20} 1·4904.

The nitrile reacts normally with magnesium phenyl bromide (2 mols.) to yield *phenyl γ-piperidinopropyl ketone*, b. p. 185—187°/12 mm., d_4^{20} 1·0238, n_D^{20} 1·5345 (*semicarbazone*, m. p. 164°), which, on reduction, gives *phenyl-γ-piperidinopropylcarbinol*, b. p. 194—195°/12 mm., d_4^{20} 1·017, n_D^{20} 1·5321. With magnesium benzyl chloride, the nitrile yields *benzyl γ-piperidinopropyl ketone*, b. p. 191—193°/11 mm., d_4^{20} 1·010, n_D^{20} 1·5247. G. A. C. Gough.

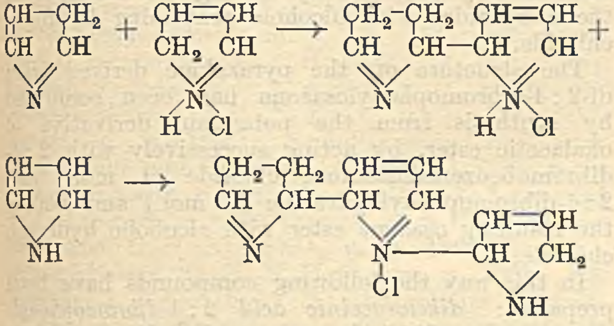
Diazomethane and *o*-nitro-compounds. II. *N*-Hydroxyisatin from *o*-nitrobenzoyl chloride. F. Arndt, B. Eistert, and W. Partale (Ber., 1927, **60**, [*B*], 1364—1370; cf. this vol., 360).—*o*-Nitrobenzoyl chloride is converted by diazomethane in ethereal solution in absence of light into *o-nitro-ω-diazoacetophenone*, $NO_2·C_6H_4·CO·CH⁚N⁚N$, m. p. 105—106°, with small amounts of *ω-chloro-o-nitroacetophenone* (*o-nitrophenacyl chloride*), m. p. 66—67°. The diazo-compound is very sensitive towards acids and is converted by concentrated formic acid in presence of glacial acetic acid into *N-hydroxyisatin*, m. p. 200—201° (decomp.) (cf. Alessandri, this vol., 572), characterised by its conversion into *N*-acetoxyisatin, m. p. 151—152°, and *N*-hydroxyisatinphenylhydrazone, m. p. 219—220°; with ethereal diazomethane, it does not appear to yield the corresponding methyl ether. It dissolves in sodium carbonate solution, is converted ultimately by sodium hydroxide into anthroxanic acid and by ammonia into anthroxanamide, m. p. 213°. *o*-Nitro-ω-diazoacetophenone is converted by concentrated hydrochloric acid in presence of glacial acetic acid into ω-chloro-*o*-nitroacetophenone, also prepared by chlorination of *o*-nitroacetophenone; it does not give the customary ketonic reactions with semicarbazide or *p*-nitrophenylhydrazine, although these are shown by *o*-nitro- and ω-chloro-acetophenone. *ω-Bromo-o-nitroacetophenone* (*o-nitrophenacyl bromide*), m. p. 55—56°, is similarly prepared. Treatment of *o*-nitro-ω-diazoacetophenone with iodine in boiling chloroform affords *ωω-di-iodo-o-nitroacetophenone*, m. p. 136—138° (decomp.), reduced by ammonium sulphide to indigotin. Hydrogen cyanide is evolved when *o*-nitro-ω-diazoacetophenone is boiled with 2*N*-sodium hydroxide. H. Wren.

Formation of heterocyclic compounds. II. H. K. Sen and U. Bose (J. Indian Chem. Soc., 1927, **4**, 51–63; cf. Sen-Gupta, J.C.S., 1915, **107**, 1347).—Moir (J.C.S., 1902, **81**, 100) gave an explanation of the mechanism of the reaction between cyanoacetamide and acetylacetone which, in the authors' opinion, is incorrect, as there is evidence that in β-diketones the ketonic group reacts through first setting up an ethylenic linking by enolisation, the ethylenic linking being more reactive than the carbonyl. Thus a negative result was obtained in attempting to condense 2-acetyl-2-methyl*cyclo*hexanone with cyanoacetamide in presence of piperidine, whereas condensation of cyanoacetamide with 2-acetyl*cyclo*hexanone proceeds readily, with formation of crystals (decomp. about 290°)—presumably a mixture of quinoline and *iso*quinoline derivatives, as from the condensation product two isomeric *methyl ethers*, m. p. 179—180° and 158°, were obtained. 2-Acetyl*cyclo*hexanone and methylcyanoacetamide condensed to give the same mixture. By using ethyl *cyclo*hexanonecarboxylate for condensation with cyanoacetamide, the enolising carbon atom was fixed, and the product was not a mixture, but 1 : 3 : 10-*trihydroxy-4-cyanohexahydro*iso*quinoline* (?), m. p. 278—280° (decomp.). Cyanoacetamide was also condensed with 2-acetyl-6-methyl*cyclo*hexanone, giving a *substance*, $C_{12}H_{14}ON_2$, m. p. 275° (decomp.) (hydrolysed *product*, $C_{11}H_{15}ON$, from this, m. p. 242—243°), with 2-acetyl-5-methyl*cyclo*hexanone, giving a *substance*, $C_{12}H_{14}ON_2$, m. p. >280° (hydrolysed *product*, $C_{11}H_{15}ON$, m. p. 200—201°), and with 2-acetyl-4-methyl*cyclo*hexanone to form a *substance*, $C_{12}H_{14}ON_2$, darkens above 270° (hydrolysed *product*, m. p. 230—232°). B. W. Anderson.

Substitution in hexahydrocarbazole derivatives. J. Gurney and S. G. P. Plant (J.C.S., 1927, 1314—1322).—Hexahydrocarbazole and 9-methylhexahydrocarbazole, m. p. 50° (cf. A., 1923, i, 142), on nitration in concentrated sulphuric acid, give *5-nitrohexahydrocarbazole*, m. p. 69°, and *5-nitro-9-methylhexahydrocarbazole*, m. p. 52°, respectively. 9-Acetylhexahydrocarbazole, when acted on by nitric acid in glacial acetic acid solution, is partly nitrated to give *6-nitro-9-acetylhexahydrocarbazole*, m. p. 150°, and partly oxidised to give 9-acetyltetrahydrocarbazole, which is then converted into a mixture of 5-nitro-9-acetyltetrahydrocarbazole and 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole. 9-Benzoylhexahydrocarbazole also undergoes oxidation to 9-benzoyltetrahydrocarbazole, which then gives 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole. In concentrated sulphuric acid, both 9-acetyl- and 9-benzoyl-hexahydrocarbazole can be nitrated to give the 6-nitro-derivative. *6-Nitro-9-benzoylhexahydrocarbazole* has m. p. 106—107°. The structures of these derivatives have been established with reference to the structures assigned to the four isomeric mononitrotetrahydrocarbazoles (J.C.S., 1921, **119**, 1825; 1923, **123**, 676). Bromination of hexahydrocarbazole and its 9-acetyl and 9-benzoyl derivatives leads in every case to the 6-bromo-compound. The following are described: *5-nitro-9-acetylhexahydrocarbazole*, m. p. 142°; *5-aminohexahydrocarbazole*, m. p. 111°; *5-acetamido-9-acetylhexahydrocarbazole*, m. p. 163°; *6-nitrohexahydrocarbazole*, m. p. 84° (*hydrochloride*, m. p. 199°); *6-aminohexahydrocarbazole*; *6-acetamido-9-acetylhexahydrocarbazole*, m. p. 213°; *7-aminohexahydrocarbazole*; *7-acetamido-9-acetylhexahydrocarbazole*, m. p. 233°; *6-bromohexahydrocarbazole*, m. p. 75°; *6-bromo-9-acetylhexahydrocarbazole*, m. p. 104°; *6-bromo-9-benzoylhexahydrocarbazole*, m. p. 125°.

The compound described by von Braun and Ritter (A., 1923, i, 142) as 7-nitro-9-ethylhexahydrocarbazole is shown to be 5-nitro-9-ethylhexahydrocarbazole. M. CLARK.

Polymerisation of pyrrole. B. V. TRONOV and P. P. POPOV (J. Russ. Phys. Chem. Soc., 1926, 58, 745—758).—The action of acids on pyrrole and its derivatives and the properties and possible structures of the resulting polymerides are discussed, with the conclusion that all earlier hypotheses are unsatisfactory. Analysis of the product of reaction of tripyrrole hydrochloride and aqueous alkali shows it to contain oxygen and so to be probably not the free amine, but the ammonium hydroxide, *i.e.*, the halogen atom is joined to a quaternary nitrogen. The various dynamic tautomeric forms of pyrrole are discussed, and possible intermolecular reactions suggested, resulting in the formation of tripyrrole.

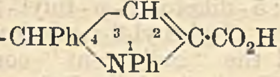
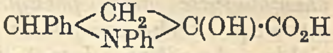


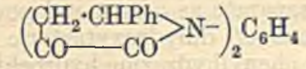
This and similar formulæ explain why only 2 mols. of pyrrole can be obtained on decomposing tripyrrole and why oxidation gives succinic acid.

The mechanism of the breaking down of the pyrrole ring and the formation of pyrrole-red and ammonia by the hydrolysis in neutral or faintly alkaline solutions of tripyrrole, is assumed to be the same as the breaking of the ring in quaternary cyclic ammonium hydroxides, by the migration of the hydroxyl to the α-carbon atom with the formation of an aldehyde and the ultimate elimination of a molecule of ammonia. The free tripyrrole, on long keeping, undergoes some transformation, as it did not give pyrrole-red so readily as before, probably due to the transformation of the quaternary ammonium hydroxide into an amine-oxide-like structure. M. ZVEGINTZOV.

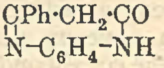
Iodising pyridine derivatives. DEUTSCHE GOLD- U SILBERSCHEIDEANSTALT VORM. ROESSLER.—See B., 1927, 507.

Production of 5-iodo-2-aminopyridine. C. RÄTH.—See B., 1927, 507.

Döbner's quinoline synthesis and its by-products. S. BODFORSS (Annalen, 1927, 455, 41—69).—The condensation of benzaldehyde, amines, and pyruvic acid and of cinnamoylformic acid with various aromatic amino-compounds has been studied in order to elucidate the mechanism of formation of quinoline derivatives, pyrrolidine, and other products obtained in the Döbner synthesis. Pyruvanilide condenses with benzaldehyde in alcohol, in presence of aniline, to yield *benzylidenepyruvanilide*, $CHPh{:}CH\cdot CO\cdot CO\cdot NHPh$, m. p. 153°. Cinnamoylformic acid reacts with aniline in cold alcohol to yield only 4 : 5-diketo-1 : 2-diphenylpyrrolidine (I) (Schiff and Bertini, A., 1897, 293), but in presence of pyridine it yields a mixture of (I) and the *anil* of cinnamoylformic acid, $CHPh{:}CH\cdot C({:}NPh)\cdot CO_2H$ (II), the latter being readily converted into the former by heating in alcohol. Pyruvic acid and benzaldehyde in ether in presence of aniline give (I), together with its anil, 5-keto-1 : 2-diphenylpyrrolidine-4-anil (III) (*nitro-derivative*, m. p. 143°). The mechanism of formation of these compounds is represented in accordance with the scheme : (II) ⟶  $CHPh<\overset{CH}{\underset{NPh}{}}>C\cdot CO_2H$ (I) or $\xrightarrow[NH_2Ph]{}$ (III), fission of the 1 : 2 linking preceding intramolecular change. The formation of (II) is assumed to occur by the interaction of benzylideneaniline with the enol form of pyruvic acid, a four-membered heterocyclic ring being formed intermediately, in accordance with the scheme : $CHPh{:}NPh+CH_2{:}C(OH)\cdot CO_2H \longrightarrow$  $CHPh<\overset{CH_2}{\underset{NPh}{}}>C(OH)\cdot CO_2H$ $\xrightarrow{-H_2O}$ (II). Similarly, by the interaction of cinnamoylformic acid with the appropriate amino-compound are obtained the β-*naphthylimide*, m. p. 138° (decomp.), p-*hydroxyanil*, m. p. 188° (decomp.) (which when heated with aniline yields I); p-*methoxyanil*, m. p. 114° (decomp.), and the p-*tolylimide*, m. p. 139° (decomp.) (which when heated with *p*-aminophenol yields the *p*-hydroxyanil) of cinnamoylformic acid. With *p*-phenylenediamine, it yields a mixture of the *substances* $[CHPh{:}CH\cdot C(CO_2H){:}N]_2C_6H_4$ and $CHPh{:}CH\cdot C(CO_2H){:}N\cdot C_6H_4\cdot NH_2$, m. p. 173° (decomp.), the latter being separated from the mixture by means of its slight solubility in acetone. Similarly, with *m*-phenylenediamine is obtained an isomeride of the first compound, and this is identical with the compound, $C_{26}H_{16}O_4N_2$, obtained by Döbner and Ferber (A., 1895, i, 72) by the action of benzaldehyde and pyruvic acid on *m*-phenylenediamine, to which a cyclic structure was erroneously ascribed. When warmed with an alcoholic solution of phenylhydrazine, it is converted into cinnamoylformic acid phenylhydrazone, m. p. 167° (Erlenmeyer, A., 1903, i, 698, gives 158°), which is oxidised by mercuric oxide to a *compound*, decomp. 190°, which is probably a tetrazone. With anthranilic and *p*-aminobenzoic acids, cinnamoylformic acid yields, respectively, 4 : 5-*diketo-2-phenyl-1-o-carboxyphenyl-*, m. p. 192° (decomp.), and -1-p-*carboxyphenyl-pyrrolidine*, m. p. 205°. When heated with alcohol or acetic acid, the various substituted cinnamoylformic acid anils are converted into pyrrolidine derivatives, and thus are obtained the following 4 : 5-diketo-1-aryl-2-phenylpyrrolidines : β-*naphthyl-*, m. p. 150°; p-*tolyl-*, m. p. 143°; p-*methoxyphenyl-*, m. p. 118° (decomp.), and 1 : 1′-p-*phenylene-bis-4 : 5-diketo-2-phenylpyrrolidine* (IV), m. p. 193°.

(IV.) 

$$\left(\begin{matrix}CH_2\cdot CHPh \\ CO\text{——}CO\end{matrix}>N-\right)_2C_6H_4$$

 (V.)

$$\begin{matrix}CPh\cdot CH_2\cdot CO \\ N-C_6H_4-NH\end{matrix}$$

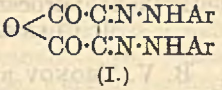
The action of pyruvic acid on various Schiff's bases has been investigated. With benzylideneaniline, (I) is obtained; benzylidene-β-naphthylamine yields 2-phenyl-β-naphthaquinolinecarboxylic acid; benzylidene-*p*-aminobenzoic acid yields *p*-[5-keto-2-phenyl-4-(carboxyanil)tetrahydropyrrole]-2-benzoic acid, m. p. 350°, identical with the "indifferent" compound obtained by Döbner; benzylidene-*o*-aminobenzoic acid yields 2-phenylquinoline-4 : 8-dicarboxylic acid; benzylidene-*p*-aminophenol yields the *p*-hydroxyanil of cinnamoylformic acid, whilst benzylidene-*p*-anisidine yields this compound together with α-phenylquininic acid and *5-keto-2-phenyl-*1-p-*anisylpyrrolidine-*4-p-*methoxyanil*, m. p. 196°; benzylidene-*p*-toluidine yields 4 : 5-diketo-1-*p*-tolyl-2-phenylpyrrolidine (above), 2-phenyl-6-methylquinoline-4-carboxylic acid, and the "indifferent" compound $C_{24}H_{22}ON_2$, m. p. 205°, obtained by Döbner; cinnamylidene-β-naphthylamine yields 2-cinnamyl-β-naphthacinchonic acid. The compound (II) when fused with *p*-nitroaniline at 160—167° for 20 min. yields *5-keto-*1 : 2-*diphenylpyrrolidine-*4-p-*nitroanil*, m. p. 258° (decomp.), and with phenylhydrazine it yields *γ-anilino-α-keto-γ-phenylbutyric acid phenylhydrazide*, m. p. 132° (decomp.). The compound (I) with phenylhydrazine yields 1-*anilino-5-keto-2-phenylpyrrolidine-4-phenylhydrazone*, m. p. 229° (also obtained by the action of phenylhydrazine on cinnamoylformic acid); with hydroxylamine, it yields the corresponding *monoxime*, and with *o*-phenylenediamine it yields a *compound*, m. p. 250° (decomp.), probably (V), which is also obtained by the action of *o*-phenylenediamine on cinnamoylformic acid. J. W. Baker.

Nitro- and amino-acridines. K. Lehmstedt (Ber., 1927, 60, [*B*], 1370—1372; cf. Jenson and Friedrich, this vol., 575).—Graebe's α-nitroacridine is shown to contain the substituent in position 3, since it is oxidised by chromic acid in glacial acetic acid to 3-nitroacridone (cf. Ullmann and Bader, A., 1907, i, 843); 3-nitro-9-*p*-dimethylaminophenylacridine has m. p. 225°. Similarly, Graebe's β-nitroacridine, m. p. 172° (corr.), is oxidised to 1-nitroacridone, m. p. 259° (cf. Mayer and Stein, A., 1918, i, 36), and is thus 1-nitroacridine. Reduction of 1-nitroacridine with stannous chloride in glacial acetic acid affords 1-*aminoacridine*, m. p. 125° (*picrate*).
H. Wren.

Unsaturated dipeptide-anhydrides and dehydration of amino-acid derivatives. E. Abderhalden (Z. physiol. Chem., 1927, 167, 177—178).—A reply to Bergmann's claim for priority (this vol., 474). A. Wormall.

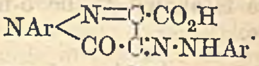
Action of halogen-substituted phenylhydrazines on dihydroxytartaric acid. F. D. Chattaway and W. G. Humphrey (J.C.S., 1927, 1323—1328).—Improved methods for the preparation of dihydroxytartaric acid and the halogen-substituted phenylhydrazines are described; the latter are best prepared by the reduction of the corresponding diazonium salts by means of sodium sulphite.

The halogen-substituted phenylosazones of dihydroxytartaric acid separate as orange-red powders when aqueous solutions of dihydroxytartaric acid and the corresponding phenylhydrazine hydrochloride are mixed. On crystallisation from any solvent, these osazones lose a molecule of water to give *anhydrides* of the general formula (I), together with *pyrazolone* derivatives of the general formula (II)



$$O<\begin{matrix}CO\cdot C{:}N\cdot NHAr\\ |\\ CO\cdot C{:}N\cdot NHAr\end{matrix}$$

(I.)



$$NAr<\begin{matrix}N{=\!=}C\cdot CO_2H\\ |\\ CO\cdot C{:}N\cdot NHAr\end{matrix}$$

(II.)

The *anhydrides*, obtained by heating the osazones with acetic anhydride or benzoyl chloride, are deep red, crystalline solids which are unaffected by boiling with water. When heated with alcohols containing hydrogen chloride they give esters of the isomeric pyrazolone acids. The pyrazolones are obtained from the osazones by crystallisation from acetic acid or by acidification of solutions of their sodium salts. In the last reaction, a varying amount of the isomeric anhydride is simultaneously produced. The free pyrazolonecarboxylic acids are yellow and are esterified only with difficulty. The esters are more readily prepared by boiling the osazones or the anhydrides with alcohols containing hydrogen chloride.

The structure of the pyrazolone derived from di-2 : 4-dibromophenylosazone has been confirmed by synthesis from the potassium derivative of oxalacetic ester, by acting successively with 2 : 4-dibromobenzenediazonium chloride (1 mol.) and 2 : 4-dibromophenylhydrazine (1 mol.) and boiling the resulting osazone ester with alcoholic hydrogen chloride.

In this way the following compounds have been prepared: *diketosuccinic acid* 2 : 4-*dibromophenylosazone*, m. p. 205° (decomp.) [*anhydride*, m. p. 267° (decomp.)]; 1-2 : 4-*dibromophenyl*-4 : 5-*diketo-3-pyrazolinecarboxylic acid* 4-2″ : 4″-*dibromophenylhydrazone*, m. p. 248° (decomp.) (*methyl* ester, m. p. 233°; *ethyl* ester, m. p. 229°; n-*butyl* ester, m. p. 175°); *ethyl diketosuccinate* 2 : 4-*dibromophenylhydrazone*, m. p. 95°; *ethyl diketosuccinate* 2 : 4-*dibromophenylosazone*, m. p. 197°; *diketosuccinic acid* p-*bromophenylosazone*, m. p. 201° (decomp.) [*anhydride*, m. p. 262° (decomp.)]; 1-p-*bromophenyl*-4 : 5-*diketopyrazoline-3-carboxylic acid* 4-p-*bromophenylhydrazone*, m. p. 260° (decomp.) (*methyl* ester, m. p. 213°; *ethyl* ester, m. p. 191°); *diketosuccinic acid* 2 : 4-*dichlorophenylosazone*, m. p. 198° (decomp.) [*anhydride*, m. p. 242° (decomp.)]; 1-2′ : 4′-*dichlorophenyl*-4 : 5-*diketopyrazoline-3-carboxylic acid* 4-2″ : 4″-*dichlorophenylhydrazone*, m. p. 252° (decomp.) (*ethyl* ester, m. p. 212°); *diketosuccinic acid* p-*chlorophenylosazone*, m. p. 195° (decomp.) [*anhydride*, m. p. 257° (decomp.)]; 1-p-*chlorophenyl*-4 : 5-*diketopyrazoline-3-carboxylic acid* 4-p-*chlorophenylhydrazone*, m. p. 254° (*ethyl* ester, m. p. 190°). G. A. C. Gough.

Dicarbazyls. III. Oxidation of carbazole and *N*-alkylcarbazoles in acid solution. P. Maitland and S. H. Tucker (J.C.S., 1927, 1388—1392).—Acetic acid solutions of carbazole, 9-methylcarbazole, and 9-ethylcarbazole are oxidised by sodium dichromate and sulphuric acid, yielding, respectively, 3 : 3′-dicarbazyl, 9 : 9′-*dimethyl*-3 : 3′-*dicarbazyl*, m. p. 200—202°, and 9 : 9′-*diethyl*-3 : 3′-*dicarbazyl*, m. p. 188—190°. The two last-named compounds are alternatively prepared by direct alkylation of 3 : 3′-dicarbazyl (this vol., 162). The mechanism of the acid oxidation of carbazole is considered to be closely allied to that of the corresponding oxidation of diphenylamine to diphenylbenzidine (Wieland, A., 1913, i, 1386). The production of NN′-*dimethyldiphenylbenzidine*, m. p. 170°, by acid oxidation of *N*-methyldiphenylamine lends support to Wieland's theory that the benzene nuclei unite directly without formation of an intermediate product. Repetition of the experiments of Marqueyrol and Muraour (A., 1914, i, 577) fails to confirm the data on which they base their theory of intermediate compound formation.

