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General, Physical, and Inorganic Chemistry.

Spectrum of doubly-ionised nitrogen (N III). L. J. FREEMAN (Proc. Roy. Soc., 1928, A, 121, 318-343).—The spectrum was examined from λ 8000 to λ 850. The N III lines observed are tabulated and their positions compared with those found by J. L. BUCHAN. calculation.

Structure of the band spectrum of helium. V. W. E. CURTIS and A. HARVEY (Proc. Roy. Soc., 1928, A, 121, 381-401; cf. A., 1928, 449).—Details are given of four new bands and of one of the "ordinary" orthohelium family. The new bands are : $3D(1) \rightarrow$ 2P(1) of o-He₂ near λ 5750; $3X \rightarrow 2P$ of p-He₂ near λ 6250; $3Z \rightarrow 2P$ of o-He₂, and $4Z \rightarrow 2P$ of ZP of D-He₂ near λ 5750; $Z \rightarrow 2P$ of p-He₂ o-He₂. These last two bands are very similar to $3Z \longrightarrow 2P$ of p-He₂ near λ 6300, which is also described. J. L. BUCHAN.

Hyperfine structure in the arc spectrum of cæsium and nuclear rotation. D. A. JACKSON (Proc. Roy. Soc., 1928, A, 121, 432-447).—The cæsium vapour was mixed with helium at about 2 mm. pressure in a discharge tube and excited by external electrodes. It was necessary to warm the tube in order to obtain the cæsium spectrum, chiefly the 1s-3p lines, and at the same time that due to helium was extinguished. On raising the temperature the yellow, red, and infra-red lines of cæsium develop and those of the principal series become broader and blurred, their hyperfine structure being extinguished. In the principal series the lines were close doublets of equal intensity. Tables of measurements are given and those lines found to be simple are also tabulated. The results are discussed and a theory is put forward to account for the doublets.

J. L. BUCHAN. Absorption bands in the spectrum of cadmium vapour. A. JABLONSKI (Bull. Acad. Polonaise, 1928, A, 163-170).—The absorption spectrum of cadmium vapour has been investigated with a view of finding the positions of bands corresponding with the fluorescence bands, and to show that both series have the same convergence point. The apparatus used is described. The frequency of the bands is plotted against the difference of frequency between one band and the next, and it is found on extrapolating the curve that the point of convergence of the bands is at a wave-length of 2561 Å. Assuming that this is connected with the dissociation of the cadmium molecule, Cd_2 , and activation to the state 2^3P_1 of one of the atoms resulting from the dissociation, the energy of dissociation of the cadmium atom is calculated to be 1.035+0.031 volts, a value in good

agreement with that calculated by consideration of the system Cd II (1.023+0.006 volts). The absorption spectrum of cadmium shows a great predominance of continuous absorption over band absorption, an observation which shows the existence of metastable states of long duration. It seems probable that the only essential difference between the molecules of cadmium (and mercury) and other diatomic molecules (e.g., iodine, selenium, tellurium, etc.) consists in the existence of metastable states of these A. J. MEE. molecules.

Origin of the band λ 2476.3—2482.7 in the spectrum of mercury. S. PIENKOWSKI (Bull. Acad. Polonaise, 1928, A, 171-179).—The band of wave-lengths 2482.72—2476.35 Å. has been resolved into rays which can be arranged in a series of seven doublets. In each of the branches of these doublets there is an irregular ray; the displacement occurs for the same quantum number in both branches and in opposite directions. The moment of inertia of the molecule emitting the light is calculated and it is concluded that the band is due to a mercury hydride, the hydrogen having been supplied probably by a trace of water vapour. All photographs of spectra of hydrogen and mercury vapour show the presence of the band. A. J. MEE.

Wave-lengths and Zeeman effects in yttrium spectra. W. F. MEGGERS (U.S. Bureau Stand. Res Paper No. 12, 1928, 319-341).-The wave-lengths corresponding with approximately 1000 lines photographed in the arc and spark spectra of yttrium were measured relative to secondary standards in the iron spectrum, the values extending from 2127.99 Å. in the ultra-violet to 9494.81 Å. in the infra-red. Four classes of lines were distinguished; about 500 are ascribed to neutral atoms and constitute the YI spectrum; 240 originate with singly-ionised atoms, the Y II spectrum; 10 belong to doubly-ionised atoms, the Y III spectrum, and most of the remainder describe the band spectrum characteristic of molecular compounds, presumably yttrium oxide. Tables are given of the wave-lengths, line intensity estimates, wave numbers, and classification. Measurements of Zeeman effects for 220 lines from 3173 to 6896 Å. are N. M. BLIGH. included.

Spectra of mercury at atmospheric pressure. W. H. CREW and L. H. DAWSON (J. Opt. Soc. Amer., 1928, 17, 261-270).-The light emitted from a mercury are in quartz was photographed through a quartz spectrograph. As the current through the arc was increased the lines of the line spectrum

broadened, and under the influence of a condensed discharge thirteen lines were found to be self-reversed. Two of these were spark lines and eight were lines of the diffuse series. Hence lines of the diffuse series are the most readily reversed. The reversal of the line of wave-length 1942 A. supports the view of Carrol, Turner, and Compton that it is a member of the first doublet of the principal series of Hg+. The continuous spectrum appeared in four discrete bands when a high current was passed through the arc. Three of these bands have intensity maxima near the three spectral series limits, i.e., 4580, 3320, and 2240 Å. A modification of Bohr's theory which accounts for bands of continuous radiation by the recombination of electrons with atomic or molecular ions agrees with the observations. Theoretically, a velocity distribution of the free electrons in the arc corresponding with a temperature of 2500° Abs. gives an intensity distribution of the continuous spectrum in agreement with that observed. Some observations made by Rayleigh agree with the theory.

A. J. MEE.

"Ultimate rays " of mercury and aluminium. A. T. WILLIAMS (Compt. rend., 1928, 187, 761-763) .- Contrary to Croze's rule (A., 1924, ii, 1), the ultimate rays of mercury have been found to be 2537 and 1942 A., the latter being the least refrangible of the ${}^{2}S^{2}P$ series of the ionised mercury atom. The persistence of the resonance rays ${}^{1}S^{3}P$ of cadmium, zine, and mercury is in direct relationship with the value of the difference $2^{3}P_{1}-2^{1}P_{3}$. The ultimate rays of aluminium are probably 1862.90, 1854.67 ($^{2}S^{2}P$), 1980.80 ($^{1}P^{1}D$), and 1670.98 ($^{1}S^{1}P$). The ultimate rays corresponding with those of the neutral atom of the elements of the first column of the periodic table (${}^{2}S^{2}P$ doublets) are the doublets of the ionised and doubly-ionised atoms of the elements in the second and third columns, respectively. In the fourth column silica has as an ultimate ray a doublet of a singly-ionised atom. J. GRANT.

Interpretation of the continuous spectrum of hydrogen. Y. TAKAHASHI (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 963-966).—Theoretical. It is suggested that the continuous spectrum of hydrogen is caused by the collision with molecules of free electrons having a kinetic energy intermediate between those corresponding with the resonance and dissociation potentials (cf. A., 1927, 1004).

A. R. POWELL. Light-emission from atoms. J. KLEIBER (Ann. Physik, 1928, [iv], 87, 461-468).—Starting from the idea of electronic shells, it is shown that the mechanical analogy of a spiral spring moving like a pendulum is of assistance in picturing the atomic disturbances which lead to emission of light. Each shell is regarded as possessing a characteristic frequency, equal to the Rydberg constant divided by i², where i is the number of the shell, R. A. MORTON.

Rate of decay in the Balmer series. J. PORT (Ann. Physik, 1928, [iv], 87, 581-589).—Hydrogen canal rays projected into a high vacuum through a narrow slit give out light decreasing in intensity along the path of the particles. The decrease corresponds accurately with an exponential law. No deviation from this law is recorded in the neighbourhood of the slit, so that observations made by Wien and Stark cannot be ascribed to atomic properties. In opposition to the requirements of the classical theory, the rate of decay in the Balmer series is independent of wave-length. R. A. MORTON.

Oscillating discharges in hydrogen. Z. BAY and W. STEINER (Z. Elektrochem., 1928, 34, 657– 662).—The continuous hydrogen spectrum is obtained on passing oscillating discharges of high frequency through intensively dried gas. The character of the spectrum is independent of the frequency (Lawson, A., 1913, ii, 911). Suitable electrodeless discharge tubes of quartz are described; they afford useful sources for light between 3300 and 1900 Å. (cf. A., 1927, 1117). S. K. TWEEDY.

Lyman bands of hydrogen. E. C. KEMBLE and V. GUILLEMIN, jun. (Proc. Nat. Acad. Sci., 1928, 14, 782—787).—The B—A bands of hydrogen have been re-examined to see whether an interpretation based on the two-branch hypothesis might not be more desirable than the one favoured by Hori (A., 1927, 1005), namely, that the Lyman bands consist of P, Q, and R branches. Frequency data are given and also the intensities of the emission lines, and an analysis of the data appears to favour this alternative hypothesis. M. S. BURR.

Stark effect of helium. Y. ISHIDA and G. KAMI-JIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 117-140) .- Photographs obtained using transformer electrical supply are compared with those obtained using battery supply and found to be in satisfactory agreement. Photographs were obtained for the first time of the lines parahelium $6631\cdot89$ (2P-3P); $4054\cdot8$ (2S-4S); $5043\cdot6$ (2S-4S)3D), orthohelium 6068.77 (2p-3p); 4277.1 (2s-3s), and their polarisation and deflexion found. 5380.3 (2S-3S) of parahelium at a high electric field was observed with a direct-vision spectroscope. Results are in general agreement with the theoretical work of Foster (A., 1928, 101) based on the new quantum mechanics, and are considered to justify the use of a high electric field with an electrical supply not totally rectified. N. M. BLIGH.

Stark effect of lithium. Y. ISHIDA and M. FUKUSHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 141—150).—Using a special cathode the effect was investigated and photographed, and was observed for the first time for the following lines: $6708\cdot2(1s-2p \text{ and } 2p-1s), 6103\cdot77(2p-3d), 4971\cdot98$ (2p-3s), and $4273\cdot3(2p-4s)$. Further analogies of line combinations with those of orthohelium are noted. The inverse Stark effect for the *p*-component of the line $4132\cdot4(2p-5f)$ was observed.

N. M. BLIGH. Structure of the $1'S_0 - 2'P_1$ and other lines in the cadmium spectrum. (FRL.) A. SCHRAMMEN (Ann. Physik, 1928, [iv], 87, 638-652).—The work of Wood (A., 1926, 986) on the cadmium line at 2288 Å. $(1'S_0 - 2'P_1)$ indicated resolution into two lines 0.021 Å. apart. The data are, however, consistent with self-reversal, and as a result of a close investigation of the absorption and emission of this line, an attempt is made to demonstrate the existence of a satellite (not separated) at a distance $d\lambda =$ -0.35×10^{-3} Å, from the main line. The structure of a few other cadmium lines is given: Wood's resolution of the 2537 Å, mercury line into five components is confirmed. R. A. MORTON.

Intensities of "forbidden" lines in a magnetic field. W. C. VAN GEEL (Z. Physik, 1928, 51, 51— 61).—The intensities of the "forbidden" lines in the pd-multiplet of the neutral zine atom have been investigated with respect to their dependence on a magnetic field and the ratios of their intensities to those of the non-forbidden lines. The results are in general accord with the theory, but the observed intensities are a little higher than those calculated. Some anomalies exist, however. J. W. SMITH.

Intensity calculations for the partial Paschen-Back effect. A. ZWAAN (Z. Physik, 1928, 51, 62–70; cf. van Geel, A., 1927, S3).—Mathematical. The matrix theory of Jordan and Heisenburg is used to calculate the intensities of the Zeeman components in the (2p-3d)-multiplet ($\lambda = 3300$ Å.) of the zinc iodide spectrum in terms of the strength of the magnetic field applied. The intensities of the forbidden lines $2p_0-3d_3$, $2p_1-3d_3$, and $2p_0-3d_2$ are also calculated. The results are compared with those of Darwin (A., 1927, 707). J. W. SMITH.

Spark spectrum of argon. H. T. L. DE BRUIN (Z. Physik, 51, 108-113; cf. A., 1928, 450).-By generating an argon spark spectrum in a Geissler tube at a pressure of about 2 cm. a number of new lines have been found and measured. These have been fitted into the classification scheme previously developed. From the term values, the ionisation potential of the A II spectrum is evaluated as $27.75 \pm$ 0.05 volts. Adding to this the ionisation potential of the A I atom-15.69 volts-a value of 43.44 volts is obtained for the second ionisation potential of argon, in fairly good agreement with the experimentally determined value. A table is given of 180 classified lines in the A II spectrum in the wavelength range 5300-3100 Å. J. W. SMITH.

Zeeman effect in the argon spark spectrum (A II). C. J. BAKKER, T. L. DE BRUIN, and P. ZEEMAN (Z. Physik, 1928, 51, 114-135).—The Zeeman effect has been investigated with respect to 110 A II lines, the results confirming de Bruin's analysis of this spectrum (cf. preceding abstract). It follows from the Zeeman effect that in the spectrum of ionised argon, normal and abnormal combinations appear: in the higher energy levels the combinations are abnormal. For one term group the law of summation of the g-terms has been established.

J. W. SMITH.

Origin of the green auroral line. L. A. SOMMER (Naturwiss., 1928, 16, 219; Chem. Zentr., 1928, i, 2484).—Experiments on the Zeeman effect of the green auroral line 5577.35 Å, ascribe it to neutral oxygen $({}^{3}P_{1} - {}^{1}S_{0})$; the excitation potential is 2.23 volts. A. A. ELDRIDGE.

Multiplets in the spectra of V III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 606-607).—The triad of multiplets of V III designated as

 ${}^{4}F_{2, 3, 4, 5} - ({}^{4}G_{3, 4, 5, 6}, {}^{4}F'_{2, 3, 4, 5}, \text{and } {}^{4}D_{1, 2, 3, 4})$ and the ${}^{4}F_{2, 3, 4, 5} - {}^{4}F'_{2, 3, 4, 5}$ multiplet of Cr iv have been identified. A. A. ELDRIDGE.

Multiplets in the spectra of Cr III and Mn III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 917).—The multiplet ${}^{5}F{}-{}^{5}G$ has been extended for four electron systems from Ti I and V II to Cr III, and the multiplet ${}^{6}D{}-{}^{6}F$ for five electron systems from V I and Cr II to Mn III.

A. A. ELDRIDGE.

Absorption spectra of iron, cobalt, and nickel. W. F. MEGGERS and F. M. WALTERS, jun. (Physical Rev., 1927, [ii], 29, 358—359).—Results of absorption spectra observations confirm the known spectral structures for neutral and for ionised iron, cobalt, and nickel; many new levels have been established.

A. A. ELDRIDGE.

Chemical valency and multiplicity of spectra. A. T. WILLIAMS (Contrib. Estud. Ciencias fisic. mat. La Plata, 1928, 4, 243—252; Chem. Zentr., 1928, ii, 126).—Except for rare earths, iron, cobalt, and iridium, the chemical valency $V=r\pm 1$, where r is the multiplicity of the spectrum. The derivation of the sign is discussed, and various values for an element are ascribed to particular electron configurations.

A. A. ELDRIDGE.

Effect of temperature on the auto-electronic discharge. N. A. DE BRUYNE (Proc. Camb. Phil. Soc., 1928, 24, 518-520).—When both thermionic and auto-electronic emissions are present in a discharge it is possible to find the value of the autoemission by subtracting from the total emission current the value of the thermionic emission as calculated by Schottky's relationship. This separation of the two emissions has been carried out, and it has been found that, within the limits of experimental error, the auto-emission is independent of temperature up to the highest cathode temperature used (1944°). This agrees with the theory of auto-electronic emission put forward by Fowler and Nordheim. A. J. MEE.

Determination of ionisation potentials. S. DATTA and S. SEN (Z. Physik, 1928, 50, 849-860) .-measurements have been made of the current flowing through a Bunsen flame in which metallic salt vapours may be introduced as a function of the P.D. between two platinum electrodes under the following conditions: (A) the cathode covered with a thorium preparation, (B) thorium-coated cathode and metallic salt vapour in flame, and (C) uncoated cathode and metallic salt vapour in flame. The difference between the current (B) and the sum of the currents (A) and (C) when plotted against the electrode P.D. attains maxima corresponding with $V_{-}V_{r}$ and with V_{i} , respectively, where V_r denotes the resonance potential and V_i the ionisation potential. Data are given for sodium, potassium, lithium, magnesium, calcium, strontium, barium, and mercury.

R. W. LENT.

Systematic variations of the constant A in thermionic emission. L. A. DUBRIDGE (Proc. Nat. Acad. Sci., 1928, 14, 788-793).—The data for thermionic emission from various metallic surfaces, viz., platinum, tungsten, thoriated tungsten, potassium, and liquid silver, gold, and copper, have been examined

with the view of testing the relationship, first observed by Richardson (Proc. Roy. Soc., 1915, A, 91, 524) for platinum and tungsten, that, when the work function \hat{b} of a given surface, in the equation $I = AT^2 e^{-b/T}$, is changed by any method, e.g., heating, out-gassing, coating, etc., the constant A also changes in such a way that $\log A$ is a linear function of b. This was confirmed in all cases. All the curves may be represented by a simple empirical equation, $\log_e A = \log_e A_0 + \beta(b-b_0)$, where $A_0 = 60$, β , the slope, is a constant depending on the nature of the surface, and b_0 has the same value for all the more refractory metals. It can be shown that the observed variations of Amight be ascribed to a small temperature variation of the surface work function b, which is in agreement with the conclusion reached by Bridgman (A., 1928, 682) that, in Dushman's simple theory, a term has been neglected which is related to the temperature derivative of the work function. The coefficient of the temperature change can be obtained from measurements on the shift of the photoelectric threshold with temperature. The values thus obtained are found to be of the right sign and order of magnitude.

M. S. BURR.

Photoelectric long-wave limit of potassium vapour. R. C. WILLIAMSON (Proc. Nat. Acad. Sci., 1928, 14, 793-796).-The ionisation currents, obtained by illuminating a jet of potassium vapour with ultraviolet light, have been studied by a method previously described (Physical Rev., 1923, [ii], 21, 107) using a monochromator instead of filters, and making also some slight modifications in dimensions of apparatus etc. The results give an approximate indication of the relative ionising efficiencies of the different wave-lengths of light. Ionisation sets in sharply near 3027 Å. In general the ionisation current rises to a maximum at about 2800 Å., falls to a minimum at about 2600 Å., rises sharply to a maximum at about 2150 Å., and drops again down to 2050 A. Since the spectroscopic limit for the potass-ium atom is 2856 Å., ionisation is occurring in this case at least 170 Å. above the expected limit, and may perhaps be accounted for on the basis of molecular ionisation. On this assumption the ionising potential of the molecule would be between 4.08 and 3.94 volts, corresponding with a limit between 3027 and 3131 A. for ionisation without dissociation. The 2610 A. limit gives 4.74 volts, corresponding with ionisation with dissociation. Thus the energy of dissociation of the ionised molecule is between 0.66 and 0.80 volt. From the limit for atomic ionisation, 2856 A., corresponding with 4.32 volts, the dissociation potential of the neutral molecule is 0.42 volt, which is rather low compared with the value of 0.61 volt estimated by Carrelli and Pringsheim (A., 1927, 1018). The dissociation potential of the ionised molecule appears to be larger than that of the neutral molecule, and atomic ionisation is probably obscured by molecular ionisation. M. S. BURR.

Emergent energy of photoelectrons in potassium vapour. R. C. WILLIAMSON (Proc. Nat. Acad. Sci., 1928, 14, 796-801).—Preliminary experiments are described for determining the negative photoelectronic currents obtained when potassium vapour is illuminated by ultra-violet light. Both total and monochromatic radiation have been used. M. S. BURR.

Generation of the helium spectrum by electrical excitation. L. S. ORNSTEIN, H. C. BURGER, and W. KAPUSCINSKI (Z. Physik, 1928, 51, 34-50).-The intensities of the helium lines produced by electrical excitation have been measured by a thermoelectric method, and their variation with current strength and with pressure has been followed. The cross-section of the capillary of the discharge tube was found to exert a considerable influence on the intensities of the lines at constant pressure and current density. The changes with pressure of the ratios of the intensities of the triplets and single lines at different current densities have also been measured. It is concluded that the emission is not produced by the reunion of ions and electrons, but that atomic collision plays a major rôle. In direct excitation by electronic collision, a priority rule holds which is analogous to the selection rule for radiation.

J. W. SMITH.

Effect of electric fields on the emission of electrons from conductors. A. T. WATERMAN (Proc. Roy. Soc., 1928, A, 121, 28—40).—Houston's explanation (A., 1928, 467) of the extraction of electrons from metals by intense electric fields, based on Sommerfeld's modification of the Lorentz electron theory of metals (A., 1928, 467), is shown to be inadequate. Houston's work is to be regarded as a treatment of the Schottky effect for very intense fields, but, according to Sommerfeld's theory, the Schottky equation should be modified, and this modification becomes significant at high fields. The degree of penetration of a surface electrical charge into the body of a conductor is worked out on the basis of the Sommerfeld electron theory.

L. L. BIRCUMSHAW. Time function of the light emission of active nitrogen. A. KOENIG and G. H. KLINKMANN (Z. physikal. Chem., 1928, 137, 335-351) .- The total illumination from active nitrogen is indicative of a bimolecular reaction, but little can be said of the individual bands in the spectrum. The bands in the β -group of the afterglow spectrum at 4310-4300 Å. and 4040-4025 Å. are not represented in the arc discharge spectrum, whilst the weak afterglow band at 5050 A. could not be observed. The rate of fading of the band diminishes as the wave-length decreases, being about twice as great for the red bands as for the violet. Bands of the α -group disappear with very much greater velocity than do those of the β groups. The reactivity and the intensity of the afterglow of active nitrogen do not follow parallel courses. H. F. GILLBE.

New resonance series of selenium. B. SCHMIDT (Bull. Acad. Polonaise, 1928, A, 61-68). A new series in the resonance spectrum of selenium, produced by excitation with the magnesium 4481 line, has been observed and measured. This band first becomes visible at 300°, attains a maximum intensity at 400°, and disappears at about 500°. Even under the most favourable conditions the intensity is very low. The wave-lengths of the lines may be expressed by the general formula $1/\lambda = 22312 - 362m + 1 \cdot 3m^2$. It is deduced that absorption of the exciting ray 4481 corresponds with the passage from the normal state n=14 to the excited state n'=1. On this supposition the results are in good agreement with former observations. J. W. SMITH.

Retarded luminescence observed in air. W. BERNHARDT (Bull. Acad. Polonaise, 1928, A, 69-83). ---It has been shown that the retarded luminescence of air occurs mainly in the space occupied by the positive columns and penetrates very little into the Faraday dark space. Since the intensity of the field has been shown to be very low in the positive column, it is concluded that it is the consequent longer free path of the molecules which permits the formation of molecules capable of giving rise to this luminescence. New types of retarded luminescence have been observed in air under pressures varying from hundredths of a mm. to 170 mm. Below 1 mm. pressure the luminescence is pale green, at 1 mm. darker green. This luminescence may be propagated to distances of 80 cm. and more. Above 1 mm. pressure the colour is emerald-green and it is propagated only about 10 cm. Using relatively high pressures (30-40 mm.) and a high-tension discharge, a yellow retarded luminescence may be obtained. The time of retardation of the green luminescence diminishes with pressure, varying from 20 to 0.01 sec. In all cases the spectra of the luminescence are of a continuous nature. The temperature limits between which the effect can be obtained are -130° and J. W. SMITH. -+200°.

Absolute magnitude effects in stellar spectra. E. A. MILNE (Nature, 1928, **122**, 840-841).

Polarisation of Compton scattering according to Dirac's new relativistic dynamics. Y. NISHINA (Nature, 1928, **122**, 843).

Atomic moments. P. WEISS and G. Fofix (Compt. rend., 1928, 187, 744—746).—The published values of the atomic moments of iron, nickel, cobalt, oxygen, copper, chromium, platinum, palladium, and vanadium in various states of combination but corrected for the diamagnetism of the atoms concerned are assembled, and their probable accuracies discussed. With the exception of that of the cobaltous ion in the hexagonal sulphate (25.67) and of ferrous iron in the ammonium sulphate (26.5) they are all approximately whole numbers and multiples of Bohr's theoretical magneton (equal to 5 experimental magnetons). J. GRANT.

Liberation of secondary electrons by electrons of 1-30 kilovolts. E. BUCHMANN (Ann. Physik, 1928, [iv], 87, 509-535).—The number s of secondary electrons liberated in a 1 cm. path at 1 mm. of mercury by electrons of $1-30 \times 10^3$ volts has been determined to within 3% for air, argon, carbon dioxide, and hydrogen. Earlier results are confirmed. At the K-limit for argon (2.9 kilovolts), s exhibits no sudden change. For a few velocities, the total number of electrons S has been measured directly and found to vary as the energy of the primary electron. The mean energy e necessary for the formation of an ionpair is 31 ± 3 volts. The range of the electrons has been calculated from S, s, and e. R. A. MORTON.

Polarisation of canal-ray light in weak electric fields. II. The accompanying emission of \mathbf{H}_{β} in various arrangements of the field. E. Rurr (Ann. Physik, 1928, [iv], 87, 285—297; cf. A., 1928, 454).—In homogeneous fields parallel or at right angles to the canal rays, no influence is noticeable on the polarisation. If the weak electric field is directed at an angle of 45° to the canal rays, periodic variations of the polarisation ratio occur which are in accordance with the theory of anharmonic oscillators. W. E. DOWNEY.

Influence of positive ions on the electronic space charge within a two-plate system. H. COHN (Ann. Physik, 1928, [iv], 87, 543-568).-In a symmetrical two-plate tube, the gas is ionised by electrons traversing the tube. The ions formed in this way tend to neutralise the space charge. The magnitude of this effect varies as the number of gas molecules, i.e., as the pressure, also as the mass of the atoms, and inversely as the absorption of electrons by the molecules of the gas. At very low pressures, the voltage needed for neutralisation exceeds the ionisation potential, and depends on the number of electrons traversing the tube before neutralisation. The neutralisation occurs independently of the magnitude of the cathode saturation current. For different gases with the same ionising potential, the pressure necessary for the neutralisation effect at the same neutralisation voltage varies inversely as the mass of the gas atom. Positive potassium ions, according to their velocity, effect a more or less marked decrease in the space charge. Comparison of the results with potassium and argon ions shows that an ion-current of about 2 milliamp. is necessary for neutralisation R. A. MORTON. of the space charge to follow.

Mobility of ions in air. IV. Investigations by two new methods. A. M. TYNDALL, L. H. STARR, and C. F. POWELL (Proc. Roy. Soc., 1928, A, 121, 172-184).-Details are given of two new methods of mobility measurement. The advantages of the first (known as the "four-gauze" method) are that the apparatus can be made air-tight, that there is no commutator, that the method has a higher resolving power than the older method (cf. Tyndall and Grindley, A., 1926, 219), that the time of measurement is shorter, and that, within certain limits, the ions may be given any required age before their mobility is measured. The second method (the "two-slit" method) also has a high resolving power and gives ions of controlled age, but it involves the use of an alternating field of the "square-wave" type, produced by a revolving commutator, so that the time of measurement is necessarily long. Neither of the methods gives absolute values. The rate of transformation of the positive ion in air is found to be considerably higher by these methods than in earlier work (loc. cit.), and there is evidence that the transformation is a more complicated phenomenon than was supposed. In many cases the ionisationcurrent-frequency curve suggests the presence, not only of initial and final ions, but also of ions of intermediate mobility. Moreover, the results for shortage (0.016 sec.) positive ions in air containing water vapour, unlike those for negative, are found to be variable. At long ages (0.25 sec.) the results are more definite. The positive ions in air are found to have mobilities distributed over a small range with a mean value of about 1.25 cm./sec. per volt/cm., independent of the humidity of the air. No evidence is obtained of the presence of initial positive ions in very dry air or in pure nitrogen. If any are formed, they must nearly all transform in less than 1/100 sec. The mobility of both positive and negative ions in air containing propyl alcohol vapour is independent of the age of the ions from 1/65 to 2/3 sec.

L. L. BIRCUMSHAW.

Mobility of ions in air. V. Transformation of positive ions at short ages. A. M. TYNDALL, G. C. GRINDLEY, and P. A. SHEPPARD (Proc. Roy. Soc., 1928, A, 121, 185-194).-To investigate the possibility that the variable results obtained for the rate of transformation of short-age positive ions in air (cf. preceding abstract) might be partly due to products of chemical action arising from the a-rays or to impurities given off from the walls which would accumulate in a closed vessel, the effect of adding certain gases and vapours to the air in which positive ions are formed has been studied by an air-blast method. The method is identical in principle with that used by Erikson (A., 1925, ii, 79), but the brass plates are much closer together, thereby reducing the portion of the life of the ion spent in the measurement of the mobility to about 1/1200 sec. The effects of using dry air, ozonised air, ozonised oxygen, oxides of nitrogen, nitrogen, and methyl and propyl alcohol vapours were investigated. A small quantity of ozone, generated either by an ozoniser or by a point discharge, produces a marked increase in the rate of transformation, and there is evidence that sufficient ozone may be generated by a-rays from polonium in a closed vessel to produce an appreciable effect. If the rate of decomposition of ozone is accelerated by the presence of manganese dioxide in the ionisation chamber, or if a rapid air stream is blown over the polonium so that the ozone generated by the α -rays is continuously removed, an increase in the relative number of initial ions is observed, due to a decrease in the rate of transformation. It is argued that the ozone effect may explain certain discrepancies between the results of mobility measurement made by various observers using different methods. The rate of transformation is greatly retarded if, before entering the air blast, the ions are formed in the presence of methyl or propyl alcohol vapours. The significance of the results obtained is discussed. It is suggested that the initial ion depends for its formation on the presence of water vapour, and is transformed into a final stable ion on collision with an ozone molecule. The relatively slow rate of transformation may perhaps be due to the dependence of the change on some type of three-body collision.

L. L. BIRCUMSHAW.

Application of Ebert's ion counter to the determination of the number and mobilities of small ions in the atmosphere. W. J. BARANOW and E. S. STSCHEPOTJEWA (Physikal. Z., 1928, 29, 741-750). For accurate determinations of the mobilities of ions in the atmosphere, it is necessary to consider three groups of ions, larger, medium, and smaller, and to determine the mean mobility in each group by means of a special technique. R. A. MORTON.

Magnetic moments of hydrogen-like atoms. F. B. Pidduck (Nature, 1928, 122, 925).

Rate of emission of α -particles from radium. H. J. J. BRADDICK and H. M. CAVE (Proc. Roy. Soc., 1928, A, 121, 367—380).—A direct determination of Z, the number of α -particles from disintegrations taking place in 1 g. of radium in 1 sec., has been made by the "total charge" method. The apparatus and method are described and the average value of Z from a number of determinations is given as $3.68 \times 10^{10} \pm 1\%$. Radium-C was used as the source. This result is discussed with regard to the heat evolved by radium and its products, and it is concluded that there is no need to assume any other form of heat production than those already recognised.

J. L. BUCHAN.

Internal conversion of γ -rays. II. (Miss) B. Swirles (Proc. Roy. Soc., 1928, A, 121, 447-456; cf. A., 1927, 1004).—Mathematical. J. L. BUCHAN.

Quantum theory of nuclear disintegration. G. GAMOW (Nature, 1928, 122, 805-806).—A brief account of investigations which have afforded a quantitative explanation of certain features of natural α -ray disintegration and throw light on the phenomenon of artificial disintegration. The results support Rutherford's observations, in which artificial disintegration was not observed with elements heavier than phosphorus, but not those of Petterson and Kirsch.

A. A. ELDRIDGE.

Loss in velocity of α -particles in passing through metal foils. S. ROSENBLUM (Physikal. Z., 1928, 29, 737—739).—The author's data on the retardation suffered by α -particles after passing through thin sheets of various metals are summarised (cf. A., 1926, 879; 1927, 1120). Each metal is shown to be characterised by a constant K. The work of Kohlrausch (A., 1928, 455) allows K to be calculated theoretically, and comparison shows fairly close agreement with experiment for the elements of low atomic number, and agreement as regards order for elements of high atomic weight. R. A. MORTON.

Duration of excited sodium atoms as deduced from the brightness of sodium flames and the degree of dissociation of sodium salts in flame. R. LADENBURG and R. MINKOWSKI (Ann. Physik, 1928, [iv], 87, 297-306).—Polemical against Ornstein and van der Held (A., 1928, 679). W. E. DOWNEY.

Nature of active nitrogen. H. O. KNESER (Ann. Physik, 1928, [iv], 87, 717-736, and Physikal. Z., 1928, 29, 895-896).—Three mechanisms have been advanced to account for the afterglow in active nitrogen: (a) metastable excited molecules (+11 volts) revert to the normal state on impact with neutral molecules and emit light (A., 1924, ii, 803); (b) triple collisions between two nitrogen atoms and one nitrogen molecule result in the formation of one activated molecule which then reverts to the normal state as in (a) (A., 1926, 8); (c) the Cario-Kaplan explanation (A., 1928, 683) combining (a) and (b). The rate of decay of the afterglow has been calculated on the basis of the alternative mechanisms, and deactivation by the walls of the containing vessel has also been considered. The rate of decay has been studied experimentally by means of visual photometry using a Lummer cube, and varying the nature of the wall, rare gas additions, and pressure. Observations have been made on the increase in brightness in the afterglow which results from the addition of inactive particles for triple collisions. The results are definitely inconsistent with (a), consistent with (b), and with certain assumptions perhaps consistent with (c) (cf. also A., 1928, 961). R. A. MORTON.

Attempt to polarise electron waves by reflexion. C. J. DAVISSON and L. H. GERMER (Nature, 1928, **122**, 809).

Possible role of diffusion by electrons in the propagation of short waves. PONTE and Y. ROCARD (Compt. rend., 1928, 187, 942-943).-If it is assumed that the Heaviside (H) layer is not analogous to a perfect gas, but is made up of small groups of electrons forming " molecules," the distance apart (d) of which is of the order of a short wavelength, then the analogy of the diffusion of X-rays by a crystalline powder may be applied to the diffusion of wireless waves by the H-layer (cf. Eckersley, Nature, 1928, 121, 245). The great variations in the zones of silence may then be explained by relatively small variations in d, or by large variations in the height of the layer, a mean value for which of 360 km. is J. GRANT. obtained.

Wave theory of the electron. J. M. WHITTAKER (Proc. Camb. Phil. Soc., 1928, 24, 501-505).-In Darwin's method of accounting for the "duplexity' of the atom without using the spinning electron hypothesis, the work can be given invariance of form only by replacing the four wave functions by sixteen. This complication is avoided by specifying the electron wave as a six-vector analogous to the electromagnetic force vector, the first three components being the components of a space vector analogous to the electric force, and the last three the components of a space vector analogous to the magnetic force. The differential equations satisfied by these functions are obtained by assuming that in a null magnetic field they admit a solution representing a plane wave advancing with uniform velocity. The theory leads to the correct energy levels for the fine structure of the hydrogen atom, and gives correct results for the free motion of the electron. A. J. MEE.

Quantum theory of atomic nuclei. G. GAMOW (Z. Physik, 1928, 51, 204-212).—The mechanism of the emission of α -particles is analysed by wave mechanics and a theoretical basis is found for the relationship between the decay constant and the energy of the α -particle. R. W. LUNT.

Reason why an elementary quantum of electricity cannot split up into still smaller charges. W. ANDERSON (Ann. Physik, 1928, [iv], 87, 536— 542).—If a particle of mass m_0 and charge e "explodes" into n_1 equal parts, these must have mass m_0/n_1 and charge e/n_1 . In a vessel of finite volume, the null-point energy of the gas must be smaller than

 m_0c^2 , where c is the velocity of light. This is conditional on the original charge being greater than a definite universal minimal charge e_{\min} . Calculation shows that e_{\min} is certainly greater than 1.14×10^{-11} e.s.u., probably greater than 1.14×10^{-10} e.s.u., and perhaps even greater than 1.14×10^{-9} . The lastnamed limit gives a simple reason for the stability of electrons and protons with a charge of 4.774×10^{-10} e.s.u. R. A. MORTON.

Origin of magnetism based on the structure of atoms. K. HONDA (Sci. Rep. Tôhoku, 1928, 17, 997-1009).—See A., 1928, 568.

Is it possible to test by a direct experiment the hypothesis of a spinning electron ? L. BRIL-LOUIN (Proc. Nat. Acad. Sci., 1928, 14, 755—763).— The possibility of determining by direct experiment whether or not the multiplet structure of line spectra is due to rotation of the electron and the influence of the magnetic field on its angular momentum and magnetic moment is discussed mathematically, and a former assumption (cf. Compt. rend., 1927, 184, 82) corrected. A form of electromagnet suitable for such a purpose is described. M. S. BURR.

Structure of the atom. F. J. VON VISNIEWSKI (Physikal. Z., 1928, 29, 716—720).—An attempt is made to develop an atomic structure on the supposition that each atom contains one electron in the K energy level, one in the L-level, and one in one of the 5M-levels etc. J. W. SMITH.

Dynamics of an electron. D. MEKSYN (Phil. Mag., 1928, [vii], 6, 977—991).—The general theory of relativity is applied to the dynamics of an electron. W. E. DOWNEY.

Homopolar combination in excited hydrogen molecules. E. A. HYLLERAAS (Z. Physik, 1928, 51, 150—158).—Mathematical. With the help of wave mechanics, calculations are made of the reciprocal action between hydrogen atoms, of which one is in the fundamental state and the other in an excited state. Of the four solutions to the wave equation, two apply to elastic reflexion and two to molecule formation. Of the latter, both show symmetry in both nuclei, but the electrons are symmetrical in the one case and asymmetrical in the other, corresponding with a para- and an ortho-term of the hydrogen molecule. In such a state the energy of dissociation is less and the moment of inertia is greater than in the fundamental state. J. W. SMITH.

Limitation of the system of elements. W. Kossel (Naturwiss., 1928, 16, 298–299; Chem. Zentr., 1928, i, 2689).—A possible explanation of the absence of atomic numbers greater than 92 is based on a consideration of the relative importance of electrostatic and magnetic attraction within the atom. A. A. ELDRIDGE.

Heat of dissociation of nitrogen. R. T. BIRGE (Nature, 1928, 122, 842).—The author gives reasons for considering that the heat of dissociation of nitrogen cannot well be greater than 9.5 volts (cf. Gaviola, A., 1928, 1075, 9.8 volts; Birge and Sponer, A., 1926, 993, 11.4 volts). Other probable values of heat of dissociation are : oxygen 7.0, carbon monoxide 11, nitrie oxide 7 volts. A. A. ELDRIDGE. [Heat of dissociation of nitrogen.] R. S. MULLIKEN (Nature, 1928, 122, 842—843).—A consideration of the products of dissociation supports the value 9.5 volts for the heat of dissociation of nitrogen (see Birge, preceding abstract).

A. A. ELDRIDGE.

Fluorescence and photo-sensitisation in aqueous solution. I. W. WEST, R. H. MULLER, and E. JETTE (Proc. Roy. Soc., 1928, A, 121, 294-298).—A discussion of the problem.

J. L. BUCHAN.

Fluorescence and photo-sensitisation in aqueous solution. II. E. JETTE and W. WEST (Proc. Roy. Soc., 1928, A, 121, 299-312).—The apparatus used is described. Two photo-electric cells were connected differentially with a standard solution in front of one and the solution under investigation in front of the other. By this means fluctuations in the intensity of the source (a mercury lamp) were automatically corrected. The effect of various salts in extinguishing the fluorescence of different substances has been studied, and the results are expressed as percentage extinction of the fluorescence due to the pure fluorescent substance. Tables are given showing the extinction of the fluorescence of quinine hydrogen sulphate by various salts and it is concluded that the effect is due chiefly to the negative ions. Silver ions, however, exert some influence. Non-electrolytes, such as sucrose and carbamide, were practically without effect, whilst the influence of electrolytes seemed to be decreased by a high viscosity of the solution. When solutions of disodium fluorescein were used instead of quinine hydrogen sulphate much the same extinction effect was observed, but higher concentrations of the added salt were necessary to produce the same percentage extinction. The amount of added salt necessary to reduce the fluorescence of uranyl sulphate to zero has also been found. From an examination of these substances the inhibiting power of various ions has been shown to be I'> $CNS'>Br'>Cl'>C_2O_4''>Ac'>SO_4''>NO_3'>F'$. The cause of this effect is discussed and it is pointed out that the order of the ions in the above series is the same as in that of their deformabilities. The deformability of the silver ion is greater than that of other cations. It is concluded that the energy of the activated fluorescent molecule is used to deform the inhibiting ion with which it collides, instead of being given out as light. J. L. BUCHAN.

Fluorescence and photo-sensitisation in aqueous solution. III. R. M. MÜLLER (Proc. Roy. Soc., 1928, A, 421, 313–317; cf. preceding abstract).—The fluorescence of 0·1*M*-uranyl sulphate solution in the presence of varying amounts of oxalic acid has been measured. It has been shown that the greater the concentration of oxalic acid the less is the amount of light emitted and the greater is the amount of oxalic acid decomposed photochemically, until the ratio $H_2C_2O_4/UO_2$ becomes unity, after which it remains constant. The order in which anions diminish the photolysis of oxalic acid is the same as that in which they extinguish the fluorescence of uranyl salts. J. L. BUCHAN.

Depolarisation of the secondary radiation in the complex light resulting from the molecular diffusion of monochromatic light. J. CABANNES (Compt. rend., 1928, 187, 654-656).-The depolarisation of secondary radiations observed by Raman (A., 1927, 1127; 1928, 1075) has been studied for benzene and ethyl ether, and the following conclusions are reached: (1) If the liquid is illuminated with different radiations N, N'_1, \ldots , all the secondary rays $N-n_1, N'-n_1, \ldots$ with the same diminution in frequency have the same depolarisation. (2) This depolarisation varies within wide limits according to the particular diminution in frequency. The results indicate that the molecules fall into groups, each group producing its own diminution in frequency and depolarisation. The groups probably represent molecules in different orientations relative to the incident ray. W. HUME-ROTHERY.

New bands of mercury hydride in the ultraviolet. H. JEZEWSKI (Bull. Acad. Polonaise, 1928, A, 143-162).-The existence of a new series of bands in the ultra-violet emitted when a discharge is passed through a mixture of hydrogen and mercury vapour has been demonstrated. The apparatus used is described, and the conditions for appearance of the bands are enumerated. The spectrum is analysed. and equations are given showing the frequency of the rays as a function of the quantum number. From the equations the moment of inertia of the molecules and the distance apart of the nuclei are calculated. It is shown that the use of fractional quantum numbers is justified. The purity of the hydrogen and mercury used leaves no doubt that the bands are emitted by some combination of the two. The moment of inertia of the molecules, however, is smaller than that of the molecules emitting Hulthén's bands; also the bands degrade towards the red, instead of towards higher frequencies as in Hulthén's case. These observations, together with the fact that the bands are always accompanied by a spark spectrum, indicate that the molecules are ionised. This is confirmed by an application of Ludloff's rule. The emission is probably due to the considerably deformed molecule of mercury hydride. A. J. MEE.

X-Ray phosphorescent and thermophosphorescent radiations of kunzite. O. STUHLMAN and A. F. DANIEL (J. Opt. Soc. Amer., 1928, 17, 289-293).—The spectral distribution of phosphorescence excited in kunzite crystals by X-rays was determined. There are two emission bands, one weak and of wavelength about 0.50 μ , the other stronger and having a maximum at 0.65μ . The thermophosphorescence was also determined. A rose-coloured light began to be emitted at about 168°, the radiation being composed of a broad orange band with a maximum near 0.64 µ and a weaker band with a maximum near 0.50 µ. As the temperature was raised the bands gradually widened up to a temperature of 400°, when the phosphorescence suddenly ceased. The colour changes of kunzite on heating or on exposure to ultra-violet light, X-rays, or radium radiation may be explained on an oxidation and reduction hypothesis connected with the manganese contained in the mineral. A. J. MEE.

Scattering of light by crystals. G. LANDSBERG and L. MANDELSTAM (Z. Physik, 1928, 50, 769–780). —The light scattered by quartz and calcite when mercury arc light is incident on these crystals has been examined spectroscopically. It has been found that each line in the incident radiation appears in the light scattered by the crystal together with a number of satellites of greater and of less frequency. The frequency difference between the satellite lines and the incident line for quartz correspond with the wave-lengths 9.0, 13.5, 21.5, 48, and 81 μ and for calcite with 9.1 and 34 μ . The relation of these wave-lengths to known infra-red wave-lengths is discussed. R. W. LUNT.

Delayed green fluorescence of mercury vapour. S. PIEŃKOWSKI (Bull. Acad. Polonaise, 1928, A, 241—256, and Z. Physik, 1928, 50, 787—792).—The average duration of the delay of the fluorescence of mercury vapour excited by ultra-violet rays was measured and found to be of the order 10⁻⁵ sec. and decreased with increasing vapour density. The intensity of the fluorescence was examined with the aid of photo-micrometric curves, and was shown to increase from the moment of excitation and to reach a maximum. The rate of intensity rise and of extinction increased with the vapour density. Evidence pointed to the existence of an intermediate state of the mercury, from which the fluorescence arises as a molecular and not as an atomic phenomenon.

N. M. BLIGH.

Ultra-violet fluorescence of iodine bromide. A. FILIPPOV (Z. Physik, 1928, 50, 861-873).—When iodine bromide vapour is irradiated with radiation of shorter wave-length than 2000 Å. the fluorescent light consists of a number of bands between 2750 and 4900 Å. Arguments are advanced to show that the fluorescence must arise from excited IBr molecules. The spectrum is modified by the addition of nitrogen or helium, the structure of some of the bands being more clearly defined; the spectrum from an iodine chloride-nitrogen mixture is similar.

R. W. LUNT.

Absorption of ultra-violet light by the inversion products of sucrose. L. KWIEUŃSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1928, A, 257—261).—If the inversion products of sucrose contained only dextrose and d-lævulose, only a faint absorption band due to the latter would be expected (cf. A., 1928, 346). Absorption measurements made at various stages of the inversion process show that other products of unknown nature are formed.

N. M. BLIGH.

Absorption of ultra-violet light by the glucosans. L. KWIEDIŃSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1928, A, 263—269).— β -Glucosan was purified by repeated recrystallisation. The absorption of ultra-violet light by the successively purer crystallisation products, and by the products recovered from the mother-liquors, showed a band weakening and finally disappearing in the former case, and stronger in the latter, due to the accumulation of unknown impurities. An unpurified sample of α -glucosan showed a band the position of which indicated that impurities, if present, were not identical with those

in β-glucosan. Results were supported by molar extinction coefficients, given in all cases. N. M. BLIGH.

Absorption of ultra-violet light by arabinose, maltose, sucrose, raffinose, and by mannitol and dulcitol. L. KWIECIŃSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1928, A, 271-282; cf. preceding abstract).—Highly purified specimens of each of the above carbohydrates showed no selective absorption. Sucrose required especially careful purification, the extent of which was determined with certainty by measurement of extinction coefficients. N. M. BLIGH.

Formation of phosphorescence centres in calcium sulphide. F. BANDOW (Ann. Physik, 1928, [iv], 87, 469-508).-Preparatory to a more accurate determination of the absolute energy output from a phosphor, i.e., the maximum number of electrons separable from one heavy metal atom, it has been necessary to investigate more closely the rôle of the flux. For the three emissions CaS-Cua, CaS-Mna, and CaS-Bia, the maximum light-sum with ordinary preparations considered with reference to a definite heavy metal content can be obtained only when fluorides are added to form a flux. Fluoride additions do not affect the distribution of phosphorescence centres corresponding with emissions differing in duration, which is obtained with sodium sulphate or borax additions. The fluoride addition necessary for maximal effect varies directly as the metal content. Secondary factors such as volatilisation of metal etc. are not influenced.

"Nursulfidphosphores," *i.e.*, phosphors in which the base consists solely of calcium sulphide, exhibit without addition of fluoride the maximum effect, which is obtained only by adding fluoride to the ordinary phosphors. The increase in initial photoelectric effect which appears in mechanically disturbed phosphors without irradiation has been studied in relation to the effect of various added substances on the formation of centres, but considerable difficulties are encountered. Phosphors containing additions of sodium chloride are in many respects abnormal. In phosphors to which calcium oxide has been added, the light-sum decreases regularly with increasing lime content, but a rearrangement of the types of centres occurs.

Addition of fluoride does not cause the appearance of new centres, but rather acts directly on the atoms of heavy metal, apparently by changing the number of electrons separable from a single atom. It seems possible that the phosphorescence centre must contain every constituent of the phosphor.

R. A. MORTON.

Ultra-violet luminescence of calcium oxide and calcium sulphide excited by X-rays. E. RUMPF (Ann. Physik, 1928, [iv], 87, 590—594).—Under the action of X-rays (Cu-K α), calcium oxide and calcium sulphide exhibit ultra-violet luminescence, due apparently to traces of impurity which cannot be eliminated. In the case of the oxide, the emission shows a strong band with a maximum near 345— 375 µµ, and a weaker band extending from 280 to 330 µµ, with a maximum near 320—330 µµ. Addition of traces of copper or manganese excites another band near $450 \,\mu\mu$. The emission from calcium sulphide is similar, but the wave-lengths are about $10 \,\mu\mu$ greater, and the luminescence is very much weaker. The work provides a test for the presence of appreciable quantities of oxide in sulphide preparations. R. A. MORTON.

Light absorption and the nature of molecular combination in gases and vapours. (MISS) H. SPONER (Z. Elektrochem., 1928, 34, 483–489).— Atomic molecules (e.g., non-polar molecules like hydrogen, halogens, and polar molecules like silver halides) are dissociated by absorption of light into a normal and an excited atom. In ionic molecules this dissociation may also be accompanied by dissociation into two normal atoms. S. K. TWEEDY.

Fluorescence and solid solution. (MISS) M. K. SLATTERY (Proc. Nat. Acad. Sci., 1928, 14, 777-782; cf. A., 1926, 659).-When activated by traces of uranium, which must be in solid solution in the salts, alkali fluorides fluoresce under excitation by ultraviolet light at the temperature of liquid air. A spectrum of fine lines is obtained, the position of these being independent of the amount of activator present. The lines can be arranged in four sets of constant frequency separation with a slightly different interval for each set, the intervals being 17.9, 17.6, 17.2, and 16.7 units, respectively. The lines for fluorescent lithium fluoride can be arranged in four sets with the same separation as those of sodium fluoride. Three of the sets are slightly displaced from the sodium fluoride positions, but the one with the 17.2 interval is identical with that of sodium fluoride. The average of these frequency intervals is 17.6, the interval for uranium. The meaning of constant frequency emission for a solid is not very clear, but the different intervals are probably dependent on vibrating systems of slightly different moments of inertia. An attempt was made by the X-ray powder method to determine whether the introduction of uranium into the crystal, although in such small quantity-one part in 200 parts at the most-might not produce a measurable change in the crystal structure of the solid solvent surrounding it. No such change was observed. This contradicts the view put forward by Ewles (A., 1926, 455). The fluorescence of mixtures of sodium and lithium fluorides when mixed with uranium in the proportion of one part of the latter to 2000 parts of the former has been studied. There is a gradual change of colour of fluorescence towards the green as the amount of lithium increases, and both lithium and sodium lines are shifted, sodium about 3Å. towards shorter wave-lengths and lithium to a smaller extent in the opposite direction. The amount of shift was the same for all mixtures, contrary to what was observed by Travniček (A., 1928, 106) for calciumstrontium sulphide mixtures with samarium. Corresponding changes in the crystal structure were also observed by X-ray methods, and these, too, were constant for all mixtures. Hence an increase in crystal dimensions causes an increase in wave-length of fluorescence. In order of size of lattice lithium fluoride is 2.007 Å., sodium fluoride 2.310 Å., and potassium fluoride 2.664 Å. The fluorescence colours are green, yellow, and orange, respectively. M. S. BURR.

Valency. XI. Molecular conductivities and extinction coefficients of derivatives of cyclotelluropentane. F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 2658-2667; cf. A., 1928, 349, 1098).-The extinction coefficients in dry alcohol and conductivities in water of the dihalides of the three series (i) C_5H_{10} :TeX₂, (ii) C_5H_{10} :TeX·CH₂·[CH₂]₃·CH₂X, (iii) C_5H_{10} :TeX·CH₂·[CH₂]₃·CH₂:TeX: C_5H_{10} (Morgan and Burgess, A., 1928, 435) have been measured. The following compounds have also been prepared and examined : monocyclic base, C5H10Te(OH)2, and the following derivatives, hydroxy-halides, C₅H₁₀Te(OH)X, tetraiodide C₅H₁₀TeI₄; dicyclic base, $(C_5H_{10})_3Te_2(OH)_2$ and derivatives, bistribromide and bistri-iodide, (C₅H₁₀)₃Te₂I₆. The dihalides of series (ii) and (iii) behave as binary and ternary electrolytes, respectively, but those of series (i) give anomalous values due to hydrolysis to hydroxy-halides. The monocyclic di-iodide is found to resemble a-dimethyltelluronium di-iodide rather than the isomeric β-di-iodide in its absorption spectrum and its behaviour towards iodides and alkalis. This resemblance is further borne out in the conductivity of the monocyclic base and the form of the curve obtained from potentiometric titration which has also been determined. The curve obtained by the latter method for the dicyclic base is anomalous. R. N. KERR.

Ultra-violet bands of alkaline-earth sulphide phosphors. O. SCHELLENBERG (Ann. Physik, 1928, [iv], 87, 677-715).-In the preparation of phosphors showing the maximum emission of ultraviolet light the important factor is the heavy metal content. Accepting as "normal" the proportion of heavy metal recommended by Lenard and Klatt for the preparation of phosphors emitting visible light, decreasing the heavy metal content causes a marked increase in the intensity of the ultra-violet bands, e.g., for CaS-Bi very good results are obtained at 1/1600N. Conditions for preparing alkaline-earth sulphide-iron phosphors emitting ultra-violet light are described for the first time, and CaS-Zn, together with sulphide phosphors of bismuth, lead, silver, and antimony, are also described and studied with special reference to ultra-violet phosphorescence. In conformity with the known shift of the visible bands in the direction of longer wave-lengths for the calciumbarium-strontium sulphide phosphors, a similar shift is recorded for the ultra-violet bands. The relation between temperature and emission has been studied; as regards the upper momentary state the phosphors can be divided into two classes, those in which it begins at 70° and at 100°; as regards duration. the phosphors are noteworthy for the short range of temperature over which the time-emission extends.

The 368 $\mu\mu$ band of CaS-Pb is shown to be connected with the known blue β -band. At the temperature of liquid nitrogen it has been possible to obtain resolution into fine bands, using calcium sulphide phosphors (CaS-Pb β).

The long wave-limit of the excitation-distribution for the ultra-violet bands has been fixed at 280 $\mu\mu$ for the first band and 237 $\mu\mu$ for the remaining bands. A number of new visible bands are recorded and fully characterised. R. A. MORTON. Vibration and rotation spectra of a molecule of the type CH_4 . W. ELERT (Z. Physik, 1928, 51, 6-33).—On the assumption that the equilibrium arrangement of a molecule which is composed of four similar nuclei and one other is a regular tetrahedron with the odd nucleus at the centre, the nature of the vibrational and rotational spectra of such a molecule has been deduced. The specific heat of methane has also been calculated from this supposition.

J. W. SMITH.

Raman effect in the X-ray region. M. PONTE and Y. ROCARD (Compt. rend., 1928, 187, 828— 829).—The work of Davis and Mitchell (A., 1928, 1168) shows that after diffusion by a body the structure of an X-ray is more complex than that of the incident ray, and therefore when rays of high frequency are used for the production of the Raman effect the phenomena fall in the domain of X-rays, and should be explained by a theory of light quanta in place of the classical theory. J. GRANT.

Ultra-violet absorption curves of *iso*eugenol and eugenol. J. SAVARD (Bull. Soc. chim., 1928, [iv], 43, 1072—1075).—The curves of both substances are similar, showing two bands and the start of a third in the extreme ultra-violet; the maxima are eugenol 2807, 2288 Å., *iso*eugenol 2925, 2565 Å. The first band is attributed to the phenol-phenolic ether grouping and the second to the ethylenic linking. Both curves are similar to that obtained for veratrol; the resemblance is very close for eugenol, but there is a displacement towards the red, especially marked in the second band, for *iso*eugenol. This is attributed to the ethylenic linking in the latter compound being in the $\alpha\beta$ -position in the side-chain and therefore conjugated with the benzene nucleus. R. N. KERE.

Band spectra and flame phenomena. K. F. BONHOEFFER and F. HABER (Z. physikal. Chem., 1928, 137, 263—288).—The reactions and energy relationships existing in a burning gas are discussed in the light of the flame spectra, especially with reference to hydrogen, carbon monoxide, and hydrocarbons. H. F. GILLBE.

Band spectra and electron terms of the molecules Na₂, NaK, and K₂. R. RITSCHL and D. VILLARS (Naturwiss., 1928, 16, 219–220; Chem. Zentr., 1928, i, 2484).—The calculated isotope effect for $(K^{39})_2$ and $(K^{39}K^{41})$ was observed. With Na₂ and K₂, two systems correspond with equal atomic excitation if the excited molecules dissociate.

A. A. ELDRIDGE.

Rotation of molecules induced by light. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, 122, 882).—In agreement with the view that the probability of a spin being induced in a molecule when it collides with a light quantum should depend (among other factors) on the degree of optical anisotropy of the molecule, benzene, toluene, and piperidine exhibit wings accompanying mercury arc lines after scattering, whilst carbon tetrachloride, ether, and alcohol do not. The effect is marked with carbon disulphide.

A. A. ELDRIDGE.

Secondary radiations observed in the molecular diffusion of light by fluids (Raman effect). P. DAURE (Compt. rend., 1928, 187, 826-

828; cf. A., 1928, 813).—If N is the frequency of the exciting ray and n the characteristic frequency of the substance studied, then the frequencies of the so-called positive and negative rays situated symmetrically on the short and long wave-length sides of the exciting ray, respectively, are given by the expressions (N+n) and (N-n), respectively. The intensities of rays of opposite characteristic frequencies excited by the mercury line 4358 Å. have been compared photometrically, and also those $(I_1 \text{ and } I_2)$ of the two secondary rays of the same characteristic frequency excited by two different radiations (4358 and 5460 Å.). If D_1 and D_2 are the intensities of those radiations normally diffused by the fluid, and S_1 and S_2 are those of the corresponding Raman rays, then $D_2/D_1: I_2/I_1=D_2/I_2: D_1/I_1=2\cdot5$, and $S_2/S_1: I_2/I_1=S_2/I_2: S_1/I_1=1\cdot5$.

observed in the radiations Secondary molecular diffusion of light (Raman effect). P. DAURE (Compt. rend., 1928, 187, 940-941).-The Raman spectra of phosphorus tribromide, carbon, silicon, titanium, and tin tetrachlorides, and the trichlorides of phosphorus, arsenic, antimony (at 100°), and bismuth (in hydrochloric acid) consist of four principal rays (a, b, c, d), the characteristic frequencies of which decrease regularly with the atomic weights of the constituent elements. Of the negative rays the a and c rays were always of equal intensity, and equal to that of the b rays for the carbon series but four times as strong as those of the phosphorus series. The intensities of the d rays were variable and usually the weakest. Positive rays were also observed.

J. GRANT.

Molecular spectra in sunspots. G. PICCARDI (Nature, 1928, 122, 880).—Comparison of Gale, Monk, and Lee's measurements of the secondary (molecular) spectrum of hydrogen (A., 1928, 1166) with observations on sunspot spectra discloses numerous coincidences (± 0.03 Å.) between 6400 and 4450 Å. All the lines presumed to be those of the secondary spectrum of hydrogen show no trace of the Zeeman effect. A. A. ELDRIDGE.

Influence of substitution of halogens, alkyl and amino-groups on the colour and absorption spectra of indigotin, thioindigotin, and indirubin. J. FORMÁNEK (Chem. obzor, 1928, 3, 133-141).—Introduction of chlorine, and particularly of bromine, atoms into the benzene nucleus of indigotin displaces the absorption bands towards the red, to an extent which increases with the number of halogen atoms. Introduction of alkyl groups into the benzene nucleus of indigotin displaces the absorption slightly, but into the imino-group considerably. Analogous observations with monothioindigotin, thioindigotin, and indirubin are described.

CHEMICAL ABSTRACTS.

Ionisation accompanying oxidation of nitric oxide. A. PINKUS and L. HENRY (Bull. Soc. chim. Belg., 1928, 37, 285–303; cf. A., 1918, ii, 286; 1924, ii, 463).—Measurements of the ionisation accompanying the reversible reaction $2NO+O_2 \implies 2NO_2$ have been made in an apparatus in which it is possible to detect currents of the order of 10^{-15} amp. At temperatures of about 100° the replacement of oxygen

in the ionisation chamber by a mixture of oxygen with nitric oxide or nitrogen peroxide produces only momentary electric effects, which are attributed to the difference in dielectric constant of oxygen and nitrogen peroxide. In the region of 300° , however, ionisation currents of from 10^{-14} to 5×10^{-13} amp. are obtained, whatever the sign of the field applied. The current intensity increases with the potential applied and with the proportion of oxides of nitrogen, provided sufficient oxygen is present to bring about the complete oxidation of the nitric oxide. The ions are not of thermionic origin, since neither gas separately produces any electrical effect. The fact that no ionisation can be detected below 100° may be explained either by supposing that it is due solely to the dissociation of the peroxide into nitric oxide and oxygen, or by assuming the presence on the electrodes of an insulating adsorbed layer of molecules of nitrogen peroxide in the form of oriented dipoles, preventing the discharge of ions by the metal at low temperatures (cf. Brewer and Daniels, A., 1923, ii, 721; 1924, ii, 745). M. S. BURR.

Ionisation accompanying the thermal decomposition of ozone. A. PINKUS and R. RUYSSEN (Bull. Soc. chim. Belg., 1928, 37, 304-325; cf. A., 1921, ii, 368).-By passing ozonised oxygen through an ionisation chamber at 220-240°, and combining measurements of the ionisation current with analyses of the gases entering and leaving the chamber, it is shown that the decomposition of 10⁻⁶ to 10⁻⁷ g.-mol. of ozone per sec., in a field of 845 volts per cm., produces currents of 10⁻¹¹ to 10⁻¹² amp. The ionisation current increases in direct proportion to the number of molecules of ozone dissociated per sec. The current intensity is independent of the sign of the electric field, indicating the formation of equivalent numbers of positive and negative ions of similar mobility. In a field of 845 volts per cm. only about one elementary charge reaches the electrodes for 1010 mols. of ozone decomposed. The ionisation current increases rapidly with the intensity of the electric field, but saturation is not reached, even with a potential gradient of 3000 volts per cm. The results obtained are substantially in agreement with those of Brewer and Daniels (A., 1923, ii, 721; 1924, ii, 745). A theory of the mechanism of the thermal dissociation of ozone is suggested. There are probably two stages in the process, viz., ionisation by collisions between molecules of ozone, resulting in the formation of positive and negative ions which are charged atoms of oxygen, followed by recombination of the ions with the formation of neutral molecules of oxygen.

M. S. BURR .

Lattice constants of calcium oxide and calcium hydroxide. E. RUMPF (Ann. Physik, 1928, [iv], 87, 595—596).—For calcium oxide (sodium chloride lattice type) the constant is 4.799 ± 0.002 Å., and for calcium hydroxide (hexagonal lattice of the calcium iodide type), $a=3.582\pm0.001$ and $c=4.904\pm0.008$ Å. R. A. MORTON.

Ionisation potential of the molecule of water. R. GRINFELD (Contrib. Estud. Ciencias fisic. mat. La Plata, 1928, 4, 283—293; Chem. Zentr., 1928, ii, 125).—A critical potential, corresponding with the change $(H_2O)^+ + e$, was observed by Lenard's method at 18.0 volts. A. A. ELDRIDGE.

Electric moments of molecules and the intermolecular forces. P. DEBYE (Z. Elektrochem., 1928, 34, 450—452).—The molecular refraction method of measuring dipole moments eliminates that part of the moment due to orientation and measures only the deformation polarisation. Intermolecular forces are likewise made up of two parts. The relation between the dissymmetry of compounds, as characterised by the dipole moments, and the constitution is discussed with the aid of examples. The dielectric method enables conclusions to be reached regarding the formulation of compounds. S. K. TWEEDY.

Dielectric constants of solutions of electrolytes. H. HELLMANN and H. ZAHN (Ann. Physik, 1928, [iv], 87, 716).—An addendum (cf. A., 1928, 1089). R. A. MORTON.

Application of the resonance method to the measurement of the dielectric constants of conducting liquids. H. KNIEPKAMP (Z. Physik, 1928, 51, 95-107).-The theory is worked out for the influence of a non-inductive capacity shunt on the standardisation of the current and voltage resonance in a vibration circuit. It is shown that current resonance is dependent on the capacity shunt, but not the voltage resonance. Hence the latter measurements are much preferable to the former in the determination of dielectric constants of conducting liquids. Measurements made on solutions of sucrose and carbamide confirmed these predictions, the values obtained by voltage measurements being in agreement with those of previous workers. J. W. SMITH.

Dielectric constants of aqueous solutions of methyl-orange, helianthin, and other ampholytes. A. THIEL and E. HORN (Z. anorg. Chem., 1928, 176, 403-415).—The variation of dielectric constant with concentration in solutions of methylorange, helianthin, o- and p-aminobenzoic acids, δ-amino-n- and α-aminoiso-valeric acids, and glycylglycine has been determined. Contrary to the observations of Blüh (A., 1923, ii, 823; 1924, ii, 658), the dielectric constant falls with increasing concentration of methyl-orange or aminobenzoic acids. The dielectric constant of helianthin solutions does not deviate to an appreciable extent from that of the solvent alone, whether water or solutions of acetic or hydrochloric acid in water. This may be due to the small solubility. The dielectric constant for aliphatic amino-acids falls to a minimum with increasing concentration, and then rises to much higher values than for water alone. This may be explained by the fact that, whilst ordinary ions cause a lowering of the dielectric constant of the solvent, the doublet ion, being really a polar molecule, causes an increase. At higher concentrations, the proportion of doublet ion increases until its influence predominates. This dielectric behaviour is in agreement with both optical and electrochemical observations on the presence of the doublet ion. M. S. BURR.

Influence of an electrostatic field on the dielectric constant of liquid crystals. M. JEZEV-SKI (Z. Physik, 1928, 51, 159-164).-Measurements have been made of the dielectric constant of p-azoxyphenetole and p-azoxyanisole in the form of liquid crystals in an electrostatic field of 0—1000 volts per cm. A diminution in the dielectric constant was found which decreased with the intensity of the field and came asymptotically to a limiting value.

J. W. SMITH. Measurement of dielectric constants in liquids at high electrical field strengths. J. MALSCH (Physikal. Z., 1928, 29, 770-777) .- A method is described for measuring dielectric constants of conducting liquids in very high fields with an accuracy of 0.06%. The principal source of error is the change in conductivity with field strength described by Wien. The data on water, nitrobenzene, and alcohol show that $\varepsilon = \varepsilon_0 (1 - \alpha E^2)$, E being the field strength. This expression agrees with the Debye theory, and from the point of view of the dipole theory the variations arise partly from association phenomena. The absolute values $\Delta \varepsilon/\varepsilon$ at 250,000 volts/cm. are 0.7, 1.0, and 1.5%, respectively, for water, nitrobenzene, and alcohol, so that the effect varies inversely as the dielectric constant. The simple Debye theory, using the Clausius-Mosotti relation for calculating the inner field and neglecting association phenomena, leads to values considerably greater than those R. A. MORTON. observed.

Refractometric researches. VII. Deformation of ions and molecules and refractometric data. K. FAJANS (Z. Elektrochem., 1928, 34, 502-518).—Most substances exhibit a type of chemical combination which falls between the limits of the ideal ionic and the non-polar combinations, which may be explained by the displacement of the electron orbits of the anion towards the cation to an extent controlled by the polarising (or deforming) action of the latter. In a molecule or lattice, then, the combination will be further removed from the ideal ionic type to the non-polar type the smaller the cation and the higher its charge, and the more the anion is capable of deformation. Further, under similar conditions, cations which have not the inert gas character (e.g., Ag', Cu'') will produce greater deformation than those which have the inert gas structure.

From these points of view the influence of the four fundamental ionic properties, viz., charge, size, and structure of the electron orbits, and polarisability, on the type of combination in compounds is investigated with the aid of previously published data (Wulff, following abstract) In almost all cases of combination of ions with ions or with neutral molecules, or even combination of neutral molecules with each other, deviation from the additive rule of molecular refractivity (Lorentz-Lorenz) results, in agreement with the above conclusions. S. K. TWEEDY.

Refractometric researches. VI. Interferometric method of determining the refractive index of crystals. P. WULFF (Z. Elektrochem., 1928, 34, 611-616).—The crystal (0.5-10 mm.) is immersed in a liquid, the composition of which is varied until its refractive index equals that of the crystal. The latter stage is determined accurately by an interferometric method. Some values for

inorganic salts are recorded (cf. Fajans, Kohner, and Geffeken, A., 1928, 477). S. K. TWEEDY.

Degree of association in liquid dielectrics. M. WOLFKE (Physikal. Z., 1928, 29, 713-716).—A statistical theory of association in liquid dielectrics has been developed and the degree of association deduced as a function of the concentration and temperature of the mixture. The values so calculated are found to be in good agreement with practical data. J. W. SMITH.

Optical properties of arsenic. II. E. GRYSZ-RIEWICZ-TROCHIMOWSKI and S. F. SIKORSKI (Rocz. Chem., 1928, 8, 405—422).—The refractive index of a number of derivatives of tervalent arsenic has been measured. The atomic refraction of arsenic is affected to the same extent by combination with chlorine, hydrogen, or aliphatic radicals. It is diminished by the substitution of fluorine, cyanogen, methoxy-, or ethoxy-groups, and is augmented by the introduction of aryl groups, bromine, or iodine.

R. TRUSZKOWSKI.

Expression of refractive power. R. DE MALLE-MANN (Compt. rend., 1928, 187, 888-890; cf. A., 1928, 1310).—From a consideration of the molecular discontinuities of a substance in the gaseous and liquid states the expression $M(n^2-1)/d[1+(n^2-1)/\alpha]$ is derived as a first approximation for the refractive power of the gas, where d is the density of the liquid and α a pure number (4.4 according to Henriot) depending on the nature and diameter of the molecules. The rotatory power is obtained when (n^2-1) is replaced by the rotation, and in the case of isotropic substances two independent expressions are then obtained. J. GRANT.

Co-ordinative combination and the electronic theory of valency. N. V. SIDGWICK (Z. Elektrochem., 1928, 34, 445-450).—A general account from the point of view of "effective atomic numbers" dealing with the co-valency rule, valency groups, and the distinction between electro- and co-valent combination. Recent work of Debye (this vol., 12) renders it likely that the capacity of an acceptor to enter into co-ordinative combination depends on the existence of a dipole in which it is positive. Association in the liquid state also is probably a co-ordination phenomenon. S. K. TWEEDY.

Stereoisomeric carbonisation theory. D. WIELUCH (Z. Oberschles. Berg- u. Hüttenmannisch. Ver. Katowice, 1928, No. 3, 6 pp.; Chem. Zentr., 1928, i, 2567).—The theory postulates that the molecules of carbonised substances contain "inorganic" as well as "organic" carbon linkings. Graphite belongs to the hydroaromatic series. Carbonisation is not associated with aromatic structure.

A. A. ELDRIDGE.

Theory of valency of boron, and the constitution of the simplest boron hydride. E. MÜLLER (Z. anorg. Chem., 1928, **176**, 205-208).— Polemical against Wiberg (cf. A., 1928, 936).

H. F. GILBE.

Production and absorption of soft X-rays and secondary electrons. E.RUDBERG (Proc. Roy. Soc., 1928, A, 121, 421-432; cf. A., 1928, 1173).—The work of several investigators is considered, and it has

been calculated that the number of photoelectrons produced in a solid conductor by soft X-rays is of the same order of magnitude as the number produced in gases by the same radiation. Also the number of primary electrons inside the conductor is about ten times the number escaping from the surface. In the case of the production of secondary by primary electrons, it is suggested that the apparent loss in efficiency may be accounted for (1) by the absorption of slow electrons by the body in which they are produced, (2) by collisions which reduce the energy of the escaping electron, and (3) by the fact that there may be slow electrons the energy of which is not sufficient to overcome the surface field. It is therefore concluded that all the energy of the bombarding electrons can be converted into that of secondary electrons within the target. The source of the secondary electrons has been considered and it is concluded that on the whole the evidence points to their origin as being the free electrons initially present in the conductor.

J. L. BUCHAN.

Reflexion of soft X-rays. J. E. HENDERSON and E. R. LAIRD (Proc. Nat. Acad. Sci., 1928, 14, 773— 777).—A method is described for investigating reflexion in the region of long wave-length X-radiation, using a mirror of polished iron and also one of optically flat glass. It was found that there is no sharplydefined total reflexion such as occurs in the hard X-ray region, with the possible exception of the 4000-volt radiation reflected from glass. The results may be explained in the case of glass by taking into account the adsorption. In practice, the reflecting power of iron appears to fall more rapidly with increase of glancing angle than for glass. This is contrary to theory, and the results suggest the presence of iron oxide. M. S. BURR.

Continuous X-radiation from thin aluminium foil. H. KULENKAMPFF (Ann. Physik, 1928, [iv], 87, 597-637).-With a massive anticathode, the properties of the continuous X-ray emission are masked by velocity losses and diffusion of cathode particles. When, however, the anticathode consists of a very thin strip of metal, e.g., aluminium foil 0.6μ thick, these disturbing factors are reduced to a minimum. An arrangement is described whereby the X-rays can be studied over the angle range 22-150° with the direction of the stream of cathode particles; intensity measurements are made by means of ionisation, and data involving wave-length are obtained by the use of filters, as the intensity of the radiation is so low that spectrometric measurements are precluded. Control determinations with a massive anticathode and a thin foil anticathode, using definite thicknesses of aluminium for the purpose of intensity calibration, indicate that at 90° and 31 kilowatts the spectral intensity distribution from foil follows the relation i_p =const. No marked differences occur when the direction of emission is varied between 90° and 55°, but at 30° and 140° the radiation is softer. whilst the maximum hardness occurs at about 67°. A fair degree of homogeneity can be attained by the use of silver, tin, and zirconium as selective filters, so that the voltage-intensity curve can be followed in relation to wave-length. Over a limited range of

voltages the intensity decreases approximately as 1/V. The voltage/intensity curves for different angular settings of the ionisation chamber show that over the range 27—40 kilovolts the intensity decreases slowly with increasing voltages over the range 140—40°, the rate of decrease being least marked at either extreme, whilst at 22° the intensity is independent of voltage.