M. Clark.

Triazoles and their derivatives. VII. R. Grüner, Z. Beneš, E. Schubert, and M. Arman (Monatsh., 1927, 48, 37—46).—The formation of triazole derivatives by the action of diacylamides on monosubstituted hydrazines in presence of the sodium salts of the corresponding acids (Brunner, A., 1915, i, 1007) is of general application, and the method has been applied to the preparation of the following triazoles: 3 : 5-*diethyl*-1 : 2 : 4-*triazole*, m. p. 61—62° (*hydrochloride*, m. p. 173—174°; *silver* compound; *mercurichloride*, $C_6H_{11}N_3,2HgCl_2$, m. p. 158°); 1-*phenyl*-3 : 5-*diethyl*-1 : 2 : 4-*triazole*, m. p. 37—38° (*mercurichloride*, $C_{12}H_{15}N_3,HgCl_2$, m. p. 117—118°; *picrate*, m. p. 154°); 3 : 5-di*iso*propyl-1 : 2 : 4-triazole (Stollé and Gutmann, A., 1904, i, 696) in the pure state has m. p. 146°; 1-α-*naphthyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 69° [*picrate*, m. p. 198°; *additive* compound, $C_{14}H_{13}N_3,AgNO_3$, m. p. 274° (decomp.); *mercurichloride*, $C_{14}H_{13}N_3,HgCl_2$, m. p. 82°]: 1-β-naphthyl-3 : 5-dimethyl-1 : 2 : 4-triazole (cf. Gastaldi, A., 1924, i, 717) (*picrate*, m. p. 158°; *mercurichloride*, $C_{14}H_{13}N_3,HgCl_2$, m. p. 155°).

J. W. Baker.

Action of aromatic amines on thiosemicarbazide, hydrazodithiodicarbonamide, and their derivatives. I. Macurevitsch (Bull. Soc. chim., 1927, [iv], 41, 637—663, and J. Russ. Phys. Chem. Soc., 1927, 59, 27—68).—The action of aromatic amines on thiosemicarbazide affords in the first place hydrazodithiodicarbonamide, $2NH_2\cdot CS\cdot NH\cdot NH_2 \longrightarrow (NH_2)_2+NH_2\cdot CS\cdot NH\cdot NH\cdot CS\cdot NH_2$, which subsequently yields heterocyclic compounds which are not in general either diazole or triazole derivatives, but disubstituted tetrazines.

These products are crystalline substances which decolorise solutions of bromine in acetic acid or methyl alcohol, but with excess of bromine give resinous products. They also decolorise iodine–potassium iodide solution and react instantly with potassium permanganate in cold sodium carbonate solution. When heated with either sodium peroxide and sodium carbonate or with dry sodium hydroxide they afford (phenyl)carbylamine. They possess acidic properties, two of the hydrogen atoms, probably those in the thiocarbamide groups, being replaceable by metals. The same products are obtained by the action of amines on monosubstituted hydrazodithiodicarbonamides. In addition to these crystalline products, resinous products of similar character are formed. These resinous products afford characteristic colour reactions with alcoholic alkalis, and, like the crystalline products, yield insoluble complex silver salts. Derivatives of diazole and triazole are also produced together with basic by-products, the constitution of which has not been determined. In addition to ammonia and hydrogen sulphide, the gaseous products contain sulphur dioxide. With an aralkylamine, such as benzylamine, the main product is the corresponding *s*-thiocarbamide, *e.g.*, *s*-dibenzylthiocarbamide, together with a small quantity of a *substance*, m. p. 161—162°, probably a triazole derivative.

Aniline and thiosemicarbazide at 180—185° afford a *substance*, $C_{16}H_{16}N_8S_2(+1H_2O$ or $2H_2O)$, m. p. 260—261° (*silver* salt, $C_{16}H_{14}N_8S_2Ag_2,2AgNO_3$), together with 3 : 5 - dianilino - 4 : 1 : 2 - thiodiazole (Fromm and Nerz, A., 1923, i, 1239); hydrazodithiodicarbonamide affords the same substance, m. p. 260—261°, together with a *substance*, m. p. 297—298°, and a volatile *product*, m. p. 137—139°. Aniline and phenylhydrazodithiodicarbonamide, m. p. 169—170° (cf. Arndt, Milde, and Tschenscher, A., 1922, i, 375), yield similarly the product m. p. 260—261°, a volatile substance, m. p. 137—139°, and a little of a substance, m. p. 201—202·5°, probably 2-phenylimino-5-thio-1-phenylurazole (Arndt and Milde, A., 1921, i, 813), whilst hydrazothiophenyldicarbonamide affords a volatile product, m. p. 140—142°, a brown, resinous substance, and 2-anilino-5-thiol-1-phenyl-1 : 3 : 4-triazole, m. p. 206° (Busch and Ulmer, A., 1902, i, 575).

o-Toluidine and thiosemicarbazide or hydrazodithiodicarbonamide afford a *substance*, $C_{18}H_{20}N_8S_2,2H_2O$, m. p. 228—229°, together with a volatile product, m. p. 142—143°, a *substance*, $C_4H_8N_8S_2$, m. p. 297—300° (decomp.) (*silver*, *lead*, and *mercury* salts); an isomeric *substance*, $C_4H_8N_8S_2$, m. p. above 370° (*silver*, *lead*, and *mercury* salts), a resinous product, and traces of a *substance*, m. p. 269—270° (decomp.), which contains carbon, hydrogen, nitrogen, and sulphur. *o*-Toluidine and phenylhydrazodithiodicarbonamide afford a volatile *substance*, m. p. 149—150°, which appears to contain an amino- but no mercaptan group, a *substance*, $C_{17}H_{18}N_8S_2,2H_2O$, m. p. 219—220°, and a white *substance*, decomp. 300°, giving silver, mercury, and lead salts, analogous to that obtained with hydrazodithiodicarbonamide. It is possible that in this case a phenyl group is replaced by a tolyl group. *m*-Toluidine and thiosemicarbazide afford a *substance*, $C_{18}H_{20}N_8S_2,2H_2O$, m. p. 259—260°, and a resinous product; the substance, m. p. 234—236°, previously described (A., 1925, i, 984) could not be obtained. Hydrazodithiodicarbonamide yields the same substance, m. p. 259—260°, a substance, decomp. 300°, probably identical with the product, m. p. 297—300°, (decomp.), described above, and a substance, $C_4H_8N_8S_2$, decomp. 297—298°. *p*-Toluidine and hydrazodithiodicarbonamide afford a volatile *substance*, m. p. 170—172°, containing nitrogen and sulphur, the substance, m. p. 272—273° (Macurevitsch, *loc. cit.*), a crystalline product, decomp. 297—298°, and a product, m. p. above 370° (silver salt, $C_4H_6N_8S_2Ag_2,8AgNO_3$). There is some evidence that the product, m. p. 297—300°, is readily converted into its isomeride, m. p. above 370°.

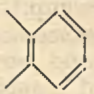
R. Brightman.

Preparation of 1 : 3 : 5-triazine-2 : 4 : 6-tricarboxyl chloride [and vat dyes therefrom]. E. Ott.—See B., 1927, 470.

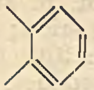
Dicyclic compounds and their analogy with naphthalene. III. K. Fries (Annalen, 1927, 454, 121—324; cf. A., 1912, i, 656; 1914, i, 569).—The behaviour of a variety of dicyclic compounds in certain critical reactions is examined in order to determine their "benzoid" or "naphthoid" character, those compounds being designated naphthoid in which two types of *ortho*-positions exist (corresponding with αβ and ββ in the naphthalene series). The reactions chosen are: (i) coupling of primary amino-derivatives to give diazoamino-compounds (benzoid) or aminoazo-compounds (naphthoid); (ii) Skraup reaction, in which naphthoid amines give no linear (ββ) ring systems; (iii) nitration and halogenation of "β" derivatives, both *ortho*-positions being attacked in benzoid compounds; (iv) formation of dihalogeno-derivatives (benzoid) or of keto-chlorides and *o*-quinones (naphthoid) by further halogenation and oxidation; (v) conversion of benzylidene-"β"-amino-compounds into acridine derivatives easily (naphthoid) or with difficulty (benzoid).

Benztriazoles are definitely naphthoid in character, benzthiodiazoles less certainly so. Tetralene (tetrahydronaphthalene) and coumarone are completely benzoid. Benziminazoles, benzthiazoles, and benz*iso*thiazoles are mainly benzoid, but show certain analogies with naphthalene which are more clearly exhibited by indazoles. The naphthoid or benzoid character probably depends on whether the compound exists in one or both of the isomeric forms (*a*) and (*b*),

(*a*)

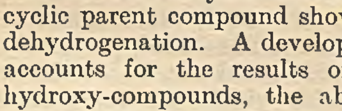


(*b*)

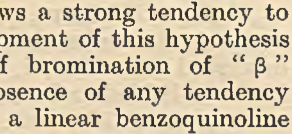


and this again is related to the ease of formation and the stability of the simple heterocyclic dihydro-derivatives. Thus in contrast with the unstable dihydrobenzenes, dihydroiminazoles and dihydrothiazoles are readily formed and are very stable. *CC*-Dihydro-1 : 2 : 3-triazoles are, on the other hand, unknown. If the dicyclic compound be supposed to exist as an equilibrium of the forms (*a*) and (*b*), then naphthoid characters will be present when the equilibrium amount of (*b*) is very small; this will be the case when the dihydro-derivative of the simple heterocyclic parent compound shows a strong tendency to dehydrogenation. A development of this hypothesis accounts for the results of bromination of "β" hydroxy-compounds, the absence of any tendency in β-naphthylamine to give a linear benzoquinoline by Skraup's reaction, and other similar observations.

Benztriazoles. [With E. Sudhoff and A. Brettschneider.]—If in the preparation of 5-hydroxy-2-phenylbenztriazole from the diazotised 5-amino-compound (Fries and Roth, A., 1912, i, 657) a less concentrated sulphuric acid is used, the main product is 5-hydroxy-2 : 2′-diphenyl-4 : 5′-azobenztriazole (I), m. p. 258°, which is also obtained by coupling the components in the usual manner. 5-Hydroxy-2-phenylbenztriazole condenses in the 4 : 4′-positions with formaldehyde in presence of 2*N*-sodium hydroxide, giving 5 : 5′-*dihydroxy*-2 : 2′-*diphenyl*-4 : 4′-*bis*-*benztriazolylmethane*, m. p. 263° (*diacetate*, m. p. 229°), which could not be anhydrised to a xanthen derivative. The corresponding *phenylmethane*, $C_{31}H_{22}O_2N_6$, m. p. 263° (*diacetate*, m. p. 195°), obtained from benzaldehyde, is readily converted by phosphoryl chloride in toluene at 100° into 5-*phenyl*-3 : 4 : 6 : 7-*bis*(*phenyltriazolo*)*xanthen* (5-phenyl-3 : 4 : 6 : 7-bisphenyl-ψ-aziminoxanthen) (II), m. p. 277°. Nitration of 5-acetamido-2-phenylbenztriazole gives the 4-*nitro*-derivative, m. p. 254°, which is hydrolysed by warm concentrated sulphuric acid to 4-*nitro*-5-*amino*-2-*phenylbenztriazole*, m. p. 310°. The 4 : 5-*diamino*-compound, m. p. 126° (*diacetyl* derivative, m. p. 258°), obtained by reduction of the nitro-amine, condenses with benzil to give a *quinoxaline*, $C_{26}H_{17}N_5$, m. p. 262°. 5-Hydroxy-2-phenylbenztriazole, like β-naphthol, reacts easily with oxalyl chloride to form a *phenyltriazolocoumarandione*, $C_{14}H_7O_3N_3$, m. p. 203°.



(I.)



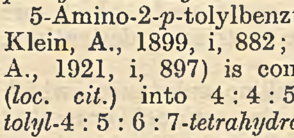
(II.)

For the preparation of 5-*amino*-6-*methoxy*-2-*phenylbenztriazole*, m. p. 185° (*acetyl* derivative, m. p. 146°), 2 : 4-diaminoanisole, m. p. 67°, is coupled with diazobenzene, and the resulting 2 : 4-diamino-5-methoxyazobenzene, m. p. 134°, is boiled with aqueous alcoholic ammoniacal copper sulphate.

4 : 4 : 5 : 7 : 7-Pentachloro-6-keto-2-phenyl-4 : 5 : 6 : 7-tetrahydrobenztriazole (Zincke and Scharff, *A.*, 1910, i, 140) is converted by fuming nitric acid into the 2-p-*nitrophenyl* compound, decomp. 172°. This, with sodium hydrogen sulphite at 100°, yields 4 : 5 : 7-*trichloro*-6-*hydroxy*-2-p-*nitrophenylbenztriazole*, m. p. 215° (*acetate*, m. p. 194°; red, sparingly soluble *sodium* salt), which by oxidation with nitric acid in acetic acid at 100° is converted into 4 : 5-*dichloro*-6 : 7-*diketo*-2-p-*nitrophenyl*-6 : 7-*dihydrobenztriazole*, m. p. 193°. The *o*-quinone, heated at 100° with aniline and acetic acid, gives the hydroxyquinone-anil, 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-2-p-*nitrophenyl*-4 : 7-*dihydrobenztriazole*, m. p. 236°.

5-Amino-2-*p*-tolylbenztriazole (Willgerodt and Klein, A., 1899, i, 882; Schmidt and Hagenböcker, A., 1921, i, 897) is converted by Zincke's method (*loc. cit.*) into 4 : 4 : 5 : 7 : 7-*pentachloro*-6-*keto*-2-p-*tolyl*-4 : 5 : 6 : 7-*tetrahydrobenztriazole*, m. p. 197° (decomp.), from which are prepared, by a similar series of reactions, 4 : 5 : 7-*trichloro*-6-*hydroxy*-2-p-*tolylbenztriazole*, m. p. 188°, 4 : 5-*dichloro*-6 : 7-*diketo*-2-p-*tolyl*-6 : 7-*dihydrobenztriazole*, m. p. 223°, and 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-2-p-*tolyl*-4 : 7-*dihydrobenztriazole*, m. p. 236°; reduction of the *o*-quinone with stannous chloride gives 4 : 5-*dichloro*-6 : 7-*dihydroxy*-2-p-*tolylbenztriazole*, m. p. 203° (*diacetate*, m. p. 197°).

5-*Benzylideneamino*-2-*phenylbenztriazole*, m. p. 156°, when boiled in glacial acetic acid for a few minutes, is converted into the corresponding *dihydroacridine* (III), m. p. 315°, which is oxidised by bromine in nitrobenzene to 5-*phenyl*-3 : 4 : 6 : 7-*bis*-(2′-*phenyltriazolo*)*acridine*, m. p. 294°.



(III.)

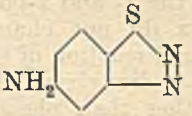
5-*Benzylideneamino*-2-p-*tolylbenztriazole*, m. p. 150°, gives in similar manner a *dihydroacridine*, m. p. 321°. 5-*Benzylideneamino*-1-*phenylbenztriazole*, m. p. 137°, when heated with 5-amino-1-phenylbenztriazole hydrochloride in a little alcohol, yields (like the corresponding β-naphthylamine derivative) an acridine, 5-*phenyl*-3 : 4 : 6 : 7-*bis*-(1'-*phenyltriazolo*)*acridine*, m. p. 336°. 5-*Benzylideneamino*-1-*methylbenztriazole*, m. p. 165°, is yellow and gives a yellow *acridine*, m. p. 364° (the 1-phenyltriazole compounds are colourless).

[With A. Madjid.]—5 : 6-(2'-*Phenyltriazolo*)*quinoline*, m. p. 160°, prepared by Skraup's reaction from 5-amino-2-phenylbenztriazole, is converted by way of the *methiodide*, m. p. 266° (decomp.), into N-*methyl*-5 : 6-(2'-*phenyltriazolo*)-2-*quinoline*, m. p. 218°. 5 : 6-(1'-*Phenyltriazolo*)*quinoline*, m. p. 122° (*methiodide*, m. p. 258°), and the *methylquinoline*, m. p. 215°, are similarly obtained. 5-Amino-1-methylbenztriazole gives 5 : 6-(1'-*methyltriazolo*)*quinoline*, m. p. 167° (*methiodide*, m. p. 244°). By chlorinating 5-acetamido-1-methylbenztriazole in boiling acetic acid there is obtained the 4-*chloro*-derivative, m. p. 214°, hydrolysed by aqueous alcoholic hydrogen chloride to 4-*chloro*-5-*amino*-1-*methylbenztriazole*, m. p. 178°. No triazoloquinolines are obtainable from the 4-chloro-5-amino-derivatives of 1-methyl-, 1-phenyl-, and 2-phenyl-benztriazoles by Skraup's reaction under a variety of conditions.

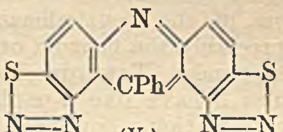
[With A. Arnemann.]—2-Bromo-3 : 5-dinitro-*p*-xylene, m. p. 115°, fails to react with phenylhydrazine alone or in presence of cuprous iodide, and with alcoholic ammonia in presence of cuprous iodide or copper-bronze. By boiling together equal parts of 2-bromo-3 : 5-dinitro-*p*-xylene and aniline for 2 hrs., a 61% yield of 2 : 4-*dinitro*-3 : 6-*dimethyldiphenylamine*, m. p. 132°, is obtained. Reduction of this with sodium sulphide gives the 4-*nitro*-2-*amino*-compound, m. p. 171° (*acetyl* derivative, m. p. 203°, cannot be converted into a benziminazole), from which by the action of nitrous acid 5-*nitro*-1-*phenyl*-4 : 7-*dimethylbenztriazole*, m. p. 208°, results. The 5-*amino*-compound, m. p. 179° (*acetyl* derivatives, m. p. 206°), obtained by reduction, couples with diazobenzene to give a *diazoamino*-compound, m. p. 161°, whereas 5-amino-1-phenylbenztriazole yields an azo *dye*, $C_{18}H_{14}N_6$, m. p. 231° (*acetyl* derivative, m. p. 207°). The aminodimethylbenztriazole is chlorinated in concentrated hydrochloric acid to give 4 : 6 : 6 : 7-*tetrachloro*-5-*keto*-1-*phenyl*-4 : 7-*dimethyl*-4 : 5 : 6 : 7-*tetrahydrobenztriazole*, m. p. 170°, which on reduction with stannous chloride in acetic acid yields 6-*chloro*-5-*hydroxy*-1-*phenyl*-4 : 7-*dimethylbenztriazole*, m. p. 168° (*acetate*, m. p. 174°). Treatment of the chlorohydroxy-compound with fuming nitric acid gives 6-*chloro*-4-*nitro*-5-*keto*-1-*phenyl*-4 : 7-*dimethyl*-4 : 5-*dihydrobenztriazole*, m. p. 124° (decomp.), from which by boiling the acetic acid solution, 6-*chloro*-4-*hydroxy*-5-*keto*-1-*phenyl*-4 : 7-*dimethyl*-4 : 5-*dihydrobenztriazole*, m. p. 201°, is obtained. As in the naphthalene series, there is here no tendency to form a ββ(5 : 6)-quinone.

Oxidation of 5-amino-2-phenylbenztriazole with permanganate gives in 50% yield 2-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (von Pechmann, A., 1891, 1110; Beretta, A., 1926, 182), m. p. 255° (decomp.), which, contrary to the statements of von Pechmann and Beretta, when heated forms no anhydride, but is decarboxylated to 2-phenyltriazole-4-carboxylic acid, m. p. 191° (methyl ester, m. p. 54°). The 4 : 5-dicarboxylic acid gives a *chloride*, m. p. 122°, *diamide*, m. p. 274°, and *dianilide*, m. p. 213°. The *methyl* ester, m. p. 91°, is converted by way of the *dihydrazide*, m. p. 232°, *diazide* (detonates by rubbing or shock), and *diurethane*, m. p. 135°, into 4 : 5-diamino-2-phenyl-1 : 2 : 3-triazole dihydrochloride (Thiele, A., 1897, i, 377), which condenses with benzil to form a *quinoxaline*, but gives no benziminazole derivatives. By the action of nitric acid on 5-amino-2-phenylbenztriazole there is obtained 2-p-*nitrophenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylic acid*, m. p. 253° (decomp.; *methyl* ester, m. p. 163°; *dianilide*, m. p. 258°), which also gives no anhydride. 2-p-*Carboxyphenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylic acid*, m. p. 232° (decomp.); *methyl* ester, m. p. 128°; *chloride*, m. p. 110°; *triamide*, m. p. 308° (+3AcOH) or 330° (not quite pure); *trianilide*, m. p. 238° (+AcOH), obtained by oxidation of 5-amino-2-*p*-tolylbenztriazole with permanganate, gives no anhydride, but when rapidly sublimed yields 2-p-*carboxyphenyl*-1 : 2 : 3-*triazole*, m. p. 282° (*methyl* ester, m. p. 128°). 5-Amino-1-phenylbenztriazole is oxidised to 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (Zincke and Petermann, A., 1901, i, 104; Beretta, *loc. cit.*), m. p. 149° (methyl ester, m. p. 127°; *dihydrazide*, m. p. 168°).