The azimuthal intensity distribution has been investigated over the range 22—150°, both in relation to wave-length and voltage. The greatest differences occur with the limiting wave-lengths, and it is probable that the intensities increase from zero at 0° to a maximum near 60—70° and slowly decrease to zero at 180°. The maximum hardness occurs at 73—64° depending only on the electron velocity over the range 16.4—37.8 kilovolts. R. A. MORTON.

Dependence of the intensity of X-ray spectral lines on the tube voltage, with special reference to the K series of aluminium. E. LORENZ (Z. Physik, 1928, 51, 71-94).—The changes of the intensities of X-ray spectral lines with voltage were investigated up to very high potentials, 30-40 times the excitation potential. The shortest wave-length Stielstrahlung," which have been measured from a tungsten anticathode, are explained as due to the emission of secondary electrons from the point of impact on the anticathode. From the P.D. between the shortest wave-lengths of the "Brennfleckstrahlung" and of the "Stielstrahlung" the energy level of the tungsten atom from which the secondary electrons arise may be deduced. These measurements also lead to the conclusion that the emission of secondary electrons ceases when the tube voltage reaches about 40 times the excitation potential of the energy level. This was proved by measurement of the intensity-voltage curve of the K series of aluminium, up to 33 times the excitation potential. A maximum was reached at about 11 times the excitation potential and then a decrease was observed. J. W. ŜMITH.

Intensity distribution of the general and characteristic X-radiation from molybdenum. L. R. G. TRELAAR (Phil. Mag., 1928, [vii], 6, 1008—1019).—Using a Bragg spectrometer and a Shearer tube fitted with a molybdenum target, measurements were made to determine the intensity distribution of the general radiation at various voltages, the corresponding intensities of the $K\alpha$ and $K\beta$ lines, and the ratio of the homogeneous to the general radiation.

W. E. DOWNEY. Quantitative study of the reflexion of X-rays by sylvine. R. W. JAMES and G. W. BRINDLEY (Proc. Roy. Soc., 1928, A, 121, 155—171; cf. A., 1928, 112, 225, 462).—An extension to sylvine of previous work on the intensity of reflexion of X-rays from rock salt (*loc. cit.*). It is found that, from the temperature of liquid air up to about 400° Abs., the dependence of the intensity of reflexion from sylvine on temperature is in quantitative agreement with the Debye–Waller formula. The decrease of intensity for higher temperatures is much greater than that indicated by the law. The value of the temperature factor found from observations at the ordinary temperature and at the temperature of liquid air is in good agreement with that calculated from the elastic constants of the crystal and also with that calculated from the Debyc-Waller law. The observed results are compared with calculations from atomic models. L. L. BIRCUMSHAW.

Soft X-ray levels of iron, cobalt, nickel, and copper. O. W. RICHARDSON and F. C. CHALKLIN (Proc. Roy. Soc., 1928, A, 121, 218-236; cf. A., 1928, 692) .- In a previous investigation of the excitation of soft X-rays from iron, cobalt, nickel, and copper by the photo-electric method (loc. cit.), a considerable number of discontinuities which had been detected were attributed to transitions from provisional X_1 and X_2 levels and a series of Rydberg terms. An attempt has now been made to arrange the remaining discontinuitics which have been observed into the same scheme. Experimentally observed breaks are attributed to transitions from levels denoted by X_3 and X_0 to the b/n^2 terms, so that there are now four initial states from which jumps can be made to the "b" series of terms. The values in volts of all the L and X levels for the four metals are tabulated, and the values of the square roots are plotted as a Moseley diagram against atomic number. The L levels are found to fall accurately on a straight line, in agreement with the view that this level is unaffected by the external atom-building. The X_1 , X_2 , and X_3 levels are practically the same for each element, the slight variations shown being common to all these levels. The X_0 level shows a variation very similar to the shape of the Moseley diagrams of the L and M levels when they are being completed. This may explain the constancy of the X_1 , X_2 , and X_3 levels. If the number of electrons in the X_0 level increases by unity from element to element with increasing atomic number, the approximate constancy of the factor b for all the virtual orbit levels b/n^2 would be accounted for. Some of the soft X-ray level differences show a marked agreement with corresponding X-ray emission transitions. The value of the constant b corresponds in each case with an effective nuclear charge of $13 \cdot 2e - 13 \cdot 3e$. The case for the inclusion of copper in the suggested scheme is not so definite as that for the other metals. The $L_{\text{II}} \xrightarrow{\text{III}} X_2$ transition and the $X \xrightarrow{} X$ transitions are absent, and their important differences are found. It was at first considered that the X levels were identical with the M levels, but evidence has since been obtained that the systems of levels here described are only parts of much larger systems, so that any association between the X and M levels now appears to be highly improbable.

L. L. BIRCUMSHAW.

Measurement of the size of crystal particles by X-rays. A. L. PATTERSON (Z. Krist., 1928, 66, 637-650; Chem. Zentr., 1928, i, 2692).

Crystallographic optics of X-rays. W. EHREN-BERG, P. P. EWALD, and H. MARK (Z. Krist., 1928, 66, 547-584; Chem. Zentr., 1928, i, 2692).

Method of increasing the accuracy of Debye-Scherrer photographs. A. E. VAN ARKEL (Z. Krist., 1928, 67, 235-238: Chem. Zentr., 1928, i, 2773).—The higher order lines are received in the middle of the film. A. A. ELDRIDGE.

Structure of topaz $[A1(F,OH)_2SiO_4]$. N. A. ALSTON and J. WEST (Proc. Roy. Soc., 1928, A, 121, 358-367).—The structure of a topaz has been examined and is believed to be essentially the same as that of other specimens. It is holohedral in character. The aluminium and silicon atoms are distributed through a core of oxygen and fluorine atoms. These latter form a close-packed arrangement of a new type, which is a combination of the hexagonal and cubic forms. The unit cell, containing four molecules, has sides a = 4.64(1), b = 8.78(3), c = 8.37(8)Å.

J. L. BUCHAN.

Röntgenographic and chemical investigations of oxides of iron and cobalt. S. B. HENDRICKS and W. H. ALBRECHT (Ber., 1928, 61, [B], 2153-2161).-The interferences of tricobaltic tetroxide are distributed similarly to those of magnetite, but the differences in the lattice dimensions indicate closer proximity of the atoms in the cobalt compound. The crystalline structure is identical in each case. The diagram of the ferromagnetic oxide, CoO, Fe₂O₃, prepared by the gradual addition of M-solutions of cobalt chloride and ferric ammonium sulphate to boiling 10% sodium hydroxide (cf. Hilpert, A., 1909, ii, 672) is identical with that of tricobaltic tetroxide and magnetite. The oxide, Co2O3,Fe2O3, can be obtained in the homogeneous state only if potassium persulphate is present at the moment of precipitation of the lower oxide (contrast Hilpert, loc. cit.); it is paramagnetic. The compound cannot be completely dchydrated at 100°, the residual water being merely adsorbed. Examination of the magnetic susceptibility of preparations oxidised in varying degree indicates an increase of this property with diminishing content of Co2O3,2Fe2O3, the value for the homogeneous material being $\chi = 45.6 \times 10^{-6}$. The oxidised product exhibits the same interferences as the oxide, CoO, Fe2O3, but the lines are less defined. When the substance is heated, the lines become more distinct and completely identical with those of the lower oxide if the temperature has been raised above 250°. H. WREN.

Constitution of hydroxides and hydrates. II. Complexes containing water of co-ordination. G. NATTA (Gazzetta, 1928, 58, 619-626; cf. A., 1928, 822).-In order to determine the nature of the water present in crystalline lattices, an X-ray examination has been made by the Laue and powder methods of the two complex cobalt salts [Co(NH₃)₆]I₃ and $[Co(NH_3)_5H_2O]I_3$. Both compounds crystallise in the cubic system. The unit cell contains four molecules and has a length 10.88 and 10.84 Å., respectively; $d_{\text{cale.}}$ 2.83 and 2.81. Each cobalt atom is at the centre of an octahedron the vertices of which are occupied by the ammonia and water groups, which behave as isomorphous groups. The substitution of a molecule of ammonia by one of water produces a slight contraction in the lattice, which otherwise remains O. J. WALKER. unaltered.

Orientation of single crystals of zinc. K. TANAKA (Mem. Coll. Sci. Kyōtō, 1928, **11**, **A**, 361— 365).—Commercial zinc plates 1.5 mm. thick were rolled to 20-70% reduction in thickness, and large crystals grown by annealing at 400° for 1 day. X-Ray examination showed that in most of these crystals the base of the hexagonal crystal was parallel to the plane of the plate. A similar arrangement was found when the plates were extended instead of being rolled before annealing. On drawing commercial zinc wires 1.5 mm. diameter through a 0.5-mm. die and then annealing, most of the resulting crystals had their [1120] axes parallel to the axis of the wire. A rather random distribution was obtained after annealing a wire extended for a small percentage only. When a circular zine plate is melted, and then cooled gradually from the circumference, large crystals grow towards the centre, and most of them grow parallel to the plane of the base of the hexagonal crystal.

W. HUME-ROTHERY.

Arrangement of micro-crystals in compressed magnesium and aluminium plates. S. Tsubor (Mem. Coll. Sci. Kyōtō, 1928, 11, A, 375-382).--A circular plate of magnesium 2.4 mm. thick was compressed to a thickness of 0.4 mm., and the arrangement of the micro-crystals investigated by X-ray analysis. Most of the crystals were arranged fibrously with the principal axis of the hexagonal crystal in the direction of compression, but the arrangement was not exact. Aluminium sheets of 1.8 mm. thickness were similarly reduced to 0.13 mm. by compression, both circular and approximately elliptical specimens being used. The micro-crystals tended to take up a fibrous structure with the (110) planes parallel to the surface of the plate, and their [112] axes parallel to the direction of flow of the metal. Consequently, with the elliptical specimens the arrangement was different at the extremities of the major and minor axes owing to the different directions of flow.

W. HUME-ROTHERY.

Arrangement of micro-crystals in bismuth and antimony deposited by electrolysis. H. HIRATA (Mem. Coll. Sci. Kyōtō, 1928, 11, A, 429-450).--The arrangement of crystals of antimony and bismuth deposited electrolytically has been studied by X-ray analysis. The bismuth was deposited on a cathode of sheet copper, the anode being bismuth, and the electrolyte various solutions of bismuth hydroxynitrate and hydrochloric acid in water. The apparently non-metallic deposits obtained under some conditions are in reality small, irregularly oriented micro-crystals of metallic bismuth, and are not a bismuth compound. When the current density and concentration of the electrolyte are high, the crystals are not deposited in a fibrous form, but at lower current densities and concentrations a perfect fibrous form is obtained in which the crystals have their [211] axes parallel to the fibrous axis. At very low current densities and concentrations, comparatively large acicular crystals are formed with the [211] axis in the direction of the needle, and with most of the crystals in the same orientation. With antimony deposited from a solution of the sulphide in aqueous sodium carbonate, the apparently amorphous deposits are also really irregularly oriented micro-crystals.

W. HUME-ROTHERY.

Crystal structure of potassium sulphate. F. P. GOEDER (Proc. Nat. Acad. Sci., 1928, 24, 766—771).— Crystallographic data for potassium sulphate have been obtained by the X-ray powder method. The following lattice constants are given: $a_0=5.771$, $b_0 = 10.064$, and $c_0 = 7.518$ Å. These are similar to the results of other investigators obtained by reflexion measurements on a rotating crystal. A quantitative three-dimensional structure for the potassium sulphate molecule is deduced from the geometrical theory of space-groups and is confirmed by experimental results. In agreement with the observations of other investigators, the SO₄ ion appears to be an entity of the molecule and to maintain its tetragonal structure irrespective of the compound of which it forms a constituent. M. S. BURE.

Structure of crystals of heulandite. P. GAU-BERT (Compt. rend., 1928, 187, 829-831).—The sectors and bands in the cleavage planes of crystals of heulandite are due to the presence of foreign matter which may produce various orientations of the plane of the optical axes. In almost every case the angle of the optical axes is smaller in the sector corresponding with the face a'(101) than with the face p(001). Pure heulandite contains hydrated silicoaluminates of sodium, potassium, strontium, and barium in solid solution, or forming mixed crystals with the pure heulandite. J. GRANT.

Crystal structure of some rhombic formates. I. NITTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 151-163).-Using the Laue photographic and ionisation spectrometric methods, the crystal structure of some orthorhombic formates was investigated. The dimensions of the unit cells are as follows: strontium formate, a=6.86, b=8.72, c=7.24; strontium formate dihydrate, a=7.30, b=11.99, c=7.13; barium formate, a=6.78, b=8.89, c=7.68; lead formate, a=6.52, b=8.75, c=7.41. In the last four salts the number of molecules in the unit cell was 4, and space-group V4. Lithium formate monohydrate (4 molecules in the unit cell, spacegroup C_{2r}^{9} or V_{h}^{16}), a=6.49, b=10.01, c=4.85; calcium formate (8 molecules in the unit cell, space-group V_{h}^{15}), a=10.16, b=13.38, c=6.26. The accepted isomorphism of the formates of strontium, barium, and lead was confirmed. The space-group V_{h}^{15} for calcium formate is different from V_h^a assigned by Yardley (A., 1925, ii, 430). The former V_{h}^{15} contains V^{4} as a subgroup. The molecules of the formates of these bivalent metals are all structurally asymmetric. N. M. BLIGH.

Crystal structure of silver subfluoride. H. TERREY and H. DIAMOND (J.C.S., 1928, 2820-2824). —Photographs taken by the powder method indicate a hexagonal unit cell, a=2.989, c=5.710 Å.; one molecule of Ag₂F per unit cell requires d 8.78 (found 8.64). A "cadmium iodide" structure is suggested in which fluorine occupies the position (0, 0, 0) and silver the positions $(\frac{1}{3}, \frac{2}{3}, \mu)$ and $(\frac{2}{3}, \frac{1}{3}, \mu)$; the value of μ is deduced from intensity considerations to be 0.3. Such a structure gives values for the atomic diameter of silver with respect to silver and with respect to fluorine equal to the atomic diameter of silver in the metallic state and in normal combination, respectively; some support is obtained therefore for the existence of sub-ions. R. N. KERE,

Crystal structure of mercury, copper, and copper amalgam. H. TERREY and C. M. WRIGHT (Phil. Mag., 1928, [vii], 6, 1055-1069).-The structures

were determined by means of a Shearer tube with a copper target and a camera similar to that used by McLennan and Wilhelm for their work on solid carbon dioxide and oxygen. At -150°, mercury was found to have a rhombohedral structure. The value for the plane spacing of copper was found to be 3.603+ 0.002 Å. Copper amalgams appear to be merely mechanical mixtures of the two metals so long as the amalgam is soft. When the amalgam sets a change in structure takes place and a definite compound containing 30-35% Cu is formed. This compound appears to possess a simple tetragonal lattice with axial ratio 0.64 and a composition Cu₃Hg₄.

W. E. DOWNEY.

X-Ray spectrography of copper and some brasses. J. LOISEAU (Rev. Mét., 1928, 25, 572-584).-Laue spectrograms for hard-rolled copper. 67:33 and 60:40 brass. and 60:40 brass with lead after varying periods of anneal at temperatures up to the m. p. are reproduced and discussed. In copper. the orientation of the (100) planes to the direction of rolling determines the recrystallisation and grain growth. The appearance of separate spots on the spectrogram indicates that overheating occurs at 1000°, but even at 1050° traces of the original rolling structure can be detected, and these disappear only on melting. Recrystallisation of 67:33 brass commences at 300°, is rapid at 400°, and continues up to 500°. At 600°, reflexion from the (110) planes and at 700° from the (111) planes commences to take place, but no change in the crystal structure is apparent until 875°. Similar effects are obtained with 60:40 brass and, as lead has no effect on the crystal structure, it does not influence the character of the spectrograms. The value of X-rays in determining the mechanical and heat treatment which copper and brass have undergone is discussed. A. R. POWELL.

Rontgenographic interpretation of the nature of the C-C linking. A. REIS and W. SCHNEIDER (Z. physikal. Chem., 1928, 137, 126-130).-The crystal structures of a number of symmetrical compounds having the C-C linking have been correlated from the stereochemical point of view. The only space-groupings so far found for the C_2 and V crystal classes are C_2^2 and V^4 , wherein unsymmetrical molecules are oriented along spiral axes. In the D_3 and D_4 classes, however, the only space-groupings known are formed from the C_2 unit. For all the cases studied Weissenberg's theory of crystal structure is substan-H. F. GILLBE. tiated.

Banded structures in metal crystals. C. F. ELAM (Proc. Roy. Soc., 1928, A, 121, 237-244) .--Crystals of aluminium are rarely formed with a banded structure after treatment which would normally produce it, although the metal has the same crystal structure (face-centred cubic) as copper, silver, and gold, which form twins of the spinel type. It is found, however, that when a large aluminium crystal is strained about 10% and heated until it recrystallises, the new crystals have very straight boundaries, and some of these take on the typical banded structure of twinned copper. The plane of composition can be the-twin plane, but is not always so. In one case, in which the orientation of each part relative to the CHNILA

BIBLIOTEKA SLUWNA.



In an appendix, G. I. TAYLOR discusses the connexion between the formation of "mechanical twins" and the known manner in which aluminium crystals are distorted under tensile stress. If the laws previously discovered regarding the distortion of aluminium crystals are applied to the case of a tensile specimen of which the longitudinal axis lies in a cubic crystal plane and close to the normal to an octahedral plane, "mechanical twins" of the type described above might have been predicted as possible, and the orientation of the two sets of crystal axes would bear the same relationship to the plane of union and the longitudinal axis of the specimen as L. L. BIRCUMSHAW. that actually found.

Change in lattice spacing at a crystal boundary. J. E. LENNARD-JONES and (MISS) B. M. DENT (Proc. Rov. Soc., 1928, A, 121, 247-259).-The recent work of Davisson and Germer (A., 1927, 492; 1928, 683) on the reflexion of electrons by a crystal of nickel has directed attention to the conditions at a crystal boundary. With the view of explaining their results, the change in spacing at a (100) boundary of a crystal of the sodium chloride type is considered theoretically. Two effects are anticipated : (a) a change of spacing between planes at the boundary; (b) a change of spacing between atoms in the surface layer itself. These effects are considered separately, assuming that their mutual action is a correction of the second order. It is found that the contraction of the lattice at the boundary is due almost entirely to the polarisation of the surface layer and is of the order of 5%. An upper limit is found for the decrease in the interatomic spacing in the surface layer, also of the order of 5%. The surface tensions of a number of crystals of the sodium chloride type are calculated. The general results obtained provide independent evidence against the contraction theory of Davisson and Germer, for they show that the contraction is too small and localised to produce an observable effect on the reflexion pattern of an electron stream.

L. L. BIROUMSHAW.

Structure of the benzene ring. K. LONSDALE (Nature, 1928, 122, 810) .- Hexamethylbenzene, triclinic, contains 1 mol. in the unit cell. Variations in reflexion intensities prove the existence of pseudohexagonal or hexagonal symmetry in the benzene ring, and show that the ring in hexamethylbenzene is almost, if not quite, flat, with distance between the centres of neighbouring carbon atoms 1.42-1.48 A. A. A. ELDRIDGE.

Crystal form of magnesium tungstate. F. MACHATSCHKI (Z. Krist., 1928, 67, 163–165; Chem. Zentr., 1928, i, 2591).—Magnesium tungstate, $MgWO_4$, is monoclinic, prismatic, a:b:c=0.8263:1:0.8703; β 89° 40′. A. A. ELDRIDGE.

Structure of zirconium silicide. H. SEYFARTH (Z. Krist., 1928, 67, 295–328; Chem. Zentr., 1928, i, 2775).—Zirconium silicide, ZrSi₂, forms small, rhombic crystals, d 4.88; it is rhombic-bipyramidal, a 3.72, b 14.61, c 3.67 Å., with 4 mols. in the unit cell. A. A. ELDRIDGE.

Crystal structure of the soluble modification of germanium dioxide. W. ZACHARIASEN (Z. Krist., 1928, 67, 226—234; Chem. Zentr., 1928, i, 2775—2776).—Water-soluble germanium dioxide has a 4.972 ± 0.005 , c 5.648 ± 0.005 Å. (for α -quartz, 4.903 and 5.393, respectively), space-group D_4^4 or D_5^6 . A. A. ELDRIDGE.

Production of corrosion faces with precious stones. M. SEEBACH (Deut. Goldschmiede-Ztg., 1925, 28, 159—163; Chem. Zentr., 1928, i, 2795).— The use of chemical reagents is described.

A. A. ELDRIDGE. Titanium cyanonitride. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1927, 390—393; Chem. Zentr., 1928, i, 2692).—The crystal structure of "titanium cyanonitride" is of the sodium chloride type, with edge of unit tube 4.243 ± 0.002 Å. The intensity data support the view that the substance consists of mixed crystals of titanium carbide and nitride. A. A. ELDRIDGE.

Crystal structure of skutterudite and smaltitechloanthite. I. OFTEDAL (Z. Krist., 1928, 66, 517— 546; Chem. Zentr., 1928, i, 2693).—The edge of the unit cube of skutterudite is $8\cdot189\pm0\cdot002$ Å., and of smaltite $8\cdot240\pm0\cdot005$ Å. The formula is RAs₃. The space-group is T_{4}^{5} . A. A. ELDRIDGE.

Crystal structure of monoethylammonium bromide and iodide. S. B. HENDRICKS (Z. Krist., 1928, 67, 119—130; Chem. Zentr., 1928, i, 2777).— Monoethylammonium bromide and iodide have d_{010} 8·30 and 8·67 Å., respectively. There are 2 mols. in the unit cell; the space-group is C_2^2 .

A. A. ELDRIDGE. Crystal structure of monomethylammonium halides. S. B. HENDRICKS (Z. Krist., 1928, 67, 106-118; Chem. Zentr., 1928, i, 2777).-Monomethylammonium chloride has a 4.28, c 5.13 A., with 1 mol. in the unit cell; the bromide has a 5.09, c 8.76 Å. and the iodide a 5.11, c 8.97 Å., each with 2 mols. in the unit cell. The forms of ammonium bromide and iodide stable at high temperatures have the sodium chloride structure, whilst those stable at low temperatures are of the cæsium chloride type. Monomethylammonium chloride possesses a modified ammonium chloride structure of the form stable at the ordinary temperature, whilst monomethylammonium bromide and iodide crystallise according to the type of ammonium bromide stable at high temperatures. The distances between the atoms have been determined.

A. A. ELDRIDGE.

Crystal structure of tetramethylammonium halides. R. W. G. WYCKOFF (Z. Krist., 1928, 67, 91—105; Chem. Zentr., 1928, i, 2777).—Tetramethylammonium iodide has a 7.96, c 5.75 Å.; bromide, a 7.76, c 5.53 Å.; chloride, a 7.78, c 5.53 Å.; spacegroup D_{45}^{17} , with 2 mols. in the unit cell. The positions of the atoms are discussed. A. A. ELDRIDGE.

Theory of crystal growth. W. KOSSEL (Nachr. Ges. Wiss. Göttingen, 1927, 135-143; Chem. Zentr., 1928, i, 2689).

Crystal structure of chromite from Tiszafa. L. TOKODY (Z. Krist., 1928, 67, 338-339; Chem. Zentr., 1928, i, 2795-2796).—The structure is cubic, a 8.05 Å.; space-group O_h^* , with 8 mols. in the unit cell. A. A. ELDRIDGE.

Test of crystals for piezoelectricity. S. B. ELINGS and P. TERPSTRA (Z. Krist., 1928, 67, 279-284; Chem. Zentr., 1928, i, 3040).—Positive results were obtained with : zinc blende, boracite, sodium bromate, hexamethylenetetramine, potassium lithium sulphate, nepheline, potassium bromate, cinnabar, mercuric cyanide, potassium dihydrogen phosphate and arsenate, ammonium dihydrogen arsenate, strychnine sulphate, melinophane, willemite, strychnine, sodium santonate, benzophenone, cinchonidine, glutamic acid, hippuric acid, nickel sulphate heptahydrate, strontium, barium, and lead formates, iodic acid, tartar, tartar emetic, lactose, α-rhamnose, glucosamine hydrochloride, hæmatoxylin trihydrate, skolezite, and strontium hydrogen tartrate. Negative results were obtained with : diamond, zinc oxide, benitoite, carborundum, lead molybdate, sulphur, and potassium dichromate. A. A. ELDRIDGE.

Comparative X-ray examination of lime-soda silicates. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1928, A, 129—138; Chem. Zentr., 1928, i, 2796). —Gehlenite has a 11·11, c 5·06 Å., with 4 mols. in the unit cell; it is regarded as $CaSiO_4, Al_2O_3$, with isomorphous replacement of the alumina by magnesium silicate. Melilite has a 11·12, c 5·09 Å., with 4 mols. of $CaO(0.527CaSiO_3, MgSiO_3+0.069CaSiO_3, FeSiO_3+$ $0.164CaSiO_3, Al_2O_3+0.238NaAlSi_2O_6)$ in the unit cell Sarkolite has a 17·6, c 15·6 Å., with 6 mols. of $3CaO+(0.825NaAlSi_3O_8+1.080CaAl_2Si_2O_8+$ $0.057Na_2Al_2Si_2O_8)$ in the unit cell.

A. A. ELDRIDGE. X-Ray examination of o- and m-nitroaniline. K. HERRMANN and M. BURAK (Z. Krist., 1928, 67, 189—225; Chem. Zentr., 1928, i, 2778—2779). o-Nitroaniline has a 10.09, b 29.44, c 8.52 Å., axial ratios 0.3427:1:0.2894. The unit cell contains 16 mols.; the space-group is considered to be V_{1}^{h} . m-Nitroaniline has a 19.23, b 6.48, c 5.06 Å.; axial ratios 2.9676:1:0.7808. The unit cell contains 4 mols.; space-group probably C_{2}^{s} .

A. A. ELDRIDGE. Isomorphism in cubic crystals of hexamminoand pentammino-aquo-complex salts. O. HAS-SEL (Norsk geol. Tidsskr., 1928, 10, 92-96; Chem. Zentr., 1928, i, 3030-3031).—The salt

 $[Co(NH_3)_6](ClO_4)_3$, which has a structure similar to that of the corresponding iodide, contains 4 mols. in the unit cell. The six ammonia groups are equivalent. In $[Co(NH_3)_5H_2O](ClO_4)_3$ the water and ammonia groups appear to be crystallographically equivalent. The salt $[Co(NH_3)_5H_2O]I_3$ is not very stable; it forms optically isotropic octahedra, a 10.81 Å., and exhibits differences in the positions of the ammonia and water groups. The iodosulphate has the fluorite structure, calcium being substituted by the complex cation and fluorine by the two anions. The action of substituents on the lattice constant is shown by the following values : [Co(NH₃)₆]SO₄I 10.71, $\begin{array}{l} [\operatorname{Co}(\operatorname{NH}_3)_6] \mathrm{SO}_4 \mathrm{Br} \quad & 10\cdot51, \quad [\operatorname{Co}(\operatorname{NH}_3)_5 \mathrm{H}_2 \mathrm{O}] \mathrm{SO}_4 \mathrm{I} \quad & 10\cdot62, \\ [\operatorname{Co}(\operatorname{NH}_3)_3 \mathrm{H}_2 \mathrm{O}] \mathrm{SO}_4 \mathrm{Br} \quad & 10\cdot45, \quad [\operatorname{Co}(\operatorname{NH}_3)_6] \mathrm{SeO}_4 \mathrm{I} \quad & 10\cdot79 \ \mathrm{A}. \end{array}$

A. A. ELDRIDGE.

Comparative X-ray studies of lime-soda silicates. IV. Melilite, gehlenite, sarkolite, and skapotite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1928, A, 167-181; Chem. Zentr., 1928, ii, 7).-Skapolite and sarkolite, which are distinct both chemically and structurally from the melilitegehlenite group, are structurally related. The unit cell is a face-centred prism with edges 17.25, 7.65 Å. and 17.6, 15.59 A., respectively. Skapolite contains 4 mols. in the unit cell, and has space-group C_{4h}^{i} or C_{sh}^{s} ; sarkolite contains 12 mols., and the space-group is probably C_{4h}^3 or C_{4h}^5 . Melilite and gehlenite, spacegroup $D_{4b_2}^{a}$ have a tetragonal prismatic unit cell with a 11.1, c 5.09 Å. and a 11.12, c 5.06 Å., respectively, A. A. ELDRIDGE. containing 4 mols.

Structure of rutile. L. TOKODY (Math. Therm. Ertesitö, 1927, 44, 247-254; Chem. Zentr., 1928, ii, 28).-Rutile has a 4.4923, c 2.8930 A., with 2 mols. in the unit cell; d_{cale} , 4.511. The shortest distance between titanium and oxygen atoms is 2.11 Å.

A. A. ELDRIDGE.

Occurrence of titanium in titaniferous slags. C. W. CARSTENS (Z. Krist., 1928, 67, 260-278; Chem. Zentr., 1928, i, 3045).—Titanium in slags may be present as titanium-augite. In basic reduced slags the titanium may be present as an independent mineral which may be black in colour, and contains less oxygen than the dioxide. The extent of the reduction depends on the temperature. In ultra-basic slags and "alcement" clinker, titanium monoxide occurs as branched crystals of fulvite. The monoxide obtained from the dioxide and titanium by heating at 1450-1500° in a reducing atmosphere belonged (BRÄKKEN) to the cubic system; it was of the sodium chloride type, having a 4.235 Å., $d_{cnlc.}$ A. A. ELDRIDGE. 5.53, H 6.

Piezoelectric method for determining crystal classification. W. SCHNEIDER (Z. Physik, 1928, 51, 263-267).—An extension of the technique of Giebe and Scheibe (ibid., 1925, 33, 760) is described suitable for the detection of piezoelectric properties in crystals. A large number of crystals have been examined in this way. All substances having a centre of symmetry show no piezo-effect; the following substances show the effect : sucrose, isohydrobenzoin, lithium sulphate, lead formate, asparagine, ammonium oxalate, sodium chlorate, rubidium tartrate, potassium bromate, pentaerythritol, succinic anhydride, R. W. LUNT. and acetamide.

Magnetostriction of a single crystal of nickel. Y. MASIYAMA (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 945-961).—The longitudinal and transverse effects of magnetic elongation of a single erystal nickel ellipsoid have been determined for different

orientations and for varying strengths of magnetic fields. Contraction always takes place in a longitudinal direction and elongation in a transverse direction. The contraction is greatest in the (100) direction and least in the (111) direction, the converse being true for the transverse elongation. With a constant field, the variation of these effects with respect to the orientation of the ellipsoid is periodic, the period being 90°, 180°, and 60° for the planes (100), (110), and (111), respectively.

A. R. POWELL. Magnetic susceptibility of single crystals of zinc and cadmium. J. C. McLENNAN, R. RUEDY, and (MISS) E. COHEN (Proc. Roy. Soc., 1928, A, 121, 9-21).-Single crystals of zinc and cadmium, of about 0.5 cm. in diameter and 6 cm. long, were prepared by the method of very slowly lowering the molten metal, contained in a pyrex mould, out of an electric furnace. The glass moulds were of a special constricted shape, designed to increase the probability of obtaining a single crystal through the whole length of the tube. The magnetic susceptibility χ_{I} (parallel) and χ_{\perp} (normal) to the hexagonal axis of each metal was determined by the Gouy method, the crystal being weighed in the presence and absence of a strong magnetic field. The values, in c.g.s.u.×10⁻⁶, are found to be : cadmium, $\chi_{\parallel} = -190$, $\chi_{\perp} = -145$; zinc, $\chi_{\parallel} = -261$, $\chi_{\perp} = -160$. From these values, the magnetic susceptibilities of isotropic aggregates of zinc and cadmium crystals arranged at random would be -0.160×10^{-6} and -0.194×10^{-6} , respectively. An attempt was made to grow single crystals of mercury by the same method, the metal being lowered from the ordinary temperature into a tube surrounded by liquid air. On rotating the solid mercury thus prepared about its vertical axis, the pull caused by the magnetic field remained constant, indicating either that the metal was not in the form of a single crystal, or, more probably, that the mercury was crystallised and in a rhombohedral form. L. L. BIRCUMSHAW.

Determination of the piezoelectric moduli of sodium ammonium tartrate. W. MANDELL (Proc. Roy. Soc., 1928, A, 121, 130-140).—The general theory of piezoelectricity as applied to crystals of the rhombic system is discussed, and it is shown that in the case of sodium ammonium tartrate all the moduli vanish excepting d_{14} , d_{25} , and d_{36} , so that excitation takes place only through pressures Y_z , Z_x , and X_y . To measure the moduli, rectangular slabs of the required orientations were cut from the crystals and placed vertically on hard rubber blocks, similar blocks being placed on the upper ends. Two copper electrodes were fixed on the side faces of the crystal slab, one electrode being connected to a pair of quadrants of an electrometer, the other electrode and the second pair of quadrants being earthed. It was found necessary to use specimens as large as possible, and to carry out the measurements under the driest conditions obtainable. The following values, in c.g.s.u.×10⁻⁸, were found: d_{14} =+56·0, d_{25} = -149·5, and d_{36} =+28·3. For the piezoelectric constants: e_{14} =+6·37×10⁴, e_{25} =-4·11×10⁴, and e_{36} =+2·39×10⁴. The values of the moduli for the potassium salt are : $d_{14} = +1000 \times 10^{-8}$, $d_{25} = -165 \times 10^{-8}$

10⁻⁸, and $d_{36} = +35.4 \times 10^{-8}$. Thus for pressures in the direction bisecting the *bc* axes, the polarisation along the *a* axis decreases by about 95% on substituting the ammonium group. An investigation of the effect of temperature on the piezoelectric response showed that, between -17° and $+30^{\circ}$, there was no appreciable change for the ammonium salt, but on raising the temperature above 30° , the crystal gradually became conducting, the charges leaking away in a few minutes. L. BIRCUMSHAW.

Magneto-resistance effect in single crystals of nickel. S. KAYA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 1027—1037).—The electrical resistance of single crystal nickel rods with a rectangular crosssection has been measured in magnetic fields parallel to and perpendicular to the direction of the current. In the case of the longitudinal effect, the resistance increases with the orientation of the axis of the rod in the order (100), (110), and (111). In the case of the transverse effect, the resistance varies with the direction of the magnetic field, the curves having an undulating form, the shape of which varies with the orientation of their longitudinal axis.

A. R. POWELL.

Magnetism of hydrated zirconia. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1928, 187, 886— 888).—Since the specific susceptibility of hydrated zirconia prepared by precipitation from ammonia and pure zirconium tetrachloride is a linear function of its water content for more than 5% of water, this substance is considered to be a weakly paramagnetic mixture of water and the hypothetical oxide ZrO₂, the susceptibility of which, calculated by extrapolation, is of the order 0.4×10^{-7} . Anhydrous zirconia, obtained by prolonged calcination at 500°, is diamagnetic, but the results are vitiated by the high temperatures required for the removal of less than 5% of water. J. GRANT.

Loosening, electrical conductivity, and reactivity of the crystal lattice. J. A. HEDVALL (Svensk Kem. Tidskr., 1928, 40, 65–98; Chem. Zentr., 1928, i, 2902–2903).—A survey of the results of investigations on reactions between solid substances. A. A. ELDRIDGE.

Enantiotropy and monotropy. II. N. NAGA-SAKO (Bull. Chem. Soc. Japan, 1928, 3, 209-217) .--The dimorphism of carbon and phosphorus is studied. By the application of the Nernst heat theorem, the affinity of transition can be obtained if the specific heats over a range of temperature and the heat of transition are known. The method is of value especially in the case of diamond and graphite, where it is almost impossible to measure the affinity directly. It is found that from 0° to 1100° Abs. graphite is more stable than diamond, and that the dimorphism of the system is truly monotropic, and not pseudomonotropic as has previously been supposed. The heat of transition changes sign at 850° Abs. Above this temperature diamond changes into graphite with absorption of heat. For the dimorphism of phosphorus it is found that red phosphorus is more stable than white from 0° Abs. to the m. p. of white phosphorus, the system being truly monotropic. Where this method is difficult to apply, e.g., when a modification exists over a narrow range of temperature over which the specific heats are not known or are difficult to find, an approximate formula can be used if the m. p. and latent heats are known. Using this method it is shown that the dimorphisms of ethyl ether, iodine monochloride, benzophenone, bromonitrobenzene, phthalide, acetamide, monochloroacetic acid, nitrop-toluidide, and erythritol are monotropic. The effect of pressure on the affinity of transition is investigated, and it is found that the diamond-graphite transformation will probably be enantiotropic at high pressures, whilst the phosphorus transition will remain monotropic. (Cf. A., 1928, 709.) A. J. MEE.

Electrical conductivity and optical absorption of metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, 14, 802—811; cf. A., 1928, 825).—Theoretical. The various hypotheses as to the relation of electrons in metals to the electrical conductivity are discussed. It is considered that the evidence is, on the whole, in favour of the view that the electric current is maintained in part by free electrons sharing the energy of heat agitation, but mainly by an interchange of electrons in encounters between atoms and positive ions, the latter being, naturally, just as numerous as the free electrons. M. S. BURR.

Electrical conductivity of metals as a function of pressure according to the Sommerfeld electron theory. A. T. WATERMAN (Phil. Mag., 1928 [vii], 6, 965—970).—A formula is developed for the effect of hydrostatic pressure on the electrical conductivity of metals. W. E. DOWNEY.

Variations in the resistivity of thin layers of platinum as functions of thickness and temperature. A. FERY (Compt. rend., 1928, 187, 819— 821; cf. A., 1928, 353).—For thicknesses above 287 mµ the resistance of films of platinum-black produced by cathodic sputtering is $4 \cdot 19 \times 10^{-4}$. Such films are considered to be composed of massive metal, but differ from ordinary metallic platinum, which may, however, be produced by a discharge at 340°. From studies of the catalytic properties and changes in resistance with temperature of these films, it is concluded that there are a large number of forms of platinum intermediate in properties between bright and black platinum. J. GRANT.

Electrical conductivity of metals. R. RUEDY (Nature, 1928, 122, 882).

Theoretical meaning of the relations between electrical conductivity and voltage and frequency. G. Joos (Physikal. Z., 1928, 29, 755— 760).—The theoretical interpretation of the work of Wien (cf. this vol., 32) is considered in the light of the new theory of electrolytes developed by Debye, Hückel, Onsager, and Falkenhagen. Calculation of approximate solutions of the Debye-Onsager differential equations leads to relations between conductivity and voltage which agree well with Wien's data. The ionic forces require a finite time before coming into play, and both for rapidly alternating fields and high voltages the interionic forces decrease or disappear entirely. True values for the degree of dissociation should therefore be obtainable in this way, since the values obtained by the older methods are unduly low owing to the actions between ions. R. A. MORTON.

Conduction of electricity and discharge in dielectric liquids. A. NIKURADSE (Physikal. Z., 1928, 29, 778-781).—An attempt has been made to elucidate the discharge phenomenon by means of current/voltage relationships at low voltages, especially just before the discharge occurs. The relations between conductivity, viscosity, temperature, pressure, and breakdown voltage have been studied, and ionic constants at spontaneous ionisation have been determined for highly purified transformer oil. The relation between conductivity and ionic constants has been investigated for various temperatures and pressures. R. A. MORTON.

Thermal conductivities of carbon monoxide and nitrous oxide. H. GREGORY and C. T. ARCHER (Proc. Roy. Soc., 1928, A, 121, 285—293; cf. A., 1926, 231).—The thermal conductivities of nitrous oxide and carbon monoxide have been measured at various pressures and the results tabulated. The conductivities have also been measured at different temperatures and the temperature coefficient is given. The same apparatus has also been used to determine the thermal conductivity of air. J. L. BUCHAN.

Heat capacity at low temperatures of zinc oxide and of cadmium oxide. R. W. MILLAR (J. Amer. Chem. Soc., 1928, 50, 2653—2656).—The specific heats of the oxides are recorded between 70 and 300° Abs. (cf. A., 1928, 936); the results may be represented by the sum of Debye and Einstein functions over limited temperature ranges. The calculated molar entropy and heat of formation at 25° are 10-28 g.-cal./1° and -83,130 g.-cal. for zinc oxide; for cadmium oxide, the molar entropy is 13-17 g.-cal./1° and the free energy of formation -54,200 g.-cal./mol. S. K. TWEEDY.

Absolute velocity of a water molecule emitted on the dehydration of a crystalline hydrate. II. A. PREDVODITELEV (Z. Physik, 1928, 51, 136—149).— A method has been developed for calculating the velocity of molecules emitted on the breakdown of a solid material, and the velocity of the water molecules emitted on the dehydration of the crystal hydrates $(CO_2H)_2, 2H_2O$, Na₂S₂O₃, 5H₂O, and Na₂B₄O₇, 10H₂O has been determined. The heats of hydration calculated from these velocities are in good agreement with the values obtained by thermochemical methods. J. W. SMITH.

Thermal expansion of air-sensitive crystalline salts. W. KLEMM (Z. Elektrochem., 1928, 34, 523-528).—The mean coefficients of cubical expansion, α , between 20° and 150°, of some metal halides, hydroxides of lithium, sodium, and potassium, and some organic substances were measured by a dilatometric method. The results are discussed in the light of theoretical considerations. Halides with ionic lattices have values of α which are smaller the higher the charges on the cation, and agree fairly well with those calculated. A sudden change in α occurs on passing from compounds of ionic to those of molecular lattices. The relationships between α and the m. p. and α and the co-ordination number are discussed.

The ratio between α for the crystalline and molten states lies within 0.3 and 0.5, except for aluminium chloride and potassium hydroxide (cf. Biltz and Voigt, A., 1923, ii, 324). The expansion has practically no influence on the ratio of the molecular volumes in the solid and liquid states (Klemm, A., 1926, 669, 670). S. K. TWEEDY.

Hydroxyl radical in flames. K. TAWADA and W. E. GARNER (Nature, 1928, 122, 879–880).—The maximum emission of radiation is not associated with the mixture $2H_2+O_2$, which gives the highest flame temperature, but with the mixture H_2+O_2 , indicating that the hydroxyl radical may be responsible for the emission of part of the radiation from the hydrogen flame. An explanation of the mechanism of the reaction, which accounts for the observed radiationcomposition curve, is offered. A. A. ELDRIDGE.

Relations between physical constants of liquids. V. PERSCHKE (J. Russ. Phys. Chem. Soc., 1928, 60, 1019—1035).—The general relation $\log X = a + b \times \log (t_k - t)$ is derived, where X is any physical constant of a liquid, a and b are constants for the given liquid and property, and t_k and t are respectively the critical and the given temperature. This equation is verified for a number of liquids for density, surface tension, latent heat of vaporisation, viscosity, specific heat, refractive index, and conductivity of sound. Any number of physical constants can be connected by combining the same number of equations of the above type : thus for any pair of constants X and Y, $\log X = p + q \times \log Y$, where $p = a_x b_y - a_y b_x / b_y$, and $q = b_x / b_y$.

Physical constants of rhenium. (FRAU) I. NODDACK (Z. Elektrochem., 1928, 34, 629-631).-The wave-lengths of the L-series of the X-ray spectrum are tabulated. The optical spectrum contains more than 100 lines; the "later" lines, especially the triplet at 3640 Å., serve for detecting minute quantities of the element. The black metal powder obtained by heating the sulphide in hydrogen has d 10.4; metal which has been fused on the anticathode of an X-ray tube forms small, bright granules having d about 20. The m. p. and b. p. are probably higher than those of tungsten, and the mean specific heat between 0° and 20° is 0.0346. By heating the disulphide, ReS2, in hydrogen the monosulphide, ReS, is formed, and then, at about 1000°, metallic rhenium. Using this conversion, the at. wt. is found S. K. TWEEDY. to be 188.71 ± 0.25 .

Main types of first-order chemical compounds, illustrated by the carbides. A. VON ANTROPOFF (Z. Elektrochem., 1928, 34, 533-536).—Carbides are divided into two main groups : (a) carbides in which the two elements have their normal valencies ("valency compounds"), and (b) those in which the elements are combined in a manner independent of their valencies (" atom compounds" or " packed compounds," because they have atomic lattices as distinct from molecular or ionic lattices, and because there is a packing effect in the molecule). Group (a) is further divided : (i) polar compounds (infusible salt-like carbides having ionic lattices and conducting electricity well, e.g., sodium carbide); (ii) non-polar compounds (non-conducting, non-metallic carbides, mostly fluid, with molecular and pseudo-atomic lattices, e.g., carbon tetrachloride). Group (b) embraces non-polar, mostly metallic, carbides, which exhibit electrolytic conduction and have true atomic lattices, e.g., tungsten carbide. Diamond belongs to group (a), (ii). This classification is extended to other first-order compounds; e.g., water belongs to group (a), (ii), and sodium chloride to group (a), (i).

S. K. TWEEDY.

Metastability of the elements as a result of enantiotropy or monotropy. XI. Physicochemical constants of silver iodide. I. E. COHEN and W. J. D. VAN DOBBENBURGH (Z. physikal. Chem., 1928, 137, 289-334).-The discrepancies among the values given in the literature for the density of silver iodide are too great to be ascribed to the presence of chemical impurities, and cannot be due to the influence of light, which produces a negligible change of density even after long exposure; further, the temperature coefficient is relatively small. The ordinary chemically pure precipitated material consists of a number of physical modifications. A physically pure α -silver iodide of d_4^{30} 5.68 is produced by heating at 90-140° with a concentrated solution of calcium chloride or by melting and cooling to the ordinary temperature. The transition temperature of the $\alpha \Longrightarrow \beta$ change at 1 atm. pressure is 145.80°; the $\alpha = \beta$ change at 1 and potential for the β , $d_4^{43'8}$ for the α modification is 5.68₅, and for the β , 6.00_9 , whilst the volume change of the transition $\alpha = \beta = -0.0094_5$ cm.³/g. H. F. GILLBE.

Vapour pressures and chemical constants of silver, gold, copper, lead, gallium, and tin. P. HARTECK (Z. physikal. Chem., 1928, 134, 1-20) .-The vapour pressures of these metals have been measured at temperatures near 1000° and above over a pressure range of 10-4 to 10-2 mm. Except in the case of lead, where a boiling method was used, the method of Knudsen has been employed. The results of other workers are discussed. The chemical constants can be represented by the equation $j_p =$ $-1.59 + \log M^{1.5} + k$, where k has the value $+0.39 \pm 0.36$ for lead, 0.65 ± 0.40 for silver, -0.10 ± 0.40 for copper, $+0.56\pm0.40$ for gold, and +0.50 or -0.20 for carbon. The deviations from the theoretical values are all positive and approximate to 0.3 unit. A Trouton constant of 22.5 is obtained for the metals of high b. p. Langmuir's method for the measurement of small vapour pressures is discussed, and certain of the data (A., 1927, 927) are considered to be erroneous. L. S. THEOBALD.

Vapour pressure and chemical constant of chlorine. P. HARTECK (Z. physikal. Chem., 1928, 134, 21–25).—An apparatus for the determination of the saturation pressure of chlorine between pressures of 2.6 and 634 mm. (162.7—245.2° Abs.) is described. Extrapolation gives for the b. p. at 760 mm. the value $-33.95^{\circ}\pm0.10$, and the intersection of the sublimation and vapour-pressure curves gives for the triple point the value $-100.5^{\circ}\pm0.30$ at a pressure of 9.8 mm. The data agree well with those of previous workers. The chemical constant of diatomic chlorine is $1.67_5\pm0.7$ or -0.12.

L. S. THEOBALD.

Density of molten metals and alloys. Y. MATSUYAMA (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 1054—1077).—The densities of tin, cadmium, bismuth, lead, zinc, the binary alloys Sn-Cd, Sn-Bi, Bi-Pb, Zn-Sn, Bi-Cd, Cd-Pb, Cd-Zn, and the ternary alloys Sn-Bi-Cd, Bi-Cd-Pb, Sn-Bi-Pb, Sn-Cd-Pb, Sn-Cd-Zn, Cd-Pb-Zn were determined at different temperatures. It was shown that the expansion coefficient of a molten metal decreased slightly with temperature, and the density of a metal at its m. p. obtained from this coefficient was in satisfactory agreement with the value obtained by extrapolating the density-temperature curve.

In the case of alloys it was found that the atomic volume of a mixture was greater than the mean of the atomic volumes of the components by not more than 1%. The maximum deviation did not occur in mixtures containing equal molar amounts of each component, but in mixtures containing less of the component of smaller density. The equation of van Laar and Lorenz for the heat of mixing may hold for the alloys Sn-Cd, Pb-Cd, Sn-Zn, Cd-Zn.

F. S. HAWKINS.

Density of boric oxide glass and atomic weight of boron. A. COUSEN and W. E. S. TURNER (J.C.S., 1928, 2654-2657).—The density of boric oxide glass prepared by fusing boric acid at 1400° and annealing the product thoroughly has been determined both by the specific gravity bottle and the flotation method; over the temperature range 18° to 25° d=1.844. Inadequate annealing or fusion of the boric acid at too low a temperature is shown to give a glass with a lower density; this explains the low value obtained by Briscoe, Robinson, and Stephenson (A., 1926, 219). As the variations obtained by these authors in the density results of boric oxide glass from six different terrestrial sources can readily be ascribed to varying degrees of strain, it is not justifiable to use them as evidence of variation in the atomic weight of boron.

R. N. KERR.

Crystallisation of mesomorphic substances in the magnetic field. Obtaining a solid with oriented molecules. G. Foëx (Compt. rend., 1928, 187, 822-823).—The molecular orientation of the solid prepared by almost completely melting *p*-azoxyanisolephenetole in a magnetic field and allowing it to cool has been shown by the author's method (A., 1925, ii, 755) to be the same as that of the oriented nematic phase produced as a result of fusion. Crystallisation of the smectic phase of ethyl *p*-azoxybenzoate in a magnetic field also gives an anisotropic solid, but the diamagnetism is stronger in the direction of the orienting field than perpendicular to it.

J. GRANT.

Molecular state of liquids. W. KISTIAKOVSKI (Z. physikal. Chem., 1928, 137, 383-392).— Liquids are classified in seven groups: (1) Nonassociated, (2) slightly associated, (3) moderately associated, (4) strongly associated but yielding normal vapours, (5) strongly associated and yielding associated vapours, (6) electrolytes, (7) those exhibiting metallic conductivity. Modern conceptions of molecular structure have been applied to the problem of the physical state of liquids, assuming the completion of an eight-electron shell to be a hindrance to association as it is to chemical reactivity. The ease of association of the elements is periodic, conforming to the long periods of the Mendeléev system. Molecular association in liquids is frequently caused by the hydrogen atom, but only to a considerable extent if the hydrogen is combined with oxygen or nitrogen. The whole problem of the association of liquids is closely related to the deformation of the electron shells. H. F. GILLBE.

Quantum theory of the specific heat of hydrogen chloride. E. HUTCHISSON (Physical Rev., 1927, [ii], 29, 360—361).—The specific heat of hydrochloric acid at various temperatures has been recomputed using new quantum theory a priori probabilities. The curve rises to a maximum above the classical value at about 12° Abs. A. A. ELDRIDGE.

Dilatometric measurements of the expansion with heat of crystalline salts. W. KLEMM, W. TILK, and S. VON MÜLLENHEIM (Z. anorg. Chem., 1928, 176, 1—22).—Dilatometric determinations have been made of the coefficients of expansion of a large number of inorganic salts and of some organic compounds, and in certain cases density measurements have been made. H. F. GILLBE.

Oxides of ruthenium and osmium. F. KRAUSS and G. SCHRADER (Z. anorg. Chem., 1928, 176, 385– 397).—Densities of the dioxides and tetroxides of ruthenium and osmium have been determined and the atomic volume of oxygen at 0° Abs. has been calculated to be about 10.7. According to the work of other investigators, crystallised specimens of the dioxides may be obtained in which the atomic volume of oxygen is only half this value. The possibility of the existence of two modifications of OsO_2 and RuO₂ is discussed. M. S. BURR.

Volume chemistry. IV. Mixed oxygen compounds. I. Carboxyl group. F. WRATSCHKO (Pharm. Presse, 1928, 33, 124-126, 138-139, 160; Chem. Zentr., 1928, i, 2897).

Change in elastic properties on replacing the potassium atom of sodium potassium tartrate by ammonium. W. MANDELL (Proc. Roy. Soc., 1928, A, 121, 122–130; cf. *ibid.*, 1927, A, 116, 623). -The nine elastic moduli and nine elastic constants of crystals of sodium ammonium tartrate, prepared by very slow cooling from 28° of a concentrated solution of the salt, have been determined by the method previously used for sodium potassium tartrate (loc. cit.). In the bending and twisting experiments, the results with the ammonium salt were much more satisfactory than those with the potassium salt, the deflexions acquiring their maximum values almost immediately except for the stretching experiment in the direction of the a axis. The ammonium salt, both for the twisting and stretching experiments, is less elastic than the potassium salt, and the deformation magnitudes are increased fairly uniformly with the former salt. There is a considerable amount of similarity between the elastic curves of the two salts, which, however, show some small differences, especially in the directions where tensions or pressures give a maximum piezoelectric response. The general

results agree with what is to be expected from the fact that the salts are isomorphous, but it is considered remarkable that the simple chemical change made in so complex a molecule should diminish the elastic properties in all directions of the crystal. A comparison of the elastic properties of isomorphous crystals which have already been determined indicates that, in a salt of simple constitution, individual atomic forces exert a marked influence on the elasticity in certain directions, whilst in more complex substances the individual effects are more or less marked by the large number of other forces in the molecule.

L. L. BIRCUMSHAW.

Determination of cohesion temperatures [of powders]. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1928, 176, 46–48).—The temperatures at which various powdered salts, oxides, and silicates commence to cohere have been determined by observing the effect of allowing air to impinge on the substance. The quantity T_z/T_f , where T_z is the cohesion temperature and T_f the m. p., is for the oxides and salts about 0.52, and for the silicates about 0.88. H. F. GILLBE.

Fused salts. III. W. HERZ (Z. Elektrochem., 1928, 34, 682-684).—The capillary constants of the fused alkali halides at the m. p. and b. p. have been calculated from the equation $a^2=2\gamma/d$, using the data of Jaeger (A., 1918, ii, 33). Except in the case of cæsium chloride, the values obtained obey the law of corresponding states, the ratio a_c^2/a_s^2 (where a_c^2 is the capillary constant at the m. p., and a_s^2 that at the b. p.) having the approximate value 1.63. The formulæ connecting capillary constant with mol. wt. given by Walden, $Ma_c^2/T_c=C$ (cf. A., 1909, ii, 119, 122), and Kistiakowsky, $Ma_s^2/T_s=C$ (A., 1906, ii, 655), are calculated for the fused salts, and the molecular state of the substances under investigation is discussed in the light of the results obtained. Walden's ratio is found to increase with increasing atomic weight of anion or cation, *i.e.*, the lighter ion has the greater tendency towards association. L. BIRCUMSHAW.

Viscosity of gases and vapours. II. Mercury, cadmium, and zinc. H. BRAUNE, R. BASCH, and W. WENTZEL (Z. physikal. Chem., 1928, 137, 447— 457).—The viscosities of vaporised mercury, zinc, and cadmium relative to that of air have been measured by the rotating disc method at temperatures between 214° and 677°, and at pressures between 16 and 244 mm. The values of Sutherland's constant derived from these measurements are, respectively, 942 for mercury between 217° and 607°, 1053 for cadmium between 517° and 627°, and 876 for zinc between 607° and 677°. Using these values in Sutherland's equations the experimental viscosities agree with the calculated to within 1%. Over the respective temperature ranges, the thermal conductivities, calculated from the viscosities, are, for mercury from 1.678×10^{-5} to 2.305×10^{-5} , for cadmium 3.96×10^{-5} to 5.197×10^{-5} , and for zine 7.158×10^{-5} to 9.275×10^{-5} . The calculated diameters of the atoms for mercury, cadmium, and zine are, respectively, 2.53×10^{-8} cm., 2.46×10^{-8} cm., and 2.33×10^{-8} cm. These values, like that for argon, are 0.8 times those derived from X-ray measurements. These results are discussed from the point of view of Debye's theory of molecular forces. F. G. TRYHORN.

Influence of molecular attraction forces on the viscosity and heat conductivity of gas mixtures. Н. SCHMICK (Physikal. Z., 1928, 29, 633-640).-Earlier work (cf. A., 1928, 1180) is described together with additional experiments on viscosity. Heteropolar compounds cause deviations from the simple mixture law for both viscosity and thermal conductivity. R. A. MORTON.

Jaeger's method as applied to the determination of the surface tension of mercury. R. C. gas, the surface tension of mercury was found to be 472 and 477 dynes/cm. for glass and platinum jets, respectively, at 18° (cf. Bircumshaw, A., 1928, 1084). W. E. DOWNEY.

Internal friction of some gases and vapours. Air and bromine. H. BRAUNE, R. BASCH, and I. W. WENTZEL (Z. physikal. Chem., 1928, 137, 176-192).—A quartz apparatus is described containing a disc of 36 mm. diameter suspended by a quartz fibre between two fixed discs of 46 mm. diameter. Measurement of the logarithmic decrement of the rotational vibration of the movable plates when the apparatus is filled with gas at a given temperature and pressure has been employed to determine the internal friction of the gas. Results have been obtained for air and for bromine vapour over a wide range of temperature and pressure, and are compared with those obtained by other observers.

Aluminium-calcium alloys. G. Bozza and C. SONNINO (Giorn. Chim. Ind. Appl., 1928, 10, 443-449).—Alloys containing up to about 5% of calcium have been examined. Donski's equilibrium diagram (A., 1908, ii, 278) requires slight modification in the liquidus curve between the m. p. of aluminium and the first eutectic point. The differences between Donski's and Arndt's results (cf. B., 1905, 676) for the alloys corresponding with the region of partial miscibility in the liquid state are explained. The electrical conductivity and the density of the alloys diminish linearly with increasing calcium content. The hardness varies little, and the brittleness becomes very marked as soon as a small proportion of calcium is present. The tensile strength is somewhat lower than that of pure aluminium. The conditions of casting influence the properties of the alloys appreciably, but their industrial application scarcely seems feasible. T. H. POPE.

Electrical resistance of some silver alloys. W. SCHMIDT (Z. Metallk., 1928, 20, 400-402).-The slope of the curves which are obtained by plotting the increase of resistance against the atomic composition of solid silver alloys increases with the nature of the alloying element in the order : cadmium, magnesium, zinc, manganese, aluminium, tin, antimony.

A. R. POWELL. Mixed crystals and alloys. L. VEGARD and H. DALE (Z. Krist., 1928, 67, 148-162; Chem. Zentr., 1928, i, 2573) .- The systems lead nitratebarium nitrate and copper-nickel, but not coppercobalt, exhibit complete miscibility. The lattice dimensions show that the additivity law holds. The copper lattice can accommodate up to 13% Co and the cobalt lattice up to 8% of copper. The cubic form of the cobalt lattice is stabilised by traces of copper. Rapidly cooled copper-gold alloys were in accord with the additivity law. No mixed crystals were observed in the system sodium bromideammonium bromide. A. A. ELDRIDGE.

Application of the Fourier functions to diffusion. E. L. LEDERER (Kolloid-Z., 1928, 46, 169-173).-Application of the Fourier functions has led to diffusion coefficients for sodium chloride and sucrose. The values are in good agreement (although somewhat higher throughout) with those in the Stefan-Kawalki tables. E. S. HEDGES.

Optical striation. F. EMICH (Monatsh., 1928, 50, 269–283).—An improved apparatus is described for microscopical observation of the optical striation which occurs when a stream of one liquid flows through a jet into a second of different refractive index. The striation phenomena are classified as positive or negative according as the entering liquid is more or less refractive, and as rising or falling according as it is lighter or heavier than the second liquid. The method is sensitive to a difference of about 0.0001 in refractive index, and quantitative measurements of the intensity of striation may be made. The method is applicable to testing the purity of liquids. R. K. CALLOW.

Determination of the solubility curves of mixed crystals at low concentrations and the segregation of the foreign substance on heating. G. TAMMANN and A. HEINZEL (Z. anorg. Chem., 1928, 176, 147-151).-The solubility of a metal which is but sparingly soluble in another may be determined by microscopical examination of the residual film left after dissolving a rolled sheet of the metal in 50% ammonium nitrate solution. By this method the solubility of lead in cadmium at 270° has been shown to be greater than 0.1% and that of copper to be between 0.05 and 0.1%. The changes in the appearance of the film after the metal has been heated above the cutectic temperature are described. H. F. GILLBE.

Invasion and solvation of gases in water. G. M. SCHWAB and E. BERNINGER (Z. physikal. Chem., 1928, 138, 55-74).-A method is described for measuring at 10° intervals between 20° and 80° the solubility and "invasion coefficients" in water of oxygen, hydrogen, nitrous oxide, carbon dioxide, ethylene, and acetylene. With rising temperature, the solubilities of carbon dioxide and acetylene pass through minimum values, that of nitrous oxide falls abruptly, and that of ethylene is little influenced. The invasion coefficients of these gases, calculated from the solubility measurements, are approximately of the same magnitude but possess different temperature coefficients which are attributed to differences in the water layers round the gas molecules. Comparison of the hydration values for 20° and 60°

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shows that, relative to other gases, carbon dioxide and acetylene, which alone pass through a minimum solubility with rise of temperature, have abnormal positive temperature coefficients for the hydration number. Taking into account the influence of the viscosity of water, it is found that the temperature coefficients of the hydration number of all gases investigated are positive, and show analogy with the temperature coefficient of solubility at higher temperatures at which the effect of the dynamic allotropy F. G. TRYHORN. of water disappears.

Solubilities of some inorganic fluorides in water at 25°. R. H. CARTER (Ind. Eng. Chem., 1928, 20, 1195) .- The solubilities of various fluorides and the p_{π} values of these saturated solutions have been determined. The solubilities (g./100 c.c.) range from sodium fluoride 4.054 to calcium fluoride 0.004. C. IRWIN.

Crystallisation at the surface of fused masses. A. SCHUBNIKOV and G. LÄMMLEIN (Z. Krist., 1928, 67, 329-338; Chem. Zentr., 1928, i, 3027-3028). -On seeding supercooled fused phenyl salicylate the spherolites separate, and on continued rotation move radially from the point of seeding. An explanation is offered. A. A. ELDRIDGE.

Influence of foreign substances in solution on the growth of crystals. L. KHMELEWSKAJA (Nachr. Don. Staatsuniv. Rastow, 1925, 5, 4 pp.; Chem. Zentr., 1928, i, 2770) .- A discussion of the fact that in presence of borax, alum solutions yield a precipitate of basic aluminium sulphate and aluminium hydroxide, and of the appearance of different A. A. ELDRIDGE. forms of crystals.

Adsorption of vapour on a quartz or glass wall. A. SMITS (J.C.S., 1928, 2952-2954; cf. McHaffie and Lenher, A., 1925, 11, 854; Len-her, A., 1926, 898; 1927, 198; Frazer and others, A., 1927, 722).-By extrapolation of the vapourpressure data of the author and Purcell it is shown that at 379° and 480 mm. pressure ammonium bromide is adsorbed by glass to an extent which corresponds with the formation of a layer 300 molecules thick. This result is similar to that obtained by Rinse (A., 1928, 829) for mercuric iodide on glass and by Smith (ibid., 1087) for water on platinum F. J. WILKINS. surfaces.

Helium. III. Behaviour of helium towards glass and palladium, and the question of helium compounds. F. PANETH and K. PETERS (Z. physikal. Chem., 1928, B, 1, 253-269; cf. A., 1928, 1341).-Glass is appreciably permeable to helium at the ordinary temperature; at 0.5 atm. pressure about 10-11 c.c./cm.2/hr. passes through glass of thickness 0.5 mm. At a higher temperature, the rate is considerably higher, and since the rate of diffusion of neon is under the same conditions extremely small, neon-free helium may be obtained with little difficulty. Since, on the other hand, palladium is almost completely impermeable to helium at all temperatures, hydrogen and helium may be separated with ease. Unsuccessful attempts to prepare helium compounds are described.

H. F. GILLBE.

Heat of adsorption of oxygen on charcoal. III. D. MCKIE (J.C.S., 1928, 2870-2889; of. A., 1927, 1134).-The heat of adsorption of small quantities of oxygen on charcoal has been measured at temperatures up to 200°. After the adsorption the pressure of the gas is so low that the apparatus serves as a vacuum calorimeter. A few measurements were also made of the adsorption of oxygen and nitrogen and their mixtures on charcoal. Pure oxygen or nitrogen adsorbed on charcoal cannot be removed by pumping out at the temperature of adsorption. When mixtures of oxygen and nitrogen are admitted either to a clean charcoal surface or to one containing adsorbed oxygen or nitrogen a portion of the gas can be desorbed by evacuation. No gas, however, can be pumped off when nitrogen is adsorbed on a surface already containing adsorbed oxygen. In agreement with the results of Saussure (Ann. Physik, 1814, 47, 113) it is found that the amount of gas adsorbed from a mixture of oxygen and nitrogen is greater than is to be expected from what is known

of the separate adsorptions of these gases. F. J. WILKINS. Electro-capillary phenomena. IV. Rôle of physical factors. W. ARCISZEWSKI, E. CZARNECKI, W. KOPACZEWSKI, and W. SZNKIEWICZ (Protoplasma, 1928, **3**, 345-356; Chem. Zentr., 1928, i, 2366-2367).—A study of the influence of concentration, dialysis, viscosity, surface tension, and age of solutions of various colloidal substances (dyes etc.) on the electrocapillary penetration in filter-paper. A. A. ELDRIDGE.

Gelatin and copper sulphate solutions. M. CHANOZ (Compt. rend. Soc. Biol., 1928, 98, 695-697; Chem. Zentr., 1928, i, 3078; cf. A., 1928, 1271).—With a gelatin diaphragm copper sulphate solution behaves as with an animal membrane. The electrolytic behaviour was studied. Gelatin is coloured blue by 0.001N-copper sulphate solution, but on addition of acid the colour is discharged, or a faint pink colour is produced. A. A. ELDRIDGE.

Simple micro-electrodialysis apparatus. E. BAER (Kolloid-Z., 1928, 46, 176-178).-A microelectrodialysis apparatus is described, which can be made mainly from pieces of glass tubing in the laboratory at a triffing cost. Directions are given for the preparation of a chromate-gelatin anode and a parchment cathode. The former is made by immersing crepe-georgette in a freshly-prepared potassium chromate-gelatin mixture, washing out the excess of potassium dichromate with water, and removing the last traces by electrodialysis. The electrodes consist of platinum wire in the form of a flat spiral, but the cathode may be made of silver E. S. HEDGES. wire or silvered brass wire.

Rotatory dispersion of solutions of nicotine in the ultra-violet. (MME.) MILWARD-LIQUIER and R. DESCAMPS (Bull. Soc. chim. Belg., 1928, 37, 345-350; cf. A., 1927, 827).-The specific rotations of aqueous solutions of nicotine (0.1 g.-mol./litre) containing increasing quantities of hydrochloric acid have been measured for wave-lengths between 5780 and 2967 Å., in continuation of previous measurements made in the visible region. Aqueous solutions of nicotine containing hydrochloric acid up to the amount necessary for the complete neutralisation of one of the basic groups behave as mixtures of two optically active constituents having different dispersions. These are the undissociated molecule of the hydrochloride and the nicotine cation.

O. J. WALKER.

Specific heats of magnesium sulphate solutions of various concentrations between 16° and 100°. F. SEROWY (Mitt. Kali-Forschungs-Anst., 1922, 2, 133—141; Chem. Zentr., 1928, i, 2701).

Thermochemistry and refractometry of strong electrolytes. E. LANGE (Physikal. Z., 1928, 29, 760-770).-Measurements carried out with a differential calorimeter accurate to 10⁻⁶ degree C. show that the heat of dilution in the limiting region (e.g., <0.01M-potassium chloride solutions) is positive and varies as M^{\ddagger} , in accordance with the requirements of the Debye-Hückel theory. Above a concentration of 0.01M, deviations from the simple theory are to be expected and do in fact occur, due possibly to residual undissociated molecules. For concentrations above 2N, the molecular refraction of strong electrolytes varies with the concentration, and the sign and magnitude of the variations indicate the formation of ionic aggregates without intermediate molecules of water, *i.e.*, undissociated molecules. Whilst these results do not prove the existence of undissociated molecules of strong electrolytes, a series of observations on heats of dilution, molecular refraction, and on the absorption spectra of nitrates strongly indicate incomplete dissociation. R. A. MORTON.

Application of the Fourier functions to sedimentation. E. L. LEDERER (Kolloid-Z., 1928, 46, 173-176).—Calculations have been made of the number of particles of colloid at various heights in a sol and at various times before the state of sedimentation equilibrium is reached. The results agree well with the data obtained by Perrin and do not support the arguments of Burton and Bishop (Proc. Roy. Soc., 1922, 100, 414). E. S. HEDGES.

Suspensions of kaolin. R. DUBRISAY and ASTIER (Compt. rend., 1928, 187, 978–980).—The rate of settlement of water-washed kaolin, purified by sedimentation and suspended in water or in a dilute solution of hydrochloric acid, or of sodium, lithium, or potassium hydroxide, decreases regularly with an increase in the $p_{\rm H}$ value of the solution. Phosphate buffers and very dilute solutions of the alkaline-earth bases show exceptional behaviour.

J. GRANT. Heterogeneity of colloidal solutions and sedimentation in a centrifugal field. T. SVEDBERG (Nobel Prize Address, 14 pp.).—The construction of centrifuges is described. Measurement of the rate of sedimentation and sedimentation equilibrium lead independently to values of the mol. wt. of substances. CHEMICAL ABSTRACTS.

Colloidal gold solution. Preparation of gold solutions and their titration with permanent hydrogen-ion concentration standards. V. CHRISTINA and C. S. GREEN (J. Lab. Clin. Med., 1928, 13, 678-681).—In Zsigmondy's method, conductivity water and a larger amount of alkali are used. Phenol-red is employed as indicator, and the $p_{\rm ff}$ determined with permanent inorganic standards. CHEMICAL ABSTRACTS.

Preparation of a lead sulphide hydrosol and its combination with phosphate ions. J. BROOKS (J. Physical Chem., 1928, 32, 1717-1724).-A lead sulphide sol has been prepared from a solution of lead acetate and hydrogen sulphide using 0.5% of gelatin as a protective agent with the subsequent addition of sodium hydrogen carbonate to neutralise the acetic acid formed. The percentage transformation of lead salt into colloidal sulphide depends on the initial concentration of the former, and above a certain concentration the amount of colloid formed decreases abruptly. The results are similar to those obtained with lead selenide hydrosol (A., 1928, 704). The rate of combination of the lead sulphide particles with phosphate ions at 15°, 25°, and 37.5° has been measured. It is slow in comparison with the rate of diffusion of phosphate ions to the surface and is independent of the phosphate concentration. At 15°, the rate is proportional to the surface of unchanged particle, but at the higher temperatures aggregation of the particles causes a decrease in reacting surface in addition to the decrease due to combination. L. S. THEOBALD.

Osmotic pressure of egg-albumin. J. MAR-RACK and L. F. HEWITT (J. Physiol., 1928, 66, Proc. Physiol. Soc., v).—The osmotic pressure of isoelectric egg-albumin has been measured by the use of sodium chloride solutions buffered with sodium acetate and acetic acid as external fluid. The calculated mol. wt. is 43,000. B. A. EAGLES.

Ultra-microscope and colloidal solutions. R. ZSIGMONDY (Nobel Prize Address, 12 pp.).—A description of studies on gold hydrosols and of observed relations between electric charge and coagulation. CHEMICAL ABSTRACTS.

Structure of colloidal particles and composition of sols and gels. H. FREUNDLICH (Bcr., 1928, 61, [B], 2219-2233).—A lecture. H. WREN.

Constitution of micelles. IV. Colloidal oxides of iron and aluminium. R. WINTGEN and O. KÜHN (Z. physikal. Chem., 1928, 138, 135–157; cf. A., 1924, ii, 156, 534).—Previous studies of the dialysis, ageing, electrical conductance, migration velocity, and ultra-filtration of ferric hydroxide and chromium oxide sols have been extended to sols of aluminium oxide. F. G. TRYHORN.

Alumina gels. D. G. R. BONNELL (Z. anorg. Chem., 1928, 176, 416—422).—The adsorptive power of different alumina gels for dyes is independent of differences in the other colloid-chemical properties of the gels. Acid dyes are more strongly adsorbed than basic. Fractional ultra-filtration of the hydrosols produced by peptisation with hydrochloric acid indicates that poly-disperse systems are formed. The particle size diminishes with increasing acid concentration. Curves are given showing the relation between vapour pressure and water content of the gel during hydration and dehydration. The vapour pressures of the dehydration curve are lower than those of the hydration curve. M. S. BURK. Constitution and stable end-state of hydrogels. A. SIMON (Kolloid-Z., 1928, 46, 161-169).—A critical discussion of the constitution of hydrogels, with particular reference to the state of the aqueous phase. The water is supposed to be bound partly osmotically and partly chemically, an equilibrium existing between the two. Attempts to separate the two forms are described. E. S. HEDGES.

Theory of charge alternation of colloidal particles. A. EUCKEN (Z. physikal. Chem., 1928, B, 1, 375–378).—Theoretical. The relation of the stability of a colloidal solution to the electrolyte concentration is discussed on the basis of Debye's theory of electrolytes. M. S. BURR.

Dielectric constant of emulsions of water and mercury in oil. A. PIEKARA (Bull. Acad. Polonaise, 1928, A, 201-222).-The formulæ proposed for the dielectric constant of a mixture express the latter as an additive function of the dielectric constants of the constituents. The various forms of this function, in particular that of Lorenz and Lorentz, have been tested by measurements on emulsions of water and mercury in oil, with concentrations of the disperse phase between 0.0002 and 0.005. The dielectric constants were measured by the resonance method, sensitivity being increased by the application of the cathodic lamp. The values obtained for the emulsions are much greater than the calculated values, and depend to a greater extent on the concentration and dielectric constant of the disperse phase than is provided for by the formula. They also increase with the degree of dispersion, and are further shown to depend on the diameter of the particles of the disperse phase, of which the formula takes no account.