Benzthiodiazoles. [With M. Vorbrodt and G. Siebert.]—4-*Nitro*-2-*aminothiophenol*, m. p. 183° (*methyl thioether*, m. p. 105°; *disulphide*, m. p. 211°), prepared from 2-bromo-5-nitroaniline and sodium polysulphide, gives with acetic anhydride 4-*nitro*-1-*methylbenzthiazole*, m. p. 139°, and with nitrous acid 5-*nitrobenzthiodiazole*, m. p. 144°, which is reduced by tin and hydrochloric acid to 5-*aminobenzthiodiazole* (IV), m. p. 94° (*acetyl* derivative, m. p. 161°). This amine behaves like β-naphthylamine. Its *benzylidene*-derivative, m. p. 90°, reacts with the hydrochloride in hot alcohol to give 5-*phenylacridine*-3 : 4 : 6 : 7-*bis*-*diazosulphide* (V), m. p. 216°. The amine couples in acetic acid with diazobenzene to give directly an aminoazo *dye*, m. p. 222° (decomp.) (*acetyl* derivative, m. p. 231°). On chlorination in hydrochloric acid, the amine forms 4 : 4 : 6 : 6 : 7-*pentachloro*-5-*keto*-4 : 5 : 6 : 7-*tetrahydrobenzthiodiazole*, m. p. 149° (decomp.), reducible by stannous chloride in acetic acid to 4 : 6 : 7-*trichloro*-5-*hydroxybenzthiodiazole*, m. p. 187° (*acetate*, m. p. 122°), from which by chlorination 4 : 4 : 6 : 6 : 7 : 7-*hexachloro*-5-*keto*-4 : 5 : 6 : 7-*tetrahydrobenzthiodiazole*, m. p. 151°, is obtained. The trichloro-compound is oxidised by nitric acid to 6 : 7-*dichlorobenzthiodiazole*-4 : 5-*quinone*, m. p. 164°, which condenses with *o*-phenylenediamine to form a *quinoxaline*, m. p. 287°, and is reduced by stannous chloride to the corresponding *dihydroxy*-compound, m. p. 219° (*diacetate*, m. p. 137°). 5-Aminobenzthio-



(IV.)



(V.)

diazole is diazotised in concentrated sulphuric acid solution, and by heating the diluted diazo-solution, 5-*hydroxybenzthiodiazole*, m. p. 161° (*acetate*, m. p. 122°), is obtained. This yields on halogenation 4-*bromo*- (m. p. 196°) and 4-*chloro*- (m. p. 197°) derivatives. 4-*Nitro*-5-*hydroxybenzthiodiazole*, m. p. 206°, results from nitration of the 5-hydroxy-compound or of its 4-bromo-derivative.

6-*Hydroxybenzthiodiazole*, m. p. 211°, prepared by demethylation of the methyl ether (Fries and Engelbertz, A., 1915, i, 155), yields on bromination the 7-*bromo*- (m. p. 210°) and, less easily, the 5 : 7-*dibromo*-derivative, m. p. 228° (decomp.). Nitration of 6-hydroxybenzthiodiazole or of its 7-bromo-derivatives gives 7-*nitrobenzthiodiazole*, m. p. 180° (*sodium* salt described). 6-Hydroxybenzthiodiazole is converted by chlorine into the 7-*chloro*-derivative, m. p. 200°, which is also obtained by demethylation of 7-*chloro*-6-*methoxybenzthiodiazole*, m. p. 114°, synthesised from 6-chloro-5-methoxy-1-phenylbenzthiazole (Fries and Buchler, below) by hydrolysis with alcoholic alkali to 6-*chloro*-2-*amino*-5-*methoxythiophenol*, followed by diazotisation. Further chlorination of 6-hydroxybenzthiodiazole yields first an *o*-quinone dichloride, probably 7 : 7-*dichloro*-6-*keto*-6 : 7-*dihydrobenzthiodiazole*, then a sulphur-free diazo-salt, probably 2 : 3 : 3-*trichloro*-4-*keto*-3 : 4-*dihydrobenzenediazonium chloride*, m. p. 155—160° (decomp.), which gives with 2-naphthol-3 : 6-disulphonic acid a red *dye*, and by reduction with stannous chloride 2 : 3-*dichloro*-4-*hydroxyphenylhydrazine*, m. p. 158° (decomp.); the final chlorination product is 2 : 3 : 4 : 6-tetrachlorophenol, m. p. 67° (lit., 70°; benzoate, m. p. 166°). 6-Methoxybenzthiodiazole is similarly converted by way of a diazonium salt into 2 : 3-*dichloro*-4-*methoxyphenylhydrazine*, m. p. 200° [p-*nitrobenzylidene*-compound, m. p. 210° (decomp.)].

Benziminazoles. [With E. Modrow, B. Raeke, and K. Weber.]—Substituents in the 1- and 2-positions in the benziminazole series do not change appreciably the benzoid or naphthoid reaction of the compounds. Towards chlorine, 5-hydroxybenziminazoles behave like β-naphthol rather than phenol; dibromination, however, gives the 4 : 6-dibromo-derivatives; 5-aminobenziminazoles couple with diazobenzene to form diazoamino-compounds as in the benzene series, and the Skraup reaction gives both linear and angular tricyclic quinolines. Moreover, a 5 : 6(*i.e.*, ββ)-quinone is obtainable.

Chlorination of 5-acetamido-1-phenyl-2-methylbenziminazole (von Walther and Kessler, A., 1904, i, 348), m. p. 233°, gives after hydrolysis with aqueous-alcoholic hydrochloric acid 4-*chloro*-5-*amino*-1-*phenyl*-2-*methylbenziminazole*, m. p. 257° (*acetyl* derivative, m. p. 228°), and the 6-*chloro*-isomeride, m. p. 208° (*acetyl* derivative, m. p. 199°). The latter base is synthesised from 5-chloro-2 : 4-diaminodiphenylamine and acetic anhydride. 5-*Hydroxy*-1-*phenyl*-2-*methylbenziminazole*, m. p. 243° (*acetate*, m. p. 141°), prepared by decomposition of the diazotised 5-amino-compound, is brominated in water to the 4-*bromo*-derivative, m. p. 266°, and in acetic acid with 2 mols. of bromine to the 4 : 6-*dibromo*-derivative, m. p. 190°. 4-*Chloro*-5-*hydroxy*-1-*phenyl*-2-*methylbenziminazole*, m. p. 287° (*acetate*, m. p. 161°), obtained by chlorination, is converted with great difficulty into a dichloro-derivative, m. p. 215° (impure), the main product, even when only one further molecule of chlorine is used, being a *keto-chloride*, which is reducible by stannous chloride to the pure 4 : 6-*dichloro*-5-*hydroxy*-1-*phenyl*-2-*methylbenziminazole*, m. p. 216° [*hydrochloride*, m. p. 283° (decomp.); O-*acetate*, m. p. 183°]. Nitration of the 4-chloro-5-hydroxy-compound gives no chloronitro-ketone (a naphthoid reaction), but 4-*chloro*-6-*nitro*-5-*hydroxy*-1-*phenyl*-2-*methylbenziminazole*, m. p. 211°.

5-*Nitro*-1-p-*chlorophenyl*-2-*methylbenziminazole*, m. p. 210°, is prepared from 4′-*chloro*-4-*nitro*-2-*aminodiphenylamine*, m. p. 176° (*monoacetyl* derivative, m. p. 210°), the sodium sulphide partial reduction product of 4′-chloro-2 : 4-dinitrodiphenylamine, and gives on reduction 5-*amino*-1-p-*chlorophenyl*-2-*methylbenziminazole*, m. p. 170°. This amine couples with diazobenzene to form a *diazoamino*-compound, m. p. 194° (decomp.), and is converted by way of its diazo-salt into the 5-*hydroxy*-compound, m. p. 228°. Chlorination of the latter gives 4-*chloro*-5-*hydroxy*-1-p-*chlorophenyl*-2-*methylbenziminazole*, m. p. 270° (*acetate*, m. p. 186°), and eventually a *keto-chloride*, reducible to the 4 : 6-*dichloro*-5-*hydroxy*-compound.

From 2′-chloro-2 : 4-dinitrodiphenylamine a similar series of reactions gives 2′-*chloro*-4-*nitro*-2-*aminodiphenylamine*, m. p. 117°, 5-*nitro*-1-o-*chlorophenyl*-2-*methylbenziminazole*, m. p. 140°, the 5-*amino*- (m. p. 130°) and 5-*hydroxy*- (m. p. 245°) compounds, and 4-*chloro*-5-*hydroxy*-1-o-*chlorophenyl*-2-*methylbenziminazoles*, m. p. 250°. 5-*Hydroxy*-1-*phenylbenziminazole*, m. p. 244° (*acetate*, m. p. 88°), obtained from 5-amino-1-phenylbenziminazole (Reissert and Goll, A., 1905, i, 248), behaves like the other 5-hydroxybenziminazoles on chlorination; the 4-*chloro*-derivative has m. p. 220°.

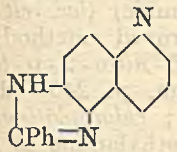
Similar relations are found in the 1-*p*-tolylbenziminazole series. 5-*Amino*-1-p-*tolylbenziminazole*, m. p. 128° (*acetyl* derivative, m. p. 210°; *benzylidene*-derivative, m. p. 142°, gives no acridine), yields with *p*-nitrodiazobenzene a *diazoamino*-compound, m. p. 214° (decomp.). 4-*Chloro*-5-*amino*-1-p-*tolylbenziminazole*, m. p. 128° (*acetyl* derivative, m. p. 209°; *formyl* derivative, m. p. 178°), is prepared by chlorination and hydrolysis of the acetyl derivative.

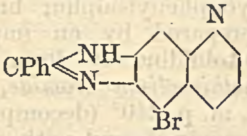
5-*Chloro*-2 : 4-*dinitro*-4′-*methyldiphenylamine*, m. p. 154°, is converted by sodium sulphide into 2 : 2′ : 4 : 4′-*tetranitro*-5 : 5′-*di*-p-*toluidinodiphenyl sulphide*, m. p. 252°, or by tin and hydrochloric acid into the 2 : 4-*diamino*-compound, which condenses with formic acid to give 6-*chloro*-5-*formamido*-1-p-*tolylbenziminazole*, m. p. 195°. 5-*Hydroxy*-1-p-*tolylbenziminazole*, m. p. 239° (*acetate*, m. p. 133°), yields by chlorination the 4-*chloro*-derivative, m. p. 217°, and a *keto-chloride*.

4-*Chloro*-5-*aminobenziminazole*, m. p. 102° (+EtOH; *hydrochloride*; *formyl* derivative, m. p. 222°), is obtained by the action of tin and hydrochloric acid on 5-nitrobenziminazole. 6-*Chloro*-5-*formamidobenziminazole*, m. p. 205°, and 4 : 6-*dichloro*-5-*formamidobenziminazole*, m. p. 225°, are prepared from 3-chloro-4 : 6-dinitroaniline by reduction with stannous chloride, or with tin and hydrochloric acid, respectively, followed by condensation with formic acid.

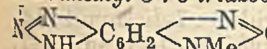
[With A. Abdurrachman.]—5-Amino-2-phenylbenziminazole gives by Skraup's reaction the *ang.*-quinoline, *2′-phenyl-5′ : 4′-benziminazolo-2 : 3-pyridine* (VII), m. p. 90—95° (+H_2O), or 270° (anhyd.; *methiodide*, m. p. 295°). *4-Bromo-5-amino-2-phenylbenziminazole*, m. p. 238—239° (obtained by hydrolysis of the *acetyl* derivative, m. p. 160°), gives with equal ease the *lin.*-quinoline, *4′-bromo-2′-phenyl-6′ : 5′-benziminazolo-2 : 3-pyridine* (VIII). Similarly, 5-amino-1-phenylbenziminazole is converted into an ang.-*quinoline*, m. p. 165° [*methiodide*, m. p. 280° (decomp.)], and its 4-*chloro*-derivative, m. p. 143° (*acetyl* derivative, m. p. 205°), into a lin.-*quinoline*, m. p. 199—201° (*methiodide* described). The corresponding 1-*p*-tolyl compounds melt, respectively, at 180° (*ang.*) and 235° (*lin.*; chloro-compound).

(VII.)



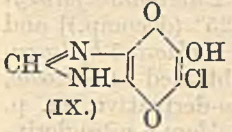


(VIII.)

5 : 6-Diamino-2-methylbenziminazole (Kym and Ratner, A., 1913, i, 102) is converted by chlorine in hydrochloric–acetic acid into *4 : 4 : 7 : 7-tetrachloro-5 : 6-diketo-2-methyl-4 : 5 : 6 : 7-tetrahydrobenziminazole* (*hydrochloride*, decomp. 300° without melting), which is more easily obtained by chlorination of its reduction product, *4 : 7-dichloro-5 : 6-dihydroxy-2-methylbenziminazole* (base and *hydrochloride* decomp. 300° without melting; *diacetate*, m. p. 267°). This dihydroxy-compound, unlike the 6 : 7-dichloro-4 : 5-dihydroxy-isomeride, is not convertible into a quinone by oxidation. *5-Nitro-1 : 2-dimethylbenziminazole*, m. p. 226°, prepared from *p*-nitro-*o*-aminomethylaniline and acetic anhydride, gives on nitration a mixture of the 5 : 6- and 4 : 5-*dinitro*-compounds, m. p. 232° and 170°, respectively. The former is reduced by sodium sulphide to the 5-nitro-6-amino-compound, m. p. 309°, and by tin and hydrochloric acid to the 5 : 6-*diamine*, m. p. 279°, which gives with benzil a *quinoxaline*, m. p. 232°, and with nitrous acid *1 : 2-dimethyl-5 : 6-triazobenziminazole*,  $N\!\!\lessgtr\!\!{}^{N-}_{NH}\!>C_6H_2<^{——N}_{NMe}\!\!>CMe$, m. p. 311°. The diamine is converted into a *keto-chloride*, $C_9H_6O_2N_2Cl_4$ (decomp. about 200°), and thence by reduction into *4 : 7-dichloro-5 : 6-dihydroxy-1 : 2-dimethyl-5 : 6-triazobenziminazole* (base and *hydrochloride* blacken at about 300°; *diacetate*, m. p. 200°). *5-Amino-1 : 2-dimethylbenziminazole*, m. p. 167° (*acetyl* derivative, m. p. 239°), gives by chlorination and reduction a mixture of *di-* and *tri-chloro*-compounds, which are oxidised by nitric–acetic acid to the quinone, *6 : 7-dichloro-4 : 5-diketo-1 : 2-dimethyl-4 : 5-dihydrobenziminazole*, m. p. above 300°, reducible to a *dihydroxy*-compound.

On nitration of 5-nitro-1-*p*-chlorophenyl-2-methylbenziminazole, the new nitro-group enters the phenyl residue *ortho* to the chlorine, giving a *product*, m. p. 226°, which condenses with aniline to form *5-nitro-1-(m-nitro-p-anilinophenyl)-2-methylbenziminazole*, m. p. 199°.

[With O. Dieckmann and A. Fingerling.]—Keto-chlorides, quinones, and dihydroxy-compounds are obtainable by the methods above described from benziminazole and its 2-methyl, 2-phenyl, and 1-phenyl-2-methyl derivatives. The following are new: *4 : 6-Dichloro-5-hydroxybenziminazole*, m. p. above 250° (*acetate*, m. p. 212°); *6 : 7-dichloro-4 : 5-diketo-4 : 5-dihydrobenziminazole*, decomp. 280° [*nitrate*, m. p. 162° (decomp.); corresponding *dihydroxy*-compound, m. p. 196° (*diacetate*, m. p. 213°)]; *6-chloro-7-phenylimino-5-hydroxy-4 : 7-diketo-4 : 7-dihydrobenziminazole*, decomp. 280°, obtained from the quinone and aniline, hydrolysable to the 4 : 7-*quinone* (IX), m. p. above 250°; *4 : 6-dichloro-5-hydroxy-2-methylbenziminazole* [*hydrochloride*, m. p. above 250° (decomp.)]; *6 : 7-dichloro-4 : 5-diketo-2-methyl-4 : 5-dihydrobenziminazole*, decomp. above 280° [corresponding *dihydroxy*-compound, m. p. above 250° (decomp.; *diacetate*, m. p. 148°); 7-*anil*, decomp. above 250°]; [with K. Fink] *4 : 4 : 6 : 7-tetrachloro-5-keto-2-phenyl-4 : 5-dihydrobenziminazole*, m. p. 199° (decomp.); *4 : 6-dichloro-5-hydroxy-2-phenylbenziminazole*, m. p. 240°; *6 : 7-dichloro-4 : 5-diketo-2-phenyl-4 : 5-dihydrobenziminazole*, m. p. 305° (decomp.); *6 : 7-dichloro-4 : 5-diketo-1-phenyl-2-methyl-4 : 5-dihydrobenziminazole*, m. p. 229° [corresponding *dihydroxy*-compound, m. p. indefinite above 160° (decomp.)]. 5-Nitro-2-phenylbenziminazole is best prepared by the action of alcoholic potassium hydroxide on *4-nitrodibenzoyl-o-phenylenediamine*, m. p. 234°.



(IX.)

Benzthiazoles. [With W. Buchler.]—Benzthiazoles, like benziminazoles, yield "α" derivatives when nitrated. The β-amines couple with diazobenzene to form diazoamino-compounds, and their benzylidene-derivatives are not convertible into acridines. The more purely benzoid character of benzthiazoles as compared with benziminazoles is further shown by the formation of 4 : 6-dichloro- and 4-bromo-derivatives from the 5-hydroxy-compounds.

Thiobenz-p-anisidide, m. p. 135°, oxidised with alkaline ferricyanide, yields *5-methoxy-1-phenylbenzthiazole*, m. p. 117°, which is converted by alcoholic alkali into 2 : 2′-diamino-5 : 5′-dimethoxydiphenyl disulphide, m. p. 81°, and by hydrobromic–acetic acid into *5-hydroxy-1-phenylbenzthiazole*, m. p. 227° (*acetate*, m. p. 140°). *5-Hydroxy-1-methylbenzthiazole*, m. p. 162°, is prepared from the 5-methoxy-compound (Fries and Engelbertz, A., 1915, i, 155).

5-Hydroxy-1-phenylbenzthiazole gives on chlorination the 6-*chloro*-compound, m. p. 165° (*methyl ether*, m. p. 138°), and by further chlorination the 4 : 6-*dichloro*-derivative, m. p. 199°, but no keto-chloride. The dichloro-compound is oxidised by nitric acid to an *o-quinone*. Bromination, on the other hand, gives *4-bromo-5-hydroxy-1-phenylbenzthiazole*, m. p. 169°, from which the 6-*chloro-4-bromo*-compound, m. p. 205° (*acetate*, m. p. 211°), and the 4 : 6-*dibromo*-compound may be obtained, but no keto-bromide; the dibromo-compound is oxidised by nitric–acetic acid to *4-bromo-5 : 6-diketo-1-phenyl-5 : 6-dihydrobenzthiazole*, m. p. 163° (impure). *6-Nitro-5-hydroxy-1-phenylbenzthiazole*, m. p. 171°, obtained with a little 4-*nitro*-compound by direct nitration, is reduced to the 6-*amino*-compound, m. p. 178° (decomp.). *4-Bromo-6-nitro-* and *6-chloro-4-nitro-5-hydroxy-1-phenylbenzthiazoles*,

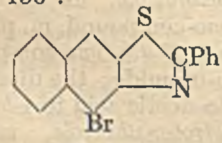
m. p. 189° (decomp.) and 203°, respectively, are similarly prepared by nitration.

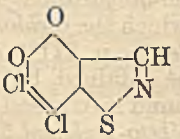
2 : 5-*Dichloro*-4-*nitrophenol*, m. p. 117° (*acetate*, m. p. 89°; 2 : 5-*dichloro*-4 : 6-*dinitrophenol*, m. p. 146°), prepared from 2 : 5-dichlorophenol by nitration in chloroform, reacts with sodium disulphide to give 4 : 4′-*dichloro*-2 : 2′-*dinitro*-5 : 5′-*dihydroxydiphenyl disulphide*, m. p. 277° (decomp.; *diacetate*, m. p. 194°), which is converted, by reduction to 4-*chloro*-2-*amino*-5-*hydroxythiophenol* [*hydrochloride*, m. p. 225° (decomp.)] and subsequent benzoylation, into 4-*chloro*-5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 219°, obtained as *benzoate*, m. p. 152°. The 4-*chloro*-6-*bromo*-derivative, m. p. 196° (*acetate*, m. p. 225°), the 4-*chloro*-6-*nitro*-derivative, m. p. 189°, and the 4-*chloro*-6-*amino*-derivative are prepared from the 4-*chloro*-compound; the amine gives on chlorination the tetrachloroketo-chloride, m. p. 177° (see below).

Chlorination of 5-hydroxy-1-phenylbenzthiazole gives successively 4 : 6-*dichloro*-5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 198°, 3 : 3 : 4 : 4 : 6 : 6-*hexachloro*-5-*keto*-1-*phenyl*-3 : 4 : 5 : 6-*tetrahydrobenzthiazole*, m. p. 204°, and finally a *hepta*- and an *octa-chloroketo-chloride*. The hexachloro-compound is reduced by stannous chloride in acetic acid to 3 : 4 : 6-*trichloro*-5-*hydroxy*-1-*phenylbenzthiazole*, m. p. 173°, obtained also by hydrolysis of its *methyl ether*, m. p. 201° (prepared by chlorination of 5-methoxy-1-phenylbenzthiazole). 3 : 3 : 4 : 4-*Tetrachloro*-5 : 6-*diketo*-1-*phenyl*-3 : 4 : 5 : 6-*tetrahydrobenzthiazole*, m. p. 177°, the chlorination product of 6-amino- or of 4-chloro-6-amino-5-hydroxy-1-phenylbenzthiazole, is reduced to 3 : 4-*dichloro*-5 : 6-*dihydroxy*-1-*phenylbenzthiazole*, m. p. 247°, which is oxidised to the *quinone*, m. p. 231°, obtainable also from the above trichloro-compound of m. p. 173°.

Thiobenz-p-*nitroanilide*, m. p. 147°, gives on oxidation with alkaline ferricyanide at 90—100° 5-nitro-1-phenylbenzthiazole, m. p. 193°, prepared also by direct nitration; cold oxidation yields *bis*-p-*nitrophenyliminobenzoyl disulphide*, m. p. 145°. 5-Benzylideneamino-1-phenylbenzthiazole shows no tendency to form an acridine derivative when heated with its hydrochloride. The free 5-amino-compound couples with *p*-nitrodiazobenzene to form a *diazoamino*-compound, m. p. 209° (decomp.). 2 : 4-Dinitrophenyl thiobenzoate is converted quantitatively by chlorination into 2 : 4-*dinitrophenyl chloromercaptan*, $(NO_2)_2C_6H_3{\cdot}SCl$, m. p. 99°. *Benz*-1-*bromo*-2-*naphthylamide*, m. p. 159°, prepared by benzoylation of 1-bromo-2-naphthylamine or by bromination of benz-β-naphthylamide, gives with phosphorus pentasulphide the *thioamide*, m. p. 161°, which is oxidised to the linear 3-*bromo*-1-*phenyl*-ββ-*naphthathiazole* (X), m. p. 156°.

(X.)





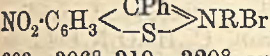
(XI.)

The angular βα-naphthathiazole, m. p. 109°, is similarly prepared from benz-β-naphthylamide. Attempts to obtain 5-methoxy-1-phenylbenzthiazole from benz-*p*-anisidide or benzylidene-*p*-anisidine were unsuccessful. By the action of hydrogen sulphide on benzylidene-aniline or -*p*-anisidine, polymeric thiobenzaldehyde results in quantitative yield.

Benz*iso*thiazoles. [With K. Eishold and B. Vahlberg.]—The reactions of benz-4′ : 5′-*iso*thiazoles show a purely benzoid character, except in the formation of a keto-chloride and a dichloro-*o*-quinone from 5-hydroxybenz*iso*thiazole. Several new benz*iso*thiazolium salts are described (cf. Fries and Brothuhn, A., 1923, i, 842). 4-Nitro-2-aldehydophenyl bromomercaptan (5-nitro-2-bromothiolbenzaldehyde, 4-nitro-2-aldehydophenylsulphur bromide) (*loc. cit.*), m. p. 171°, prepared by an improved method, reacts with *p*-toluidine to form 5-*nitro*-2-p-*tolylbenz*-4′ : 5′-iso*thiazolium bromide*, m. p. 240° [decomp.; *chloride*, m. p. 240° (decomp.); *chloroplatinate*, m. p. 265° (decomp.)], and with methylamine to give the corresponding 2-*methyl* compound, m. p. 212° (decomp.; *chloroplatinate*). These, like the 2-phenyl compound (*loc. cit.*), are converted by alcoholic ammonia into 5-nitrobenz-4′ : 5′-*iso*thiazole, m. p. 151°; the action of sodium hydroxide, carbonate, or acetate is different in the case of the aryl compounds, the products being the *di*(*phenylimine*), m. p. 183°, and *di*-(p-*tolylimine*), m. p. 202°, of 4 : 4′-dinitro-2 : 2′-dialdehydodiphenyl disulphide, $[ArN{:}CH{\cdot}C_6H_3(NO_2){\cdot}S{\cdot}_2]$. The *di*(*methylimine*), m. p. 165° (decomp.), is obtained only by prolonged action of sodium carbonate solution. The di(arylimines) on chlorination in warm chloroform regenerate 5-nitro-2-arylbenz-4′ : 5′-*iso*thiazolium chlorides.

5-*Aminobenz*-4′ : 5′-iso*thiazole*, m. p. 130° [*hydrochloride*, m. p. 225° (decomp.); *acetyl* derivative, m. p. 172°], obtained by reduction of the 5-nitro-compound, is converted by decomposition of its *diazo*-compound in concentrated sulphuric acid into 5-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 156° [*benzoate*, m. p. 125°; *hydrobromide*, m. p. 240° (decomp.)]. Chlorination of the hydroxy-compound yields successively the 4-*chloro*-derivative, m. p. 195°, the 4 : 6-*dichloro*-derivative, m. p. 176°, and finally 4 : 4 : 6 : 6 : 7-*pentachloro*-5-*hydroxy*-4 : 5 : 6 : 7-*tetrahydrobenz*-4′ : 5′-iso*thiazole*, m. p. 183°, reducible to 4 : 6 : 7-*trichloro*-5-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 234°, from which by oxidation with nitric acid 6 : 7-*dichloro*-4 : 5-*diketo*-4 : 5-*dihydrobenz*-4′ : 5′-iso*thiazole* (XI), m. p. 145°, is obtained. 4-*Bromo*- [m. p. 247° (decomp.)] and 4 : 6-*dibromo*- (m. p. 171°) derivatives are prepared by bromination of 5-hydroxybenz-4′ : 5′-*iso*thiazole. 4-*Nitro*-2-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 145°, and its 6-*bromo*-derivative, m. p. 185°, are obtained by direct nitration of the 4-bromo- and 4 : 6-dibromo-compounds, respectively, the former also from 5-hydroxybenz-4′ : 5′-*iso*thiazole. Oxidation of the 4 : 6-dibromo-compound with nitric acid in acetic acid yields 6-*bromo*-4 : 5-*diketo*-4 : 5-*dihydrobenz*-4′ : 5′-iso*thiazole*, m. p. 131° (decomp.; *anilino*-derivative described), also obtainable from 4-*chloro*-6-*bromo*-5-*hydroxybenz*-4′ : 5′-iso*thiazole*, m. p. 186°, the product of bromination of the 4-chloro-compound. 5-Aminobenz-4′ : 5′-*iso*thiazole (*benzylidene*-derivative, m. p. 101°, is not convertible into an acridine) couples with diazobenzene to form a *diazoamino*-compound, but with *p*-nitrodiazobenzene to give an *aminoazo*-compound, m. p. 225° [decomp.; *acetyl* derivative, m. p. 270° (decomp.)].

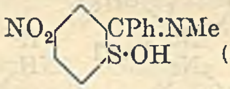
3-*Nitro*-6-*thiolbenzophenone*, m. p. 125° (*methyl ether*, m. p. 89°; *disulphide*, m. p. 177°), is prepared from 6-chloro-3-nitrobenzophenone, m. p. 86° (Ullmann and Ernst, A., 1906, i, 205), by the action of sodium sulphide and sulphur. By using less sulphide, there is obtained 4 : 4′-*dinitro*-2 : 2′-*dibenzoyldiphenyl sulphide*, m. p. 205°, and, by subsequent bromination in boiling carbon tetrachloride, 3-*nitro*-6-*bromothiolbenzophenone*, m. p. 146° (decomp.), which is converted by ammonia into 5-*nitro*-3-*phenylbenz*-4′ : 5′-iso*thiazole*, m. p. 124°. The bromo-mercaptan reacts as usual with aniline, *p*-toluidine, and methylamine to give *benz*iso*thiazolium bromides*,



$$NO_2\cdot C_6H_3<\begin{matrix}CPh\\ -S-\end{matrix}>NRBr$$

melting and decomposing at 303—306°, 319—320°, and 201°, respectively. By the action of aqueous ammonia or sodium hydroxide on a cold alcoholic solution of the phenobromide, there is formed 5-*nitro*-2-*anilinothiolbenzophenone* (XII), m. p. 147°, which is stable to alkali, but is converted by hydrogen bromide in cold benzene into aniline hydrobromide and the bromo-mercaptan. The *p*-tolyl compound similarly gives 5-*nitro*-2-p-*toluidinothiolbenzophenone*, m. p. 148°. The methobromide, on the other hand, gives with ammonia 5-nitro-2-phenylbenz-4′ : 5′-*iso*thiazole, and with sodium hydroxide a *compound*, $C_{14}H_{12}O_3N_2S$ (probably XIII), m. p. 110°, which regenerates the methobromide when ground with dilute hydrobromic acid. A similar, but much less stable, *compound* is obtained by the action of sodium hydroxide on 5-nitro-2-methylbenz-4′ : 5′-*iso*thiazolium bromide. 5-*Amino*-3-*phenylbenz*-4′ : 5′-iso*thiazole*, m. p. 131° (*hydrochloride*, m. p. 266°; *acetyl* derivative, m. p. 109—110°), prepared by reduction of the 5-nitro-compound, is diazotised in 50% sulphuric acid, forming a *diazonium sulphate*, m. p. 166° (decomp.; couples normally with R-salt and dimethylaniline), which when heated in acetic acid gives 5-*hydroxy*-3-*phenylbenz*-4′ : 5′-iso*thiazole*, m. p. 226° (decomp.; *acetate*, m. p. 100°; *methyl ether*, m. p. 80°), or in alcohol with copper powder gives 3-*phenylbenz*-4′ : 5′-iso*thiazole*, m. p. 71°. From the 5-hydroxy-compound are prepared the 4-*chloro*- (m. p. 206°; *acetate*, m. p. 81°), 4 : 6-*dichloro*- (m. p. 216°; *acetate*, m. p. 170°), 4-*bromo*- (m. p. 216°; *acetate*, m. p. 89°), 4 : 6-*dibromo*- (m. p. 201°; *acetate*, m. p. 162°), and 4-*nitro*- [m. p. 220° (decomp.); *acetate*, m. p. 159°] derivatives; no keto-halide is formed. Nitration of 5-acetamido-3-phenylbenz-4′ : 5′-*iso*thiazole gives the 4-*nitro*-derivative, m. p. 222°, and on hydrolysis the 4-*nitro*-5-*amino*-compound, m. p. 208°, which gives with diazobenzene a *diazoamino*-compound, m. p. 140—143°.

(XII.)

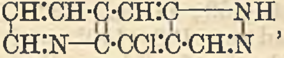


(XIII.)

Indazoles. [With H. Tampke.]—In the indazole series, linear quinolines, keto-chlorides, and *o*-quinones are obtainable, but the naphthoid character is not well marked. 5-Aminoindazole, m. p. 181° (von Auwers and Lange, A., 1922, i, 684; *acetyl* derivative, m. p. 165°), is best obtained as *sulphate* from the *zinc chloride* double salt, prepared by reduction of the nitro-compound in alcohol with zinc and hydrochloric acid. Methylation of 5-nitroindazole with methyl sulphate gives a mixture of 5-nitro-1-methylindazole, m. p. 129° (Noelting, A., 1904, i, 690), and 5-*nitro*-2-*methylindazole*, m. p. 163°, separable by extraction of the former with 20 parts of water at 90°. Both give the same *methiodide*, m. p. 203° (decomp.), and are reduced by ferrous sulphate and ammonia to the corresponding *amines*, m. p. 105° and 127°, respectively. Attempts to prepare 5-hydroxyindazoles by decomposition of diazotised 5-aminoindazole and -2-methylindazole give only azo-compounds, 5-*hydroxy*-4 : 5′-*azoindazole*, decomp. 290° (*triacetyl* derivative, m. p. 245°), and 5-*hydroxy*-2 : 2′-*dimethyl*-4 : 5′-*azoindazole*, m. p. 215° (decomp.; *acetyl* derivative, m. p. 206°). Isomeric 2-*chloro*-5-*nitrobenzophenonephenylhydrazones*, red crystals, m. p. 171°, and yellow crystals, m. p. 134°, separable by means of alcohol, are both converted by warm aqueous-alcoholic sodium hydroxide into 5-*nitro*-1 : 3-*diphenylindazole*, m. p. 181°, reducible by stannous chloride to the *amine*, m. p. 60—65° [*hydrochloride*, m. p. 312° (decomp.); *acetyl* derivative, m. p. 163°; stable *diazonium sulphate*, m. p. 165° (decomp.), coupling normally with R-salt, but giving no hydroxydiphenylindazole on decomposition]. Reduction with tin and hydrochloric acid gives 4-*chloro*-5-*amino*-1 : 3-*diphenylindazole*, m. p. 149° (*acetyl* derivative, m. p. 233—234°). 5-Amino-1 : 3-diphenylindazole is converted by chlorination into a keto-chloride, 4 : 4 : 6 : 7 : 7-*pentachloro*-5-*keto*-1 : 3-*diphenyl*-4 : 5 : 6 : 7-*tetrahydroindazole*, m. p. 159° (decomp.), which on reduction yields difficultly separable *di*- and *tri-chloro*-5-*hydroxy*-1 : 3-*diphenylindazoles*. 6-Aminoindazole (Witt, Noelting, and Grandmougin, A., 1893, i, 46) forms a triacetyl derivative, 6-*diacetylamino*-2-*acetylindazole*, m. p. 133° (*monoacetyl* derivative, m. p. 248°; *diacetyl*, m. p. 184—185°), and is converted by Skraup's reaction into 5 : 6-*pyrazoloquinoline*,

$$\begin{array}{l}CH{:}CH\cdot C\text{————}C\text{——}NH\\ CH{:}N-C\cdot CH{:}CH\cdot C\cdot CH{:}N\end{array}$$

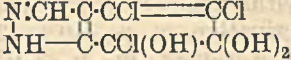
m. p. 278° (*methiodide*, m. p. 220°). 7-*Chloro*-6-*aminoindazole*, m. p. 179°, obtained in the form of its *acetyl* derivative, m. p. 215°, by chlorination of 6-acetamidoindazole, gives the linear 8-*chloro*-7 : 6-*pyrazoloquinoline*,



$$\begin{array}{l}CH{:}CH\cdot C\cdot CH{:}C\text{——}NH\\ CH{:}N-C\cdot CCl{:}C\cdot CH{:}N\end{array}$$

m. p. 228° (*hydrochloride*, m. p. 212°).

[With R. Weldert.]—6-Aminoindazole is converted by chlorination into a *keto-chloride*, not obtained pure, which when heated with dilute acetic acid yields 4 : 5 : 7-*trichloro*-7-*hydroxy*-6-*keto*-6 : 7-*dihydroindazole hydrate*,



$$\begin{array}{l}N{:}CH\cdot C\cdot CCl\text{====}CCl\\ NH\text{——}C\cdot CCl(OH)\cdot C(OH)_2\end{array}$$

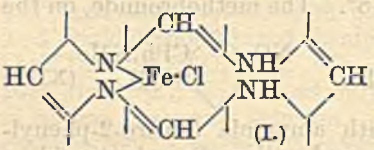
m. p. 155—160° (decomp.), hydrolysable to an *o*-quinone. Reduction of the keto-chloride gives 4 : 5 : 7-*trichloro*-6-*hydroxyindazole*, m. p. 220° [decomp.; *diacetyl* derivative, m. p. 172° (decomp.)], which is readily converted into the same *o*-quinone, 4 : 5-*dichloro*-6 : 7-*diketo*-6 : 7-*dihydroindazole*, exploding above 350°, and the corresponding *dihydroxy*-compound (*diacetate*, m. p. 243°). The *o*-quinone condenses with aniline to form 5-*chloro*-4-*phenylimino*-6-*hydroxy*-7-*keto*-4 : 7-*dihydroindazole*, m. p. above 500° (decomp.), which is hydrolysed by hydrochloric acid to give the 5-*chloro*-6-*hydroxy*-4 : 7-

quinone (*acetate*, m. p. 174°). This is oxidised by chlorine to 5 : 5-*dichloro*-4 : 6 : 7-*triketo*-4 : 5 : 6 : 7-*tetrahydroindazole*, m. p. 183° (decomp.), and further by nitric acid to the 4 : 5 : 6 : 7-*tetraketone*, m. p. above 300° (decomp.). The dichlorotriketone and the tetraketone condense with *o*-phenylenediamine, giving, respectively, the *compounds*, $C_{13}H_6ON_4Cl_2$ and $C_{19}H_{10}N_6$, both melting and decomposing above 300°. Treatment of the tetraketone with sodium carbonate solutions converts it into the 5 : 6-*dihydroxy*-4 : 7-*quinone*, m. p. 290° (decomp.), similar in properties to *iso*naphthazarin. Pyrazolone-4 : 5-dicarboxylic acid, m. p. 244°, results from the oxidation of 4 : 5-*dichloro*-6 : 7-*diketo*-6 : 7-*dihydroindazole* with bleaching-powder solution. C. Hollins.

Thiazole series. I. Action of hydrochloric acid on allylthiosemicarbazide. S. C. De (J. Indian Chem. Soc., 1927, **4**, 6—10).—δ-Allylthiosemicarbazide (I), when heated with hydrochloric acid in a sealed tube, yielded 2-*hydroxy*-5-*methylthiazole*, m. p. 200° (*acetyl* derivative, m. p. 242°; *benzoyl* derivative, m. p. 243°; *nitroso*-derivative, m. p. 138°). An unsuccessful attempt was made to prepare a thiazolehydrazine by hydrolysis of thiazoles similarly derived from α-substituted δ-allylthiosemicarbazides. The action of benzaldehyde on (I) gave α-*benzylidene*-δ-*allylthiosemicarbazide*, m. p. 125°, which, when treated as above, yielded 2-*benzylidenehydrazido*-5-*methylthiazole*, m. p. 141° (*acetyl* derivative, m. p. 119°; *benzoyl* derivative, m. p. 150°; *nitroso*-derivative, m. p. 120°), and this, on hydrolysis, gave the same hydroxymethylthiazole. From α-phenyl-δ-allylthiosemicarbazide was obtained 2-*phenylhydrazido*-5-*methylthiazole*, m. p. 94° (*acetyl* derivative, m. p. 190°; *benzoyl* derivative). Treatment of (I) with boiling phenylthiocarbimide yielded α-thiocarbanilido-δ-allylthiosemicarbazide, and this, when heated with hydrochloric acid, formed 2-*allylimino*-5-*thion*-1 : 3 : 4-*thiodiazole*, m. p. 136°. B. W. Anderson.

Action of carbamide on thiosemicarbazides: simultaneous formation of thiourazoles, aminoketothiodiazoles, endoxytriazole, and aminothioltriazoles. P. C. Guha and P. C. Sen (J. Indian Chem. Soc., 1927, **4**, 43—50; cf. A., 1922, i, 875).—Carbamide was heated at 130—140° with various δ-arylthiosemicarbazides for 5—6 hrs. Four types of compound were simultaneously formed in each case, the formation of which can be explained by assuming that both *syn*- and *anti*-forms of the δ-arylthiosemicarbazides take part in the reaction. Thus from δ-phenylthiosemicarbazide 4-phenylthiourazole (*dimethyl* derivative, m. p. 110°); 2-*anilino*-5-*thiol*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 210° (*methyl* derivative, m. p. 209°); 2 : 5-*endoxy*-1 : 3 : 4-*triazole*, m. p. 250° (*acetyl* derivative, m. p. 242°), and 5-*anilino*-2-*keto*-2 : 3-*dihydroxy*-1 : 3 : 4-*thiodiazole*, m. p. 246°, were obtained. Similarly, δ-(*p*-tolyl)thiosemicarbazide yielded 4-p-*tolylthiourazole*, m. p. 175° (*dimethyl* derivative, m. p. 142°); 2-p-*toluidino*-5-*thiol*-1-p-*tolyl*-1 : 3 : 4-*triazole*, m. p. 187° (*benzoyl* derivative, m. p. 100°; *methyl* derivative, m. p. 178°); endoxytriazole, and 5-p-*toluidino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 227°, and δ-xylylthiosemicarbazide yielded 4-*xylylthiourazole*, m. p. 195° (*disulphide*, m. p. 240°); 2-*xylylamino*-5-*thiol*-1-*xylyl*-1 : 3 : 4-*triazole*, m. p. 200°; endoxytriazole, and 5-*xylylamino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 218—219°. The endoxytriazole was also formed when carbamide reacted with thiosemicarbazide or semicarbazide. B. W. Anderson.

Catalytic hydrogenation of hæmin. R. Kuhn, L. Braun, C. Seyffert, and M. Furter (Ber., 1927, **60**, [*B*], 1151—1159).—Contrary to the observations of Fischer and Hahn (A., 1914, i, 887), hæmin adds only 1 mol. of hydrogen in sodium hydroxide solution in presence of palladised charcoal or platinum oxide; from this solution the product cannot be isolated, but if the operation is performed in a mixture of pyridine and chloroform, *dihydrohæmin*, $C_{34}H_{32}O_4N_4FeCl$, is obtained. The absorption spectra of hæmin and dihydrohæmin are very closely similar, but the substances are distinguished from one another by their catalytic activity and by the possession of 3 and 5 "active hydrogen atoms," respectively. The formation and properties of the new compound lend support to Küster's hæmin formula, and indicate the probable presence of the grouping (I). The observation that triphenylmethyl chloride does not evolve gas when treated with magnesium methyl halide deprives Fischer's supposition that the third "active hydrogen atom" of hæmin is actually the chlorine atom attached to iron of some of its support. The presence of 5, 3, 3, and 3 "active hydrogen atoms" in *meso*porphyrin dihydrochloride, *meso*porphyrin, the complex copper salt of *meso*porphyrin, and *meso*hæmin, respectively, appears to strengthen the view of Kunz and Kress that a FeCl group with univalent iron is present in hæmin.



(I.)

In aqueous-alkaline solution, the hydrogenation of hæmin at a platinum oxide or other contact cannot be caused to proceed beyond the dihydro-stage; in piperidine–chloroform, the strongly basic *perhydrohæmin* is formed, which gives the characteristic hæmin spectrum.

Ability of hæmin and its derivatives to effect the catalytic decomposition of hydrogen peroxide appears to be intimately connected with the chemical constitution of the molecule. The sequences of activity vary greatly with the experimental conditions. H. Wren.

Hæmochromogen and hæmoglobin. W. Küster (Ber., 1927, **60**, [*B*], 1139—1141).—Repetition of Clement's work has shown that the action of sodium hydroxide on hæmin in absence of air and reducing agents yields a sodium salt of hydroxyhæmin which does not give the hæmochromogen spectrum unless, as in Clement's experiments, hydrazine hydrate is added to its solution. It is therefore unnecessary to abandon the hypothesis (cf. A., 1926, 315) that hæmin has its radical nature masked because the unsaturated position is not localised.

Hæmatin is converted by hydrogen bromide in acetic acid into two *porphyrins*, $C_{34}H_{34}O_5N_4$ and $C_{34}H_{35}O_3N_4Br$; the latter substance is a monobasic acid containing one methoxyl group. H. Wren.

β-Pyridyl-α-pyrrolidine (nornicotine). M. Polonovski and M. Polonovski (Compt. rend., 1927, 184, 1333—1335; cf. A., 1926, 367).—*N-Acetylnornicotine*, $[\alpha]_D$ −13·6°, and N-*benzoylnornicotine*, prepared from the *N*-oxide of nicotine, give on hydrolysis, *nornicotine*, $[\alpha]_D$ −20° [*picrate*, m. p. 135° (*mono*- and *di-hydrochloride*), *chloroaurate*, m. p. 210—212° (decomp.), *nitroso*-derivative]. E. H. Sharples.

Vasicine—an alkaloid present in *Adhatoda vasica*. II. T. P. Ghose (J. Indian Chem. Soc., 1927, 4, 1—5).—Vasicine, when treated with phosphorus oxychloride and pentachloride, yields *chlorovasicine*, $C_{11}H_{11}N_2Cl$, m. p. 136—137°, which on reduction gives a *base*, $C_{11}H_{12}N_2,0{\cdot}5H_2O$, m. p. 87—88° (*hydrochloride*, m. p. 255—256°; *chloroplatinate*). Vasicine is oxidised by potassium permanganate to 4-hydroxyquinazoline, and yields *o*-aminobenzoic and acetic acids when fused with potassium hydroxide. Thus vasicine is probably either 2-propyl- or 2-*iso*propyl-4-hydroxyquinazoline. B. W. Anderson.

Microchemical reactions of codeine. M. Wagenaar (Pharm. Weekblad, 1927, 64, 671—676). —A summary of the optical properties of the alkaloid, and of its commoner reactions. S. I. Levy.