N. M. BLIGH.

Relation between the dielectric constant of an emulsion of mercury in vaseline and the degree of dispersion. A. PIEKARA (Bull. Acad. Polonaise, 1928, A, 223-239; cf. preceding abstract) .- It is suggested that the divergence between the experimental and calculated values of the dielectric constant of emulsions may be due to the secondary influence of the movements of droplets constituting the disperse phase and to surface charges on the droplets. This was tested experimentally by measuring the dielectric constant of emulsions of mercury in vaseline to eliminate such movements. No appreciable effect due to these secondary factors could be detected. Evidence was obtained for a negative effect diminishing the dielectric constant, which is attributable to the directing influence of the charged particles on the dipoles of the liquid phase; this appears to increase with the concentration and dispersion and thus resembles the orienting effect found in the case of colloidal solutions. N. M. BLIGH.

Hofmeister ionic series in the precipitation of the hydrophilic colloids. K. ANDO (Nagoya J. Med. Sci., 1927, 2, 110–123).—In the precipitation of the hydrophilic colloids the Hofmeister series is valid except with the buffer salts. Precipitation according to valency occurs, and increases with the distance of the $p_{\rm fr}$ from the isoelectric point. At the isoelectric point the hydrophilic colloids have a minimal stability towards ethyl alcohol. On both

sides of the point the sensitiveness to salts increases abruptly. CHEMICAL ABSTRACTS.

C-Potential and the lyotropic series. D. R. BRIGGS (J. Physical Chem., 1928, 32, 1646-1662). -The effect of ions on the ζ-potential at an inert interface of cellulose and water has been measured by the streaming-potential method recently described (A., 1928, 713). The ions affect the ζ-potential in the order of their mobilities, which are thus inverse measures of the attraction between an ion and its dispersion medium. The ζ-potential arises from the relative attractions of ions for the phases of a system in which the ions are distributed. The effect of a salt solution on the ζ-potential is a function of all the ions present in a system to which the interface is accessible, and the potential varies with salt concentration in a manner similar to that of the partial molal free energy, the equation representing the former variation being $c = ae^{i\xi}$. In certain cases, the change in ζ-potential with ionic concentration is secondary in effect to other free surface energy changes, and is not, per se, the determining factor in the adsorption phenomenon. L. S. THEOBALD.

. Empirical equation for K. HIROTA (J. Biochem. II. Coagulation. gelation velocity. Japan, 1928, 9, 103-115) .- Measurements have been made of the viscosity of sols of Merek's powdered gelatin (2.5-5%) by the use of a viscosimeter in which the fluid travels through the capillary under a constant pressure. Results are obtained which are in harmony with the equation of Shoji (A., 1919, ii, 498). The critical concentration of gelatin is 3.8% when $\lambda = \infty$ and the rate of change of the constant with concentration, which is linear for higher and lower concentrations, increases suddenly at this point. The viscosities of agar-agar sols change with time similarly to those of gelatin sols, but it has not been found possible to apply the above equation in this case. When heated for some time at 98° both gelatin and agar sols undergo irreversible W. O. KERMACK. changes.

Influence of lyophile colloids on the stability and electric charge of lyophobe sols. W. REIN-DERS and W. M. BENDIEN (Rec. trav. chim., 1928, 47, 977-988) .- In acid solutions of pu value lower than that of the isoelectric solution colloids such as gelatin, casein, and sodium lysalbuminate, which are nitrogenous, lyophile, and amphoteric in character, behave as salts with multivalent cations towards gold sols. From observation on coagulation and cataphoresis it was found that very small amounts of these colloids discharge and coagulate gold sols. The same sols are charged positively and rendered stable in the presence of larger amounts of the above colloids. A second precipitation zone occurs at higher concentrations in circumstances in which the reagent is incompletely soluble in the solution of the given acidity and, in being precipitated, carries with it the gold particles. In solutions a little less acid than the isoelectric solution and in which the gold particles retain their negative charges for all concentrations of the added colloid, the protective action of the latter becomes predominant and the sol remains stable in spite of its low electrical charge. The gold

number of these colloids is markedly dependent on and decreases with the $p_{\rm H}$ value of the solution. Non-amphoteric, nitrogen-free colloids such as dextrin, gum arabic, and tannin coagulate gold sols in both acid and alkaline solutions, but are unable to reverse the sign of the electric charge on the particles.

F. G. TRYHORN.

Ion antagonism in colloidal models. I. Regularities in ion antagonism in the coagulation of hydrophilic sulphur sols. II. Influence of anions on the antagonism of cations in the coagulation of hydrophilic sulphur sols. W. A. DORTMAN (Kolloid-Z., 1928, 46, 186-198, 198-201).-I. A study of the ion antagonism encountered in biological problems has been made in a simpler system by observing the effects of pairs of electrolytes on hydrophilic sulphur sols. The strongest antagonistic effects were observed when the hydrogen ion formed one of the pair, and the lithium ion comes next in importance in this respect. No antagonism was observed between sodium and potassium ions. In general, the more remote the two ions in the order of coagulation values the greater is the antagonistic effect. In accordance with the Schulze-Hardy rule, the degree of antagonism increases with rising valency of the ions concerned, but quadrivalent thorium is a notable exception. The curves showing the dependence of the coagulation values of magnesium chloride, calcium chloride, and sodium chloride on the amount of hydrochloric acid previously added to the sol pass through a maximum at an abscissal value correspond. ing with 50% of the coagulation value for hydro-chloric acid. For the pair hydrochloric acid-aluminium chloride, the maximum is displaced to the right, but in this case antagonism begins later. Dilution of the sol reduces the coagulation values of uni- and multi-valent cations and raises the corresponding values of bivalent cations. The ion antagonism is less marked in the dilute sols. Reversal of charge of the sol diminishes the degree of hydration; cation antagonism disappears, and no corresponding anion antagonism is observed. The factors concerned in determining these effects are considered to be the charge on the particles and the degree of hydration.

II. The effect of substituting sulphuric acid for hydrochloric acid in the experiments described above is to increase the antagonistic effect of the cations. This increase was observed in the pairs sulphuric acid with sodium chloride, magnesium chloride, or aluminium chloride and was particularly noticeable in the pair sulphuric acid-thorium nitrate. The effect is shown only by substitution of the anion of the first member of the pairs, a slight decrease in degree of antagonism being observed when sulphate is substituted for chloride in the second member of the pairs. E. S. HEDGES.

Spectrophotometric and cataphoretic experiments on the adsorptive power of gelatin for methylene-blue hydrochloride. A. FODOR and K. MAYER (Kolloid-Z., 1928, 46, 201-207).—The spectrophotometric and cataphoretic methods of measuring the adsorption of methylene-blue hydrochloride developed earlier by the authors (A., 1926, 1091) have been applied to gelatin as adsorbent. Experiments on the direction of migration of mixtures of gelatin and methylene-blue hydrochloride in an electric field with addition of acid or alkali show that the dye migrates in the same direction as the gelatin. With a solution containing 1.68% of gelatin and 0.002% of methylene-blue hydrochloride, both constituents migrate together to the cathode at $p_{\rm H}$ 4.6 and in more strongly acid solutions, whereas at p_{μ} 4.9 and above migration occurs in the direction of the anode. Gelatin alone behaves in a precisely similar way, but it was established that methyleneblue hydrochloride alone always wanders to the cathode, whatever the hydrogen-ion concentration of the solution. Experiments were also carried out on the velocity of diffusion of methylene-blue hydrochloride into gelatin gels containing added electrolytes. The presence of neutral salts scarcely alters the rate of diffusion from that in pure, dialysed gelatin, but alkalis and alkaline salts diminish the velocity and acids and acid salts increase it. The formation of rings was observed in the diffusion into gels containing neutral salts and alkalis, but not in the gels containing acids. The course of adsorption was also followed by the spectrophotometric method. The amount of adsorption depends on the thickness of the gelatin layer and it is inferred that there is no essential difference between adsorption by gelatin and by animal charcoal (cf. Fodor and Schönfeld, A., 1922, ii, 688). E. S. HEDGES.

Influence of adsorbed silver and bromide ions on light absorption by silver bromide hydrosols. H. FROMHERZ (Z. physikal. Chem., 1928, B, 1, 324-345).-The absorption spectra of samples of silver bromide hydrosols of approximately equal particle size and containing adsorbed silver and bromine ions, respectively, have been measured in an apparatus previously described (cf. ibid., 301). The sol containing adsorbed silver ion, in contrast to bromine ion, shows increased absorption in the yellow and green due to a shift of the absorption curve 150-200 A. towards the long-wave region. This is in agreement with earlier observations according to which the general photochemical sensitivity of silver bromide, free from any binding agent, is increased by the presence of adsorbed silver ion and its spectral sensitivity is extended to longer wave-lengths. In order to equalise the particle size of the two sols relative measurements of the degree of coagulation have been made on the basis of the light scattering produced by the particles. By measuring the rate of coagulation with time and its dependence on the excess of silver or bromine ion in the solution the necessary data may be obtained. M. S. BURR.

Influence of adsorbed ions on the light absorption and photochemical sensitivity of silver bromide-gelatin emulsions. H. FROMMERZ and G. KARAGUNIS (Z. physikal. Chem., 1928, B, 1, 346— 361; cf. preceding abstract).—Experiments carried out with mirrors covered with an emulsion of silver bromide in gelatin washed with solutions of various salts have shown that the extinction curves for adsorbed silver or bromine ions are similar to those for hydrosols. The extinction coefficient of the emulsion containing silver ion in comparison with

that containing bromine ion is increased by about 17% in the near ultra-violet and blue, and by about 60-70% in the yellow-red, resulting in an extension of the absorption region by 500 Å, towards the longer-wave region. The thallous ion has a similar effect to the silver ion, but only half as great. Experiments on the spectral and photochemical sensitivity of emulsions with different adsorbed ions indicate that the hydroxyl, sulphite, and thallous ions extend the sensitivity towards the red, the sulphate and chlorate ions have no influence, and the bromine ion decreases it. The extension of sensitivity towards the red by the thallous ion amounts to 700 Å. These results are in agreement with corresponding observations on silver bromide sol alone and with absorption M. S. BURR. measurements.

Theory of the solid-phase rule. A. VON BUZAGH (Kolloid-Z., 1928, 46, 178-185) -In continuation of previous work (A., 1927, 310), the relation between the amounts of colloid peptised and the amount of the disperse phase present in the massive state is discussed and the conclusion is reached that factors other than adsorption are involved in the so-called solid-phase rule. Experiments conducted with suspensions of animal charcoal, calcium carbonate, barium sulphate, zinc oxide, red lead, and mercuric oxide in water show that the solid-phase rule holds in such coarsely disperse systems in the absence of an additional peptising agent. The same effect is also observed in the preparation of sols (e.g., mastic) by the method of exchange of the dispersion medium. The relative amounts of dispersed material (or degree of peptisation) depends, not only on specific adsorption, but also on the concentration of the gel suspension; these factors determine whether or not peptisation in the narrow sense takes place. It is probable that the variation of particle size of the suspension with the concentration also plays a part.

E. S. HEDGES.

Effect of the spatial position of substituent groups on acidic strength. B. FLÜRSCHEIM (J.C.S., 1928, 3039-3040).-A claim for priority over the views of Hey (A., 1928, 1188).

F. J. WILKINS.

Ionisation of aromatic nitro-compounds in liquid ammonia. II. W. E. GARNER and H. F. GILLBE (J.C.S., 1928, 2889-2904; cf. A., 1925, ii, 792) .- The velocity of ionisation of m-dinitro-compounds in liquid ammonia solution obeys a first-order law, even in cases where the ionisation does not proceed to completion. Measurements of the change in conductivity and extinction coefficients of these solutions show that at high dilution the ionic concentration is proportional to the conductivity. It is suggested that the ionisation is the result of two consecutive reactions, $R(NO_2)_2 + 2NH_3 \rightarrow R(NO_2)_2, 2NH_3 \rightarrow R(NO_2)_2^{--} + (NH_3)^{++}$, the first of which governs the velocity of the process and proceeds to completion. The critical increment of the reaction is 7250 g.-cal. Vapour-pressure measurements give no indication of the existence of molecular complexes of the type $R(NO_2)_2, xNH_3$. F. J. WILKINS.

Hydrolysis of tin chloride and the chlorostannates. L. SMITH [with A. PERSSON] (Z. anorg. Chem., 1928, 176, 155-180) .- The concentration of chlorine ions and hydrogen ions in aqueous stannic chloride solutions have been determined, the latter by calorimetric, potentiometric, and polarimetric methods. Conductivity and f.-p. determinations have also been carried out. In dilute solution the hydrogen and chlorine ions are present in equal concentrations, but for solutions of greater concentrations than 0.1M an excess of chlorine ions is present. For old solutions the f. p. and conductivities are in good agreement with the values calculated on the assumption of the existence of univalent positive tin complexes, whereas for newly-prepared solutions the observed conductivities for 0.1-0.4M-solutions are 15-20% less than the calculated. Sodium salts lower the hydrogen-ion concentration appreciably more than do potassium salts. The influence of acids and salts at concentrations up to about 4N has been studied by means of solubility measurements and determination of partition coefficients between ether and water. Even in N-hydrogen chloride solution the true concentration of stannic chloride and of chlorostannate ions must be small; complete inhibition of hydrolysis does not take place even in presence of 4N-acid. It is probable that the stannic chloride and chlorostannate-ion concentrations are of similar magnitude. The percentage hydrolysis is influenced to a very variable extent by different chlorides; their repressive influence increases in the order ammonium, potassium, barium, sodium, magnesium.

H. F. GILBE.

Transformation of hydrated ortho-ferric oxide into hydrated meta-ferric oxide. A. KRAUSE (Z. anorg. Chem., 1928, 176, 398-402; cf. A., 1928, 1202) .- When kept under water, hydrated orthoferric oxide gradually changes into the meta-form, and the change is very much accelerated by the presence of hydroxyl ions. At the same time the isoelectric point changes from p_{π} 5.2 to 7.7. The dried metacompound contains less water than the ortho-, is brownish-yellow instead of black, is more friable, and adheres more firmly to glass. The meta-oxide can also be readily peptised by either dilute acid or ammonia, whilst the ortho-oxide cannot.

M. S. BURR.

Decomposition pressures of nitrides. R. LORENZ and J. WOOLCOCK (Z. anorg. Chem., 1928, 176, 289-304) .- The different methods employed in the investigation of the decomposition pressures of nitrides are reviewed. A method is described by which the formation of nitrides from the metal, or carbide, and nitrogen may be quantitatively studied, using a "Kurzschluss" vacuum furnace. The product formed by passing nitrogen over zirconium carbide gives up some gas again by heating above 1400°, but cannot be made to reabsorb nitrogen at a higher pressure. Although some nitrogen is absorbed by tantalum and titanium, no reversible equilibrium can be obtained. Between 750° and 1800°, and at a pressure of 1 atm. of nitrogen there is no appreciable absorption by molybdenum. The decomposition pressures of boron nitride have been observed between 1695° and 2045°. The results are reversible and reproducible and the relation between $\log p$ and 1/T is approximately linear. The heat of formation of boron nitride per g.-mol. is calculated to be 28100 g.-cal. It has been shown by Shukov's method (A., 1910, ii, 254) that the nitrogen pressures in equilibrium with compounds of uranium and nitrogen increase continually with increasing nitrogen content. It is possible to obtain reversible equilibrium values, but these are not satisfactorily reproducible and a straight line is not obtained by plotting log p against 1/T. The behaviour is similar to that of chromium and manganese (Shukov, loc. cit.), and may be due to the dissolution of nitrogen or nitride in the metal.

M. S. BURR. System zinc oxide-water. A. GUTBIER and H. R. BARFUSS-KNOCHENDÖPPEL (Z. anorg. Chem., 1928, 176, 363-371).-The preparation of three different samples of hydrated zine oxide is described : A, the crystallised monohydrate ZnO,H2O; B, an amorphous zinc oxide hydrate subjected to ageing and having a composition corresponding with the formula $ZnO_{,0}.342H_2O_{,0}.027CO_2$; C, freshly-prepared amorphous zinc oxide hydrate, $ZnO_{,0}.275H_2O_{,0}.005CO_2$. The vapour pressure of preparation A is not measurable at the ordinary temperature but undergoes a marked rise at 73°. All but a very small fraction of the water, about 0.06 mol., can be readily removed, but the process is not reversible at the ordinary temperature, even in the presence of liquid water. This and other observations indicate that the crystallised monohydrate is not stable at the ordinary temperature (cf. Roth and Chall, A., 1928, 593). Preparation B gives up water less readily than C. The ratio of the adsorptive power of B to that of C for silver is 31:9, so that ageing diminishes the adsorptive power. On examination of the X-ray spectrograms C was found to give no interference, B showed broad diffused interference bands corresponding in position with those of zinc oxide and not with the crystallised monohydrate, whilst A showed sharp interference lines, the positions being different from those of zinc oxide lines. It is concluded that the ageing process in the system zinc oxide-water results in the formation of the oxide and liquid water, but that there is an intermediate stage consisting in the formation of the monohydrate. M. S. BURR.

Fusion diagram of highly refractory oxides. H. VON WARTENBERG, H. LINDE, and R. JUNG (Z. anorg. Chem., 1928, 176, 349-362).-The construction of a furnace made of zirconium oxide and heated by the oxy-hydrogen or oxy-coal gas flame is described. The furnace has been employed for the study of the m.-p. curves of the following binary mixtures of refractory oxides: $CaO-Al_2O_3$ (determined merely as a test of the behaviour of the furnace); ZrO_2 -Al₂O₃; and CaO-ZrO₂. Softening points and m. p. of aluminium oxide mixtures were observed up to 20% of zirconium oxide. From 20% to 60%, at a little above 1900°, there was one m. p. only, evidently the eutectic. At 80% there was only a softening point. So much deformation took place that no m. p. could be observed. No evidence of compound formation was obtained. The m. p. of mixtures of calcium oxide and zirconium oxide of high zirconium oxide content were rendered uncertain by the volatility of calcium oxide at the temperatures required for fusion, but there appears to be a well-defined eutectic at 2230° with less than 60% zirconium oxide. A second eutectic mixture with a higher zirconium content is formed at 2380°. Between these two there should be a compound, probably the meta-compound CaO.ZrO₂, with 69% of zirconium oxide.

M. S. BURR. Lithium chloride ammonia complexes. S. C. COLLINS and F. K. CAMERON (J. Physical Chem., 1928, 32, 1705-1716).-Vapour-pressure measurements of the system lithium chloride-ammonia have been made at 0°, 33°, 45.2°, 54.5°, 58.3°, 66.4°, 74.9°, and 86.9°, and of the system lithium chlorideammonia-water at 25°. In the former system, between 0° and 66°, either the mono-, tri-, or tetraamminolithium chloride may be formed, but at 66.4° the only stable complex is the monoammino-chloride. Excepting the case of this complex, the measurements agree well with those of Bonnefoi (A., 1901, ii, 653), but, contrary to this worker, the existence of a diammino-complex could not be established. In the latter system, either the monohydrate, lithium monoamminochloride, or triamminochloride may be a stable solid phase, but no diammino-complex was L. S. THEOBALD. found.

Phase rule investigation of cupric bromide in aqueous and hydrobromic acid solutions. S. R. CARTER and N. J. L. MEGSON (J.C.S., 1928, 2954-2967).-The solubility of cupric bromide in water between 0° and 50° shows the existence of two solid phases, $CuBr_{2}, 4H_{2}O$ and $CuBr_{2}$. The transition temperature is 17.97° (cf. Kurnakov and Sementschenko, A., 1899, ii, 287).

The system CuBr₂-HBr-H₂O has been investigated at 0° and 25°. The results at 0° indicate two stable solid phases, $CuBr_{2,}4H_2O$, and the violet β -CuBr₂. Up to a concentration of 59% of hydrobromic acid the stable solid phase is $CuBr_2$, which exists in two forms, the transition between α -CuBr₂ and β -CuBr₂ occurring at 26.0% hydrobromic acid. A metastable region exists which has a solid phase of composition corresponding with $3CuBr_2, 2HD1, 0H_2O$. been obtained of the existence of $CuBr_2, 2H_2O$. F. J. WILKINS. sponding with 3CuBr₂,2HBr,6H₂O. No evidence has

Interaction of acids and neutral salts with stannic oxide and its relation to electrical charge. B. N. GHOSH (J.C.S., 1927, 3027-3038) .- Solutions of neutral salts develop an acid reaction in contact with both α - and β -stannic acids. The concentration of the liberated hydrogen ions varies with the amount of stannic acid taken. The *x*-acid has a greater number of replaceable hydrogen ions than the β-acid, a result which is in accord with Mecklenburg's view that the former has a larger active surface than the latter. The capacity of cations to liberate hydrogen ions is in the order Mg' > Ba' > Sr' > Li > Na' > K'. This is in agreement with Mukherjee's theory of the adsorption of ions (Phil. Mag., 1922, [vi], 44, 321).

In the presence of acids, hydrated stannic oxide is positively charged and the adsorption of an acid is greater the smaller the positive charge on the surface. The capacity of an anion to diminish the positive charge of the adsorbent increases with the adsorbability of the anion. F. J. WILKINS.

System ammonium sulphate-sulphuric acidethyl alcohol. H. B. DUNNICLIFF, A. L. AGGARWAL, and R. C. HOON (J. Physical Chem., 1928, 32, 1697-1704).-An investigation of this system at 18.1° shows equilibrium to be established more rapidly than in the case of the corresponding system with sodium sulphate. The solid, 3(NH₄)₂SO₄, H₂SO₄, formed by the action of alcohol on ammonium hydrogen sulphate is amorphous, but the solid phases resulting from the action of alcoholic sulphuric acid on this salt are crystalline. When the ratio of the weight of ammonium hydrogen sulphate to that of alcohol is unity or greater than unity the formation of a compound of the formula 2(NH4)2SO4, H2SO4 is indicated, but this solid phase is not formed when alcoholic sulphuric acids react with the ammonium salt. Solid phases of the $composition 3(\mathrm{NH_4})_2 \mathrm{SO_4}, 2\mathrm{H_2SO_4} \mathrm{and} (\mathrm{NH_4})_2 \mathrm{SO_4}, \mathrm{H_2SO_4}$ are produced at various ranges of acid concentration, but when the total acidity reaches 80% or more, no solid phase results at -18° from the action of the alcoholic acid on the ammonium salt. The phase diagram indicates that equilibrium is controlled by factors other than the concentration of free sulphuric L. S. THEOBALD. acid.

Equilibria of sulphides and silicates in fusions. W. JANDER [with K. ROTHSCHILD] (Metall-Wirtschaft, 1928, 7, 580—585; Chem. Zentr., 1928, i, 2897).— By fusion of the constituents in a graphite crucible, the contents being stirred with a magnesium rod, and analysis of the cooled mass, the following reactions were studied: $FeS+PbSiO_3 \implies PbS+FeSiO_3$; $Cu_2SiO_3+FeS \implies FeSiO_3+Cu_2S$; $NiSiO_3+FeS \implies$ $FeSiO_2+NiS$; $PbSiO_3+Cu_2S \implies Cu_2SiO_3+FeS \implies$ $FeSiO_3+NiS \implies NiSiO_3+Cu_2S$; $NiSiO_3+FeS \implies$ $PbSiO_3+NiS \implies NiSiO_3+Cu_2S$; $NiSiO_3+PbS \implies$ $PbSiO_3+NiS$. With lack of iron in the sulphide layer, larger amounts of the more noble metal pass into the silicate layer. Except for the lead-copper equilibrium the values of K obtained directly and by calculation from two equations are in accord.

A. A. ELDRIDGE.

Systematic doctrine of affinity. XLVII. Relationship of mercury to certain metals. W. BILTZ and F. MEYER. XLVIII. Heats of formation of uranium tetrachloride, trichloride, and trioxide. W. BILTZ and C. FENDIUS. XLIX. Relationships of chlorine and other halogens with gold. W. FISCHER and W. BILTZ. L. Pneumatolytic transference of gold by chlorine. W. BILTZ, W. FISCHER, and R. JUZA (Z. anorg. Chem., 1928, 176, 23-45, 49-63, 81-111, 121-142).-XLVII. The mercury vapour tensions of gold amal-gams containing 7-25% of mercury have been measured at temperatures from about 250° to 350° . Several series of mixed crystals exist, together with one compound, HgAu4. The phase of composition HgAu₃ is a saturated mixed crystal; with a mercury percentage greater than 25 this phase exists in contact with an immiscible mercury phase. The amalgamation of gold by liquid mercury is feebly endotehrmic, the affinity of the process being less than 0.5 kg.-cal./g.-atom of mercury. Tensimetric measurements with cerium amalgams, which are extremely

pyrophoric, indicate the existence of CeHg4, which is but slightly soluble in mercury, and does not dissolve metallic cerium; the heat of formation, referred to solid cerium, is 5.8 kg.-cal./g.-atom of mercury. Calorimetric determinations yield for the heat of formation of Hg₅Tl₂, referred to liquid mercury at 0°, 2.5 kg.-cal., and for solid mercury at -39°, -0.4 kg.-cal.; the density of the solid amalgam at 0° is 13.16, and of the liquid at 25°, 12.94; the zero molecular volume is nearly equal to the sum of those of the components. The heats of formation in kg.cal./g.-atom of liquid mercury of the sodium amalgams are NaHg₄ 1.9, NaHg₂ 7.8, Na₇Hg₈ 5.3, NaHg 13.2, Na₃Hg₂ 11.4, and Na₃Hg 9.3. The relative magnitudes of the heats of amalgamation are in agreement with the hypothesis of a relationship between the stability of intermetallic compounds and the "nobleness " of the components.

XLVIII. By measurement of the heats of dissolution of uranium and its tetra- and tri-chlorides in hydrogen chloride solutions, the following heats of formation have been determined: U (solid)+ $2Cl_{2}(gas)=UCl_{4}(solid)+251$ kg.-cal., and U(solid)+ $3/2Cl_{2}(gas)=UCl_{3}(solid)+213$ kg.-cal. Uranium is thus, with regard to chlorine, a less noble metal than iron, and resembles thorium closely. The heat of formation of the trioxide, calculated from the heats of dissolution of the chlorides and oxide in iodine trichloride and ferric chloride solutions, is 292 kg.-cal.

XLIX. The dissociation pressures of aurous chloride and bromide and auric chloride have been determined at various temperatures. The heats of reaction, calculated from the van 't Hoff equation, are in close agreement with those obtained by calorimetric measurements. The values in kg.-cal. are 2Au(solid)+ $Cl_{2}(gas) = 2AuCl(solid) + 16.5$ (16.8), $Cl_{2}(gas) = AuCl_{2}(solid) + 18.7$ (19.9), $Br_{2}(gas) = 2AuBr(solid) + 18.7$ (19.9), AuCl(solid)+ $Cl_2(gas) = AuCl_3(solid) + 18.7$ (19.9), $2Au(solid) + Br_2(gas) = 2AuBr(solid) + 13.7(14.2)$, and $AuBr(solid) + Br_2(gas) = AuBr_3(solid) + (16.9)$; bracketed values refer to calorimetric values. These results differ 2Au(solid)+ widely, for the first and third reactions, from those of Thomsen, and the discrepancies cannot be ascribed to the existence of different modifications of the metal. The possibility of formation of gold dichloride has been investigated, but no evidence has been obtained for its existence or for the formation of double salts between the dichloride and potassium chloride.

L. The system gold-chlorine has been investigated at temperatures up to 1250° at I atm. pressure of chlorine, and at 900-1000° and up to 500° with varying pressures. At temperatures above 475° the vapour phase contains Au₂Cl₂ molecules having a heat of sublimation of about -36 kg.-cal. in the neighbourhood of 900°; the heat of formation of the double molecule of aurous chloride from solid gold is, at this temperature, -22 kg.-cal. Although isobars lead to the double formula for auric chloride at high temperatures, isothermal measurements indicate that more complex molecules are present, and the discrepancies cannot be explained by assuming the existence of a dissociation equilibrium such as H. F. GILLBE. $\operatorname{Au_4Cl_{12}} \rightleftharpoons 2\operatorname{Au_2Cl_6}$.

Solubilities and transition points of the ferrous chloride hydrates in aqueous solution. F. SCHIMMEL (Z. anorg. Chem., 1928, 176, 285–288).— The system ferrous chloride-water has been investigated between -50° and $+117\cdot5^{\circ}$. The di-, tetra-, and hexa-hydrates exist in contact with the solution as stable phases, the transition temperatures being for FeCl₂,2H₂O = FeCl₂,4H₂O, 76.5°, and for FeCl₂,6H₂O = FeCl₂,4H₂O, 12.3°. The b. p. of the saturated solution, which contains 50.4% of ferrous chloride, is $117\cdot5^{\circ}$. Considerable supercooling may take place below the eutectic temperature of ice and the dihydrate, viz., $-36\cdot5^{\circ}$; the eutectic mixture contains 30.4% of ferrous chloride. H. F. GILLBE.

Quaternary system $Na_2C_2O_4-H_2SO_4-Na_2SO_4$ (or $H_2C_2O_4$)- H_2O at 25°. E. ELOD and E. ACKER (Z. anorg. Chem., 1928, 176, 305-324).-The above system has been examined at $24.71^{\circ}\pm0.05^{\circ}$, and the existence of a new compound, acid sodium sulphateoxalate with the empirical formula Na3H3(SO4)2C2O4, has been established. It is incongruently soluble in water with the separation of NaHC₂O₄, H₂O. The compound appears in ten different crystallographic forms according to the conditions under which it is obtained. The range of existence of the sulphateoxalate extends over a sulphuric acid concentration interval of 21-67%, and the hydrogen oxalate forms one of the solid components in equilibrium with solutions varying in composition through a wide range. This means that, by the action of sulphuric acid of different concentrations on sodium oxalate at 25°, the probability of the formation of hydrogen oxalate or sulphate-oxalate is very great. The results of the solubility determinations have been plotted on Jänecke's four-co-ordinate diagram. By graphical analysis of the isothermal course of crystallisation on removing the products formed, two real rystallisation end-points may be observed. At one of these Na₂SO₄,10H₂O, NaHC₂O₄,H₂O, and Na₂C₂O₄ separate, whilst at the other is formed the stable salt pair Na₂SO₄,10H₂O-NaHC₂O₄,H₂O with congruent solubility. There is a third point which might be regarded as a "virtual" crystallisation point, since crystallisation comes to an end before this is since crystallisation comes to an end before this is reached and only a syrupy liquid, consisting of strongly acid sodium sulphate and oxalic acid dissolved in concentrated sulphuric acid, is obtained. M. S. BURR.

Heat of formation of cementite. T. WATASÉ (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 1091—1109). —The heat of combustion of a mixture of sucrose and cementite obtained by the electrolysis of a steel containing 2% C has been determined and from this the heat of formation of cementite has been calculated using published data for the heat of formation of ferrosoferric oxide and carbon dioxide. The results obtained were : $F_3C + 3O_2 = Fe_3O_4 + CO_2 + 366\cdot3$ kg.cal. at 20°, whence $3Fe+C = Fe_3C - 4\cdot8$ kg.-cal. at 20°. A. R. POWELL.

Heterogeneous reactions between elements. I. Action of chlorine on copper. L. FROMMER and M. PÓLÁNYI (Z. physikal. Chem., 1928, 137, 201-208).—Determinations of the yields of cupric chloride obtained by the action of chlorine on copper under various conditions of temperature and pressure lead to the value 2 kg.-cal. as the heat of activation of the reaction. H. F. GILLBE. Selenium cells as colorimeters. II. A. MICK-WITZ (Z. anorg. Chem., 1928, 176, 271-282).—The solubility of freshly-precipitated lead sulphide, expressed as percentage of lead, is given by the selenocolorimetric method as 68×10^{-6} , in good agreement with Weigel's conductimetric value, viz., 74×10^{-6} . The concentration-light absorption curves exhibit a break, due probably to the formation of submicroscopic aggregates of lead sulphide at higher concentrations. The method yields more accurate results than the usual colorimetric method, the average error of a determination being about $\pm 4.5\%$. H. F. GILLBE.

Electrolytic conduction of crystal surfaces and the free ion conduction of solid salts. O. BLÜH and W. JOST (Z. physikal. Chem., 1928, B, 1, 270— 274).—The electrolytic conduction of α -silver iodide has been shown to be not markedly influenced by the presence of interfaces; the conclusion is therefore reached that the presence of internal interfaces is not the cause of the conductivity of such salts.

H. F. GILLBE.

Electrical conductivity of compressed salt mixtures. P. FISCHER (Z. Elektrochem., 1928, 34, 756—758; cf. A., 1926, 478; 1927, 23, 717).— By means of the method previously employed (*loc. cit.*), measurements have been made of the conductivities of the following ternary mixtures: lead, mercuric, and potassium iodide; lead, cadmium, and potassium iodide; lead, cadmium, and silver iodide. In many cases the conductivity of the ternary mixture is greater than that of a binary mixture of any two of the components. Values obtained with direct current and with alternating current agree closely. Measurements of the loss in weight of the silver anode show that Faraday's law holds, so that the conduction is electrolytic in nature. It is suggested that the results depend on deformations of the crystal lattices present. L. L. BIRCUMSHAW.

The Ohm-Fourier law of conduction. S. RAY (Z. Elektrochem., 1928, 34, 753-756).—A paper read before the Indian Science Convention, Calcutta, in 1919. Ohm's law is so modified that it can be treated by means of Fourier's law and compared in this way with the flow of heat through a conductor. Numerous relations are obtained and discussed. The author's suggestions have received support from subsequent work. L. L. BIRCUMSHAW.

Deviations from Ohm's law for electrolytes. M. WIEN (Physikal. Z., 1928, 29, 751-755) .- On account of uncertainties in the measurements of the relation between equivalent conductivity and concentration, the Debye-Hückel theory of strong electrolytes does not compel assent. New observations are necessary forrigid proof. The author's work (cf. A., 1928, 244) on the variation of conductivity with field strength is summarised. In strong fields the conductivity increases with the field strength. being proportional to the square of the field at the lower values. The proportionality constant varies approximately as the square of the product of the valencies of the ions, and is greatest at lower concentrations and lower dielectric constants. In very strong fields the conductivity approaches a limiting value, the more readily so the lower the concentration. Within experimental error, this limiting value agrees with the conductivity at infinite dilution. When the field is at right angles to the *P.D.* used for measuring the conductivity, no increase is observed. The above phenomena require a modified theory of electrolytic dissociation for their explanation. R. A. MORTON.

Electrode potential of nickel. Effect of occluded hydrogen on the electrode potential of nickel. K. MURATA (Bull. Chem. Soc. Japan, 1928, 3, 253-261).-It was previously found that nickel electrodes prepared from powdered nickel oxide by reduction in hydrogen gave a reproducible electrode potential although they probably contained occluded hydrogen (cf. A., 1928, 596). Prolonged cathodic polarisation of the nickel electrode in dilute acid and in an atmosphere of hydrogen did not cause any increase but rather a slight decrease in the initial of the cell $Ni|NiSO_4(0.05M)|KC|$ sat.]),Hg₂Cl₂|Hg. This slight decrease is E.M.F. $\mathrm{KCl}(0.1N),\mathrm{Hg}_{2}\mathrm{Cl}_{2}|\mathrm{Hg}.$ ascribed to the presence of a trace of free acid used in the polarisation in the cell. Reduced nickel powder was not rendered less noble by cathodic polarisation, although previous authors have found that metals of the iron group become less noble when subjected to cathodic polarisation. The occluded hydrogen in nickel has no effect on the true electrode potential. Addition of a trace of oxygen to the cell causes the E.M.F. to fall often by as much as 30 millivolts. Subsequent treatment with hydrogen causes the electrode to return to its active state. During the measurement of the electrode potential of nickel oxygen must be rigorously excluded.

H. INGLESON.

Anodic behaviour of palladium in chloride solutions. F. MÜLLER (Z. Elektrochem., 1928, 34, 744-752).-It has been shown (A., 1928, 713) that the anomalous behaviour of palladium when used as an indicator electrode in oxidation-reduction reactions is connected with the presence of hydrogen chloride in the solutions. In solutions containing chlorine and hydrogen ions, of not too high p_{π} , the electromotive behaviour of palladium is found to be quite different from that of the other metals of the platinum group. By passing chlorine into the solution, or by anodic polarisation, the metal first dissolves quantitatively at relatively low potentials, but becomes suddenly passive on reaching a certain critical current density. The effect of increasing the concentration of the added hydrochloric acid is to cause complete passivity to occur at higher potentials, and in pure concentrated hydrochloric acid the metal remains active up to very high current densities. Palladium differs from other base metals, such as iron and nickel, in that it remains completely passive, like platinum, on anodic polarisation in solutions free from chloride, whereas iron and nickel in, e.g., sulphuric acid are at first active, and become passive only at higher current densities. Polarisation also renders a palladium anode active in solutions containing bromine and chlorine ions. In the transition from the active to the passive condition, characteristic pulsations sometimes occur. These are most marked in the case of iodide solutions, but are also sometimes observed in chloride solutions.

The observed phenomena are discussed, and it is suggested provisionally that they may be ascribed to the formation of a sparingly soluble film of unknown nature on the surface of the electrode.

L. L. BIRCUMSHAW.

Velocity coefficient of a homogeneous bimolecular gas reaction. R. G. W. NORRISH (Nature, 1928, 122, 923—924).—The thermal change $2NO_2 =$ $2NO+O_2$ affords by Hinshelwood's method a value of the critical increment of 33,200, in agreement with the value, 32,000, derived from the temperature coefficient. Thus further confirmation of the theory of kinetic activation is afforded.

A. A. ELDRIDGE.

Reactions of the third order. F. E. E. GERMANN (J. Physical Chem., 1928, **32**, 1748—1750).—In the case of reactions of the type A+2B = $R_1+R_2+\ldots$, errors have arisen in the derived mass-law equations through confusion in the use of equivalents per litre and mol. per litre as the units of concentration. Such cases are pointed out (Getman, "Outlines of Theoretical Chemistry," 1927, 433; Taylor, "Treatise on Physical Chemistry," 1924, **2**, 872) and corrected equations are given. L. S. THEOBALD.