Microchemical detection of alkaloids. II. A. Heiduschka and N. I. Meisner (Arch. Pharm., 1927, 265, 455—461).—Tables are given showing the smallest quantities of caffeine, theobromine, strychnine, brucine, quinine, morphine, and codeine that can be detected by various reagents in simple aqueous solution and in a 2% aqueous solution of lactic acid. W. A. Silvester.

Identification of alkaloids. W. M. Cumming (Proc. Roy. Phil. Soc. Glasgow, 1927, 54, 26—31).—See A., 1925, i, 572.

Phosphino-magnesium compounds. A. Job and G. Dusollier (Compt. rend., 1927, 184, 1454—1456).—Phenylphosphine and magnesium ethyl bromide react in benzene–ethereal solution to give ethane in amount corresponding with the equation $PH_2Ph+2PhMgBr=PPh(MgBr)_2+2C_2H_6$. The greenish-brown solution probably contains dimagnesium phenylphosphine dibromide. Since it is decomposed by water, yielding phenylphosphine, and affords a white precipitate with carbon dioxide, probably of $PPh(CO_2MgBr)_2$, whilst with ethyl chloroformate in benzene it gives *ethyl phenylphosphinodicarboxylate*, $PPh(CO_2Et)_2$, b. p. 150—153°/4—5 mm. Similarly, diphenylphosphine affords *magnesium diphenylphosphine bromide*, $PPh_2{\cdot}MgBr$, yielding *ethyl diphenylphosphinocarboxylate*, b. p. 185—188°/5—6 mm. Phosphine and magnesium ethyl bromide afford a white powder in which two phosphine hydrogen atoms have apparently been replaced by magnesium bromide. Only one hydrogen atom in phenylphosphine could be replaced by zinc iodide when treated with zinc ethyl iodide (cf. Gal, A., 1883, 653). R. Brightman.

Organic compounds of arsenic. V. Electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid. K. Matsumiya and H. Nakata (Mem. Coll. Sci. Kyoto, 1927, 10, 199—210).—Electrolytic reduction (in an atmosphere of carbon dioxide) of 3-nitro-4-hydroxyphenylarsinic acid with a mercury cathode in presence of hydrochloric acid gives 3-amino-4-hydroxyphenylarsine hydrochloride or 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene hydrochloride (salvarsan), according as the hydrochloric acid is below or above 4·7*N*. The arsine is the sole product if the hydrochloric acid is replaced by sulphuric acid of varying concentration. The effects of different cathodes, current density, and temperature were studied; the results are tabulated. H. Burton.

Manufacture of asymmetrically acylated amino-derivatives of arylarseno-compounds. G. Newbery, and May & Baker, Ltd.—See B., 1927, 507.

Manufacture of asymmetrical aryl-arseno-compounds. G. Newbery, F. J. Paxon, and May & Baker, Ltd.—See B., 1927, 507.

Porphyrins. E. Mertens (Z. physiol. Chem., 1927, 167, 179—187).—The spectrochemical reaction with bromine (Schumm, A., 1926, 538) and the grating-spectrometer of Schumm (this vol., 437) are used to differentiate between the different porphyrins, spectra of the bromine compounds showing marked differences. Aqueous and alcoholic solutions of bromine give similar results, except in the case of mesoporphyrin, and this compound can be distinguished from all the other porphyrins investigated by this alcoholic bromine test. Eight preparations of Nencki's hæmatoporphyrin gave absorption bands practically identical with those previously recorded by Schumm (A., 1914, ii, 401). A. Wormall.

Isolation of some hitherto undescribed products of hydrolysis of proteins. IV. S. B. Schryver and H. W. Buston (Proc. Roy. Soc., 1927, B, 101, 519—527).—The diamino-nitrogen fraction of the amino-acids formed from gelatin by hydrolysis is increased if the gelatin is first treated with cold hydrochloric acid. This is entirely accounted for by an increase in the arginine and lysine and by the presence of *dl*-lysine. It is improbable that the *dl*-lysine arises from racemisation of the active lysine normally present (cf. A., 1926, 749, 1049). W. O. Kermack.

Mol.-wt. determinations of proteins in phenol. N. Troensegaard and J. Schmidt (Z. physiol. Chem., 1927, 167, 312—313).—A reply to the criticism by Cohn and Conant (A., 1926, 891) of a previous paper (A., 1924, i, 581). A. Wormall.

Analysis of proteins and the products of their degradation by adsorption. E. Waldschmidt-Leitz and A. Schäffner (Ber., 1927, 60, [*B*], 1147—1151).—The product is submitted to fractional adsorption, and comparative determinations of some analytical characteristic of it are made in the residual solutions. The constancy or inconstancy of the quotients from the data thus supplied (*e.g.*, nitrogen content, free amino-group content, or specific rotation) is a criterion of the homogeneous or heterogeneous nature of the product. The behaviour of clupeine, salmine, scombrine, and histone towards ferric hydroxide causes them to be regarded as homogeneous.

Tryptoclupeon in neutral or acid media is separated by ferric hydroxide into a more complex, readily adsorbed portion, the individuality of which is not established at a less complex, difficultly adsorbed portion which appears homogeneous as judged by the constancy of the specific rotation or the ratio N/NH_2 in the residual solutions. In alkaline solution tryptoclupeon behaves as an individual towards ferric hydroxide, since the basic properties of the components are too pronounced and too similar to permit separation under these conditions. H. Wren.

Volumetric determination of hexamethylenetetramine. (Mrs.) C. Kollo and B. N. Angelescu (Bul. Soc. Chim. România, 1926, 8, 17—20).—Hexamethylenetetramine (0·15—0·2 g.) is treated with an excess of 0·5N-picric acid solution, and after separation of the precipitated hexamethylenetetramine picrate, m. p. 157°, the excess of picric acid is determined by titration with standard sodium hydroxide solution. The method is accurate to ±0·3%, and can be used for the determination of small amounts of hexamethylenetetramine in wine. H. Burton.

Biochemistry.

Determination of respiratory quotient of small animals. L. G. Wesson (J. Biol. Chem., 1927, 73, 499—506).—An apparatus of the closed-circuit type is described, in which the air is circulated by a pump; the carbon dioxide is determined by absorption in standard sodium hydroxide solution, with subsequent titration; the oxygen used up is replaced from a graduated container, so as to maintain a constant pressure, and is thus determined volumetrically. C. R. Harington.

Blood as a physicochemical system. V. Composition and respiratory exchanges of normal human blood during work. A. V. Bock, D. B. Dill, L. M. Hurxthal, J. S. Lawrence, T. C. Coolidge, M. E. Dailey, and L. J. Henderson (J. Biol. Chem., 1927, 73, 749—766; cf. A., 1924, i, 780).—Tables, and a nomographic representation, are given of the changes occurring in normal human blood as the result of work sufficient to raise the oxygen consumption to seven times the basal value. By such work, the oxygen capacity was raised about 10%; there was a 10% increase in the concentration of serum-proteins and a slight increase in that of base; the lactic acid is increased, and the hydrogen carbonate, to a much less extent, decreased. C. R. Harington.

Colorimetric determination of oxygen saturation of blood. J. Holló and S. Weiss (Biochem. Z., 1927, 185, 373—378).—A colorimeter of the Duboscq type is so modified that a layer of hæmolysed blood 1 mm. thick can be matched against a 20 mm. layer of the same blood 20 times diluted and fully oxygenated or fully reduced plus a layer of similarly diluted blood fully reduced or fully oxygenated. The thickness of the last-mentioned layer, determined by experiment, indicates the proportion of hæmoglobin to oxyhæmoglobin, or *vice versa*, in the undiluted blood. The error of the method is about 5%. C. R. Harington.

Total carbon dioxide content of the blood of marine and of fresh-water invertebrates. M. Duval and P. Portier (Compt. rend., 1927, 184, 1594—1596).—The total carbon dioxide content of the blood of marine invertebrates ranges from 5 to 17 c.c. (at 0° and 760 mm.) per 100 c.c. of blood, that of fresh-water invertebrates from 21·5 to 62 c.c. These values do not, apparently, bear any relationship to the amount of carbon dioxide in the particular water in question. The corresponding value for the blood of terrestrial gastropods is from 45 to 60 c.c. Figures are given for typical crustaceans, gastropods, and cephalopods. G. A. C. Gough.

Regulation of [H˙] of the blood. I. Course of the potential of blood measured with the quinhydrone electrode. II. Influence of process of dissolution of quinhydrone on course of the potential. III. Potentials of serum, plasma, red blood-corpuscles, and hæmoglobin solutions. S. K. Liu (Biochem. Z., 1927, 185, 242—254, 255—262, 263—274).—I. The quinhydrone electrode indicates a slightly higher p_H for blood than does the hydrogen electrode. The potential of blood diluted with 3 vols. of water as observed by the quinhydrone method, using a platinum electrode, shows a sharp rise in the first minute, a constant level for 1—2 min., and thereafter a steady fall of about 1 millivolt per min.; the effect is exaggerated by insufficient mixing of the solution. A less marked variation is obtained by the use of a gold electrode.

II. The variation in potential observed with quinhydrone, owing to the slow process of dissolution of the substance, is largely suppressed by the presence of buffers; the more acid the solution the less the variation and the more easily it is suppressed; whole blood is a much more efficient buffer, in this respect, than a simple phosphate mixture or than urine.

III. Potential variations, of the type described above for diluted whole blood, are observed in an exaggerated form with diluted serum and plasma and, to a much less extent, with solutions of hæmoglobin and suspensions of red blood-corpuscles which are rich in buffer substances. In view of these results, the quinhydrone electrode is not adapted to the investigation of poorly-buffered tissue fluids. C. R. Harington.

Permeability of human red blood-corpuscles. A. M. Wakeman, A. J. Eisenman, and J. P. Peters (J. Biol. Chem., 1927, 73, 567—580).—After addition to human blood *in vitro* of various sodium and potassium salts in amounts of 29·1—100·4 milliequiv. of base per 1000 c.c. of blood-serum, the changes observed, as between red blood-corpuscles and serum, consisted entirely in a transfer of water, carbon dioxide, and chlorine across the cell membrane; no evidence could be obtained that the latter was permeable to the cations. C. R. Harington.

Determination of chlorine in organs and in blood. M. Delaville and D. Broun (Bull. Soc. Chim. biol., 1927, 9, 621—623).—The dried material is destroyed by fuming nitric acid in presence of silver nitrate at 100°. Small additions of potassium permanganate accelerate the decomposition, and the excess may be removed by means of oxalic acid. The silver chloride so obtained is purified by reprecipitation, dried, and weighed. E. A. Lunt.

Distribution of non-protein sulphur of the blood between serum and corpuscles. L. Reed and W. Denis (J. Biol. Chem., 1927, 73, 623—626).—In human blood, inorganic sulphates are present almost exclusively in the plasma, whilst in the dog, the ox, and the goat they are distributed more or less equally between plasma and corpuscles. Neutral sulphur, in all species investigated, is present for the most part in the corpuscles.

C. R. Harington.

Proteolytic enzymes in blood-serum. VIII. Possibility of fundamental unity of blood enzymes. M. von Falkenhausen (Biochem. Z., 1927, **185**, 334—343).—Galvialo's preparation (*ibid.*, **177**, 266) shows diastatic, lipolytic, and proteolytic activity in a non-specific alkaline medium; in the first two cases, the activity is somewhat enhanced by the presence of the electrolytes of saliva and of duodenal juice, respectively, but the proteolytic activity is greater in the alkaline medium than in presence of the electrolytes of gastric juice; moreover, by fractional heating the various enzymic activities are destroyed at different temperatures, so that it is improbable that they pertain to a single substance.

C. R. Harington.

Sugar content of capillary and venous blood after muscular activity. M. Dörle and W. Liehr (Biochem. Z., 1927, **185**, 365—372).—Moderate localised muscular activity raises the concentration of sugar in the capillary blood of the limb immediately concerned; activity carried to the point of fatigue reverses the effect, the venous blood-sugar in both cases being little affected. General moderate muscular activity raises the sugar content of both capillary and venous blood of relatively inactive parts; extreme general activity has the reverse effect on capillary blood-sugar and leaves venous blood-sugar unchanged. Variations in blood-sugar could not, in these experiments, be related to changes in lactic acid.

C. R. Harington.

Determination of blood-sugar by the method of Hagedorn and Jensen. L. Csik and A. Juhász (Biochem. Z., 1927, **185**, 420—422; cf. A., 1923, ii, 265, 440).—The blood is weighed in a special vessel on a torsion balance. C. R. Harington.

Micro-determination of sugar in blood. E. Martinson (Biochem. Z., 1927, **185**, 400—404).—The accuracy of the method of Hagedorn and Jensen (A., 1923, ii, 265, 440) depends on exactness of measurement of the potassium ferricyanide; by allowing 5 min. for drainage of the latter from the pipette before proceeding to the titration, the error of the method is reduced to 2%. C. R. Harington.

Ovomucoid. J. Needham (Biochem. J., 1927, **21**, 733—738).—The carbohydrate content of the ovomucoid molecule increases as the egg develops, only 7·4% calculated as dextrose being present on the 5th day, against 15·4% on the 18th day. The average figure is about 11·5%. An enzyme which hydrolyses ovomucoid appears to exist in the yolk and the yolk-sac of the hen's egg at the 5th day of development, possibly also in the white and the blastoderm, but not in the embryo. S. S. Zilva.

Application of the Copaux method for the determination of small amounts of phosphorus in tissues. (Mme.) H. Hinglais (Bull. Soc. Chim. biol., 1927, 9, 540—553).—The Copaux method of determining phosphorus by measuring the volume of a water–ether–phosphomolybdic acid complex can be adapted to give accurate results and has been applied successfully to plant-tissues. E. A. Lunt.

Determination of iron in muscle by means of titanium chloride. V. Henriquès and (Mme.) A. Roche (Bull. Soc. Chim. biol., 1927, 9, 527—539).—Experiments on the non-pigment iron content of muscle from the cat, dog, rabbit, rat, codfish, eel, lobster, frog, and mussel have failed to establish a constant value for any given species. The mean value for the lobster and mussel is sensibly the same as that of the rabbit. E. A. Lunt.

Adenylic acid and muscle function. I. Presence of adenylic acid in skeletal muscle. G. Embden and M. Zimmermann (Z. physiol. Chem., 1927, **167**, 137—140).—Appreciable quantities of this acid have been isolated from rabbit muscle. After recrystallisation from hot water, the dried substance had m. p. 195° (uncorr.). The physiological significance of this acid and its relationship with inosic acid are briefly discussed. A. Wormall.

Cystine content of hair and other epidermal tissues. R. H. Wilson and H. B. Lewis (J. Biol. Chem., 1927, **73**, 543—553).—The following values were obtained for the cystine content of various keratin-containing tissues, as determined by the colorimetric method of Folin and Looney (A., 1922, ii, 539); human hair 15·6—21·2%, sheep wool 8·0—10·9%, feathers 7·05—12·2%, rabbit hair 11·9—14·0%, tortoise shell 6·4—8·1%, rat hair 14·1%, cat hair 13·1%, dog hair 18·0%; human skin and connective tissue 1·82—2·34%. For the keratin of any given species the nitrogen : sulphur ratio is more constant than the actual content of nitrogen and sulphur. The figures given above are higher than those obtainable by the gravimetric method of determination, owing to the losses inherent in this method due to the solubility of cystine. No considerable amounts of non-cystine sulphur were detected, nor could any correlation be found between the cystine content of the hair and the age, sex, or colouring of the individual. C. R. Harington.

Presence of arginine in the spleen. W. S. Gulevitsch and S. J. Kaplanski (J. Russ. Phys. Chem. Soc., 1926, 58, 620—622; cf. Gulevitsch and Jochelson, A., 1901, ii, 29).—Fresh ox-spleen was rapidly extracted with water at 60°, to avoid autolysis of the proteins, and the extract treated in turn with phosphotungstic acid, silver nitrate, copper nitrate, bismuth iodide, and absolute alcohol, the solid in each case being removed and examined. No trace of arginine could be found, its detection by Gulevitsch and Jochelson (*loc. cit.*) being due to autolysis. The autolysis of spleen at the ordinary temperature is more rapid than that of tendon, liver, and spleen, being detectable after 3 hrs., as compared with 9 and 6 hrs. for the other organs. The chemical analysis of the spleen, consequently, should be carried out not later than 2 hrs. after the death of the animal.

M. Zvegintzov.

Compounds extracted from tendon. XXIV. Carnosine and carnitine as specific constituents. W. S. Gulevitsch (J. Russ. Phys. Chem. Soc., 1926, **58**, 610—619).—A review of the work of the author and others, and a description and discussion of the chemistry and physiology of carnosine and carnitine.

M. Zvegintzov.

Detection of iron in ashed sections of spinal cord. W. Keuscher (Mikrokosmos, 1927, 20, 126—127).

Chemical Abstracts.

Shell-depositions in oysters. J. H. Orton and C. Amirthalingam. **Composition of chalky deposits on the shells of *Ostrea edulis*.** H. O. Bull (J. Marine Biol. Assoc., 1927, **14**, 935—954).—The function of the chalky deposit is to fill in rapidly grooves and hollows which are inimical to efficient functioning in the changing needs of the individual.

The chalky deposits consist of a powder mainly crystalline in appearance under the microscope, and of the composition, $CaCO_3$, 78·5%; water and organic matter 19·2%; undetermined, 2·3%.

W. Robson.

Tubular sheath of *Spirographis Spallanzani*. S. Fränkel and C. Jellinek (Biochem. Z., 1927, **185**, 379—383).—After exhaustive digestion of the sheath secreted by *Spirographis Spallanzani*, first with pepsin and then with trypsin, there was obtained an insoluble residue which gave no protein reactions, except Millon's reaction. After purification by dissolving in ammonia and precipitation with acetic acid, the substance had the formula $C_{38}H_{68}O_{17}N_8S$; it had two acidic groups, one of which was a sulphonic acid group. Hydrolysis with hydrochloric acid and analysis of the products indicated the presence of two tyrosine groups and one arginine group in the molecule.

C. R. Harington.

***Limulus polyphemus*.** S. Fränkel and C. Jellinek (Biochem. Z., 1927, **185**, 384—388).—The carapace of *Limulus polyphemus* differs from that of typical crustaceans in containing no calcium carbonate, and in containing 70% of protein; the chitin obtained after removal of the protein has a higher content of carbon and hydrogen and a lower content of nitrogen than chitins which have been previously investigated.

C. R. Harington.

Edible Holothuria. S. Fränkel and C. Jellinek (Biochem. Z., 1927, **185**, 389—391).—Certain edible Holothuria were exhaustively digested first with pepsin and then with trypsin. More than 90% of the substance of the animals passed into solution under the action of the pepsin. Figures are given for the nitrogen distribution in the substance of the animals, determined by the method of Van Slyke.

C. R. Harington.

Reaction changes of human saliva. G. W. Clark and K. L. Carter (J. Biol. Chem., 1927, **73**, 391—404).—Whilst saliva obtained directly from the glands is only very slightly more acid than saliva freshly expectorated, resting saliva is markedly more acid than activated saliva obtained by chewing paraffin wax. The carbon dioxide content of saliva kept in an open vessel alters scarcely at all, owing, probably, to equilibrium between loss and production of carbon dioxide. Chloroform is without effect on the formation of carbon dioxide, and slightly inhibits that of ammonia; mercuric chloride strongly inhibits both processes; these processes are therefore regarded as being enzymic rather than bacterial in character.

C. R. Harington.

Constituents of sweat, urine, and blood. I. Chlorides. G. A. Talbert and C. O. Haugen. **II. Total nitrogen of sweat and urine; total non-protein nitrogen of blood.** G. A. Talbert, S. Silvers, and W. Johnson (Amer. J. Physiol., 1927, **81**, 74—80, 81—85).—I. There is some correlation of the concentration of chlorides in the sweat with that in the blood, but none with the chlorides in the urine.

II. The total nitrogen of the sweat is, in general, more than double the non-protein nitrogen of the blood, but there is no definite correlation between these quantities or between them and the total nitrogen of the urine.

R. K. Cannan.

Determination of bismuth in urine. H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou (Dansk Tidsskr. Farm., 1927, 1, 391—403).—Small amounts of bismuth present in urine (0·05—0·4 mg.) can be determined as follows: 100 c.c. of urine are mixed with 50 c.c. of 68% nitric acid and cautiously heated until the mass is almost dry. After cooling, 3 c.c. of sulphuric acid are added, and the mixture is evaporated until fumes are evolved; 1—2 c.c. of nitric acid are added, drop by drop, and the evaporation is continued: more nitric acid must be added if necessary, until the liquid is quite colourless after cooling. Finally, 10 c.c. of a saturated solution of oxalic acid are added, and the solution is evaporated until copious fumes appear, to ensure complete removal of nitric acid. The cooled liquid is diluted with hot water to 20 c.c., filtered, and 1 c.c. each of 10% potassium iodide, 15% sodium citrate, and 10% sodium sulphite solutions are added. The resultant yellow liquid is diluted to 25—50 c.c., and the tint matched in a colorimeter against a standard solution of bismuth; the solution must not be exposed to direct sunlight, nor kept for very long before comparison, or incorrect results will be obtained owing to liberation of iodine. Chlorides render the result low, but mercuric salts and the salts usually present in urine have no effect on the reaction; the presence of ferric salts leads to high results, but their effect can be counteracted by the addition of citric acid. Instead of employing a colorimeter, the light absorption of the solution for the blue line 4359 Å. may be measured, the absorption being compared with that produced by a similar solution of known bismuth content. The results are accurate to about 5%.

H. F. Harwood.

Chemistry of cancerous tissue. Enselme and (Mme.) Enselme (Compt. rend., 1927, 184, 1353—1354).—From a study of the amounts of lipoid and nucleic phosphorus in cancerous and normal tissue both before and after irradiation with ultra-violet light, the following conclusions are reached. In cancerous tissue there is a notable increase of nucleic phosphorus compared with that in the healthy organ; *e.g.*, in tumours of the breast, uterus, and thyroid the nucleic phosphorus (mg./100 g. of fresh tissue) varies from 28 to 30 and in the normal tissues of the same organs the amounts are 18, 13, and 21, respectively. Irradiation causes this excess to disappear, and the nucleic phosphorus content of the irradiated cancer is no larger than that of the normal tissue. On the other hand, lipoid phosphorus increases in the irradiated tumour at the same time as the proportion of fat, and thus under the influence of irradiation the tendency is for the nucleic constituents to be decreased and for the cancerous tissue to be transformed into fat. E. H. Sharples.

Nitroprusside reaction in normal tissues and tumours. E. L. Kennaway and I. Hieger (Biochem. J., 1927, 21, 751—759).—Analyses of normal tissues and of tumours in man and in the fowl show that tumours are not distinguished by any deficiency in glutathione. S. S. Zilva.

Chemical constitution of gallstones and bile in relation to cholelithiasis. A. A. F. Peel (Z. physiol. Chem., 1927, 167, 250—284).—A chemical analysis has been made of the whole stone, kernel, and cortex of the various types of gallstones and an analysis of the bladder bile, in an attempt to determine the chemical differences between the different groups of stones and between the different parts of these stones, and the extent to which these differences may be attributed to changes in the bile. The precipitation of cholesterol crystals cannot be explained simply by a rise in the cholesterol content of bladder bile. The three main groups of stone kernels—pure cholesterol stones, pure pigment stones, and cholesterol–pigment–chalk stones—are quite different chemically, whilst the stones of each group give more or less constant values. These differences in the different groups are attributed to different changes in the bile, and a transformation of any stone into one of a different type is regarded as improbable. That condition of bile, mainly a metabolic change such as an increase in the cholesterol content, which leads to the formation of a pure cholesterol stone is entirely different from that producing a cholesterol–pigment–chalk kernel. For the formation of a pure pigment stone, the presence of copper is necessary. Three other types of stones are mentioned, and single stones of two of these groups have been examined. The chemical analysis of the different stones supports the morphological classification of Aschoff.
A. Wormall.

Does diabetic blood-serum influence the permeability of cells to dextrose? E. Bissinger (Biochem. Z., 1927, 185, 229—237).—The uptake of dextrose by the surviving liver of the frog is largely suppressed by addition of diabetic (frog or human) blood-serum to the perfusion fluid; at the same time the amount of free dextrose in the liver is greater than can be accounted for by that taken up during the perfusion; it appears therefore that the effect of the diabetic serum is to slow down the process of diffusion of dextrose by increasing the concentration of the latter in the liver cells, rather than that it alters the permeability of the cell-wall (cf. Geiger and Loewi, Pflüger's Arch., 1923, 198, 633).
C. R. Harington.

Blood-sugar. II. Magnitude of non-dextrose fraction under various conditions. B. Sjollema (Biochem. Z., 1927, 185, 355—364; cf. this vol., 476).—Cows suffering from *post partum* paralysis, and excreting lactose in the urine, show an increase in the non-dextrose fraction of the blood-sugar; in ketosis a similar increase is observed, but is accompanied by a decrease in the dextrose. In glycolysis of ox-blood, the non-dextrose fraction is very little decreased, and in starvation in rabbits it is somewhat increased. In diabetic blood, it is of normal magnitude and it is not markedly affected by administration of insulin. Hexosemonophosphates are partly adsorbed by charcoal in presence of acetic acid, but not in presence of ether; compounds of this type may therefore form part of the non-dextrose fraction of the blood-sugar. The latter fraction is contained for the most part in the red blood-corpuscles.
C. R. Harington.

Inorganic salt content of blood and the acid–alkali equilibrium of blood in fever. I and II. M. Akiya (Proc. Imp. Acad. Tokyo, 1927, 3, 187—190).—Clinical data on the variation of the calcium, sodium, potassium, chlorine, and protein content of serum, the hæmoglobin and solid content of blood in typhus fever are compared with the corresponding data relating to the pyrexia following piqûre in dogs.
E. A. Lunt.

Chemical composition of the liver in experimental spirochætosis. J. Inada (Proc. Imp. Acad. Tokyo, 1927, 3, 175—176).—The influence of icterohæmorrhagic spirochætosis and of yellow fever on the water, solid matter, total and non-protein nitrogen, coagulable protein, glycogen, fat, and sodium chloride content of the liver of guinea-pigs has been investigated. E. A. Lunt.

Cerebrospinal fluid in nephritis. J. D. Lyttle and L. Rosenberg (Arch. Int. Med., 1927, 39, 808—816).—In chronic nephritis, the cerebrospinal fluid is usually clear, has a cell-count varying from 2 to 16 per mm.^{3} (the cells are all lymphocytes), has an increased non-protein nitrogen content (the ratio of the cerebrospinal non-protein nitrogen to the blood non-protein nitrogen, normally 46%, rises to 80% in presence of nitrogen retention), shows an unaltered chloride content, an increase in albumin and globulin, and an increased value for the ratio of the blood-sugar to the cerebrospinal sugar. In acute nephritis, the cerebrospinal fluid in absence of uræmic manifestations is normal; in their presence it shows a rise in protein content. E. A. Lunt.

Total sugar content of cerebrospinal fluid and the influence of syphilis. B. Glassmann, L. Zwilling, and M. Israilsohn (Z. physiol. Chem., 1927, 167, 245—249).—The total sugar values for

47 cases, obtained by the colorimetric method of Glassmann (A., 1926, 192), varied from 0·083 to 0·183%, with a mean value of 0·135%. In three cases of syphilis only were definitely high sugar values obtained. No relationship was found between the total sugar content and the results of the Wassermann and the mastic reactions or the lymphocyte count. The polysaccharide content of the fluid is 0·085% (as dextrose), but the protein-sugar of the normal fluid is very small. A. WORMALL.

Rickets in rats. I. Metabolism on diets high in calcium and low in phosphorus. II. Effect of adding phosphate to diet of rachitic rats. S. KARELITZ and A. T. SHOHL (J. Biol. Chem., 1927, **73**, 655—664, 665—677).—I. In young rats suffering from rickets as the result of a diet lacking vitamin-*D*, rich in calcium, but poor in phosphorus, the retention of calcium is 50% and that of phosphorus 20% of the normal.

II. Addition of phosphate to the diet of such rats, to bring the Ca : P ratio of the diet to 1 : 1, no other factors being altered, much improves the retention of calcium and phosphorus and causes healing of the rickets. C. R. HARINGTON.

Variation in relative weight and composition of the dog's heart in certain pathological conditions. P. JUNKERSDORF and S. HANISCH (Arch. exp. Path. Pharm., 1927, **123**, 231—251).—A *résumé* is given of published and hitherto unpublished results on the variation in relative weight, dry weight, glycogen and fat content of the dog's heart induced by various diets, total starvation, pancreatic and phloridzin diabetes, and administration of adrenaline, insulin, or choline. E. A. LUNT.

Influence of menstruation on the concentration of calcium in blood-plasma. H. SHARLIT, J. A. CORSCADEN, and W. G. LYLE (Arch. Int. Med., 1927, **39**, 780—786).—Observations made on three subjects over a period of 2½ months indicate a rise in the calcium content of the blood-plasma at the approach and onset of menstruation. E. A. LUNT.

Modifications of the urinary deposit after muscular exercise. M. G. CARPENTIER and M. M. BRIGAUDET (Bull. Soc. Chim. biol., 1927, **9**, 580—587).—Microscopical examination of the urinary deposit of four subjects before and after muscular exercise suggests that incipient albuminuria and hæmaturia may be detected by such a procedure.
E. A. LUNT.

Intermediate carbohydrate metabolism. II. Ketosis in phloridzin diabetes. III. Vital action of dextrose in phloridzin diabetes. M. WIERZUCHOWSKI (J. Biol. Chem., 1927, **73**, 417—444, 445—458).—II. After administration of 1—4 g. of dextrose per kg. body-weight to completely phloridzinised dogs, 81·5% was recovered as extra dextrose in the urine; a constant sparing effect on the nitrogen metabolism was observed, and, parallel with this, a decreased excretion of ketones, 1 g. of dextrose ingested accounting for 0·1 g. of acetone. The view is therefore supported that small amounts of ingested dextrose are oxidised in the phloridzinised animal. Administration of olive oil to a phloridzinised dog causes increased excretion of ketones, and injection of adrenaline produces coma.

III. In phloridzin diabetes, ingestion of dextrose has a twofold physiological action. By raising the blood-sugar it prevents or relieves the hypoglycæmic convulsions which otherwise ensue, and by its ketolytic action it relieves the symptoms of ketosis.
C. R. HARINGTON.

Lactic acid formation in muscle extract. H. A. DAVENPORT and M. COTONIO (J. Biol. Chem., 1927, **73**, 463—475).—Fresh extracts of muscle were incubated at 25° under various conditions and the changes observed in lactic acid, phosphate, free sugar, and total sugar, the latter being determined by acid hydrolysis. No marked changes were observed in untreated extracts or in extracts to which were added phosphate alone or phosphate with fluoride. When, however, glycogen was added, lactic acid formation increased (except in presence of fluoride), whilst phosphate and total sugar decreased; increases in the free sugar owing to the action of muscle amylase on the glycogen were observed. In all cases, the difference between the decrease of total sugar and the increase of lactic acid was approximately equivalent to the decrease of phosphate; the hypothesis of the intermediate participation of a hexosephosphate in the process of lactic acid formation is therefore supported. C. R. HARINGTON.

Succinic acid in muscle. II. Metabolic relationships of succinic, malic, and fumaric acids. D. M. NEEDHAM (Biochem. J., 1927, **21**, 739—750).—In minced muscle suspended in buffer solution and placed alternately under anaërobic and aërobic conditions, there is a rise in succinic acid when in nitrogen and a fall when in oxygen. The total amount of succinic, fumaric, and malic acids also rises in anaërobiosis and fall on oxygenation. The succinic acid produced in nitrogen is formed from some other source than reversibly from fumaric and malic acids, and it is oxidised in oxygen further than to the latter acids. The malic acid content is highest in the fresh muscle. It falls to practically zero in nitrogen, and on admission of oxygen it may rise very slightly. The total amount of the acids was determined by precipitating the silver salts and titrating the latter with potassium thiocyanate. After filtering off the silver thiocyanate, malic acid was determined polarimetrically in the filtrate as the molybdenum compound.
S. S. ZILVA.

Fate of sugar in the animal body. VI. Sugar oxidation and glycogen formation in normal and insulin-treated rats during absorption of lævulose. G. T. CORI and C. F. CORI (J. Biol. Chem., 1927, **73**, 555—566).—Rats which have been starved for 24 hrs. absorb and oxidise more lævulose than those which have been starved 48 hrs. After 24 hrs.' starvation, 81·2%, in normal rats, and 89·7%, in insulin-treated rats, of administered lævulose was accounted for by oxidation and glycogen storage, but the ratio of glycogen stored to lævulose oxidised was 1·16 in the normal and 0·3 in the insulin-treated animals. Insulin therefore increases the oxidation of lævulose.

In the case of the rats starved for 48 hrs., it was necessary to continue the observations for 6 hrs. instead of 4 hrs. in the normal animals, in order to account for all of the ingested lævulose; this was due to a lag in oxidation, since, under the influence of insulin, recovery of the ingested lævulose was complete in 4 hrs. C. R. Harington.

Renal threshold for dextrose. R. L. Mackay (Biochem. J., 1927, 21, 760—764).—A number of cases have been examined for blood-sugar at intervals before, during, and after anæsthesia. The first urine passed after recovery from the anæsthetic was also examined for sugar. The explanation of the results obtained in terms of the doctrine of the renal threshold (the concentration in the blood which has to be reached before a recognisable quantity of sugar appears in the urine) for sugar at about 0·180% is unsatisfactory. S. S. Zilva.

Influence of certain bile acids on fat metabolism. S. Ikoma (J. Biochem. [Japan], 1926, 6, 383—393).—Cholic acid, in a concentration of 0·5%, causes an acceleration of the hydrolysis of fat in the liver; the same concentration inhibits the hydrolysis of fat in other organs. Deoxycholic acid, however, which stimulates the hydrolysis of fat even in a concentration of 0·3%, causes inhibition in the liver. Chemical Abstracts.

Physiological significance of the ethylenic linkings in fatty acids. E. F. Terroine, R. Bonnet, G. Kopp, and J. Véchot (Bull. Soc. Chim. biol., 1927, 9, 605—620).—Determinations of the iodine value of the natural fats in various poikilothermous animals and in moulds grown at various temperatures have shown that when growth takes place at a comparatively low temperature the naturally synthesised fat is less saturated than that formed during growth at a comparatively high temperature. *Aspergillus niger* grows more rapidly on an unsaturated than on a saturated fat, and the formation of saturated fatty acids by bacilli and moulds entails a greater expenditure of energy than the formation of unsaturated fatty acids. E. A. Lunt.

Protein test for urea-formation function of the liver. P. Cohen and S. J. Levin (Arch. Int. Med., 1927, 39, 787—798).—A new test for liver function, based on the normal conversion by the liver of amino-acids into urea, is described. After a protein meal of 1 g. per kg. body-weight, the blood-urea increases normally from 50% to 70% above the fasting level in 4 hrs. In cases of liver injury this increase is much diminished. E. A. Lunt.

Indole derivatives in connexion with a diet deficient in tryptophan. R. W. Jackson (J. Biol. Chem., 1927, 73, 523—533).—Dietary deficiency of tryptophan could not be made good by administration of β-indolealdehyde or of *r*- or *l*-3-β-indolelactic acid; nor could tryptophan, absent from the diet, be replaced by tryptophan injected subcutaneously. C. R. Harington.

Nucleic phosphorus balance and relation to the course of growth. M. Javillier, H. Allaire, and (Mlle.) S. Rousseau (Compt. rend., 1927, 184, 1351—1353; cf. A., 1926, 969, 1268).—The relationships and significance of the lipoid and nucleic phosphorus during the early growth of white mice have been examined. Determinations have been carried out at intervals from birth to 40 days after. At birth, the animal is richer in nucleic phosphorus than in lipoid phosphorus. The nucleic phosphorus of the young animal (*i.e.*, the amount of phosphorus of nucleoproteins per 100 g. of living tissue) decreases very considerably during the period between birth and the end of lactation, and then after the 21st day it rises to a level which, however, is much below that of the lipoid phosphorus. The percentage of lipoid phosphorus rises quickly during the first week, then regularly during the period of lactation and even up to the 40th day (cf. Mayer and Schaeffer, Compt. rend., 1914, 159, 102). The proportion of "transitional phosphorus" (soluble inorganic phosphorus and organic phosphorus of the intermediate synthetic and degradation products) rises quickly after birth and then oscillates within narrow limits. The relationship nucleic phosphorus/lipoid phosphorus varies largely; from 1·14 at the beginning, it falls to 0·46. Nucleic phosphorus/total phosphorus falls from 0·14 to 0·07; lipoid phosphorus/total phosphorus rises from 0·12 to 0·19. Nucleic phosphorus/active phosphorus (nucleic+lipoid+transitional phosphorus) falls in 3 weeks from 0·40 to 0·20, whilst lipoid phosphorus/active phosphorus increases from 0·35 to 0·47. E. H. Sharples.

Fate of cholesterol in the animal organism. I. Lifschütz (Arch. Pharm., 1927, 265, 450—455).—A review of the literature, with particular reference to the author's own work. W. A. Silvester.

Cholesterol metabolism and the reticulo-endothelial system. F. Goebel and H. Gnoinski (Biochem. Z., 1927, 185, 414—419).—Blocking of the reticulo-endothelial system, or removal of a considerable part of it by splenectomy, causes a reduction in the cholesterol content of the blood; this system appears therefore to be actively concerned in the metabolism of cholesterol. C. R. Harington.

Decomposition of bile acids in the organism. F. Rosenthal, L. Wislicki, and H. Pommernelle (Arch. exp. Path. Pharm., 1927, 122, 159—183).—Decomposition of bile acids may take place on either side of the intestinal wall, that occurring in the alimentary tract being bacterial in nature and attacking the cholic acid complex of the coupled bile-acid, whilst the parenteral mechanism involves enzymes which split the bile acid at the linking with glycine or taurine. The patho-physiological significance of these conclusions is discussed. W. Robson.

Influence of heat and hydrogen-ion concentration on biological transportation systems containing sulphur. F. F. Nord (J. Physical Chem., 1927, 31, 867—876).—The oxygen-additive product which brings the reduced and oxidised forms of sulphur compounds into equilibrium can be prepared at p_H 7·4—3·8, but the solutions are much less active at the lower p_H values. After destruction of the additive product by heat, re-activation by oxygen is possible. Muscle, liver, and yeast suspensions

probably form no reversible systems with oxidised glutathione after they have been boiled.
L. S. Theobald.

Sulphur metabolism. C. P. Sherwin, G. J. Shiple, and A. R. Rose (J. Biol. Chem., 1927, **73**, 607—615).—Substitution of the hydrogen of the sulphydryl group of cysteine by the benzyl group, or conversion of cysteine (or cystine) into the phenylcarbamido-derivative or the phenylhydantoin, suppresses the normal physiological oxidation of these compounds to about the same extent, viz., 30—50%. The oxidation of cysteine is entirely suppressed when both sulphydryl and amino-groups are blocked in this way; it is concluded that both groups are open to attack in physiological oxidation. Diphenylacetylcystine is efficiently metabolised. The fact that, after administration of some of these compounds, the output of sulphur becomes greater than the intake, indicates a possible disturbing effect on the sulphur metabolism as a whole.
C. R. Harington.

Metabolism of sulphur. XII. Value of cystine peptides and peptide anhydrides for nutrition of the rat. G. T. Lewis and H. B. Lewis (J. Biol. Chem., 1927, **73**, 535—542).—A diet deficient in cystine could be made good for the requirements of growing rats by addition of diglycylcystine or of dialanylcystine, but not of dialanylcystine dianhydride; the failure with the last-named compound was, however, not due to failure of absorption, since traces only could be detected in the fæces.
C. R. Harington.

Effect of diminished atmospheric pressure on the liver. A. Loewy (Biochem. Z., 1927, **185**, 287—319).—The livers of animals (especially guinea-pigs) which have been exposed to low atmospheric pressures show a general chemical and histological similarity to those of animals poisoned with phosphorus.
C. R. Harington.

Effect of turnips and turnip-juice on the blood-sugar, phosphorus, and cholesterol of rabbits. A. A. Horvath (Amer. J. Physiol., 1927, **81**, 215—221).—Subcutaneous injection of turnip-juice into rabbits produced hyperglycæmia and a fall in inorganic phosphorus and cholesterol of the blood. The boiled juice produced hyperglycæmia and a rise in inorganic phosphates.
R. K. Cannan.

Chemical activity of the spleen. I. Relation to methæmoglobin in the blood. G. B. Ray and B. B. Stimson (Amer. J. Physiol., 1927, **81**, 62—73).—Small doses of nitrobenzene caused the appearance of methæmoglobin in the blood of dogs. By comparative studies on normal and splenectomised dogs it is concluded that the spleen plays some part in hindering the formation and hastening the removal of methæmoglobin, possibly by an active reducing action.
R. K. Cannan.

Relation of connective tissue content of meat to its nutritional value. H. H. Mitchell, J. R. Beadles, and J. H. Kruger (J. Biol. Chem., 1927, **73**, 767—774).—The biological value of the nitrogen of a sample of pork containing little connective tissue was 79, that of "crackling" was 25, and that of a 3 : 1 mixture of the two was 72; the last figure indicates that there must have been a supplementary action between the constituents of the two tissues. Pork tends to have a higher and more constant biological value than beef, since in the latter the content of connective tissue is both higher and more variable.
C. R. Harington.

Pentamethylenetetrazole ("cardiazole"). VI. Elimination of cardiazole by the kidneys. H. Leppert (Arch. exp. Path. Pharm., 1927, **122**, 362—365).—A method is described by which "cardiazole," added to urine, may be approximately quantitatively measured. Only a small proportion of the cardiazole injected subcutaneously appeared in the urine.
W. Robson.

Error of determination of toxicity. J. W. Trevan (Proc. Roy. Soc., 1927, **B**, **101**, 483—514).—The principles which govern the determination of toxicity and of physiological activity in general by means of animal experiments are discussed, and fresh experimental data are presented.
W. O. Kermack.

Influence of plankton on the phosphate content of stored sea-water. R. Gill.—See this vol., 747.

Relation of plankton to chemical and physical factors in the Clyde sea area. S. M. Marshall and A. P. Orr.—See this vol., 747.

Arginase. IV. Optimum p_H and purification of arginase by adsorption. S. Edlbacher and E. Simons (Z. physiol. Chem., 1927, **167**, 76—87; cf. Edlbacher and Röthler, A., 1925, i, 1505).—The optimum reaction is found to be p_H 9·0, in contrast to the value of p_H 7·34—7·51 given by Hino (this vol., 173). Purification is effected by the removal of impurities from a glycerol extract of calf-liver by alumina, adsorption of the enzyme on kaolin, elution by a solution containing glycine, sodium chloride, and sodium hydroxide at p_H 9·0, and precipitation by acetone. The preparation is at least thirty times as active as the original material, and gives only very feeble biuret and diazo-reactions. Arginase is not identical with either histidase or histozyme.
A. Wormall.

Influence of arsenic and antimony compounds on enzymic functions of the organism. IV. Cause of inhibitory influence of tartar emetic on salivary amylase. J. A. Smorodincev and E. A. Iljin (Biochem. Z., 1927, **185**, 328—333).—In well-buffered solutions, tartar emetic has no effect on salivary amylase; the previously observed inhibitory action was due solely to its effect in increasing the acidity of the solution.
C. R. Harington.

Regeneration of invertase from certain carriers. A. Fodor and C. Epstein (Z. physiol. Chem., 1927, **167**, 1—16; cf. Fodor and Schoenfeld, this vol., 76).—The enzyme is considered as composed of two parts, the "zymohaptic" substance and the non-specific and interchangeable carrier. A macerate of air-dried top yeast loses part of its activity on treatment with dilute sulphuric acid, but if kept at the ordinary temperature for 24 hrs., the neutralised solution regains part of its activity. The activity of the untreated macerate does not alter under these conditions. The addition of lævulose to the macerate does not affect the results in either case. With an invertase preparation from autolysed yeast the results are in striking contrast. No regeneration of the enzyme occurs with either the untreated or acid-treated solutions, with or without the addition of lævulose; indeed, in the absence of lævulose, the acid-treated invertase preparation, after neutralisation, undergoes a definite weakening on keeping. The invertase present in the macerate is principally bound to its natural carriers (zymostable form), but in the preparation of the enzyme from autolysed yeast these carriers are destroyed and the enzyme is bound to secondary carriers (zymolabile form). In the former case, after inactivation of part of the enzyme by acid, there is a regeneration of active enzyme from the enzymic or zymohaptic component of the zymostable form and secondary carriers; no regeneration can take place with the invertase preparation, since practically all the enzyme is attached to secondary carriers. A. Wormall.