Calculation of theoretical combustion temperatures. P. DROSSBACH (Z. Elektrochem., 1928, 34, 783).—In a previous communication (A., 1927, 940), certain data used for the calculation of the theoretical combustion temperatures of carbon monoxide and hydrogen were assumed to involve temperatures expressed as °C., whereas they were expressed as ° Abs., and the combustion temperatures have therefore been recalculated. The values now obtained are : for carbon monoxide, 2640° (burning in oxygen) and 2000° (burning in air); for hydrogen, 3300° (oxygen) and 2250° (air). L. L. BIRCUMSHAW.

Ignition temperature of mixtures of hydrogen and air. M. PRETTRE and P. LAFFITTE (Compt. rend., 1928, 187, 763—765).—A modification of Mallard and Le Chatelier's pyrometric method for the determination of the ignition temperature of mixtures of hydrogen and air gave results in agreement with those obtained for hydrogen and oxygen by Dixon, who used the adiabatic compression method (A., 1926, 689). The temperature-composition curve is linear for 10—60% of hydrogen, but above the hydrogen content corresponding approximately with the upper limit of inflammability of hydrogen-air mixtures at the ordinary temperature (60—65%), the temperature rises very rapidly. The upper limit is 90.45% at 540° (cf. White, A., 1925, ii, 553). J. GRANT.

Oxidation of hydrocarbons. DUMANOIS and MONDAIN-MONVAL.—See B., 1928, 917.

Decomposition of carbonyl bromide. E. H. REERINK (Rec. trav. chim., 1928, 47, 989–999).— Measurements have been made of the velocity of decomposition of carbonyl bromide at temperatures between 147° and 182°. The activation energy, calculated from the temperature coefficient of the reaction velocity, is 15,000 g.-cal. The results are explicable by the assumption that a first-order wall reaction occurs which is catalysed by a thin layer on the walls of the vessel of an organic substance, derived probably from tap grease, and rendered active by the selective adsorption by it of bromine molecules. F. G. TRYHORN.

Monochloroamine and hydrazine. I. Decomposition of monochloroamine in acid solution. M. BODENSTEIN (Z. physikal. Chem., 1928, 137, 131-141).—The decomposition of monochloroamine in a solution made initially slightly alkaline with ammonia has been studied : the first autocatalytic stage ceases almost entirely when the reaction has proceeded about half-way, and the reaction then recommences in a totally different manner, reaching its end very slowly. Raschig's equation 3NH_oCl= NH_4Cl+N_2+2HCl is applicable only to the first half and to the extreme end of the reaction. It is probable, since in the second stage of the reaction hydrogen chloride is present in insufficient quantity to accord with the equation, that monochloroamine and hydrogen chloride react to form dichloroamine and nitrogen trichloride. In a solution saturated with boric acid and sodium borate the reaction is bimolecular. H. F. GILLBE.

Kinetics of the hydrolytic decomposition of a-bromopropionic acid. J. ZAWIDZKI and J. G. ZAWIDZKI (Z. physikal. Chem., 1928, 137, 72-106).-The hydrolysis of the a-bromopropionic acid in aqueous solution at 90° has been studied by titration of the evolved hydrogen bromide. The velocity of the reaction is governed by the equation, typical of a negatively autocatalytic reaction, dx/dt = $K(a-x)/x^{\frac{1}{2}}$, where x is the concentration of hydrogen bromide and a - x the instantaneous concentration of α -bromopropionic acid. At 90°, K=0.000942, whilst for the interval 80-90° the temperature coefficient is 2.99. In presence of a considerable quantity of hydrogen bromide or nitric acid, the equation dx/dt =K(a-x)/(b+x), where b is the initial concentration of acid added, yields an almost identical value for K, whilst neutral salts in general produce not more than about 4% increase of the ordinary constant. Potassium sulphate, on account of the depression of the hydrogen-ion concentration in the solution produced by the reaction, CHMeBr·CO₂H+K₂SO₄ \longrightarrow CHMeBr·CO₂K+KHSO₄, causes, when present at approximately equivalent concentration, a six-fold increase of the reaction velocity. The enormous accelerative action of potassium chloride is ascribed to an interchange of halogen atoms between the salt and the α -bromopropionic acid. H. F. GILLBE,

Reduction of methylene-blue in mixtures of lævulose and amino-acids. H. von EULER and H. JOHANSSON (Svensk Kem. Tidskr., 1928, 40, 263— 264).—Reduction of methylene-blue takes place more rapidly when both lævulose and an amino-acid, e.g., alanine or glycine, are present than when either of these compounds is used separately. The rate of reduction increases with the $p_{\rm H}$. W. O. KERMACK.

Saponification of menthyl succinate, acetate, and isovalerate. V. A. NEKRASOWA (Arch. Pharm., 1928, 266, 595—599).—Menthyl succinate was prepared by heating menthol, succinic anhydride, and a trace of sulphuric acid at 110° for 30 hrs. The following data are given, k being the velocity coefficient for saponification with 0.5N-alcoholic potassium hydroxide at the temperature indicated: menthyl succinate, m. p. 62° , k^{99-100} 3284×10^{5} ; menthyl acetate, b. p. $226-228^{\circ}$, d^{20} 0.926, k^{99-100} $99\cdot65-104\cdot68$; menthyl isovalerate, b. p. $140-146^{\circ}$, d^{15} 0.907, k^{99-100} $49\cdot77-50\cdot54$. Menthyl hydrogen succinate could not be obtained. S. COFFEY.

Chlorination of anilides. V. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFIELD and B. JONES (J.C.S., 1928, 3073–3081; cf. A., 1928, 628).—The isothermal condition $k_{X_1}^{OR}/k_{X_2}^{OR}=k_{X_1}^{OR}/k_{X_2}^{OR}$ (where $k_{X_1}^{OR}$ represents the velocity coefficient for the chlorination of X·C₆H₄·OR) derived in a previous paper has been interpreted as indicating the additivity of the energies of activation for the chlorination of ethers of the type $X \cdot C_6 H_4 \cdot OR$ by extending to these reactions the hypothesis that the product of the phase and steric factors is constant. Four other hypotheses are mentioned and expressions are derived from them which should, given sufficiently accurate experimental data, be able to be differentiated by the change in the ratio of the velocity coefficients with temperature. Some data for anisic acid and p-nitrophenetole are considered, but the experimental accuracy is not sufficient to admit of decision among the hypotheses. The problem of the nitration of ethers of the type p-RO·C₆H₄·OMe is discussed. H. INGLESON.

Kinetics of the reaction between calcium and nitrogen. A. VON ANTROPOFF and E. GERMANN (Z. physikal. Chem., 1928, 137, 209-237).-The reaction between pure crystalline calcium and nitrogen at 400-440°, which is the temperature of maximum velocity, takes place in three stages : the first is rapid and involves the actual calcium surface, the second is very slow and takes place through a thin and probably amorphous film of calcium nitride, whilst the third and rapid stage commences when the nitride film has reached a certain thickness and has probably become porous on account of the formation of a coarsely crystalline structure. The incidence of the reaction is retarded by the presence of traces of oxygen, but once the nitride film has formed the effect vanishes. Activation of the calcium surface is concerned with the elimination of the slow second stage and not with the nitride content of the metal. Minute quantities of lithium, sodium, or potassium in the calcium surface accelerate the reaction only at the beginning, probably by accelerating the crystallisation of the calcium nitride layer. Since lithium readily forms a nitride it must, to exert any such catalytic influence, be in intimate contact with the calcium surface. The activity of commercial calcium is due to the presence of sodium in minute enclosures in the metal; those near the surface have ordinarily no effect, owing to oxidation, and the acceleration of the reaction is therefore not apparent until the underlying sodium particles come into play. Variations commonly observed in the activity of commercial calcium are thus due to both the quantity of sodium present and its distribution, and to the degree of oxidation which it has undergone. Activation of calcium in practice is best produced by deposition of sodium on the surface immediately before use.

H. F. GILLBE.

Dissolution velocity of cadmium in hydrogen chloride solutions. M. CENTNERSZWER (Z. physikal. Chem., 1928, 137, 352-360).-In solutions of hydrogen chloride of concentration greater than 6N cadmium dissolves with measurable velocity. The process is characterised by an induction period, which diminishes as the acid concentration is increased, and during which the dissolution velocity increases rapidly. If the surface of the cadmium be activated by previous immersion in concentrated hydrogen chloride solution the induction period vanishes. Agitation of the acid produces noticeable effects only at concentrations above about 10N. The temperature coefficient of the reaction is approximately 2 for 10° rise. At the lower acid concentrations the process is almost entirely chemical, diffusion playing a relatively small part, but at higher concentrations and higher temperatures the latter becomes of increasing importance, as evidenced by the diminution of the temperature coefficient. H. F. GILLBE.

Corrosion of iron. H. ENDÔ.-See B., 1928, 929.

Catalytic preparation of copper sulphate. E. ABEL and O. REDLICH (Z. Elektrochem., 1928, 34, 740-744) .- The possibilities of utilising the action of concentrated sulphuric acid on copper in the presence of oxygen (air), using nitric oxide or nitrosylsulphuric acid as a catalyst, for the technical preparation of copper sulphate have been explored, but the difficulties attendant on the process appear to be insurmountable. The most important of these are the sensitiveness of the reaction between copper and nitrosylsulphuric acid to the presence of water, which exerts an auto-anticatalytic influence, and the narrow temperature limits within which the reaction (which is strongly exothermic) can occur. The cause of the negative autocatalysis of the reaction Cu+ $2HNSO_5 = CuSO_4 + 2NO + H_2SO_4$ has been traced to the formation of an inactive surface film of the copper salt of nitrosisulphonic acid. This may be partly or completely prevented by the addition of nitrogen peroxide or nitric acid, but the presence of excess of the acid exerts a retarding influence on the reaction.

L. L. BIRCUMSHAW.

Nitrite-nitrate formation from ammonia and oxygen at alkaline surfaces. K. A. HOFMANN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 26, 461-465; cf. B., 1927, 600).-A further discussion of the view previously put forward that the formation of nitrite from ammonia and air proceeds through the intermediate stage of imide. Silver, which activates the above reaction at alkaline surfaces at about 350°, does not bring about an oxidation of ammonia in aqueous solution to nitrite. Silver, however, dissolves appreciably in ammonia solution in presence of air and forms ammino-silver hydroxide, Ag(NH₃)₂OH. This process ceases after several months, long before the saturation point of ammonia solution for silver oxide is reached, and the final concentration is dependent on the amount of silver in contact with the O. J. WALKER. solution.

Behaviour of zinc oxide and zinc oxidechromium oxide catalysts in the decomposition and synthesis of methyl alcohol. H. H. STORCH (J. Physical Chem., 1928, 32, 1743—1747; cf. Smith and Hawk, A., 1928, 488).—The catalytic activity of zinc oxide, prepared in various ways, and of zinc oxide—chromium oxide mixtures in the synthesis of methyl alcohol from hydrogen and carbon monoxide (4:1) under 3000 lb. pressure at 330° and 350° has been investigated. The addition of chromium oxide increases the activity of the zinc oxide in the synthesis, but has no effect on the decomposition of methyl alcohol (at 1 atm.). L. S. THEOBALD.

Synthesis of methyl alcohol. E. AUDIBERT and A. RAINEAU; also A. C. FIELDNER and R. L. BROWN. —See B., 1928, 920.

Partial oxidation of methane and ethane in presence of catalysts. T. E. LAYNG and R. SOUKUP.—See B., 1928, 920.

Catalytic acceleration of the oxidation-reduction reaction between formic acid and methyleneblue. H. VON EULER and A. OLANDER (Z. physikal. Chem., 1928, 137, 29-44).-The reaction between methylene-blue and formic acid in presence of platinum sol has been studied by measurement of the time necessary for complete bleaching of the solution to occur. The reaction velocity, which is greatest at $p_{\rm H}$ 2-3, appears to be determined by the concentration of a complex which is formed between the formic acid and platinum. Increase of the methylene-blue concentration causes a decrease of the reaction velocity, the dye using up a certain quantity of the platinum sol. Investigation of the influence on the velocity of the acidity and formic acid concentration indicates that free formic acid, and not the formate ion, is concerned with the production of the complex catalyst. H. F. GILLBE.

Theory of molecular dislocation applied to homogeneous catalysis. J. BÖESEKEN (Trans. Faraday Soc., 1928, 24, 611-620).—A summary.

Action of accelerators and inhibitors on the oxidation of liquid hydrocarbons. T. E. LAYNG and M. A. YOUKER.—See B., 1928, 882.

Keto-enol isomerism and the mechanism of homogeneous reactions. F. O. RICE and J. J. SULLIVAN (Trans. Faraday Soc., 1928, 24, 678-682). -Determinations have been made of the rate of change of the tautomeric forms of ethyl acetoacetate, and of the effects of catalysts on this process. The percentage of enolic form was measured after different periods in mixtures which contained originally up to 40% of the enolic tautomeride. Concentrations of 4×10^{-5} mol. per litre of the catalysts piperidine, ammonia, bromine, pyridine, and quinoline increased the reaction velocity by factors between 11,400 for piperidine and 17 for quinoline. A unimolecular mechanism is suggested for the change, in which the enolic form, or a complex of this with the catalyst, undergoes a change dependent on the concentration and quite independent of the time between molecular collisions. The rate is determined by a process occurring inside the molecule or complex, and this in turn is determined by the number of internal degrees of F. G. TRYHORN. freedom.

Determination of the catalytic coefficient of the hydroxyl ion in the mutarotation of dextrose and lactose. T. M. LOWRY and G. L. WILSON (Trans. Faraday Soc., 1928, 24, 683-687) .- Careful determinations, in which the possibility of contamination by carbon dioxide was excluded, have been made of the velocity of mutarotation of lactose, dextrose, and tetramethylglucose in the presence of hydroxyl ions. The concentrations of hydroxyl ions in the solutions were computed from measurements of electrode potentials and on the basis of the assumption that the sugar forms a salt which is hydrolysed according to the law of mass action. The final values of the catalytic coefficients of the hydroxyl ion are, for lactose 5000, for dextrose 8000, and for tetramethylglucose 1600. The wide variation in these values is notable inasmuch as the mutarotation velocities of these sugars in pure water vary but F. G. TRYHORN. little.

Autoxidation and anti-oxygenic action. Catalytic properties of arsenic and its compounds. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1928, 187, 917—921).—The catalytic properties of arsenic and 21 of its compounds in concentrations of 1% are shown to have important positive or negative effects. Thus arsenic itself inhibits the oxidation of aeraldehyde for several hours and then accelerates it, whilst for *l*-pinene the order is reversed. An anti-oxygenic action is also shown towards styrene and benzaldehyde. Arsenic and its oxygenated derivatives, particularly the inorganic compounds, have relatively low activities on account of their insolubility, but the activities of the halogen derivatives are considerably higher. J. GRANT.

Acid and salt effects in catalysed reactions. XVII. Variation of catalytic activity of an acid with its concentration, and determination of ionisation constants. H. M. DAWSON, G. V. HALL, and A. KEY (J.C.S., 1928, 2844-2853; cf. A., 1928, 717).—The catalytic effects produced in the acctoneiodine reaction at 25° by acetic, chloroacetic, propionic, β-chloropropionic, succinic, and glycollic acids have been studied with reference to the variation of the catalysing power with the concentration. The connexion between reaction velocity and concentration gives a means of determining the ionisation constant of the acid as well as the catalytic activity of the undissociated acid. The constants so derived are in good agreement with those derived from conductivity measurements. In general, the catalytic activity of the undissociated acid increases with the ionisation constant. The relation between the eatalytically determined constant K and the thermodynamic constant K_a (where $K = K_a/f^2 \pm$ and $f \pm$ is the mean activity coefficient of the ions) is discussed.

H. INGLESON.

Catalytic activity of hydrogen ions in ethyl alcohol. H. GOLDSCHMIDT (Trans. Faraday Soc., 1928, 24, 662-666).—A résumé of evidence that catalytic effects are due to the undissociated acid molecules as well as to hydrogen ions in acid catalysis in ethyl alcohol solutions. F. G. TRYHORN.

Decomposition of nitrosotriacetonamine in presence of hydroxyl ion. A. W. GOODALL and W. C. MCC. LEWIS (Z. physikal. Chem., 1928, 137, 45-62).—The velocity of decomposition of nitroso-

triacetonamine is in dilute alkali determined by the activity of the hydroxyl ion, and in concentrated alkali by that of the hydrogen ion. At intermediate concentrations (0.05-0.5N) the decomposition process consists of two reactions, having different critical increments, of which the one is catalysed by hydrogen ion and the other by hydroxyl ion. The mechanisms are represented by: (I) nitrosotriacetonamine+OH' $\longrightarrow A+OH'$, and (II) $A+H^+ \longrightarrow B+H^+$, where A represents a hypothetical intermediate compound and B the final decomposition products.

H. F. GILLBE.

Electrolysis of copper sulphate solutions separated by an animal membrane. CHANOZ (Compt. rend. Soc. Biol., 1928, 98, 39–41, 42–43; Chem. Zentr., 1928, i, 3078).—With solutions less concentrated than 0.1N polarisation of the membrane results in a diminution of the current. The form of the separated copper is described. A. A. ELDRIDGE.

Electro-deposition of silver with special reference to the use of sodium cyanide. E. B. SANIGAR. --See B., 1928, 897.

Polymerisation distance between discharged ions in the preparation of persulphates. O. Essin (Z. Elektrochem., 1928, 34, 758-760).-In a previous investigation of the dependence of current efficiency on anodic current density in the preparation of ammonium persulphate (Essin and Krylow, A., 1927, 422) it was found that the sulphate ions must be discharged within a certain distance of each other in order that polymerisation (i.e., persulphate formation) may take place. Assuming the presence of a layer of activated sulphate ions at the anode, the " polymerisation distance," l, is given by : l=1.68(eh/ τ), where e is the charge on the electron, h the thickness of the layer, and v the life period of the activated ions. This is calculated to be of the order of 10⁻⁶ cm. (cf. Dhar and Mukerji, A., 1925, ii, 809).

L. L. BIRCUMSHAW.

Direct electrolytic preparation of potassium permanganate. G. RAPIN (Bull. Soc. chim., 1928, [iv], 43, 1174—1189).—A .more detailed account of work already published (A., 1928, 969). In spite of the formation of potassium silicate, the use of an electrolyte of potassium hydroxide alone is recommended on the grounds of increased yield and efficiency. The temperature should not exceed $70-75^\circ$, and compact anodes of silicomanganese (60% Mn) are preferred.

Determination of the rôle of light in thermal chemical reactions. J. PERRIN (Compt. rend., 1928, 187, 913—916; cf. A., 1927, 527).—It is concluded that since one of the preliminary requirements of all reactions sensitive to temperature is the endothermic activation of the ordinary molecules, the part played by light as distinct from molecular agitation in a purely thermal reaction is for each reactant equal to the yield of fluorescence of this reactant under the conditions concerned. This yield is defined as the ratio of the number of luminous deactivations to the number of quanta absorbed, and may be measured without changing the temperature or medium by an exposure of sufficient intensity to the activating light absorbed by the substance concerned. J. GRANT.
Energetics, quantum action, and temperature coefficient of some photochemical reactions influenced by radiation of different frequency. A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1928, 176, 372-384; cf. A., 1928, 378).-The order of reaction, velocity coefficient, temperature coefficient, and number of molecules reacting per quantum absorbed have been determined in the dark, in sunlight, and in radiation of different wavelengths, for the following reactions : decomposition of sodium cobaltinitrite solution and potassium persulphate solution, and reactions between the persulphate and iodide of potassium, bromine and methyl or ethyl alcohol, oxalic and chromic acids, acetone and iodine in presence of hydrochloric acid, lactic acid and potassium permanganate in presence of manganese sulphate, and tartaric acid and potassium permanganate in presence of manganese sulphate. All are unimolecular except that between acetone and iodine, which is of zero order. More than one molecule always reacts for each quantum absorbed, so that Einstein's law of photochemical equivalence does not hold in any of these cases. The reaction per quantum increases with rising temperature of the reactants. In sunlight, the quantum efficiency is higher than for any other radiation. It also increases with increase in frequency of the radiation employed. The temperature coefficient of a photochemical reaction is always greater than 1 and less than that of the corresponding thermic reaction. The greater the observed acceleration by light the smaller is the temperature coefficient.

M. S. BURR.

Action of luminous rays on potassium chloride. J. RISLER and F. DE COURMELLES (Compt. rend., 1928, 187, 944-945).-In order to produce an impression on a photographic plate, films of potassium chloride required the following exposures (in days) to the sources mentioned : infra-red light (incandescence lamp with an ebonite filter) >55, orange-red light (neon lamp with ruby filter) 44, 2 3650 Å. (ultra-violet lamp with a nickel oxide filter) 36, sunlight 29, and unfiltered ultra-violet light 19. Activation of potassium chloride by ultra-violet light plays an important rôle in biological processes.

J. GRANT.

Photochemical catalysis. Reaction between nitric oxide and cyanogen and its mechanism. R. G. W. NORRISH and F. F. P. SMITH (Trans. Faraday Soc., 1928, 24, 620-629) .- Two reactions, of which the former is about six times as extensive as the latter, occur when mixtures of nitric oxide and cyanogen, each at 1/2-1/3 atm. pressure, are illuminated by ultra-violet light of wave-length 360-220 $\mu\mu$: 4NO=N₂+2NO₂; 4NO+(CN)₂=3N₂+2CO₂. In the former reaction, cyanogen acts as a catalyst. but neither reaction occurs in the absence of a trace of oxygen, and therefore of nitrogen peroxide. The total reaction is auto-catalytic as a result of the accumulation of nitrogen peroxide. The existence of a comparatively stable intermediate compound is indicated by a dark reaction occurring over several days and continuing, with fall of pressure, after the ultra-violet illumination has ceased. This compound is believed to be nitrosyl evanide, and is perhaps pro-

duced according to the two opposed photo-reactions $2NO+(CN)_2 \xrightarrow{\text{light I}} 2NOCN$. Of these reactions the former is actal burned or accurational burnitzer provides $2NO+(CN)_2 \xrightarrow{\text{light II}} 2NOCN$. former is catalysed or sensitised by nitrogen peroxide. Jointly, these reactions give rise to a photochemical stationary state associated with considerable equilibrium pressures (90 mm.) of nitrosyl cyanide. This latter compound, being unstable, decays spontaneously in the dark according to the reactions $2NOCN = N_2 + O_2 + (CN)_2$ and $2NO + O_2 = 2NO_2 \Longrightarrow$ N_2O_4 . These reactions, in combination with the process $2NO+(CN)_2 = 2NOCN$, give the total change represented by $4NO=N_2+2NO_2$. The reaction $4NO+(CN)_2=3N_2+2CO_2$ results as a side reaction by the combination of the reactions NOCN+ light NO₂ $\stackrel{\text{hem}}{=}$ NO+CO₂+N₂ and 2NO+(CN)₂ $\stackrel{\text{m}}{=}$ 2NOCN. A precisely similar series of changes, which can be explained by an analogous mechanism, has been observed in the system nitric oxide-cyanogen F. G. TRYHORN. chloride.

Photochemistry of iron-carbonyl compounds and the absolute absorption spectrum of the respiratory enzyme. O. WARBURG (Naturwiss., 1928, 16, 856-861).-The photochemical decomposition of iron carbonyl with ultra-violet irradiation agrees with the equation $2 \text{Fe}(\text{CO})_5 + 1h\nu \rightarrow 2 \text{Fe}(\text{CO})_4 +$ 2CO. Carbon monoxide is likewise set free by the action of light on the hæmoglobin "carbonyl," but on account of the high velocity of the back reaction the system does not lend itself to quantitative work. Carbon monoxide-pyridine-hæmin and carbon monoxide-ferrocysteine have, however, been studied in detail and the course of the photochemical change follows the equations $2FeCO+1hv \longrightarrow 2Fe+2CO$ and 2Fe(CO)₂+1hy - 2Fe+4CO, respectively; i.e., in both cases two atoms of "carbonyl" iron are set free per quantum absorbed. The respiratory enzyme combines with 1 mol. of carbon monoxide per atom of iron, and its properties can be deduced from the respiration of the living cell under different conditions. From the changes which occur on irradiation, the absorption spectrum of the enzyme has been deduced. The curve for the carbon monoxideenzyme is very similar to that of the hæmin compound.

The absorption curve for the ferrocysteine-carbon monoxide is quite different, the maximum being at 490 µµ and the intensity of absorption about 10-2 times as great, whilst the curve for iron pentacarbonyl is 10-1 times as great as that of the hæmin compound and shows only continuous absorption between 430 and 600 µµ. The absorption spectra, therefore, indicate not merely the iron-carbonyl group as a part of the respiratory enzyme, but also show that it is attached to a hæmin-like molecule. The chemical constitution of the enzyme is therefore, in essentials, R. A. MORTON. now known.

Photochemical decomposition of glyoxal. R. G. W. NORRISH and J. G. A. GRIFFITHS (J.C.S., 1928, 2829-2840).-The photochemical decomposition of gaseous glyoxal has been measured by observing the diminution in pressure during the illumination of the gas in a water-cooled glass bulb with the unfiltered light of a 3000-e.p. mercury-vapour lamp. The light

reaching the gas was probably in the regions 436, 405, and 365 µµ and that active in promoting the decomposition at 3650 Å. The pressure-time curves conform approximately to a bimolecular law with respect to decomposing glyoxal. The final pressure even after prolonged heating is never exactly half the initial, as would be expected from the equation $2C_2H_2O_2=CO+C_3H_4O_3 \longrightarrow$ polymerised product, which reaction takes place to an extent of about 98.5%. A secondary reaction, $C_2H_2O_2=2CO+H_2$, probably occurs to a small extent. The mol. wt. of the glyoxal was determined from its vapour density as 58.7, so that thermal dissociation is excluded. A white solid produced during the decomposition of the gas appears to be the polymeride of the hitherto unknown glycerosone to which it is hydrolysed in aqueous and acid solutions. The properties of glycerosone suggest that it exists in aqueous solution in tautomeric equilibrium with an acidic hydroxymethylene form, the change from neutral to acid taking place slowly at the ordinary temperature.

H. INGLESON.

Some properties of alkali metals. L. HACK-SPILL (Helv. Chim. Acta, 1928, 11, 1003-1026).—A lecture delivered before the Swiss Chemical Society on Aug. 31, 1928. R. N. KERR.

Hydrates of beryllium halides. V. ČUPR and H. ŠALANSKÝ (Z. anôrg. Chem., 1928, 176, 241-257). —The preparation of considerable quantities of pure beryllium compounds is described. Beryllium chloride tetrahydrate, prepared by spontaneous evaporation of a clear solution of the oxide in hydrogen chloride solution, is extremely unstable in moist air, hydrogen chloride being readily evolved. The bromide tetrahydrate, precipitated in the analogous manner, does not lose hydrogen bromide in moist air; the corresponding iodide could not be prepared. The compounds $BeCl_2, 3H_2O, Et_2O$ and $BeBr_2, 3H_2O, Et_2O$ are described, but the analogous iodide has not been prepared, although evidence has been obtained for the existence of the compound $BeL_2, 2H_2O, 2Et_2O$.

H. F. GILLBE.

Cadmium acetylides. K. GEBAUER (Z. anorg. Chem., 1928, 176, 283–284).—Slow passage of purified acetylene through an acetone solution of the compound $CdCl_2$, NH₂Ph produces an orange, amorphous precipitate which when washed with acetone and dried at 110° has the composition CdC_2 , C_2H_2 , CdI_2 . By washing this substance with alcohol or water the compound CdC_2 , C_2H_2 is obtained. Both substances are stable in the air, and may be heated to about 200° without decomposition; neither is explosive.

H. F. GILLBE. New fluoboric acid. A. TRAVERS and MALA-PRADE (Compt. rend., 1928, 187, 765—767).—The curve of neutralisation of the mixture H_3BO_3+4HF with potassium hydroxide solution indicates that boric acid reacts instantaneously with hydrofluoric acid to form a new fluoboric acid, the salt of which is easily decomposed by alkali. Tetrafluoboric acid, HBF₄, is then formed slowly, particularly in the cold, until equilibrium between the two fluoboric acids is established. The time taken and the amount of the latter formed at equilibrium increase with the concentration of the reactants and with the initial acidity of the mixture (cf. Abegg, Fox, and Herz, A., 1903, ii, 540). J. GRANT.

Existence of a new type of fluoborate. A. TRAVERS and MALAPRADE (Compt. rend., 1928, 187, 891-892; cf. preceding abstract) .- In the determination of soluble or insoluble fluorides of the type MBF₄ by Travers' fluosilicate method (A., 1921, ii, 706) a preliminary alkaline fusion is required, since the reaction $H_3BO_3 + 3HF + nKF \implies BF_3, nKF +$ $3H_2O$ increases the $p_{\rm ff}$ value by destruction of the acids present, and there is no immediate precipitation of the insoluble potassium salt unless acid is added to increase the rate of formation of the acid HBF4. Fusion destroys the complex BF4' ion, and on acidification all the fluorine is converted into insoluble potassium fluosilicate, since the fluoborate produced is less stable and more soluble than KBF4. Further evidence for the existence of another fluoborate is provided by the action of boric acid on neutral concentrated solutions of potassium fluoride, and by the work of Abegg, Fox, and Herz (A., 1903, ii, 540). J. GRANT.

Measurement of bi- and quadri-valent compounds of the rare earths. I. Samarium halides. W. KLEMM and J. ROCKSTRON (Z. anorg. Chem., 1928, 176, 181-199).-Isotherms of the system samarium trichloride-ammonia indicate the existence of complexes containing 13, 8, 5, 4, 2²/₃, 2, and 1 mols. of ammonia per mol. of trichloride. There is a considerable tendency to mixed crystal formation, especially above 8 mols. of ammonia. The existence of $SmCl_3, 9.5NH_3$ and $SmCl_3, 11.5NH_3$ could not be confirmed, whilst the triammine definitely does not exist. Samarium dichloride forms complexes having respectively 2 and 8 mols. of ammonia, which exhibit considerable tendency to formation of mixed crystals. Reactions such as the following take place with great ease: $SmCl_2+NH_3 \longrightarrow Sm(NH_2)Cl_2+H$ and $Sm(NH_2)Cl_2+2NH_3 \longrightarrow Sm(NH_2)_2Cl+NH_4Cl_4$ At temperatures from 30° to 100° a sublimate of ammonium chloride is formed. There is a tendency for this type of reaction to occur with the trichloride at ammonia concentrations from 0 to 1M. The densities of samarium trichloride, tribromide, dichloride, and dibromide are 4.31 ± 0.01 , 5.40 ± 0.02 , 4.5_6 , and 5.17, respectively; the m. p. of the trichloride, prepared by the action of chlorine and sulphur chloride on the oxide, is $677\pm1^\circ$, and that of the tribromide, prepared by the action of hydrogen bromide on the powdered trichloride, is $628 \pm 2^{\circ}$. The magnetic susceptibilities of the trioxide, tribromide, and dibromide, referred to 1 g., are 9900×10^{-6} , $15600 \times$ 10-6, and 71000×10-6, respectively. H. F. GILLBE.

Hydrates and hydrogels. XI. Simplest silicic acids; aluminium hydroxide. R. WILL-STÄTTER, H. KRAUT, and K. LOBINGER (Ber., 1928, 61, [B], 2280—2293; cf. A., 1926, 36).—Solutions of monosilicic acid are obtained by passing the vapour of silicon tetrachloride into ice-cold water containing freshly-precipitated silver oxide, the success of the operation depending on the maintenance of a suitable hydrogen-ion concentration in the solution which is thus attained. When the brown colour of the silver

oxide has disappeared, the concentration of hydrochloric acid is adjusted to 0.01-0.005N by further addition of the oxide, the value of $p_{\rm H}$ (in presence of silicic acid) being 2.5-2.8. The clear solution con-tains more than 80% of the theoretical quantity of SiO2. The dissolved acid has the mol. wt. 72-75 and thus consists of 75-80% of monosilicic acid, the remainder being disilicic acid; the calculations are based on the unfavourable assumption that the total hydrochloric acid is free and completely ionised. Solutions of disilicic acid are obtained in a similar manner except that hydrogen chloride is not removed until addition of the silicon tetrachloride is complete and the acidity of the residual hydrochloric acid is adjusted to 0.01-0.001N (or the acid is removed quantitatively). In solutions 2-3 hrs. old, the mol. wt. of the silicic acid (as SiO₂) is 120-130 instead of 120, indicating the presence either mainly of disilicic acid or of a mixture of mono- and oligosilicic acids. The ability of the acid to pass rapidly and quantitatively through a fish-bladder membrane favours the former view. Solutions of monosilicic acid after preservation for 4-6 days contain mixtures of tetra- to hexa-silicic acids; the hexasilicic stage is only slowly passed during further preservation. Similar oligosilicic acids are obtained slowly from disilicic acid solutions with 0.01N-hydrochloric acid. Such preserved solutions with silicic acids of medium mol. wt. frequently do not give the Mylius reaction for β -silicic acids with egg-albumin. The volatility of silicic acid with water vapour when its solutions are distilled under diminished pressure is confined to the mono-acid. Solutions of the silicic acids can be titrated potentiometrically with sodium hydroxide. The graphs correspond with those of a very weak acid and the end-point is reached when silica and alkali are in the ratio 1:1. A second stage in the neutralisation cannot be recognised definitely. Hydrosols and gels of silicic acid behave exactly similarly to molecular solutions during titration, but the strength of the acid diminishes somewhat during condensation. Silicon dioxide, on the other hand, shows no indication of the combination with hydroxyl ions during titration and hence the gels do not behave as the dioxide with varying amounts of adsorbed water. For the titration, an antimony electrode is particularly suitable.

To α-aluminium hydroxide the structure Al(OH)₃ is assigned, whereas the γ compound is regarded as Al₂O₃, 3H₂O. The meta-compound may be regarded as [Al,O3,H2O] or as a polyaluminium hydroxide, $[-O-Al(OH)-]_n$. The gels A and B are poly-aluminium hydroxides, A consisting of chains between the range $4Al(OH)_3-3H_2O$ and $8Al(OH)_3-7H_2O$, and *B* as their hydrates with higher water content than the simplest chain formula permits.

Silicophosphoric acids. R. SCHWARTZ (Z. anorg. Chem., 1928, 176, 236–240).—Silicophosphoric acid, $H_8Si(PO_4)_4$, prepared by heating silica with the theoretical quantity of orthophosphoric acid at 125° multiple and the product with the second state of the second until the product yields a clear solution with cold water (about 240-300 hrs.), is decomposed by warm water, acids, and alkalis, silica being precipitated. The lack of stability of the compound is evidenced

by conductivity and transport measurements. The dissociation $H_8Si(PO_4)_4 + 2\hat{H}_2O \longrightarrow 4H_3PO_4 + SiO_2$ is irreversible, since the liberated silica immediately assumes the colloidal state. Salts cannot be prepared from the aqueous solution, but thermal analysis of the system Na₂O-SiO₂-P₂O₅ indicates the existence of the sodium salt, of m. p. 961°. Attempts to produce the corresponding silicoarsenic acid or its salts H. F. GILLBE. have proved unsuccessful.

Peroxides of titanium, zirconium, hafnium, and thorium. R. SCHWARTZ and H. GIESE (Z. anorg. Chem., 1928, 176, 209-232).-The hydrated peroxides of titanium, zirconium, hafnium, and cerium behave as peroxy-ortho-acids of the general formula $M(OOH)(OH)_3$. The formula of the thorium compounds is $Th_2O_{7,}4H_2O$. Zirconium alone of the group forms a basic peroxy-sulphate, Zr2O6SO4,8H2O, obtained by the action of hydrogen peroxide on an acid zirconium sulphate solution. In contradiction to the results of Melikov and Pissarjevski, potassium pertitanate and perzirconate, prepared by this method, are found to have the formulæ K, TiO, 6H2O and K_4 ZrO₈,6H₂O, respectively, and are to be regarded as salts of tetraperoxy-ortho-acids. Similar compounds of thorium and hafnium have not been prepared. The compound first prepared by Mazzuchelli and Pantanelli has the formula K2TiO2(SO4)2,3H2O, and analogous substances containing zirconium and hafnium, but not thorium, have now been prepared. The reactions underlying the new method of determining fluorine, based on the decolorisation of a solution of $K_2 TiO_2(SO_4)_2$ by hydrogen fluoride, have been elucidated. Ammonium peroxytitanyl fluoride, $(\rm NH_3)_3 TiO_2 F_5$, has been shown by conductivity measurements to yield on electrolytic dissociation four ions, and the production of the complex ion $\text{TiO}_2\text{F}_5^{\prime\prime}$ in which the $\hat{O} \cdot O$ linking occupies only one of the six co-ordination valencies, has thus been established. The substances discussed are to be regarded as true H. F. GILLBE. per-compounds.

Active nitrogen. C. N. HINSHELWOOD (Nature, 1928, 122, 404-407).- A summary and discussion. A. A. ELDRIDGE.

Active nitrogen. J. KAPLAN (Nature, 1928, 122, 771).—Polemical (cf. Hinshelwood, preceding ab-stract). A. A. ELDRIDGE. stract).

[Active nitrogen.] C. N. HINSHELWOOD (Nature, 1928, 122, 771).- A reply to Kaplan (preceding A. A. ELDRIDGE. abstract).