Catalase. II. H. von Euler and K. Josephson (Annalen, 1927, **455**, 1—16).—The effect of varying concentrations of hydrocyanic acid and of substrate (hydrogen peroxide) on the activity of liver catalase has been studied, the highly reactive specimens previously obtained (this vol., 376) being employed. The poisoning action of the hydrogen cyanide is greater the greater its concentration (a concentration of $5\times10^{-5}N$ reduces the catalase activity to 2%), but, whilst in the absence of hydrogen cyanide the unimolecular reaction constant (k) decreases continuously throughout the reaction, in presence of hydrogen cyanide it increases at first and then diminishes, owing to the destruction of the enzyme by the hydrogen peroxide, which is greater than the reactivation due to the destruction of the hydrogen cyanide. In presence of hydrogen cyanide concentrations of 2 and $5\times10^{-6}N$ and with varying concentrations of hydrogen peroxide (below $0{\cdot}02N$), the value of k extrapolated to zero time is lowered by the hydrogen cyanide independently of the substrate concentration, but the increase in k in presence of hydrogen cyanide is more rapid at higher than at lower concentrations of hydrogen peroxide. By means of these extrapolated values of k, activity–substrate curves are plotted for varying concentrations of substrate, and from these the affinity constant of the system catalase–substrate, $k_M=40$, is deduced (cf. Hennichs, A., 1926, 756, who found $k_M=22$). The poisoning action of hydrogen cyanide is independent of the amount of iron in the catalase preparation, the activity of the authors' specimen (C.F. 31,000) being reduced to one half by the presence of 1700 mols. of hydrogen cyanide/1 mol. iron (cf. Kuhn and Braun, A., 1926, 1215, who found the ratio 1500/1 for hæmin). Small concentrations of manganese chloride solution ($10^{-7}N$) have no activating effect on catalase, but higher concentrations have a slight poisoning action. J. W. Baker.

Possibility of transformation of one enzymic activity into another according to experimental conditions. M. J. Gramenitzki (Biochem. Z., 1927, **185**, 433—437).—The guaiacum reaction for the detection of blood fails if the proportion of blood be high in relation to the hydrogen peroxide. The apparent predominance of catalase action under these conditions is explained not on the ground that blood can normally act as catalase and as peroxidase, but that the normal peroxidase action, which is responsible for the guaiacum reaction, is masked in presence of high concentrations of hæmoglobin by the tendency of the active oxygen to be converted into molecular oxygen.

C. R. Harington.

Inhibition of liver esterase by esters of keto-acids. R. Willstätter, R. Kuhn, O. Lind, and F. Memmen (Z. physiol. Chem., 1927, **167**, 303—309).—In the action of liver esterase (cf. Willstätter and Memmen, A., 1924, i, 1145) on ethyl mandelate there is a distinct latent period, and this period is directly proportional to the concentration of the ester and inversely proportional to the amount of enzyme added. The delay in the hydrolysis is due to the presence in the substrate of ethyl phenylglyoxylate, and when the mandelic ester is recrystallised from light petroleum, the latent period disappears completely. The inhibitory effect is attributed to the great affinity of the enzyme for phenylglyoxylic ester and the very slow rate of decomposition of the product formed. Ethyl oxalacetate and benzoylacetate give marked latent periods, but ethyl pyruvate does not, presumably because it is very readily hydrolysed even in the absence of the enzyme.

A. Wormall.

Action of oxidoreductase on glyceraldehyde. A. N. Lebedev (J. Russ. Phys. Chem. Soc., 1926, **58**, 712—725).—Mixtures of glyceraldehyde, enzyme, water, and methylene-blue were heated at various temperatures, and the time taken for the change of colour of the dye was noted.

In all cases when oxidoreductase was present, the methylene-blue was reduced, and a solution, giving the reactions of a hydroxy-acid, obtained, thus indicating the probable presence of glyceric acid. The oxidoreductase had no action on methylglyoxal or dihydroxyacetone, but readily oxidised crotonaldehyde. M. Zvegintzov.

Liver hexose-redoxase [mutase]. H. von Euler, R. Nilsson, and D. Runehjelm (Z. physiol. Chem., 1927, **167**, 221—235).—Rat liver contains large amounts of the carbohydrate redoxase (mutase) which decolorises methylene-blue, and this reduction is accelerated by co-zymase, especially if hexosediphosphate is added as well. Preliminary attempts at purification by adsorption, dialysis, and precipitation of the proteins with acetic acid are described.

A. Wormall.

Isoelectric precipitation of pepsin. F. Fenger and R. H. Andrew (J. Biol. Chem., 1927, **73**, 371—377).—Pig's gastric mucous membrane is extracted with 50% acetone at p_H 3·5; the filtered extract is treated further with acetone to make 75% concentration of the latter; the resulting precipitate, containing the pepsin, is dissolved in dilute hydrochloric acid and the solution dialysed against water. The first and most active pepsin-containing precipitate separates at p_H 2·4—2·5; slightly less active, but more constant, preparations are obtained at p_H 2·5—

3·0 and 3·0—3·85. The above described process of extraction is carried out at 0°.

C. R. Harington.

Peptidases. V. Specific action of yeast and intestinal peptidases. H. von Euler and K. Josephson (Ber., 1927, **60**, [*B*], 1341—1349; cf. this vol., 175).—Characteristic differences are not observed in the action of yeast and intestinal peptidases towards glycylglycine, benzoylglycylglycine, or the biuret base, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$. Benzoylglycylglycine does not suffer fission under the influence of yeast erepsin, whereas the biuret base is smoothly hydrolysed. Restriction of the action of yeast peptidase by glycine and alanine is of the same order of magnitude and similarly dependent on the acidity of the medium as that of intestinal peptidase. The experiments do not support the views of Waldschmidt-Leitz, Grassmann, and Schäffner (this vol., 345) of the subdivision of peptidases into amino- and carboxy-peptidases.

H. Wren.

Proteolytic enzymes of the spleen. E. Waldschmidt-Leitz and W. Deutsch (Z. physiol. Chem., 1927, **167**, 285—302).—The p_H-activity curve for the action of spleen extracts on gelatin shows two optima, one at p_H 4·0 and another at p_H 8·0. These optima are not due to the presence of two proteases (α-protease and β-protease), but are those of a protease, which acts on proteins only and not on simple peptides, and a peptidase (erepsin), respectively. The most active enzyme extract is obtained by extracting the spleen with a glycerol solution containing a small amount of acetic acid. Separation of the enzyme by adsorption methods is described, and it is observed that neither isolated enzyme has any measurable action on proteins (gelatin) in an alkaline solution.

A. Wormall.

Plant proteases. VIII. Adsorption and separation of yeast proteases. W. Grassmann and W. Haag. **IX. Dipeptidase and polypeptidase of yeast.** W. Grassmann (Z. physiol. Chem., 1927, **167**, 188—201, 202—220).—VIII. The adsorption of the two proteases of yeast by alumina (Willstätter and Grassmann, A., 1926, 759) has been investigated further to determine the conditions which yield the best separation. Maximum adsorption of the yeast trypsin is effected in slightly acid solution from the diluted yeast autolysate, and the enzyme is obtained in the purest state from the alumina by elution with diammonium hydrogen phosphate, adsorption again on alumina from slightly acid solution, followed by elution with dilute ammonia. By modifying the separation, a yield of from 30% to 70% of the "yeast dipeptidase," free from tryptic activity, can be obtained.

IX. The dipeptidase hydrolyses all the dipeptides tested, but has no action on various natural proteins, three tripeptides, and one tetrapeptide. In this respect, it differs from intestinal and pancreatic erepsins, which hydrolyse tripeptides and even more complex peptides. The hydrolysis of tri- and tetrapeptides by autolysed yeast is due to the presence of "polypeptidase" (yeast trypsin), which hydrolyses all the natural proteins, but has no action on dipeptides, and this enzyme appears to remove dipeptide molecules from the peptide chain. The optimum reaction for the polypeptidase is p_H 6·7—7·0, and that for the dipeptidase p_H 7·8.

A. Wormall.

Phytase of malt. H. Lüers and K. Silbereisen (Woch. Brau., 1927, 44, 263—268).—Phytase possesses a sharp temperature optimum at 48° and an optimum p_H at 5·2—5·3, the activity at p_H 4 and 6 being only one half that at the optimum. The anions used in the buffering mixtures play only a secondary rôle, whilst the enzyme is just as active in an arsenate buffer as in one containing acetate or citrate. The preparations of phytase and phytin are described.

W. Robson.

Synthesis of proteins by *Saccharomyces*. J. Effront (Compt. rend., 1927, **184**, 1302—1304).—From a quantitative examination of the products of fermentation of dextrose by yeast in presence of ammonium sulphate it is shown that, under anaërobic conditions, the course of the synthesis of the protein of yeast closely approaches the formula $2nC_6H_{12}O_6+4nNH_3=(C_{12}H_{20}O_4N_4)_n+8nH_2O$. Probably hydrated pyruvaldehyde is first produced, and this with ammonia forms alanine, which, by condensation, forms substances having the nature of polypeptides. With strong aëration, it is concluded that the sugar is first transformed to acetaldehyde, and that the reaction is (1) $3C_6H_{12}O_6+3O_2=6CH_3{\cdot}CHO+6CO_2+6H_2O$; (2) $6CH_3{\cdot}CHO+3N=C_{12}H_{20}O_4N_3+2H_2O$. The presence of traces of acetaldehyde was established, the amount being greatly increased by changing the p_H value or with insufficient aëration. No alcohol was formed, but a quantity of the dextrose was completely oxidised, and the yield of carbon dioxide was much larger than that formed under anaërobic conditions.

E. H. Sharples.

Formation and decomposition of hexosediphosphoric acid in alcoholic fermentation. H. von Euler and K. Myrbäck (Z. physiol. Chem., 1927, **167**, 236—244).—Sodium hexosemonophosphate (Robison, A., 1923, i, 86) is fermented by dried bottom yeast-H and also by top yeast, but the fermentation curves show important differences. With the former, the velocity falls suddenly when half the total carbon dioxide evolution has occurred; this corresponds with the disappearance of all the hexosemonophosphate, half being fermented and the other half converted into the diphosphate. With top yeast, the curve is symmetrical and smooth, and indicates that although top yeast accumulates hexosediphosphoric acid more slowly, this compound is decomposed almost as fast as it is formed. Co-zymase is necessary for the fermentation of hexosediphosphoric acid by yeast, as it is in the case of muscle (Meyerhof, this vol., 75). Purified hexosediphosphate is fermented by yeast only when co-zymase is present, and the earlier contrary results (Euler, Nilsson, and Jansson, this vol., 697) are possibly due to the presence of co-zymase in the impure hexosediphosphoric acid used.

A. Wormall.

Products formed by *Bacterium pruni* in milk. S. L. Jodidi (J. Amer. Chem. Soc., 1927, 49, 1556—1558).—The crystalline deposit obtained when *B. pruni* is grown in skimmed milk contains tyrosine, leucine, and myristic, palmitic, and stearic acids, together with the calcium salts of these acids.

F. G. Willson.

Bactericidal action of *X*-rays. J. J. Trillat (Ann. Inst. Pasteur, 1927, 41, 583—606).—The bactericidal action of *X*-rays on *B. prodigiosus* becomes more marked as the wave-length increases, and is much increased by secondary rays, particularly from metals of high atomic weight. This secondary effect is apparently due to the bombardment of the culture by electrons liberated from the metal.

W. O. Kermack.

p_H of the blood and the response of the vascular system to adrenaline. G. E. Burget and M. B. Visscher (Amer. J. Physiol., 1927, 81, 113—123).—The adrenaline response of the vascular system of the pithed cat can be made to vary at any time by varying the p_H of the blood. From p_H 6·9—8·0 the response progressively increases. The thyroid plays no part in this reaction, which may be due to increased sensitivity of the sympathetic nervous system or to the increased alkalinity causing more rapid and complete oxidation of the adrenaline. R. K. Cannan.

Adrenaline in water and salt metabolism. S. Éderer (Arch. exp. Path. Pharm., 1927, 122, 211—218).—The hypochloruric oliguria with the transfer of salt and generally also of water from the blood to the tissues illustrates the typical adrenaline reaction. Salt transfer occurs especially in those cases where the chlorine tension between the blood and tissues is high on account of changed physico-chemical ratios, which hinder the normal equalisation of the salt between the blood and tissue.

W. Robson.

Diabetes and action of insulin. IX. Appearance in the blood after pancreatectomy of the substance antagonistic to insulin. H. Häusler and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 56—62).—The blood of a dog after pancreatectomy contains a substance which inhibits the uptake from the plasma of dextrose by human blood-corpuscles. This substance, which is dialysable and can be extracted by alcohol, is similar to that which appears in the blood of human diabetics and of adrenalinised animals. W. O. Kermack.

Diabetes and action of insulin. X. Glycæmin, the hormone antagonistic to insulin. Its importance in the mechanism of diabetes. S. Dietrich, H. Häusler, and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 63—71).—The substance antagonistic to insulin which can be extracted by dialysis and treatment with alcohol from the plasma of dogs after pancreatectomy or treatment with adrenaline causes increased glycogenolysis when added to the fluid perfusing an isolated liver. This substance, which it is proposed to call glycæmin, is considered to be of importance in effecting the increase in blood-sugar concentration which occurs in human diabetes.

W. O. Kermack.

Hormone activity after administration of dextrose. I. Secretion of insulin after subcutaneous administration of dextrose. II. Insulin and glycæmin secretion after oral administration of dextrose. III. Fasting animals. H. Häusler and O. Loewi (Arch. exp. Path. Pharm., 1927, 123, 72—87, 88—119, 120—128).—I. A method has been devised for the determination of insulin in blood based on the observation that a larger amount of dextrose is taken up by red blood-corpuscles in presence of insulin than in its absence. The quantity of insulin present in the blood increases after the subcutaneous administration of dextrose. After vagotomy, administration of atropine, or pancreatectomy, subcutaneous injection of dextrose is not followed by an increase of insulin in the blood.

II. After oral administration of dextrose, the largest quantity of insulin is found in the plasma after 3 hrs. In the case of plasma taken from animals after vagotomy or treatment with atropine, administration of dextrose actually results in a decrease in the amount of sugar taken up by red blood-corpuscles. This inhibiting action is due to glycæmin, a substance which can be dialysed and recovered from the dialysate. The dialysed plasma has no inhibiting action. The dialysate when precipitated by alcohol and injected into the animal organism causes hyperglycæmia to develop. Plasma taken from normal animals after administration of dextrose has a greater effect in increasing the uptake of dextrose by the corpuscles after dialysis than it has before dialysis.

III. The methods elaborated in the two preceding papers are applied to elucidate the cause of the abnormal hyperglycæmia which ensues when dextrose is administered to a fasting animal. It appears that this abnormal hyperglycæmia is due not to an excessive glycæmin secretion, but to defective secretion of insulin. W. O. Kermack.

Effect of insulin on respiratory exchange of fed and fasting rabbits. I. L. Chaikoff and J. J. R. Macleod (J. Biol. Chem., 1927, 73, 725—747).—Rabbits were fed on a diet rich in carbohydrates until their respiratory quotient reached unity; administration of insulin to such animals caused no change in oxygen consumption or in respiratory quotient; insulin administered to the same rabbits after starvation caused a rise in oxygen consumption and in respiratory quotient, indicating that a little less than 10% more of the total energy production was being derived from oxidation of carbohydrate. In the first set of experiments, since the unchanged oxygen consumption and respiratory quotient indicated the absence of increased oxidation of dextrose, or formation of dextrose from other substances, and since, in view of the previous dieting, the glycogen stores of the body were probably full, the results favour the hypothesis of the conversion of dextrose into an unknown intermediate product under the action of insulin. The reasons for the discrepancy between this conclusion and that reached by Burn and Dale (J. Physiol., 1924, 59, 164) and Best and others (A., 1926, 870) are discussed.

C. R. Harington.

Blood- and insulin-sulphur eliminated by hydrogen and its behaviour on treatment with hydrogen cyanide and cyanamide. J. Kühnau (Arch. exp. Path. Pharm., 1927, 123, 24—49).—When hydrogen is passed through blood, hydrogen sulphide is liberated apparently from some non-protein substance contained in the red blood-corpuscles. The liberation of hydrogen sulphide from blood is increased by hydrogen cyanide and malononitrile, but is inhibited by cyanamide. Hydrogen does not liberate hydrogen sulphide from cysteine, but the quantity of hydrogen sulphide formed from a solution of cystine is increased by potassium cyanide and decreased by cyanamide. Hydrogen sulphide is also liberated from a solution of insulin by a current of hydrogen, but in this case both potassium cyanide and cyanamide are without action. W. O. Kermack.

Effect on normal calves of administration of parathyroid extract. C. S. Robinson, C. F. Huffman, and K. L. Burt (J. Biol. Chem., 1927, **73**, 477—482).—Calves are less sensitive than dogs to the effects of parathyroid extract. Injection of large doses, however, caused an increase of the blood-calcium to 18 mg. per 100 c.c., a decrease in the blood-phosphorus, and an increase in the urinary excretion of calcium and phosphorus; the fæcal excretion of these elements was little affected. Persistent over-dosage caused drowsiness and swelling, with eventual death of the animals.

C. R. Harington.

Effect of pituitrin administration on carbohydrate metabolism. H. M. Hines, C. E. Leese, and J. D. Boyd (Amer. J. Physiol., 1927, **81**, 27—35).—Continuous intravenous injection of pituitrin along with dextrose led to a greater degree of hyperglycæmia and glycosuria than when dextrose was injected alone. There were no differences in extra-heat production or respiratory quotient. This diminished retention of carbohydrate under the influence of pituitrin is not explained by a direct action on the kidney or by changes in the acid–base equilibrium of the blood, and may be due to altered capillary circulation. R. K. Cannan.

Vitamin-*A* content of skimmed milk. J. B. Platon (Biochem. Z., 1927, **185**, 238—241).—The greatest amount that could be consumed (20 g. per diem) of skimmed milk was insufficient to supply the vitamin-*A* requirements of young rats; 1·75—2·0 g. per diem of the whole milk was sufficient for this purpose. C. R. Harington.

Antirachitic and calcifying properties of dried summer and winter milk, irradiated and non-irradiated. G. C. Supplee and O. D. Dow (J. Biol. Chem., 1927, **73**, 617—622).—Dried summer milk had greater antirachitic activity than dried winter milk; on irradiation, both products became more active, but the proportional increase of activity was greater in the case of the winter milk, so that both irradiated products exhibited approximately the same degree of antirachitic activity.

C. R. Harington.

Relationship between antirachitic activity and the dielectric constant of irradiated cholesterol solutions. P. Ellinger (Arch. exp. Path. Pharm., 1927, **122**, 238—246).—A method and an apparatus are described by which changes in the dielectric constants of liquids during irradiation with ultra-violet light may be followed. Oils and solutions of cholesterol in alcohol and paraffin on such irradiation show a rise in their dielectric constants. This rise does not take place if the irradiation is conducted in the absence of oxygen; the formation of the antirachitic factor, on the other hand, takes place in the absence of oxygen. The processes are accordingly independent of one another. The rise of the dielectric constant produced by ultra-violet irradiation may probably be traced to the formation of an oxidation product of cholesterol. W. Robson.

Influence of intense *X*-ray and γ-ray radiation on cholesterol. M. C. Reinhard and K. W. Buchwald (J. Biol. Chem., 1927, **73**, 383—388).—Irradiation of cholesterol, in solution in chloroform or alcohol with *X*-rays or γ-rays causes a shift in the ultra-violet absorption curve towards longer wavelengths. The change in optical rotatory power was slight. Pure cholesterol could not be recovered on evaporation of the irradiated solutions.

C. R. Harington.

Vitamin-*D* content of the stomach oil of the Australasian petrel (*Aestralata lessoni*). J. L. Leigh-Clare (Biochem. J., 1927, **21**, 725—727).—The presence of vitamin-*D* in amount equal to about one fifth of that present in a good cod-liver oil has been demonstrated in the oil. S. S. Zilva.

Synthesis of the antineuritic factor (torulin) by yeast. F. Hawking (Biochem. J., 1927, **21**, 728—732).—*Saccharomyces cerevisiæ* can synthesise the curative factor (torulin) for pigeons in small amounts. S. S. Zilva.

Evolution of *B*-avitaminosis in its relation with the constitution of the carbohydrates of the diet. L. Randoin and R. Lecoq (Compt. rend., 1927, **184**, 1347—1349; cf. A., 1925, i, 751).—Eleven separate diets (deficient in vitamin-*B*) having the same percentage composition, but each containing a different carbohydrate, were administered to eleven groups of pigeons. From the observations of their behaviour, together with the results of Cori (A., 1926, 429, 1271) and Reinhold and Karr (this vol., 480), the following conclusions are reached. The slower or more feeble the intestinal absorption of a given sugar [potato-starch, lactose (?)] or the greater its ability to be converted into glycogen the slower is the development of avitaminosis-*B*; conversely, the quicker the absorption (galactose, dextrose) and the smaller the ability to be transformed into glycogen (galactose) or the greater the tendency to produce hyperglycæmia (galactose, maltose), the more rapidly it produces death in complete absence of vitamin-*B*.

E. H. Sharples.

Existence of two active factors in vitamin-*B* complex. W. D. Salmon (J. Biol. Chem., 1927, **73**, 483—497).—The seeds of the velvet and soya beans have a greater protective action against neuritis or beri-beri but a less marked growth-promoting action than the leaves, for animals on a diet deficient in vitamin-*B*; on treatment of an extract of these materials with fuller's earth, the precipitate obtained was antineuritic, whilst the residue in the filtrate, which, alone, had very little physiological action, acquired growth-promoting properties when added to the precipitate. It therefore appears that vitamin-*B* is a complex of at least two active substances. C. R. Harington.

Effect of desiccation on the nutritive properties of egg-white. M. A. Boas (Biochem. J., 1927, 21, 712—724).—A diet of crude egg-white, boiled and supplemented with wheat-starch, cotton-seed oil, cod-liver oil, lemon juice, marmite, salts, and water, supports young rats in growth and health. If the egg-white is previously dried, the diet is inadequate, unless the carbohydrate is supplied in the form of potato-starch or arrowroot, or unless certain substances are added in small amounts. The condition which is developed by rats fed on this unsatisfactory diet is described in detail. The change which takes place in the dried egg-white is independent of the reaction of the solution during drying, is not due to a thermolabile enzyme, and does not appear to be a process of oxidation. Egg-white previously coagulated by boiling is not damaged by desiccation. The crude proteins of horse-serum and milk do not suffer a similar change during desiccation. The foodstuffs which possess the power of counteracting the ill effects resulting from ingesting the dried egg-white are raw potato, potato-starch, arrowroot, dried yeast, fresh egg-white, egg-yolk, milk, commercial caseinogen, crude lactalbumin, spinach and cabbage leaves, banana, and dried horse-serum. The presence of a protective factor *X* in these substances is postulated. The factor shows a similar distribution in many ways to that of the water-soluble *B*-vitamins, but is not, however, identical with either the antineuritic factor or Goldberger's pellagra-preventive vitamin. Its resistance towards heat and desiccation varies according to the substance in which it is found. There are indications that rats can store reserves of the protective factor *X*. S. S. Zilva.

Formation of fat from carbohydrate by the rat under abnormal conditions ; relationship to a possible new dietary factor. L. G. Wesson (J. Biol. Chem., 1927, 73, 507—522).—Rats were kept for several weeks on a diet of dextrin, salts, and water, or on such a diet with the addition of small amounts of oatmeal or caseinogen; they were starved for 2—3 days and then 3 g. of dextrin per 100 g. of body-weight were administered; as a result, respiratory quotients of 1·5—2·0, or higher, were observed, indicating conversion of carbohydrate into fat. Addition of very small amounts of lard or of an ethereal extract of pig's liver to the restricted diet abolished this effect, which was therefore not due to a demand for fat as such, but possibly for some unknown factor contained in the fat. C. R. Harington.

Energy of growth. X. Formation of fats from carbohydrates by micro-organisms. E. F. Terroine and R. Bonnet (Bull. Soc. Chim. biol., 1927, 9, 588—596).—Cultures of *Aspergillus niger* in media containing from 3% to 40% of dextrose show a remarkable increase in the fat content of the cells, and little change in protein, ash, and unsaponifiable matter. By means of an energy balance-sheet, it is shown that the change from dextrose to fatty acid is carried out by the cell with about 90% efficiency. E. A. Lunt.

Energy of growth. XI. Formation of carbohydrates from fatty acids by moulds. E. F. Terroine, R. Bonnet, and P. Duquénois (Bull. Soc. Chim. biol., 1927, 9, 597—604).—The rate of growth of cultures of *Aspergillus niger* in media rich in the fatty acids of butter fat, arachis oil, linseed oil, cod-liver oil, oleic acid, and castor oil is retarded, whilst the transformation of fatty acid into carbohydrate is carried out by the cells with 75—80% energy efficiency. The transformation is less efficient for saturated than for unsaturated fatty acids. E. A. Lunt.

Physiology of fruit trees. I. Seasonal starch content and cambial activity in one- to five-year-old apple branches. T. Swarbrick (J. Pomology, 1927, 6, 137—156).—The seasonal changes in starch content in one- to five-year-old branches of normal bush type apple trees have been followed, and observations made on the seasonal changes in cambial activity. Special attention was directed to the order of disappearance and reappearance of starch, and to the beginning and cessation of cambial activity. In vegetative shoots, cambial activity was early and starch disappearance tended to lag behind, whereas the reverse was the case in flowering shoots. C. T. Gimingham.

Plastic substances in stems of grape vines growing in Kakhetin. V. G. Aleksandrov and E. A. Makarevskaya (Naukh-Agron. Zhurnal [Russia], 1926, 3, 324—333).—In winter, there is much starch in the lignin portion of the medullary rays, less in the lignin itself, and little in the bark; there is also sugar in the lignins and bark. The sieve-like tubes of the phloëm, which contain proteins, are always free from sugar; the secondary tubes are full of sugar. During the first period of bleeding, starch diminishes and sugar increases. Towards the end of the sap movement in the old wood there is much starch both in the lignins and in the bark. The phloëm is filled with proteins which come from the roots. The bast fibres are also filled with protein; some proteins are found in the medullary rays. Whenever the walls of the medullary rays begin to fill with proteins, the starch begins to disappear. During the winter, there is no protein in the medullary rays. During leaf formation, the upper zones of the shoots are free from starch; the sugar content also decreases. Only in some places in the sieve-like tubes some protein still persists. During blooming, there is an abundance of crystals in the young shoots. In the upper zones of such shoots in the lignin-like medullary rays starch is present; in the last parenchyma protein is found. An abundance of crystals is also found in the outer cells of the medullary rays, in the bark. After blooming, the bast fibres of the medullary rays and the entire phloëm are free from starch. There is sugar in the thin-walled bast fibres, some in the thick-walled. In the cambium, the quantity of sugar diminishes; in the lignins, some sugar is found in the vessels, but there is more sugar in the bark. At that time the proteins are present in the upper zone of the growing shoot, where most of the sugar may be located. During the ripening of the fruit, starch begins to accumulate in the bark; the phloëm also begins to fill with starch. The proteins are located in the sieve-like tubes. In the lignins, an increase in the starch content is noticeable. Then all the fibres became filled with starch except the sieve-like tubes. The elements close to the cambium are filled less than those which are nearer to the periphery. Calcium oxalate crystals are obscured. The quantities of sugar and protein increase. This is the period during which the plant prepares to go into the so-called rest period. CHEMICAL ABSTRACTS.

Relation of antitoxic power to ionisation. L. MAUME and J. DULAC (Compt. rend., 1927, 184, 1194—1196).—An amplification of previous work (*ibid.*, 1081). It is concluded that for mixtures of sodium and calcium chlorides, the minimum toxicity of the solutions for germinating wheat is given by that quantity of the salts which, separately dissolved in a quantity of water equal in volume to that of the mixture, would give solutions having the same degree of ionisation. M. CLARK.

Influence of sodium carbonate and calcium chloride on the acidity of maize sap (*Zea mais*, L.). S. KARASIEWICZ (Compt. rend., 1927, 184, 1192—1194).—When maize is grown in culture media containing sodium carbonate the amount of acid present in the sap is diminished on account of the insoluble calcium salts formed. The use of culture media containing calcium chloride, however, gives a progressive increase of the total acidity. The amount of water-soluble acid present, whether as free acid or as soluble salt, is unaltered by either treatment. M. CLARK.

Distribution of potassium and sodium in plants. G. ANDRÉ and E. DEMOUSSY (Compt. rend., 1927, 184, 1501—1503).—The ratio of potassium to sodium shows a preponderance of the former in the older wood of ligneous plants and in the interior of tap-roots during the period of growth, but an almost equal distribution during the resting period. Figures are given for the distribution of these elements in beet, in chestnut, and in *Tamarix gallica*. G. A. C. GOUGH.

Nutrient ions of plants and ion activation of plant enzymes. G. DOBY and R. P. HIBBARD (J. Biol. Chem., 1927, 73, 405—416).—The leaves of young sugar-beet plants contain more amylase and less sucrose than those of old ones; in plants grown in sand with a synthetic nutrient medium, deficiency of potassium in the latter leads to increase in the amount of both the above enzymes. The amylase is activated by potassium and nitrate ions, and still more so by chloride ions; the sucrose is activated by nitrates and inhibited by chlorides; all effects of salts on the enzymes are exaggerated in the case of the plants grown on the medium deficient in potassium. C. R. HARINGTON.

Iodine as a biogenic element. X. Iodine content of cultivated plants. K. SCHARRER and J. SCHWAIBOLD (Biochem. Z., 1927, 185, 405—413). —Figures are given for the iodine content of numerous edible plants. Application of iodine-containing manure to plants, whether growing in pots or in the open ground, caused a great increase in their iodine content. In the case of sugar-beet, the increase occurred both in roots and leaves. C. R. HARINGTON.

Phosphorus compounds in plants. I. Solubility and distribution of phosphorus compounds in seeds. S. KOEHLER (Bull. Acad. Polonaise, B, 1926, 707—848).—The discrepancies in the mineral phosphate content of seeds, recorded in the literature, may be accounted for by the fact that the results are dependent on the nature and concentration of the acid used for extraction, and by the fact that many seeds contain phosphatases. The distribution of phosphorus in the seeds of various plants has been examined. In the seeds of the scarlet runner, in castor-oil beans, and in the seeds of dentate maize, the mineral P_2O_5 is 13·2%, 4·82%, and 5·38%, respectively, the phytin P_2O_5 is 60%, 91%, and 1·5%, respectively, whilst the organic P_2O_5 is 27%, 4%, and 13%, respectively. In maize, dentate maize, and the carob tree the embryos contain 86—90% of the total phosphorus; in castor-oil beans, the embryos contain only 3·4%, and the endosperm 95%; in the scarlet runner, the cotyledons contain 98·5%, and the rest of the seed 1·47%. Further results are given for the amounts of mineral, phytin, and organic phosphorus in each part of the seeds of all these plants. E. A. LUNT.

Hitherto unsuspected source of arsenic in human environment. R. E. REMINGTON (J. Amer. Chem. Soc., 1927, 49, 1410—1416).—Samples of American tobacco, examined by a micro-Marsh method, contained 0·05—0·27 grain of arsenious oxide per pound. Half the arsenic in pipe tobacco is evolved in the smoke, and half of that in "plug" tobacco is soluble in water. S. K. TWEEDY.

α-Hæmatin, the iron-containing porphyratin of plants, and the corresponding porphyrins. O. SCHUMM (Z. physiol. Chem., 1927, 166, 319; cf. this vol., 685).—The methyl ether of the dimethyl ester of hæmatoporphyrin, described in the original paper as being obtained by boiling α-hæmatin with a solution of hydrochloric acid in methyl alcohol and subsequent removal of the iron with hydrazine in glacial acetic acid solution, appears to be identical with Küster's tetramethylporphyrin. H. D. KAY.

Corn [maize] wax. R. L. SHRINER, F. P. NABENHAUER, and R. J. ANDERSON (J. Amer. Chem. Soc., 1927, 49, 1290—1294).—The pasty deposit obtained when crude maize oil is cooled contains a wax, which is obtained as feathery crystals, m. p. 81—82·5°, by dilution of the crude material with light petroleum, centrifuging, and recrystallising from amyl alcohol, acetone, and light petroleum. The wax is a mixture of the myricyl esters of tetracosoic acid and an iso*behenic acid*. The *amide* of the latter, m. p. 110—111°, and the *methyl* ester, m. p. 47—52°, are described. F. G. WILLSON.

Non-volatile acids of the pear, quince, apple, loganberry, blueberry, cranberry, lemon, and pomegranate. E. K. NELSON (J. Amer. Chem. Soc., 1927, 49, 1300—1302; cf. A., 1925, i, 762).—The non-volatile acids of Bartlett pears consist of citric and *l*-malic acids in the proportion 2 : 1. Quinces contain *l*-malic acid. Winesap apples contain *l*-malic acid with a trace of citric acid, whilst York Imperial apples contain *l*-malic acid only (cf. Franzen and

Helwert, A., 1923, i, 637). The non-volatile acids of the loganberry are citric (96%) and *l*-malic (4%); of the blueberry, citric, with a trace of *l*-malic; of the cranberry, citric (80%), *l*-malic (20%), and benzoic (0·069%); of California lemons, citric, with a trace of *l*-malic; and of the pomegranate, citric acid only.
F. G. Willson.

Oil of *Secale cornutum* and its daturic acid content. H. Dieterle, H. Diester, and T. Thimann (Arch. Pharm., 1927, 265, 171—187).—The oil has $d^{16\cdot2}$ 0·9259; n_D^{40} 1·5420; acid value, 13·19; saponification value, 193·3; ester value, 180·11; Hehner value, 96·13; Reichert–Meissl value, 0·47; Polenske value, 0·48; iodine value (Hübl) 69·55, (Hanus) 66—67. The oil is not a drying oil. The above data agree with those of Mjoen (A., 1896, ii, 500).

The fatty acid mixture is composed of palmitic, daturic, and other solid fatty acids (20·48% of the original oil), oleic acid (70·99%), and α-linoleic acid (4·58%). Hydroxy-fatty acids, which Mjoen supposed to be present, were not discovered. The daturic acid isolated was examined in detail, but satisfactory conclusions were not reached. Stearic acid, however, is definitely absent from the oil. No characteristic differences were found between the methyl and ethyl esters of palmitic, stearic, and daturic acids, nor between the sodium salts of the corresponding hydroxamic acids. 1·9% of the oil is unhydrolysable, consisting of hydrocarbons, phytosterols, etc. W. A. Silvester.

Kuromoji oil. H. Shinosaki and H. Makino (Rep. Imp. Ind. Res. Inst. Osaka, 1927, 7, No. 15, 27—44).—The low b.-p. fraction of kuromoji (*Lindera sericea*, Bl.) oil consists chiefly of *l*-α-phellandrene, with small quantities of dipentene and limonene. The important components of the oil are nerolidol, linalool, and geraniol. α-Pinene, camphene, a dicyclic sesquiterpene, a monocyclic (?) sesquiterpene alcohol, and an ester of an unknown acid (m. p. 126—126·5°) were also isolated. Chemical Abstracts.

Toxicity of flax lolium (*Lolium remotum*, Schrank). A. von Lingelsheim (Arch. Pharm., 1927, 265, 244—250).—*Lolium remotum*, Schrank, is poisonous, like *L. temulentum*, and is frequently present as an impurity in linseed. Data are given from many mid-European agricultural stations showing that, although the risk of fatal effects to cattle or human beings from this cause is not great, further investigation is desirable. The toxic properties appear to be connected with the presence of a parasitic fungus. W. A. Silvester.

Ether-soluble substances of cabbage-leaf cytoplasm. III. Fatty acids. A. C. Chibnall and H. J. Channon (Biochem. J., 1927, 21, 479—483).—The greater part of the fatty acids of the cytoplasm of the cabbage leaf consists of the unsaturated acids, linolenic and linoleic acids; palmitic and stearic acids constitute the saturated acids. The presence of oleic acid could not be established. There seems to be a definite difference in the amounts of fatty acids and of the unsaponifiable matter in the ethereal extracts obtained from spring and summer material. S. S. Zilva.

Helleborus. O. Keller and W. Schöbel (Arch. Pharm., 1927, 265, 238—243).—*Helleborus niger* (root) contains the two glucosides, helleborein and helleborin. Helleborin has m. p. 269—270°, and analyses (the results are very different from those of earlier authors) indicate that the composition is $C_{28}H_{36}O_6$ or $C_{27}H_{36}O_6$. *Helleborus viridis* (root) contains, together with brown colouring matter and fatty substances, the same two glucosides as *H. niger*, sucrose, and two alkaloids. These two new *bases*, together amounting to only about 0·1% of the dried root, are extracted by Stoll's method (Schweiz. med. Woch., 1921, 23). They differ in carbon content, but both contain about 3% of nitrogen. The one is easily soluble in ether, but sparingly soluble in chloroform; the other sparingly soluble in ether, and easily soluble in chloroform.
W. A. Silvester.

Ephredra nevadensis. R. E. Terry (J. Amer. Pharm. Assoc., 1927, 16, 397—407).—*E. nevadensis* contains no ephredine, which is usually present in the European and Asiatic members of the genus *Ephredra*. The plant contains a water-soluble constituent with a slight diuretic effect, the use of which in medicine is precluded by the large amount of gallotannic acid present in the aqueous extract of the plant.
E. A. Lunt.

Asarum caudatum. H. M. Burlage and E. V. Lynn (J. Amer. Pharm. Assoc., 1927, 16, 407—411).—The leaves and petioles of the plant contain little or no volatile oil, the roots and rhizomes as much as 4·06%, depending on the time of harvest. This oil contains a small amount of pinene, 60—75% of methyleugenol or closely related methoxyl compounds, 10% of azulene, and 10% or more of asarone (3 : 4 : 6-trimethoxyallylbenzene). E. A. Lunt.

Glucosides of *Caulophyllum thalictroides.* E. D. Davy and H. P. Chu (J. Amer. Pharm. Assoc., 1927, 16, 302—305).—Analysis of the rhizome and roots of *Caulophyllum thalictroides* yielded the alkaloid methylcytisine and a non-crystalline, glucosidal material which differed from that described by Power and Salway (J.C.S., 1913, 103, 193). On moistening the drug to allow enzyme action to take place before extraction, a crystalline glucoside, m. p. 243—246°, $[\alpha]_D+45°$, sparingly soluble in alcohol, and a non-crystalline glucosidal product, m. p. 230—240°, $[\alpha]_D+37°$, very soluble in alcohol, were isolated. The former may be identical with caulosaponin.
W. J. Powell.

Protoplasm. III. Proteins of the plasmodium of *Fuligo varians.* A. Kiesel (Z. physiol. Chem., 1927, 167, 141—162; cf. A., 1926, 204; this vol., 382).—The air-dried plasmodium contains crude oil 8·73%, water 9·53%, calcium carbonate 16·35%, organic water-soluble matter 15·35%, residue insoluble in light petroleum, water, or alcohol 50·04%. One of the most important constituents is a nucleoprotein, present to the extent of at least 3·1% of the dry weight, and in addition to the protein-like substance or mixture, "plastin." A. Wormall.

Glutelins. I. α- and β-Glutelins of wheat. F. A. Csonka and D. B. Jones (J. Biol. Chem., 1927, 73, 321—329).—Glutelins can be precipitated from alkaline solution by concentrations of ammonium sulphate which are too low to precipitate globulins, and may thus be separated from the latter. Wheat flour was freed from starch and gliadin and then extracted with 0·2% sodium hydroxide. Treatment of the extract with ammonium sulphate to 2% saturation precipitated 1% of *α-glutelin*; further addition to the filtrate of ammonium sulphate to 18% saturation yielded about 0·07% of *β-glutelin* (calculated on the weight of the original flour). Both proteins have an isoelectric point at p_H 6·45; figures are given for the nitrogen distribution.

C. R. HARINGTON.

Nitrogen compounds of the rice kernel as compared with those of other cereals. S. L. JODIDI (J. Agric. Res., 1927, **34**, 309—325).—The total nitrogen in oven-dried rice varies from 1·7 to 1·24% in different varieties and different seasons. Polypeptides and free amino-acids occur in the ungerminated rice kernel (brown rice). Amino-nitrogen amounts to 0·75—1·02% of the total nitrogen; corresponding figures for acid amide nitrogen are 0·14—0·23%, and for polypeptide nitrogen, 0·85—1·15%. The percentages of total nitrogen in wheat, oats, rye, maize, and rice decrease in the order named. The proportion of protein nitrogen is smaller in rye, wheat, and oats than in maize or rice, but the absolute quantity is considerably larger. The significance of the non-protein nitrogen compounds during the early stages of seed germination is discussed.

C. T. GIMINGHAM.

Immunological reactions of the globulins from the seeds of leguminous plants. Biological reactions of the vegetable proteins. IX. H. G. WELLS, J. H. LEWIS, and D. B. JONES (J. Infect. Dis., 1926, **40**, 326).—The α-globulin fractions of navy, mung, adzuki, Lima, and Georgia velvet beans have a higher sulphur and a lower nitrogen content than the β-globulins. The globulins from adzuki and mung beans are distinct from those of navy, Lima, and Georgia velvet beans, but the α- and β-globulins of adzuki and mung beans are either identical or similar. Georgia velvet bean globulins are immunologically distinct from the others. CHEMICAL ABSTRACTS.

Portable form of manometric gas apparatus. D. D. VAN SLYKE (J. Biol. Chem., 1927, **73**, 121—126).—A portable form of the apparatus of Van Slyke and Neill (A., 1924, ii, 872) is described and details of technique are given. C. R. HARINGTON.

Carbon dioxide factors for the manometric blood-gas apparatus. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1927, **73**, 127—144).—By gasometric analysis of sodium carbonate solutions, the composition of which was independently checked by three different gravimetric methods, factors for the conversion of observed pressure differences into carbon dioxide content in the use of the apparatus of Van Slyke and Neill (A., 1924, ii, 872) have been re-calculated with increased accuracy.

C. R. HARINGTON.

Determination of acetoacetic acid. L. PINCUSSEN (Biochem. Z., 1927, **184**, 359).—A reply to Lorber's criticism (this vol., 372) of the author's micro-methods. R. K. CANNAN.

Determination of lactic acid. T. E. FRIEDEMANN, M. COTONIO, and P. A. SHAFFER (J. Biol. Chem., 1927, **73**, 335—358). **Condenser unit for use in determination of lactic acid.** H. A. DAVENPORT and M. COTONIO (*ibid.*, 359—361).—The oxidation of lactic acid to acetaldehyde is rendered almost quantitative by the addition of manganous sulphate. By utilisation of this observation, development of an improved apparatus, and more rigid determination of the appropriate conditions for the titration of hydrogen sulphite bound by acetaldehyde, an improved modification of the method of Clausen (A., 1922, ii, 593) has been devised. The method is applicable to amounts of lactic acid from 0·045 to 45 mg. with an error of ±5%; the magnitude of the error which may be introduced by the presence of interfering substances in physiological material has been determined in a large number of cases, and methods for the preliminary removal of certain of these substances are indicated.

A technical modification, leading to a more compact apparatus for the above method, is described.

C. R. HARINGTON.

Use of magnesium perchlorate trihydrate and asbestos–sodium hydroxide for determination of water and carbon dioxide in metabolism experiments. M. O. LEE and J. B. BROWN (J. Biol. Chem., 1927, **73**, 69—72).—The quantitative absorption of water and carbon dioxide in metabolism experiments is conveniently accomplished by the use of magnesium perchlorate and asbestos impregnated with sodium hydroxide, respectively, these preparations offering technical advantages over the absorbents commonly employed. C. R. HARINGTON.

Nephelometric determination of small amounts of arsenic. I. Turbidities produced by a new reagent. II. Determination of arsenic in any material. H. KLEINMANN and F. PANGRITZ (Biochem. Z., 1927, **185**, 14—43, 44—62).—I. A reagent prepared by mixing 1 vol. of 1% potassium molybdate with 1 vol. of 2% cocaine and 2 vols. of *N*-hydrochloric acid exhibits a turbidity with minute traces of arsenates. By the use of this reagent, under the specified experimental conditions, amounts of arsenic from 0·06 to 0·0005 mg. can be determined nephelometrically with an error of ±1%. The determination is not affected by the presence of neutral salts up to *N*-concentration.

II. Organic material is dried at 100° and then incinerated with a mixture of sulphuric and nitric acids; the arsenic remaining in the sulphuric acid is reduced by addition of ferrous sulphate; the mixture is then treated with potassium chloride and bromide and distilled, the arsenic trichloride being collected in excess of *N*-sodium hydroxide; the arsenic in the distillate is oxidised by treatment with hydrogen peroxide, and determined nephelometrically. In this way, amounts of arsenic of the order of 0·0005 mg. may be determined in organic material. Methods are described for the removal of traces of arsenic from the reagents employed. C. R. HARINGTON.