Active nitrogen. VI. Formation of iron nitride in the iron-nitrogen arc. E. J. B. WILLEY (J.C.S., 1928, 2840—2844; cf. A., 1928, 3).—An arc using a current of 3—10 amp. at 35 volts struck between iron electrodes in a quartz bulb in an atmosphere of nitrogen gave iron nitride, Fe4N2. From 12 to 15% of the iron withdrawn by aspiration from the inner blue cone of the arc was present as nitride. The proportion fell as the sampling point receded from the hottest zone. By visual inspection of the arc with a spectrometer it was not possible to observe the bands (in the yellow) characteristic of the nitrogen afterglow spectrum. It is possible that the rate of reaction of the active nitrogen with the iron is so

H. WREN.

rapid that the quantity of the former in the free state is small. It is suggested that if the Rayleigh nitrogen be the active form in this case it is non-luminous or that under the conditions of experiment another and chemically more active form of nitrogen such as Lowry's (J.C.S., 1912, 101, 1152) is produced.

H. INGLESON.

Reaction between nitrogen peroxide and sulphur dioxide. E. BRINER, G. H. LUNGE, and A. VAN DER WIJK (Helv. Chim. Acta, 1928, 11, 1125— 1144).—Reaction proceeds between the above two substances in the liquid state according to the equation $1.5N_2O_4+2SO_2=S_2N_2O_9+NO$. The pressure produced in the reaction has been measured; this is gradual at first, but at a certain point a sudden considerable increase takes place. The substance $S_2N_2O_9$ is a white, crystalline solid with the properties of an anhydride of nitrosylsulphuric acid. Whilst it is stable at the ordinary temperature, heat decomposes it into a solid S_2NO_7 and nitric oxide; this reaction appears to be reversible to a certain extent.

The heat of formation of $S_2N_2O_9$ has been calculated from its heat of dissolution in potassium hydroxide; $2SO_2$ liq. $+1.5N_2O_4$ liq. $=S_2N_2O_9$ sol. +NO gas +112 kg.-cal. The same solid product is obtained by interaction of the two gases, but only very slowly at the ordinary temperature. Reaction is quicker at higher temperatures, but the product obtained has a nitrogen content lower than that corresponding with S₂N₂O₉. The course of the reaction has been investigated by measuring the decrease in pressure. The curve of pressure against time in all cases becomes almost parallel to the time axis at a point which corresponds with only part completion of the reaction. This abnormality is further emphasised by the fact that reaction does not take place at all between the gases if mixed at a sufficiently low pressure. The reaction is very much quicker in the presence of platinised asbestos as catalyst, but again reaction is incomplete, although it proceeds further than without the catalyst. The properties of the substance $S_2N_2O_9$ are recorded and the mechanism of its formation is briefly discussed. R. N. KERR.

Preparation of tantalum pentabromide. K. R. KRISHNASWAMI (Nature, 1928, 122, 845).—Bromine is distilled in an atmosphere of nitrogen or argon on to powdered tantalum at 260—300°.

A. A. ELDRIDGE. Decomposition of trithionate solutions. A. HORNIG (Z. anorg. Chem., 1928, 176, 423-424). —Trithionate solutions are hydrolysed giving sulphate, thiosulphate, and hydrogen ions. The presence of the thiosulphate is difficult to detect in presence of the acid formed. On adding potassium trithionate, however, to a cold saturated solution of copper acetate, and leaving for a few days in the dark, a yellow, crystalline compound separates out in transparent monoclinic prisms. The composition corresponds with the formula $K_2S_2O_3$, $Cu_2S_2O_3$, $2H_2O$. Some long, thin, yellow needles of unknown composition have also been observed. The potassium cuprous thiosulphate is not stable in air or in boiling water, copper sulphide being formed.

M. S. BURR.

Reactions of hydrogen chloride with the dioxides of selenium and tellurium between 0° and 170°. T. W. PARKER and P. L. ROBINSON (J.C.S., 1928, 2853-2857) .- By the action of hydrogen chloride on selenium dioxide two additive compounds are formed : (i) SeO₂,4HCl, a yellow solid stable at 0°, and (ii) SeO₂,2HCl, a yellow liquid, stable up to 170° and able to be distilled at this temperature with some decomposition into its constituents. This liquid dissolves hydrogen chloride in amounts varying with the temperature. There is no evidence that tellurium dioxide forms a definite additive compound within the range 0-150°. At 0°, hydrogen chloride is absorbed in varying amounts by the dioxide giving a heterogeneous product which loses water continuously in a stream of the gas as the temperature is raised. H. INGLESON.

Molybdic acid-selenic acid. E. WENDEHORST (Z. anorg. Chem., 1928, 176, 233-235).—Treatment of selenic acid with molybdic acid on the water-bath for several days, followed by removal and evaporation to the liquid layer, yields a pure crystalline mass of the composition MoO_{3} , SeO₃, which with a little water yields a hydrate having when dried at 110° the formula MoO_{3} , SeO₂, 2H₂O. No other stable hydrate exists. The acid is extremely hygroscopic. Titration with potassium hydroxide, using phenolphthalein as indicator, shows it to be tetrabasic. Alcohol and ordinary acetone cause the production of a blue colour and a precipitate of selenium, whereas pure acetone has no such effect. Permanganate does not react with the acid, but with water the orange colour due to permolybdate is produced.

H. F. GILLBE.

Denigès' phospho-cœruleo-molybdenum compound. G. DENIGÈS (Pharm. Acta Helv., 1928, 3, 52—56; Chem. Zentr., 1928, i, 2920).—Polemical (cf. Verda, A., 1928, 1104). A. A. ELDRIDGE.

Denigès' phospho-cœruleo-molybdenum compound. A. VERDA (Pharm. Acta Helv., 1928, 3, 56—59; Chem. Zentr., 1928, i, 2920).—A reply to Denigès (preceding abstract). A. A. ELDRIDGE.

Chlorine fluoride. O. RUFF and E. ASCHER [with J. FISCHER and F. LAASS] (Z. anorg. Chem., 1928, 176, 258-270).-Chlorine fluoride has been prepared by passing chlorine into a copper vessel containing fluorine and heated at 250°, and fractionally condensing the product. The compound is an almost colourless gas of characteristic odour; in quartz vessels it becomes yellower in colour, probably on account of the formation of chlorine monoxide. The white solid melts at $-161\pm0.5^{\circ}$ to a yellow liquid of b. p. $-103\pm3^{\circ}$. The reaction is exothermal, and even in presence of a large excess of fluorine some free chlorine exists. In general, chlorine fluoride reacts in a similar manner to fluorine, but exhibits greater activity towards most metals. A characteristic reaction is that with cellulose, which ignites in the cold, whereas with fluorine the reaction takes place only on warming. Glass is attacked at the ordinary temperature, the reaction being enormously accelerated by the presence of water vapour or hydrogen fluoride. H. F. GILLBE.

New salts of the tervalent iodine cation. F. FICHTER and S. STERN (Helv. Chim. Acta, 1928, 11, 1256-1264).-The following salts of the tervalent iodine cation have been prepared by Fouque's method : phosphate, bright yellow crystals, trichloroacetate, dichloroacetate, monochloroacetate, light yellow powders. The methanesulphonate, light yellow crystals, has been prepared directly from the acetate. Double salts, trichloroacetate-iodate and monobromoacetate-iodate, have also been obtained. These salts have been shown to have the required composition by analysis of the products on decomposition with water. A saturated solution of iodine acetate in acetic anhydride was electrolysed, using a silvered platinum gauze as cathode; an amount of silver iodide was deposited equivalent to the current passed. R. N. KERR.

Reactions and derivatives of iron carbonyl. III. Iron carbonyls containing pyridine. W. HIEBER and F. SONNEKALB [with G. BADER] (Ber., 1928, 61, [B], 2421-2427; cf. A., 1928, 511).-The direct action of ethylenediamine on iron pentacarbonyl affords the additive compound, Fe(CO)₅, en, without liberation of carbon monoxide. The substance is decomposed by dilute acid into its components together with iron tetracarbonyl, ferrous salt, and very small quantities of hydrogen and carbon monoxide. The substitution of carbon monoxide by ethylenediamine (loc. cit.) depends therefore on the presence of pyridine. The interaction of iron pentacarbonyl with a large excess of pyridine at 80° is accompanied by the maximal evolution of approximately 3 mols. of carbon monoxide; in the presence of 5 mols. of the base the disengagement occurs more rapidly, whereas it is invariably very slow at the atmospheric temperature. Light accelerates the change, causing the liberation of 2 mols. of carbon monoxide at the ordinary temperature. The compound Fe(CO)₅,C₅H₅N is the primary product which subsequently yields the substitution products $Fe(CO)_4, C_5H_5N$ and $Fe(CO)_3, 2C_5H_5N$. Substitution occurs only when the liberated carbon monoxide is allowed to escape. Decomposition of the compounds by dilute acids affords hydrogen, carbon monoxide, and ferrous salt; the proportion converted into the ferrous ion varies, the remainder of the metal appearing as iron tetracarbonyl. The carbon monoxide is partly reduced by the nascent hydrogen, which also H. WREN. hydrogenates the pyridine.

Complex salts. I. Preparation and properties of some selenitopentamminecobalt salts. H. L. RILEY (J.C.S., 1928, 2985-2989).-Ions possessing an electrovalency of two show varying co-ordination valencies. The carbonate ion usually occupies two positions, but sometimes only one. Those of the sulphate or sulphite type possess a greater tendency to occupy one position in the complex. An explanation of this behaviour is advanced and evidence in its favour is obtained from the study of the properties of selenitopentamminecobaltic chloride, [Co(SeO₃)(NH₃)₅]Cl, occurring as brownish-red crystals which when dissolved in water dissociates as a binary electrolyte to the extent of 97% in 0.1N-solutions, and selenitopentamminecobaltic selenite, $[Co(SeO_3)(NH_3)_5]_2SeO_3, 3H_2O$ (?),

which could not be obtained in a pure state owing to H. INGLESON. its deliquescent nature.

Metallic cyanates. III. Ammines of the simple cyanates with hexamethylenetetramine. R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 29-41; Chem. Zentr., 1928, i, 2938-2939).-Compounds of the general formula $[X(H_2O)_2C_6H_{12}N_4](CNO)_2$, where X=Co, Ni, Mn, Fe, Cu, or Cd, have been prepared: their stability and insolubility are greater than those of the simple cyanates. The compounds $[Cu(MeOH)_2C_6H_{12}N_4](CNO)_2$ and $[Cu(EtOH)C_6H_{12}N_4](CNO)_2$ were also obtained.

A. A. ELDRIDGE. Selenocyanoammines. I. G. SPACU and R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 3-22; Chem. Zentr., 1928, i, 2937-2938).-Selenocyanoammines have been prepared (1) by adding the required base to a metallic salt solution, such that no precipitation takes place, and then precipitating the selenocyanoammine by addition of alkali selenocyanate solution; (2) by causing potassium selenocyanate and a metallic nitrate to react in alcoholic solution, and addition of the required base after filtration from potassium nitrate. The following metallic pyridineand hexamethylenetetramine-selenocyanates are described: $[X(H_2O)_4C_6H_{12}N_4](SeCN)_2$, where X = Co, Ni, Mn, Fe, or Zn; $[X(C_5H_5N)_4](SeCN)_2$, where X = Co, Ni, Mn, Fe, Zn, or Cd; $[Ni(C_5H_5N)_6](SeCN)_2$; $[Zn(C_5H_5N)_2](SeCN)_2$; $[Cd(C_5H_5N)_2](SeCN)_2$.

A. A. ELDRIDGE.

Sebor's method of quantitative spectral analysis. J. KNOP (Chem. Obzor, 1926, 1, 253-256; Chem. Zentr., 1928, ii, 371).-The method whereby it is sought to determine the concentration of dyes by measurement of the width of the absorption A. A. ELDRIDGE. bands is inexact.

Gravimetric titrations and their application to microchemical determinations. B. ORMONT (Z. anal. Chem., 1928, 75, 209-228).-For microvolumetric analysis more accurate results can be obtained by weighing the standard solution in the burette before and after titrating to the end-point than by measuring the volume of solution used. The standard solution is prepared in such a way that it contains a definite fraction of the equivalent weight of the standard substance in 1 kg. of solution. A suitable burette for use in the work is described and illustrated, and the possible sources of error and the preparation of the solutions and indicators are discussed. Microchemical gravimetric titrations afford an accurate means of determining quantities between 6×10^{-4} and $2 \cdot 6 \times 10^{-7}$ g. of hydrogen chloride by acidimetry and $7 \cdot 3 \times 10^{-4} - 3 \cdot 5 \times 10^{-7}$ g. of arsenic trioxide by iodometry. A. R. POWELL.

Apparatus for colorimetric titration. E. B. POWERS (Ecology, 1928, 9, 364).

CHEMICAL ABSTRACTS.

Systematic knowledge of indicators. XIII. Solvent errors. (1) Alcohol error with methylorange and related azo-indicators. XIV. New source of error in colorimetric measurements ; the "light error" of some azo-indicators in presence of organic solvents. A. THIEL and W. SPRINGEMANN (Z. anorg. Chem., 1928, 176, 64-80, 112—120).—XIII. When alcohol is employed as solvent in titrations with azo-indicators two errors are liable to arise, one being purely optical and the other due to an alteration of the acid-sensitivity of the indicator. Measurements have been made of the extinction coefficients of methyl-orange, methylyellow, monomethyl-orange, and methyl-red in aqueous solutions containing 0—100% of ethyl alcohol. The $p_{\rm ff}$ of 0·1N- and 0·01N-solutions of hydrogen chloride in various mixtures of alcohol and water has been determined, and the values of the half stages of the four indicators in the same mixtures have been ascertained.

XIV. Disubstituted p-aminoazobenzene derivatives in presence of methyl and ethyl alcohols and acetone are bleached by the action of light, the process reaching an equilibrium but reverting in the dark in accordance with the law for unimolecular reactions. The equilibrium is influenced by the alcohol concentration, and is liable to become a source of error in colorimetric determinations. H. F. GILLBE.

Simplified potentiometric analysis. E. MÜLLER and H. KOGERT (Z. anal. Chem., 1928, 75, 235-239).—Examples are given of the results obtained by the use of the capillary-wire electrode. From these it is inferred that the new electrode may be used satisfactorily in place of the N-calomel electrode for all potentiometric titrations.

A. R. POWELL.

Rapid determination of selenium. E. BENESCH (Chem.-Ztg., 1928, 52, 878-879).—Selenium precipitated as element by any of the usual methods is collected, washed roughly, and dissolved in cold saturated sodium sulphide solution. The red colloidal solution reacts quantitatively with potassium cyanide according to the equation Se+KCN=KSeCN. The end-point is marked by the change of colour from red to yellow. S. I. LEVY.

Gas-volumetric determination of nitrogen in ammonia, carbamide, and ammonium salts. P. RISOHBIETH (Z. physikal.-Chem. Unterr., 1928, 41, 132-133; Chem. Zentr., 1928, i, 2973).--A lecture experiment. A. A. ELDRIDGE.

Determination of small quantities of nitrate nitrogen. B. G. ŠIMEK (Chem. Listy, 1928, 22, 353-357, 473-476).—The reduction methods of Devarda and of Ulsch are unsuitable for the determination of small quantities of nitrate nitrogen (less than 2 mg.), whilst that of Arnd gives a mean error of only about 1% when duraluminium is used for reduction. The Gladstone-Tribe colorimetric method gives results on the average 10% below the actual values. The Marx-Trommsdorff titration method gives good agreement for quantities of nitrogen within the limits 0.1--0.5 mg.; this method caunot, however, be applied in the presence of sodium chloride. R. TRUSZKOWSKI.

Volumetric method of determining phosphoric acid in alkali and alkaline-earth phosphates and in phosphates of iron and aluminium. DRAC-HOUSSOF and DOUCHY (Chim. et Ind., 1928, 20, 823-828).—A solution of a dihydrogen phosphate, neutral to methyl-orange and containing a sufficiency of calcium chloride, is titrated with standard sodium hydroxide solution until neutral to phenolphthalein in the cold : $2H_3PO_4+3CaCl_2+6NaOH=Ca_3(PO_4)_2+$ $6NaCl+6H_2O$. Acid phosphates of iron or aluminium which would give precipitates are determined by the difference between titrations with methyl-orange and phenolphthalein. Errors due to the presence of carbon dioxide in the reagents are corrected by a blank. If calcium chloride is being used not more than small quantities of nitrates are admissible, and ammonia must be eliminated. Free lime in dicalcium phosphate may be determined in the same operation. Natural phosphates always contain iron and aluminium and must be treated accordingly. The method is sufficiently accurate for all industrial purposes. C. IRWIN.

Test for arsenic. DAUVÉ (Ann. Chim. analyt., 1928, [ii], 10, 320—321).—The solution is treated with sodium hydroxide and a piece of aluminium foil and the gases evolved are brought into contact with a paper saturated with mercuric chloride solution. A yellow stain on the paper indicates the presence of arsenic. Silver nitrate cannot be used in the test instead of mercuric chloride, as hydrogen silicide is evolved, and this gas, like hydrogen arsenide, blackens silver nitrate paper. A. R. POWELL.

Use of 8-hydroxyquinoline in silicate analysis. J. ROBITSCHEK.—See B., 1928, 895.

Determination of carbon and hydrogen in organic substances by the dry method. D. BATESCU (Ber., 1928, 61, [B], 2336-2340).—The substance is burnt in air or oxygen, the contact agent being platinised asbestos held in position by oxidised copper gauze plugs containing the same catalyst. The tube, which is about 50 cm. long and 0.8 cm. internal diameter, is placed in a small sheet-iron furnace heated by three Teclu burners. A complete combustion requires only 0.75—1 hr. H. WREN.

Elementary micro-analysis. R. GOUBAU (Bull. Soc. chim. Belg., 1928, 37, 335-344).—A method of micro-combustion of organic substances is described which it is claimed possesses certain advantages over the ordinary Pregl method, particularly with regard to rapidity of working and simplicity of technique. The water and carbon dioxide formed by the combustion of the substance are not absorbed in the usual way, but are condensed in U-tubes cooled by means of an alcohol-carbon dioxide mixture and liquid oxygen, respectively. These tubes are sealed up after the combustion, and the actual weighing of the water and carbon dioxide formed can be postponed to any convenient time. Using 5 mg. of a substance, containing, e.g., 70% of carbon and 10% of hydrogen, the possible errors are ± 0.5 % C and ± 1.3 % H, but larger quantities may be conveniently employed, with a corresponding decrease in the possible error. The method is especially useful where small numbers of combustions are made from time to time.

O. J. WALKER.

Simultaneous determination of silver and cadmium by potentiometric titration. E. MÜLLER and H. HENTSCHEL (Z. anal. Chem., 1928, 75, 240—244).—The solution is first titrated with 0.1M-potassium bromide solution, using a silver indicator electrode and an opposed E.M.F. of +0.173 volt against the normal calomel electrode, then with sodium ferrocyanide, using a platinum indicator electrode and an opposed E.M.F. of +0.15 volt. Both titrations are made at 75°.

A. R. POWELL. Precipitation of zinc sulphide from solutions containing considerable quantities of sodium chloride. L. DEDE (Ber., 1928, 61, [B], 2248-2251).-The precipitation of zinc sulphide from neutral solutions of zinc salts by hydrogen sulphide in presence of a small quantity of sodium acetate is appreciably hindered by the addition of sodium chloride. In presence of even very small amounts of free acid, the effect of sodium chloride is so considerable that an exact determination of zinc is not possible. The deficit amounts to more than 30% when much sodium chloride is present. The zinc sulphide, precipitated by addition of colourless ammonium sulphide to solutions of zinc salts and ammonium acetate, settles more rapidly in the presence than in the absence of sodium chloride. In these cases, also, the separation of the sulphide is not quantitative, but the effect of the sodium chloride is less marked than H. WREN. in acid solution.

Sensitivity of methods of detection of impurities in cadmium and copper. G. TAMMANN, A. HEINZEL, and F. LAASS (Z. anorg. Chem., 1928, 176, 143-146).-Microscopical examination of the residue remaining after cadmium containing 0.1-0.01% of lead, bismuth, antimony, or tin has been dissolved in 50% ammonium nitrate solution demonstrates that this procedure forms a sensitive test for the presence of these metals. The limits at which antimony, bismuth, and lead may be determined in copper by this method, after dissolving in 7.5% ammonium persulphate solution, is about 0.1%, the limit for gold being about 0.01%; the presence of cuprous sulphide, in quantity corresponding with about 0.001% of sulphur, may also be detected. In general, the sensitivity of the microscopical method is increased by first rolling the metal and then heating to above the eutectic temperature, as the phase rich in the impurity aggregates in the interstices between the crystals, and the foreign material remains after dissolution in the form of coarse particles.

H. F. GILLBE.

Rapid analysis of bronze and brass without electrolysis. H. KRUG.—See B., 1928, 930.

Determination of free aluminium oxide in silicate mixtures. L. A. SCHMELEV.—See B., 1928, 895.

Metallic cyanates. V. Separation of the metals of the third analytical group. R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 104–109; Chem. Zentr., 1928, i, 2974).—The precipitate containing aluminium, zinc, manganese, chromium, iron, nickel, and cobalt is dissolved in 10% hydrochloric acid, treated with a few c.c. of "perhydrol," boiled, and filtered from sulphur; the filtrate is nearly neutralised with sodium carbonate, again boiled with ammonium nitrate (1–2 g.), and treated, with stirring, with repeated small quantities of a 2% potassium cyanate solution. Aluminium, chromium, and iron are thus precipitated; in their usual separation, aluminium

is again precipitated by means of cyanate. In the separation of the remaining metals, zinc is precipitated by means of pyridine and potassium bromide as the compound $[Zn(C_5H_5N)_2]Br_2$. A. A. ELDRIDGE.

Gallium. II. R. FRICKE and K. MEYRING (Z. anorg. Chem., 1928, 176, 325-348; cf. A., 1925, ii, 417).--A method of determining gallium quantitatively as Ga₂O₃ is described. A platinum crucible is not suitable for this purpose. The electrical conductivity and f.-p. depression of ammoniacal gallium hydroxide solutions have been determined, and it is concluded that the solubility of gallium hydroxide in ammonia solutions is largely due to the formation of salts and not of complex compounds. The hydrolysis of gallium chloride and sodium galliate has been investigated by the hydrogen electrode method. The results in the gallium chloride solution are complicated by the high hydration of the gallium ion, but, working in dilute solution, the first hydrolytic constant of gallium trichloride, [Ga++OH][H+]/[Ga+++]= 1.4×10^{-3} , giving for the third basic dissociation constant of gallium hydroxide [Ga+++][OH']/[Ga++OH]= 4×10^{-12} . The second hydrolytic constant, [Ga+(OH)₂][H+]/[Ga++OH], is 3.5×10^{-4} and the corresponding basic dissociation constant 1.6×10^{-11} . The first hydrolytic constant of sodium galliate,

 $[GaO_2''OH][OH']/[GaO_3''']=3\times10^{-3}$, from which the third acid dissociation constant is found to be $[GaO_3'''][H^+]/[GaO_2''OH]=2\times10^{-12}$. Similarly, the second hydrolytic constant and the second acid dissociation constant are $1\cdot2\times10^{-4}$ and $4\cdot8\times10^{-11}$, respectively. It is evident that the acid and basic properties of gallium hydroxide are of practically the same order of magnitude. Further, the second dissociation constant, whether basic or acidic, is only a little greater than the third, which is to be explained on the basis of Bjerrum's theory of "Zwitterion" formation in ampholytes (A., 1923, i, 444). M. S. BURR.

Influence of cobalt on the determination of manganese in steel. I. WADA and S. SAITO.—See B., 1928, 930.

Sensitivity of methods of detection of small quantities of impurities in iron. G. TAMMANN and W. SALGE (Z. anorg. Chem., 1928, 176, 152— 154).—Microscopical study of the residue left after the dissolution of iron in 15% ammonium persulphate solution enables the presence of 0.002% of sulphur, 0.05—0.02% of aluminium, 0.05% of antimony, 0.02% of zinc, or about 0.01% of silicon to be detected. H. F. GILLBE.

Metallic cyanates. IV. Chromium. Gravimetric determination of chromium. R. RIPAN (Bull. Soc. Stiinte Cluj, 1928, 4, 57—61; Chem. Zentr., 1928, i, 2973).—When a neutral or slightly acid solution of a chromium salt (0.0002 g. Cr) is boiled with a 2% solution of potassium cyanate, granular chromium hydroxide is precipitated. Zinc and manganese, if present, are kept in solution by the addition of an ammonium salt, zinc being precipitated from the filtrate as $[Zn(C_5H_5N)_2](CNO)_2$ or the corresponding thiocyanate. For the determination of chromium (0.04—0.05 g.), the salt is dissolved in 200-250 c.c. of water and boiled until carbon dioxide is evolved with ammonium chloride (2 g.) and potassium eyanate (0.3 g.), the precipitate being washed, dried, and ignited in the usual way. A. A. ELDRIDGE.

Analytical determination of uranium, thorium, and lead, as a basis for age-calculations. C. N. FENNER (Amer. J. Sci., 1928, [v], 16, 369-381).— Detailed directions are given for the determination of uranium, thorium, and lead in radioactive minerals such as euxenite, polycrase, samarskite, and monazite. C. W. GIBBY.

Control of a new method for the measurement of the temperature of a gas. M. CHOPIN (Compt. rend., 1928, 187, 935—937).—From 350° to 650° the temperature of a current of air calculated by the author's aërodynamic method (*ibid.*, 186, 1832) exceeds that indicated by an electric thermo-couple placed 6 mm. away from the orifice by 2.9° (mean), and is 3.5° (mean) below that obtained when the couple is 20—80 mm. from the orifice. Successive determinations at 600° gave values differing by less than 1°. J. GRANT.

Automatic apparatus for p_{II} measurement. A. LASSIEUR (Chim. et Ind., 1928, 20, 819—822).— The *E.M.F.* to be measured is made to charge a condenser which is then discharged through a ballistic galvanometer. The deflexion is a measure of the *E.M.F.*, further oscillations being damped out by a shunt. The condenser armatures are then shortcircuited. A switch is described which makes these successive connexions by simple rotation. If driven by clockwork, one measurement per minute can be made. The apparatus is sensitive to 0.0045 volt or a p_{II} variation of 0.07. C. IRWIN,

[Apparatus for] ultrafiltration. P. DICKENS (Chem. Fabr., 1928, 633; cf. A., 1928, 728).— Attention is directed to the author's earlier publications describing the apparatus. A diagram of a modified form is given. S. I. LEVY.

Toy balloons and filtration. J. W. GARRETT and C. D. HURD (Ind. Eng. Chem., 1928, 20, 1130).— An inflated rubber toy balloon resting on top of a Buchner funnel is an aid in laboratory pressure filtration. It is put in position when most of the solvent has been withdrawn and prevents cracking of the precipitate. C. IRWIN.

Washing by decantation. G. E. MARSH (Ind. Eng. Chem., 1928, 20, 1241).—A chart gives the relationship between number of washings by decantation, initial and final concentrations of impurity, and the proportion of the volume occupied by the settled precipitate. C. IRWIN.

Projection of Brownian movement. N. H. BLACK (J. Chem. Education, 1928, 5, 868—873).—A projection apparatus for demonstration is described. CHEMICAL ABSTRACTS.

Apparatus for working with exclusion of air or in a neutral atmosphere. P. DICKENS (Instruments, 1928, 1, 311-312).

Wing top oxygen-gas burner. G. R. ROBERT-SON (Ind. Eng. Chem., 1928, 20, 1240—1241).—For glass working with natural gas oxygen is both necessary and safe, there being no tendency to light back to the mixing chamber owing to the slow rate of flame propagation. The burner described employs a short horizontal tube as mixing chamber with a needle valve on each side from oxygen and gas supplies. C. IRWIN.

Laboratory humidity cabinet. I. C. MATTHEWS and A. M. BURGESS (Ind. Eng. Chem., 1928, 20, 1239—1240).—The cabinet is designed to maintain any temperature between 27° and 50° with humidity at any point between 80°_{0} and 100°_{0} . It is of stone with brass ducts and is fitted with a circulating fan and both water spray and steam jet. Wet- and drybulb thermometers operate automatic controls.

C. IRWIN.

Protected reservoir and burette [for solutions affected by oxygen]. B. COHEN (Ind. Eng. Chem., 1928, 20, 1238).—The reservoir has an upper and lower three-way cock; the latter connects with the burette and the supply of solution. The upper cock connects with the inert gas supply and with a by-pass around the reservoir for flushing out. The reservoir is evacuated in order to charge it with solution.

C. IRWIN.

Titration vessel with side container to avoid over-titration. J. LINDNER (Chem.-Ztg., 1928, 52, 868—869).—A side container is joined to the exterior of an Erlenmeyer flask midway between the base and the mouth. By inclining the flask a small portion of the liquid may be tipped into the side tube, and after titrating the bulk of the liquid, the rest is returned from the side tube, which is rinsed out and the titration completed. F. R. ENNOS.

Unbreakable explosion pipette. F. W. ISLES (Ind. Eng. Chem., 1928, 20, 1163).—An explosion pipette consists of a 1-in. tee with sparking plug in the side outlet and a 7.5-in. nipple screwed into the bottom. Top and bottom steel plugs carry capillary hose connexions with mercury as aspirating fluid. The joints are made with shellac. C. IRWIN.

Simplified cataphoriser. W. D. HORNE (Ind. Eng. Chem., 1928, 20, 1147).—A flattened capillary tube about 8 cm. long is enlarged at each end in a ground tapered tube in the form of a stopper. These are connected by rubber tubing to corks carrying glass tubes of 2 mm. diam. and platinum wires. The glass tubes serve for filling and emptying, and the platinum wires are only 12 cm. apart, thus enhancing the activity of the colloid particles. C. IRWIN.

Viscosimeter with double set of radiators. E. LASZLO (Chem.-Ztg., 1928, 52, 869).—A viscosimeter of the Engler type is provided with two sets of radiating vanes, one set being fixed to the inside of the outer heating bath and the other to the outside and base of the inner oil container, whereby the necessity for stirring is obviated. Other minor improvements are also described. F. R. ENNOS.

Universal siphon. G. BEETZ (Chem.-Ztg., 1928, 52, 868).—A glass siphon of the usual form is provided near the end of the lower limb with a tap, above which is a side tube also with a tap. The siphon is filled by closing the lower tap, opening that in the side tube, and blowing down a small water pump which is fixed temporarily to the side tube.

F. R. ENNOS.

Phosphate content and hydrogen-ion concentration of the surface water of the English Channel and southern North Sea, June 18-22, 1928. H. R. SEIWELL (Nature, 1928, 122, 921-922) .- For the English Channel, the average phosphate content (excluding abnormal stations) was 8.64 mg. P_2O_5 per m.³, and the average $p_{\rm H}$ (corr.) was 8.03; corresponding values for the southern North Sea were 3.44 and 8.11, respectively, and for the Straits of Dover 3.65 and 8.05. There appears to have been a greater photo-synthetic activity in the surface water of the southern North Sea than in that A. A. ELDRIDGE. of the English Channel.

Meteoric iron of Savik, C. York, N. Greenland. O. B. Bøggild (Medd. Grønland, 1927, 74, 9-30; Chem. Zentr., 1928, ii, 32).—The Savik meteorite (3401.7 kg.) contains 7.25% Ni, but no carbon, cobalt, or copper. A. A. ELDRIDGE.

Analysis of a eudialyte from Chibina steppes and its weathering products. G. P. TSCHERNIK (Bull. Acad. Sci., U.S.S.R. [Russia], 1925, 711— 720; Chem. Zentr., 1928, ii, 28—29).—The eudialyte, d 2.83-2.99, H 5-6, and its weathering product contain, respectively, TiO₂ 1·81, 3·04; Fe₂O₃ 1·54, 15·87; MnO 1·43, 2·20; H₂O 1·07, 3·25; ZrO₂ 11·91, 3·92; FeO 7·21, 3·85; Na₂O 12·97, 5·95; Cl 0·96, 0·14. A. A. ELDRIDGE.

Silicates. A. ENDRÉDY (Föld. Közlöny, 1927, 20-105; Chem. Zentr., 1928, ii, 29).-An attempt to elucidate the constitution of grossularite and adradite by "fractional" decomposition with hydrochloric A. A. ELDRIDGE. acid.

Karpholite. J. JAKOB and J. HESEMANN (Schweiz. Min. Petr. Mitt., 1928, 7, 134-137; Chem. Zentr., 1928, ii, 29).-Karpholite from Hettstedt, Harz Mts., and from Schlaggenwald, Bohemia, corresponded, respectively, with the formulæ

1.639.

Zirklerite. E. HARBORT (Kali, 1928, 22, 157-161; Chem. Zentr., 1928, ii, 30-31).—Zirklerite, from salt deposits of the N. German plain, is similar to rinneite; it contains large quantities of ferrous chloride and is coloured reddish-brown in the air. It has n 1.552, d 2.6, is optically uniaxial, and is rhombohedral hemihedral or tetartohedral hexagonal. The composition corresponds with the formula $2Al_2O_3, H_2O, 9(Fe, Mg, Ca)Cl_2, 2H_2O$

A. A. ELDRIDGE. Chemical composition of nepheline. J. Morowicz (Bull. Acad. Polonaise, 1928, A, 111-125).-The data concerning the empirical formula of nephel-ine are discussed. It is concluded that the general ine are discussed. It is $\operatorname{SolarAl_2Si_2O_8}$, where, in the formula is $K_2Al_2Si_3O_{10}$, $nNa_2Al_2Si_2O_8$, where, in the mainting of across n = 4 J. W. SMITH. majority of cases, n=4.

Alumohydrocalcite. G. BILIBINE [with TSCHERYNKH] (Mem. Soc. Russe Min., 1928, 55, 243-258; Chem. Zentr., 1928, i, 2797).-The mineral d 2.231, H 2.5, contained SiO₂ 0.67, Al₂O₃ 28.60, Fe2O3 0.45, FeO 0.35, CaO 15.46, MgO, Na2O, and K2O

Geochemistry. trace, P2O5 0.74, CO2 25.20, H2O 26.40, H2O hygroscopic 2.48%. It is monoclinic, α 1.485, β 1.553, γ 1.570. The dehydration curve indicates the formula A. A. ELDRIDGE. $CaH_2(CO_3)_2, 2Al(OH)_3, H_2O.$

Heterobrochantite, neptunite, rock salt, and syngenite.] H. BUTTGENBACH (Ann. Soc. Geol. Belg., 1926, 49, 164—180; Chem. Zentr., 1928, i, 2796).—Heterobrochantite (Chile), CuSO₄,Cu(OH)₂, *H* 2.5, *d* 3.757, is rhombic pyramidal; neptunite (Greenland) has a:b:c=1.3164:1:0.8075, $\beta=64^{\circ}$ 22'. A scratch-test distinguishes between rock salt and potassium salts. The optical constants of A. A. ELDRIDGE. syngenite are recorded.

Schefferite and richterite. J. JAKOB (Schweiz. Min. Petr. Mitt., 1927, 7, 137-139; Chem. Zentr., 1928, ii, 30).-The manganiferous pyroxenes and amphiboles frequently, sometimes exclusively, contain tervalent manganese. Schefferite contains 4.55 and richterite 3.34-7.17% Mn₂O₃. A. A. ELDRIDGE.

Micas containing rubidium and cæsium. J. JAKOB (Schweiz. Min. Petr. Mitt., 1927, 7, 139-141; Chem. Zentr., 1928, ii, 30).-Lepidolite (Nubeb, Usakos, S.W. Africa) and zinnwaldite (Zinnwald) contain, respectively : SiO2 48.80, 48.55; TiO2 trace, 0.0; Al_2O_3 24.44, 21.79; Mn_2O_3 1.48, 1.40; Fe_2O_3 2.34, 0.0; FeO 0.0, 9.51; MgO and CaO 0.0, 0.0; Li₂O 4.93, 3.73; Na₂O 2.15, 0.51; K₂O 9.26, 8.29; $Rb_{2}O 1.73, 1.49; Cs_{2}O 0.60, 0.0; H_{2}O(+) 1.88, 0.83;$ H_2O (-) 0.0, 0.0; F 4.69, 6.67; α 1.529, 1.541; A. A. ELDRIDGE. β 1.651, 1.571; $\gamma = \beta - , 1.573.$

Harz mineral fields. IV. Occurrence of pyrrhotine and origin of antimony, nickel, and cobalt in the Rammelsberg minerals. G. FRE-BOLD (Zentr. Min. Geol., 1928, A, 161-167; Chem Zentr., 1928, i, 3045-3046).-Pyrrhotine was found in zinc blende from the seventh Rammelsberg level. Calcite contained inclusions of antimonite; pyrrhotine contained pentlandite and cobalt glance. The conditions of the association of these minerals are A. A. ELDRIDGE. discussed.

Mineral constituents and origin of a certain kaolin deposit near Spokane, Washington. G. E. GOODSPEED and A. A. WEYMOUTH (J. Amer. Ceram. Soc., 1928, 11, 687-695).-In this region the rocks, which are at least pre-Tertiary, consist of metamorphics intruded by granite rocks. The kaolin deposits are classified into three types, viz., (1) deposits of lacustrine origin, (2) material transported from the wash of felspathic rocks, (3) a residual deposit. The last type, in which no trace of the former existence of felspar is apparent, occurs in dykes cutting a sandy material. In this case, the usual conception of the formation of kaolin by the weathering of felspathic rocks does not appear to be tenable. It is suggested that it may have been formed either (1) by effective endomorphic action, the whole of the pre-formed felspar being changed by the volatile constituents of an intrusion, or (2) by the direct action of a highly aqueous magmatic solution, the alumina directly forming kaolin instead of the intermediate felspar. The latter hypothesis is strengthened by the absence of secondary silica. A list and description of the minerals found in the sandy matrix and kaolinitic dykes arc given. A. T. GREEN.

Helium contents and ages of Japanese radioactive minerals from Ishikawa district. Y. KANO and B. YAMAGUCHI (Bull. Chem. Soc. Japan, 1928, 3, 244—252).—The minerals xenotime, samarskite, monazite, and ishikawaite (cf. A., 1922, ii, 861) have been examined for their helium content with the following results: 1 g. of the minerals heated to 1000° yields, respectively, 0.025, 1.42, 0.246, and 1.77 c.c. of helium. The uranium, thorium, and lead contents of ishikawaite were determined. Calculations based on the helium and lead contents give values respectively for the age of this mineral as $72\cdot3$ and 127 million years. The ages of the samarskite and the monazite are calculated as $81\cdot2$ and $73\cdot9$ million years. These three minerals from Ishikawa belong to the same geological age, either Jurassic or Cretaceous. H. INGLESON.

Radioactive minerals from Divino de Ubá, Brazil. C. N. FENNER (Amer. J. Sci., 1928, [v], 16, 382-391).—A specimen of monazite from Divino de Ubácontained 5.091% Th and 0.0927% Pb, from which its age is calculated to be 3.6×10^8 years. The age of samarskite from the same source is 3.4×10^8 years, reckoned from its content of 10.88% U, 1.64% Th, and 0.52% Pb. C. W. GIBBY.

Organic Chemistry.

Higher hydrocarbons from methane. F. H. CONSTABLE (Nature, 1928, 122, 882).—Carbon deposited on china clay is not capable of combining at any appreciable speed with hydrogen at 800—1200° (cf. Stanley and Nash, B., 1929, 7).

Scheffertte and richterite. J. Jacon (Schweiz

A. A. ELDRIDGE. Slow combustion of triacontane. S. LANDA (Compt. rend., 1928, 187, 948-949).—The slow combustion of *n*-triacontane yields aliphatic acids (formic, butyric, and valeric acids identified), aldehydes (hexaldehyde and heptaldehyde identified), small amounts of unsaturated hydrocarbons, and carbon oxides, but no alcohols or ketones. This is in agreement with the theory that the last-named products arise only from branched-chain hydrocarbons. G. A. C. GOUGH.

Interaction of Δ^{β} -pentenyl bromide and magnesium ethyl bromide. C. PRÉVOST (Compt. rend., 1928, 187, 946—948).— Δ^{β} -Pentenyl bromide reacts with magnesium ethyl bromide to give Δ^{γ} -heptene, b. p. 94°, n^{22} 1·4017, d^{22} 0·701, which yields exclusively propionic and butyric acids in equimolecular proportions on oxidation with potassium permanganate, and γ -ethyl- Δ^{α} -pentene, b. p. 85°, n^{22} 1·3966, d^{22} 0·6948, which yields diethylacetic acid on oxidation and a dibromide, b. p. 93·5°/15 mm., n^{24} 1·5006, d^{24} 1·5251. These results are in accord with the previously published theory (A., 1928, 152) and demonstrate the separation of Δ^{β} -pentenyl ion. On treatment with alcoholic potassium hydroxide, the dibromide yields an acetylenic hydrocarbon, b. p. 87°, n^{22} 1·4023, d^{22} 0·7272, which gives a precipitate with aqueous or ammoniacal silver nitrate soluble in ether, alcohol, or an excess of the hydrocarbon. G. A. C. GOUGH.

Action of metallic tin on the dihalogen derivatives of methane. K. A. KOTSCHESCHKOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1191-1197).-See A., 1928, 1212.

Decomposition of organic compounds at high temperatures and pressures. L. R. HERNDON and E. E. REID (J. Amer. Chem. Soc., 1928, 50, 3066-3073).-36 Organic compounds, mainly alcohols, acids, and hydrocarbons, have been heated at constant volume in a metal bomb at temperatures of $300-525^{\circ}$ for periods of 2-48 hrs. For details of the very complicated results the original should be consulted. The quantities of gaseous, water-soluble, and water-insoluble products formed, the b. p. range of the last-named, and the reaction products which have been identified are tabulated. The composition of the gaseous mixture obtained from methyl, ethyl, *n*-propyl, *iso*propyl, benzyl, phenylethyl, and fenchyl alcohols is given. In general, hydroxylic compounds are dehydrated and the hydrocarbon residue is converted into an unsaturated product of wide b. p. range. Aromatic hydrocarbons yield complex mixtures of polymerisation and decomposition products. *n*-Heptane, benzene, toluene, benzoic and stearic acids, benzophenone, and phenol are only slightly decomposed at 400°. H. E. F. NOTTON.

Behaviour of alkoxide solutions towards nitric oxide. H. WIELAND [with J. J. CHAVAN and F. KLAGES] (Ber., 1928, 61, [B], 2382-2387; cf. Stechow, A., 1924, i, 1157; Traube, A., 1925, i, 10). The production of the company 110).-The production of the compound CH₂[N(NO)·ONa]₂ by the action of nitric oxide on a solution of sodium ethoxide in ethyl alcohol is not due to the production of acetone but of acetaldehyde, and sodium formate is formed instead of sodium acetate as assumed previously. The complete reaction is expressed: $3EtONa + 6NO \longrightarrow CH_2[N(NO) \cdot ONa]_2 +$ $H \cdot CO_2Na + 2EtOH + N_2O$. The rate of the complete reaction is controlled by that of the dehydrogenation of ethyl alcohol, which constitutes the main change; the formation of the sodium salt is a secondary process. Benzyl alcohol, in presence of sodium benzyl oxide, is much more rapidly dehydrogenated than ethyl alcohol, but the benzaldehyde produced cannot react further with nitric oxide with production of a salt. isoPropyl alcohol also reacts more readily than ethyl alcohol and a sodium salt is formed from the resultant acetone. Methyl alcohol does not appear to be affected by nitric oxide. H. WREN.

Preparation of α s-dihydroxy-*n*-pentane (pentamethylene glycol) and α s-di-iodo-*n*-pentane. A. MÜLLER and E. RÖLZ [with A. GERÖ] (Monatsh., 1928, 50, 105—108; cf. A., 1928, 43, 270, 734).— Using the method previously described, α s-dihydroxy*n*-pentane [diphenylurethane, m. p. 174–175° (corr.), 142–143° (corr.) on remelting] was prepared in 46% yield by reduction of ethyl glutarate. α :-Dibromo*n*-pentane was obtained in 62% yield by the action of dry hydrogen bromide and α :-di-iodo-*n*-pentane in 76% yield by the action of red phosphorus and iodine on the glycol. R. K. CALLOW.

Carbohydrates and polysaccharides. XVII. Isomeric methylidene[methylene]glycerols. H. HIBBERT and N. M. CARTER (J. Amer. Chem. Soc., 1928, 50, 3120-3127).-Benzoylation of the mixture of methyleneglycerols, prepared by an improved method (cf. Schulz and Tollens, A., 1896, i, 115; Nef, A., 1905, i, 3; Peacock, J.C.S., 1915, **107**, 815), and fractional crystallisation of the product yields pure $\alpha\gamma$ -methyleneglyceryl β -benzoate (I), m. p. 72°, and $\alpha\beta$ -methyleneglyceryl γ -benzoate, m. p. 26°. The latter is hydrolysed by 20% aqueous potassium hydroxide to pure $\alpha\beta$ -methyleneglycerol (II), b. p. 84-85°/11 mm., d²⁰ 1.2113, n²⁰ 1.4477 (p-nitrobenzoate, m. p. 135°), the constitution of which is proved by its conversion by methyl iodide and silver oxide into y-methyl-aβ-methyleneglyceryl ether, b. p. 147°/760 mm., $n_{\rm D}^{20}$ 1.4213, d_4^{20} 1.0788, which is hydrolysed by dilute hydrochloric acid to a-methyl glyceryl ether. The benzoate I is similarly hydrolysed to ay-methyleneglycerol (III), b. p. $82^{\circ}/11 \text{ mm.}, n_{\text{D}}^{\circ \circ} 1.4533, d_4^{\circ \circ} 1.2256$ (p-nitrobenzoate, m. p. 185°). This is methylated to β-methyl-aγ-methyleneglyceryl ether, b. p. 152°/760 mm., $n_{\rm D}^{20}$ 1.4295, which is hydrolysed to β -methyl glyceryl ether (A., 1928, 1213). The pure methyleneglycerols do not isomerise in presence of alkali hydroxide, but II is largely converted by a trace of hydrogen chloride into III, whilst III undergoes more complex changes. The original mixture contains about 60% of II and H. E. F. NOTTON. 40% of III.

Acetylation of diethylene oxide. M. MACLEOD (J.C.S., 1928, 3092).—From the interaction of diethylene oxide with acetic anhydride in the presence of anhydrous ferric chloride (cf. Knoevenagel, A., 1914, i, 163) small quantities of glycol diacetate and $\beta\beta'$ -diacetoxyethyl ether, b. p. 110—135°/16 mm., d_{20}^{20} 1·123, n_{20}^{20} 1·4348, were isolated. A. I. VOGEL.

Reactivity of atoms and groups in organic VII. Influence of solvents on compounds. reaction velocity; adjuvance. J. F. NORRIS and S. W. PRENTISS (J. Amer. Chem. Soc., 1928, 50. 3042-3048) .- The term "adjuvance" is proposed for that property of liquids whereby a reaction proceeds with different velocities in different "indifferent" solvents. Relative values for the adjuvance of some pure solvents in the combination of pyridine and ethyl iodide, as measured by the bimolecular velocity coefficients for this reaction at 25° in 0.2-1.0M.concentrations, are: benzene, 1.00; nitrobenzene, 25; acetone, 12.8; methyl alcohol, 2.5; ethyl alcohol, 1.4; n-propyl alcohol, 1.11; n-butyl alcohol, 1.11; isopropyl alcohol, 1.07; sec.butyl alcohol, 1.00, and tert.-butyl alcohol, 0.93. The results are similar to those obtained by Menschutkin for the reaction between trimethylamine and ethyl iodide (cf. A., 1888, 901; 1890, 1366).

H. E. F. NOTTON.

Alkyl orthosilicates. A. W. DEARING and E. E. REID (J. Amer. Chem. Soc., 1928, 50, 3058-3062) .--The following alkyl orthosilicates have been obtained by adding silicon tetrachloride to the appropriate alcohols cooled below 0°: n-butyl, b. p. 160-165°/ 20 mm., d4 0.9194; n-amyl, b. p. 145-150°/3 mm., d_4^{25} 0.8933; n-heptyl, b. p. 200–215°/3 mm., d_4^{25} 0.8958, and n-octyl, b. p. 240°/3 mm. (decomp.). Phenylethyl and B-chloroethyl orthosilicates could not be purified by distillation. The latter gives with aniline hydrochloride amorphous (?) *β-anilinoethyl orthosilicate* and similar products with dimethylaniline and pyridine. Silicon tetrachloride with isopropyl alcohol yields propylene and isopropyl chloride; it reacts very slowly with ethyl mercaptan, even at 200°. Ethyl orthosilicate converts phthalic and acetic anhydrides and sulphuric and benzoic acids into the corresponding ethyl esters, and benzene in presence of aluminium chloride into hexaethylbenzene. Silica gel free from strong electrolytes and moisture may be prepared by the action of water and acetic acid, respectively, on ethyl orthosilicate. The product has similar adsorptive properties to ordinary silica gel, but is a slightly better catalyst for contact esterification.

H. E. F. NOTTON.

Formation of allyl alcohol. Decomposition of glyceryl formates by heat. R. DELABY and P. DUBOIS (Compt. rend., 1928, 187, 949—951; cf. A., 1928, 1354).—The glyceryl monoformate (1 g.mol.), obtained by esterification, decomposes smoothly at 235° to yield carbon oxides (total about 22·4 g.), hydrogen, saturated hydrocarbons, and 57% of allyl alcohol, partly as the formate. The monoformate containing 72% of the α -ester decomposes suddenly below 220° to afford a 4% yield of allyl alcohol. Hence the esterification product consists mainly of the β -formate. The $\alpha\beta$ - and $\alpha\gamma$ -diformates (1 g.-mol.) yield similarly carbon oxides (about 44·8 g.) at 255—310° and allyl alcohol (42·2—43·3 and 45—46·8 g., respectively). The diformate obtained by esterification contains probably a preponderance of the $\alpha\beta$ -ester. G. A. C. GOUGH.

Univalent iron, cobalt, and nickel. IV. Action of nitric oxide on ferrous mercaptide. W. MANCHOT and H. GALL (Ber., 1928, 61, [B], 2393—2394; cf. A., 1928, 35).—The production of nitrosylmercaptide, SEt-NO, by the action of nitric oxide on ferrous mercaptide at a low temperature or in presence of the gas diluted with nitrogen, is established by its isolation (contrast Reihlen, A., 1927, 951). H. WREN.

Complex compounds of gold with mercaptanic radicals. II. Residual affinities of chloroauric acid. P. C. Rây and K. C. BOSE-Rây (J. Indian Chem. Soc., 1928, **5**, 527-533).—When 1:4-dithian is treated with excess of aqucous gold chloride the *compounds* 2AuCl,HCl,(C_2H_4S)₂ (I) and 2HAuCl₄,3(C_2H_4S)₂,4H₂O (II) are obtained. Ammonia, pyridine, and benzylamine convert I into the *substances* Au₅Cl₂,6NH₃ (explodes when heated), 4AuCl,(C_2H_4S)₂,2C₅H₅N, and AuCl,CH₂Ph·NH₂, respectively. If dithian is heated with aqueous gold chloride the products formed are II and the *compound* AuCl₄(C_2H_4S)₂ (III). Pyridine converts III into the substance $2AuCl_{4}(C_{2}H_{4}S)_{2}$, but if the reaction is carried out in absence of light the *product* is $AuCl_{5}H_{5}N$. Treatment of II with potassium carbonate (0.5 mol.) gives potassium chloroaurate and the *salt*

KAuCl₄,HCl,3(C₂H₄S)₂,2H₂O, but with 1 mol. of the carbonate the complex salt KAuCl₄,3(C₂H₄S)₂,4H₂O is produced. The action of ammonia on II is to yield the explosive compound Au(NH₃)₃,1·5H₂O, whilst pyridine gives dithian sulphone, and the substances AuCl₃,1·5C₅H₅N, chars about 210°, and AuCl₃,2C₅H₅N.

Triethylene tetrasulphide and gold chloride afford the substance $AuCl_{1}(C_{2}H_{4})_{3}S_{2}$. H. BURTON.

Properties of butyrates and isobutyrates. F. KJELSBERG and A. MÜLLER (Deut. Parfümerieztg., 1928, 14, 235—236; Chem. Zentr., 1928, ii, 338). isoButyrates have smaller d and n than the corresponding butyrates; differences in the odours of esters and in the case of hydrolysis of esters are recorded. Terpinyl isobutyrate is specially resistant to hydrolysis. A. A. ELDRIDGE.

Oxidation of fats, nitrogenous substances, and their mixtures with carbohydrates by air, and metabolism in normal health and diabetes. C. C. PALIT and N. R. DHAR (J. Physical Chem., 1928, 32, 1663-1680; cf. A., 1926, 822).—Potassium stearate and oleate in the presence of sodium hydrogen carbonate or hydroxide are oxidised by the passage of air through their solutions at the ordinary temperature, and the amount of oxidation is increased by the addition of many of the metallic hydroxides. Mixtures of carbohydrates with potassium stearate or oleate are also oxidised by this treatment, but in these cases each component is oxidised to a smaller extent. Carbamide, hippuric acid, and glycine are also oxidised by air in the presence of reducing agents, and in alkaline solution the last two substances are oxidised even in the absence of a catalyst. When carbohydrates or fats are present, the extent of oxidation is decreased. In the presence of carbamide, the oxidation of the fat or of the carbohydrate is also diminished. Oxidation, in all cases, increases with an increase in amount of alkali present. Treatment with alkali should prove of value in metabolic diseases. L. S. THEOBALD.

Phenylstearic acid. C. M. DE MILT (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925–1926, 4, 123–126).—Oleic acid and benzene, in presence of aluminium chloride, yield (?) κ -phenylstearic acid, b. p. 250°/4 mm., n^{23} 1·4905 (sodium, potassium, lead, m. p. 86°, and silver salts; methyl ester, b. p. 228°/ 4 mm., n^{23} 1·4840; amide; anilide, b. p. 282°/4 mm.). CHEMICAL ABSTRACTS.

Determination of small amounts of lactic acid. E. LEHNARTZ (Z. physiol. Chem., 1928, **179**, 1—8).— A few changes are recommended in the Hirsch-Kauffmann (A., 1925, i, 96) and Embden (A., 1925, i, 719) modifications of the von Fürth-Charnass method for the determination of lactic acid. The error is not more than 2%. The presence of trichloroacetic acid is detrimental.

J. H. BIRKINSHAW.

Catalytic studies on acetoacetic ester. F. O. RICE and J. J. SULLIVAN (J. Amer. Chem. Soc., 1928, 50, 3048—3055).—Distillation of ethyl acetoacetate at the ordinary temperature and 10⁻⁵ mm. pressure in

quartz or Pyrex, but not in soft glass vessels, yields fractions containing 30-40% of enol, the half-life period of which is about 500 hrs. These are approximately ten times as stable as any previously obtained. The effects of measured amounts of 11 catalysts on the velocity of transformation have been determined. The results are, in general, in accordance with previous work (cf. Meyer and Hopff, A., 1921, i, 391; Rumeau, A., 1924, i, 939), but no substance has been found capable of stabilising the product, both oxalic acid and phthalic anhydride being accelerators. Attempts to increase the stability by removing traces of water by means of silica gel or acetyl chloride were unsuccessful. The temperature coefficient of the rate of change, k_{35}/k_{25} , is 4.9 or 6.3, and the heat of activation 31,200 g.-cal. H. E. F. NOTTON.

Reduction of the secondary hydroxyl group in ricinoleic acid. F. SIGMUND and F. HAAS (Monatsh., 1928, 50, 357–368).—Reduction of ethyl ricinoleate by sodium and boiling amyl alcohol yielded not more than a trace of the expected glycol (μ -hydroxyoleyl alcohol). The product was essentially oleyl alcohol, characterised by conversion into the acetate and preparation of stearyl alcohol and stearyl acetate by catalytic reduction in presence of platinum-black. The reduction of the hydroxyl group not vicinal to the double linking is anomalous, but was found also to occur in the reduction of ricinoleic acid or its derivatives by hydrogen in presence of Löw's platinumblack (cf. also Grün and Woldenberg, A., 1909, i, 284; Grün and Czerny, A., 1926, 269).

Commercial ricinoleic acid was found to contain only 85% of free acid, and it was purified by heating with sodium hydroxide and separation of the barium salt. Reduction of the acid in acetic acid yielded stearic acid, or a mixture of ricinoleic and stearic acids when hydrogenation was incomplete. Similarly, methyl ricinoleate vielded methyl stearate under all conditions tried. The action of acetyl chloride on methyl ricinoleate yielded the acetyl derivative of about 84% purity, which could not be further purified without repeated fractionation. The hydrogenation of this crude acetyl derivative yielded impure methyl λ-acetoxystearate, b. p. 239-244° (corr.)/17 mm., from which λ -hydroxystearic acid was obtained by hydrolysis. *\lambda*-Hydroxystearic acid resisted catalytic hydrogenation, and in the reduction of ricinoleic acid the hydroxyl group must, therefore, be reduced before the double linking. R. K. CALLOW.

Second form of oxalic acid? A. E. TSCHIT-SCHIBABIN (J. pr. Chem., 1928, [ii], 120, 214—220; cf. Oberhauser and Hensinger, A., 1928, 505).—A theoretical paper in which the author's views concerning the existence of a *cis-trans* type of isomerism of oxalic acid (A., 1912, i, 149) are reviewed in the light of the reported isolation of an acid isomeric, but not identical, with oxalic acid by Wassilieff (A., 1902, i, 361) and other data from the literature.

J. W. BAKER. The C₄-saccharinic acids. IV. Preparation of $\beta\gamma$ -dihydroxybutyric acid. G. LEAVELL (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925—1926, 4, 99—104).—The γ -lactone of $\beta\gamma$ -dihydroxybutyric acid is prepared in 54% yield from glycerol, by way of the α -chlorohydrin and α -cyanohydrin. $\beta\gamma$ -Dihydroxybutyric acid phenylhydrazide has m. p. 109°. Reduction of the acid with sodium and alcohol gave a liquid, b. p. 188°, probably $\alpha\beta\delta$ -trihydroxybutane.

CHEMICAL ABSTRACTS.

Plant colouring matters. X. Crocetin and lycopin. P. KARRER, A. HELFENSTEIN, and R. WIDMER (Helv. Chim. Acta, 1928, **11**, 1201—1209).— α -Crocetin (1 mol.) is reduced by titanous chloride (2·3 mols.) to dihydro- α -crocetin ($\gamma\eta\lambda$ -trimethyl- $\Delta^{\beta\delta\zeta\theta\kappa\mu}$ tetradecahexaene- $\alpha\xi$ -dicarboxylic acid), m. p. 192—193° after previous sintering, yellow, which on exposure to air absorbs oxygen (16·75%), and on treatment with ozone gives malonic acid. When the reduction is carried out with a large excess of titanous chloride the product is hexahydro- α -crocetin, an almost colourless oil, reduced by hydrogen in presence of platinum-black and acetic acid to tetradecahydro- α -crocetin. Colour reactions of these crocetins with several reagents are given. Pure γ -crocetin (A., 1928, 869) has m. p. 199—200° (uncorr.).

Phosphorus pentabromide converts dihydrophytol (Willstätter and Mayer, A., 1908, i, 383) into $\gamma\eta\lambda \circ$ -tetramethylhexadecyl bromide, b. p. 185–188°/0.6 mm., which when treated with sodium in dry benzene yields a mixture of tetramethylhexadecene, b. p. 127°/0.11 mm., and the hydrocarbon

(CHMe₂·[$\check{C}H_{2}$ ·CH₂·CH₂·CHMe]₃·CH₂·CH₂·)₂, b. p. 240— 242°/0·3 mm. The former compound resembles phytene (Willstätter and Hocheder, A., 1907, i, 784), whilst the latter is similar to perhydrolycopin, C₄₀H₈₂, d⁴⁵₄ 0·8211, n⁵₁₅ 1·45837 (cf. A., 1928, 1016).

H. BURTON.

Preparation of potassium and sodium tetrabismuth tartrates. P. A. KOBER (J. Lab. Clin. Med., 1927, 12, 962—967).—Sodium and potassium tetrabismuth tartrates, obtained from alkaline tartrate solutions and bismuth hydroxide at a low temperature, are less toxic than other bismuth tartrates. The "tribismuth tartrates" are probably mixtures of di- and tetra-bismuth tartrates.

CHEMICAL ABSTRACTS.

Sulphopyrotartaric acids. III. H. J. BACKER and J. BUINING (Rec. trav. chim., 1928, 47, 1000-1010; cf. A., 1928, 46, 273).—Propane-ααβ-tricarboxylic acid is converted by heating with sulphur trioxide, fuming and concentrated sulphuric acids, and best with excess of chlorosulphonic acid into α-sulpho-β-methylsuccinic acid (+2 $\hat{H_2}$ O), m. p. 115- 120° (decomp.), isolated through its barium salt (+6 or $9H_2O$ [calcium salt (+7H₂O)]. Treatment of the acid with strychnine gives the strychnine hydrogen salt $(+4H_2O)$, which on decomposition with sodium hydroxide affords a neutral sodium salt, $[M]_{\rm D} + 19^{\circ}$ in water (tervalent ion rotation). The free acid from this has $[M]_{D} + 35^{\circ}$ in water (univalent ion rotation). Racemisation of the acid or its salts is not effected by heating at 100°. Ethyl sodiopropane-aaβ-tricarboxylate and ethyl chlorosulphonate afford ethyl a-chloropropane-aaβ-tricarboxylate, b. p. 160-168°/ 20 mm. The results now and previously obtained (loc. cit.) show that the addition of sulphite to itaconic, mesaconic, and citraconic acids does not give the same sulphomethylsuccinic acid (cf. Wieland, A., 1871, 132). The acid described by Andreasch (A., 1897, i,

327) is probably α -sulpho- β -methylsuccinic acid. The properties of the three isomeric sulphomethyl-succinic acids are appended. H. BURTON.

[X-Ray examination of highly-polymerised organic substances.] G. MIE and J. HENGSTEN-BERG (Helv. Chim. Acta, 1928, 11, 1052).—Polemical against Ott (A., 1928, 465). H. BURTON.

Highly-polymerised compounds. XI. [X-Ray examination of highly-polymerised organic substances.] H. STAUDINGER and R. SIGNER (Helv. Chim. Acta, 1928, 11, 1047-1051).--A criticism of Ott's conclusions (A., 1928, 465) regarding the structure of highly-polymerised polyoxymethylenc compounds. Ott's conclusions appear to be based on the erroneous assumption that the elementary cell contains one molecule. It is suggested that complex molecules may be larger than the elementary cell. A determination of the methoxyl and acetyl content of complex polyoxymethylene di-methyl ethers and acetates, $RO \cdot [CH_2 \cdot O]_n \cdot R$, indicates that n is on the average about 50. The physical properties of these compounds show that n is at least 20; the larger molecules must, therefore, have n = about 100. It appears that these highly-polymerised substances are not homogeneous, but are composed of molecules of varying length.

H. BURTON.

Action of metallic sodium on trimethylacetyl chloride. V. EGOROVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1199—1210).—The action of metallic sodium on trimethylacetyl chloride in moist ether gave, instead of the expected hydroxyketone, CMe₃·CO·CH(OH)·CMe₃, the diketone, CMe₃·CO·CO·CMe₃, b. p. 165—168°, together with some trimethylacetic ester of the hydroxyketone. m. p. 37°, and a trace of a *polymeride* of the diketone of high mol. wt., m. p. 180—181°. The formation of the diketone could not be due to oxidation, as it was obtained in the absence of air, and the hydroxyketone could not be oxidised to the diketone under the conditions of the experiment. When the diketone was treated with sodium, the hydroxyketone was obtained, together with some free trimethylacetic acid. Under the same conditions, benzil yielded only traces of benzoin and benzoic acid.

M. ZVEGINTZOV.

Sugars. J. MIKŠIC (Věstnik Král. Čes. Spol. Nauk., 1926, Cl. II, 18 pp.; Chem. Zentr., 1928, i, 2704—2705).—The following compounds of importance in sugar syntheses are described : rhamnohexonamide, m. p. 194°, $[\alpha]_D^{sp} -47\cdot26^\circ$, after 2 days unchanged, after 2 hrs. on the water-bath $-21\cdot48^\circ$; rhamnohexonic acid, m. p. 151° (ammonium salt; nitrile, m. p. 145°, $[\alpha]_D^{sp} -23\cdot47^\circ$). Mannoheptononitrile, CH₂OH·[CH·OH]₅·CN, m. p. 121—122°, $[\alpha]_D^{sp}$ +31·4 to +23·11° (final); mannoheptonamide, m. p. 188—189° (slow heating), 200° (rapid heating); ammonium mannoheptonate, m. p. 154°, $[\alpha]_D^{sp} +31\cdot31°$ to +7·22° (final). α -Penta-acetylglucose, m. p. 111·5— 112°, $[\alpha]_D^{sp} +101\cdot4°$; tetra-acetyl-d-gluconolactone, m. p. 103°, $[\alpha]_D^{sp} +13\cdot46°$. Acetylation of ammonium rhamnohexonate affords tetra-acetylrhamnohexonolactone, m. p. 128·5—129°, $[\alpha]_D^{sp} +9\cdot66°$. Hexaacetyl-a-rhamnohexonamide has m. p. 71-72°; penta-acetyl-a-rhamnohexononitrile, m. p. 85-86° [a]; +76.43°; hepta-acetyl-a-galaheptonamide, m. p. 125.5- 126° , $[\alpha]_{0}^{20} + 21.79^{\circ}$ to $+23.86^{\circ}$ (after 24 hrs.); hexaacetyl-a-mannoheptononitrile, m. p. 124.5-125°, [a] A. A. ELDRIDGE. $+31.45^{\circ}$.

Mechanism of oxidation of some carbohydrates and polyhydric alcohols by hydrogen peroxide with iron salts as catalyst in acid media. A. T. KUCHLIN and J. BÖESEKEN (Rec. trav. chim., 1928, 47, 1011—1026).—Oxidation of dextrose (1 mol.) with hydrogen peroxide (1 mol.) in presence of ferrous sulphate and a small amount of sulphuric acid proceeds more rapidly at 30° than at 0°, and glucosone is shown to be an intermediate product. Provided a low concentration of hydrogen peroxide is used, auto-decomposition is very small. With lævulose oxidation proceeds more quickly, the primary effect (cf. Wieland and Franke, A., 1927, 944) being much greater than for dextrose. When lævulose is oxidised in presence of ferric sulphate, reaction proceeds more slowly and the primary effect disappears; at the end of the reaction ferrous ions are present in solution. d-Arabinose is oxidised more slowly than either lævulose or dextrose. Erythritol is oxidised in presence of ferrous sulphate giving, in addition to acid products, an osone (isolated as impure disemicarbazone, m. p. 224°). The primary effect (maximum at about $p_{\rm H} 2 \cdot 2$) is much less in this case than for the sugars, and the amount of hydrogen peroxide reacted with at the beginning of the reaction is approximately equal to the amount of catalyst present.

Dihydroxyacetone osone (disemicarbazone, m. p. 221°) is oxidised by aqueous ferric chloride or sulphate. Increase of dilution causes a decrease in the initial velocity, which is not of the expected magnitude (in one case an increase was observed). This appears to be due to oxidation being effected by FeOH" or $Fe_2(OH)_2$ " ions, which are presumed to exist in relatively larger quantities at greater dilutions. Glucosone (shown to be formed by oxidation of dextrose and lævulose by copper acetate) is oxidised by ferric salts also.

The above experiments indicate that in the production of d-arabinose from dextrose, the reaction proceeds to a great extent through the intermediates glucosone and ketoglutonic acid. H. BURTON.

Determination of acetone groups in acetone [isopropylidene] sugars. H. ELSNER (Ber., 1928, 61, [B], 2364-2367).-The substance (50-100 mg.) is placed in a Claisen flask, the straight limb of which carries a narrow tube through which carbon dioxide is passed. The curved neck supports a tap funnel, which serves for the introduction of dilute sulphuric acid (4 c.c. of acid in 30 c.c. of water) and subsequently of 80 c.c. of water during the course of the distillation. The flask is connected by rubber stoppers to a condenser and receiver cooled in ice. The distillate is made up to 100 c.c. and 30 c.c. of N-potassium hydroxide are added. Simultaneously, a comparison solution containing a known weight of acetone, approximately equal to that expected, is prepared and similarly treated. The solutions are preserved in a closed flask for 13 hrs. until the ordinary temperature has been attained, after which equal quantities (about 40 c.c.) of 0.1N-iodine are added with brisk stirring. After exactly 4 min. the solutions are acidified with about 35 c.c. of N-sulphuric acid and excess of iodine is titrated with 0.1N-sodium thiosulphate.

H. WREN.

β-Arabinosan. H. VOGEL (Helv. Chim. Acta, 1928, 11, 1210–1213).—When α -arabinose is heated at 160°/15 mm. for 2 hrs. isomerisation into the β -form occurs, but after a further 2 hrs. β -l-arabinosan

O HO.CH HO.CH ____CH2

(annexed formula), m. p. 80-81°, [a]p HC $+60.5^{\circ}$ in water, is produced. This compound does not exhibit mutarotation; it reduces hot Fehling's solution, and is converted by boiling with water into arabinose. When it is

heated with a small amount of zine chloride at 150°/15 mm. for 1.5 hrs. diarabinosan, (C5H8O4)2, m. p. 153-155°, $[\alpha]_D$ +18.9° in water, is formed.

H. BURTON.

Transformations of β -pentabenzoyl-h-glucose. H. H. SCHLUBACH, F. TREFZ, and W. RAUCHEN-BERGER (Ber., 1928, 61, [B], 2368-2371; cf. A., 1927, 858).—β-Pentabenzoyl-h-glucose is converted by liquid hydrogen chloride or hydrogen bromide into halogenated derivatives of somewhat varying specific rotation. With hydrogen bromide in glacial acetic acid followed by treatment of the mixture with water and then of the solid product with silver carbonate and acetone, it gives *tetrabenzoyl*-h-glucose, $[\alpha]_{12}^{30}$ +5.15° to +4.96° in chloroform, +11.9° to +3.5° in alcohol, characterised by re-benzoylation to β-pentabenzoylh-glucose. The tetrabenzoyl compound is converted by silver oxide and methyl iodide into β -tetrabenzoylh-methylglucoside, (+MeOH), $[\alpha]_{\rm p}^{\rm so}$ -48.6° in chloroform, from which h-methylglucoside, $[\alpha]^{20} - 16.4^{\circ}$ in water, is prepared by means of methyl-alcoholic ammonia. H. WREN.

Derivatives of the benzylidenemethylglucosides. H. OHLE and K. SPENCKER (Ber., 1928, 61, [B], 2387-2392).-Mainly according to the work of Irvine and Scott (J.C.S., 1913, 103, 575) and Freudenberg, Toepffer, and Andersen, A., 1928, 1223), the constitution I or II is to be assigned to the benzylidenemethylglucosides.



The methylglucosides do not react with acetone in the presence of anhydrous copper sulphate, production of glucose dissopropylidene ether occurring only in the presence of mineral acid. The β -isomeride is affected by much lower concentrations of acid than the α -form. Glucose diisopropylidene ether in the presence of acetone and sulphuric acid under defined conditions is partly transformed into the mono-ether and a little free dextrose, but the furoid structure remains intact. If benzylidenemethylglucoside has the structure II, its partial conversion into glucose dissopropylidene ether or the hypothetical isopropylidenemethylglucoside under these conditions is to be expected, whereas this reaction cannot take place if it has the structure I, since the pyranoid α -methylglucoside remains unchanged. Experiment shows that benzylidene- α -methylglucoside is almost quantitatively converted into benzaldehyde and α -methylglucoside, thus establishing the constitution I.

The following new compounds are described: 2:3-dibenzoyl-4:6-benzylidenc- α -methyl-d-glucoside, m. p. 148°, [α]^b₀ +96·89° in chloroform, from benzylidene- α -methylglucoside and benzoyl chloride in pyridine, and the corresponding β -compound, m. p. 185°, [α]^b₀ +15·84° in chloroform; 2:3-di-p-toluenesulphonyl-4:6-benzylidene- α -methyl-d-glucoside, m. p. 149°, [α]^b₀ +66·5° in chloroform, and the corresponding β -compound, m. p. 158°, [α]^b₀ +54·70° in chloroform. H. WREN.

Formula of digitoxin. A. WINDAUS and G. STEIN.—See this vol., 71.

Constitution of solanine. G. ZEMPLÉN and A. GERECS (Ber., 1928, 61, [B], 2294-2300).-Solanine, $C_{44}H_{71}O_{15}N$, $[\alpha]_D - 59.45^\circ$ in pyridine, is converted by sodium acetate and acetic anhydride into tridecaacetylsolanine, (?) $C_{70}H_{97}O_{28}N$, m. p. 204–205° after softening at 190°, $[\alpha]_{10}^{\infty}$ –34.96° in alcohol, which is hydrolysed by hydrobromic and acetic acids in presence of chloroform to acetylated rhamnosidogalactose (sce later) and acetylated solanidineglucoside, m. p. 115-120° (decomp.), $[\alpha]_{B}^{\infty}$ -8.01° in alcohol, yielding on further hydrolysis solanidine and dextrose (identified as \$-penta-acetylglucose). The bromoacetyl compound of rhamnosidoglucose is hydrolysed to the free biose, which could not be caused to orystallise. Its nature is deduced from the observation that it is converted by iodometric oxidation into a rhamnosidogalactonic acid which yields large amounts of methylfurfuraldehyde when distilled with hydrochloric acid. In solanine, therefore, the solanidine residue is united to a trisaccharide; the sequence of monoses is dextrose-galactose-rhamnose, the dextrose being directly combined with the solanidine. Analyses of solanidine hydrochloride indicate the formula C28H41ON for solanidine, which agrees with the composition C44H71O15N for solanine. H. WREN.

Synthesis of the fundamental substance of inulin. H. H. SCHLUBACH and H. ELSNER (Ber., 1928, 61, [B], 2358-2363).-Treatment of lævulose with acetone and hydrochloric acid (cf. Irvine and Garrett, J.C.S., 1910, 97, 1282) yields a fructose dissopropylidene ether and a non-crystalline syrup. The yields of the latter are improved if the second treatment with acctone is effected in the presence of anhydrous copper sulphate, whereby the isomerising effect of the acid is avoided, and are then at a maximum when 2% of water is present in the acetone, whereas with 0-0.5% of water the disopropylidene ether is almost exclusively formed. By treatment with alcohol and ether, the syrupy product is caused to solidify; it contains only a small proportion of isopropylidene derivatives, which can be removed by further systematic treatment with alcohol and ether. The acetone-free solid has distinct reducing power even after treatment with yeast. It is separated by absolute alcohol into a fructose anhydride, $C_6H_{10}O_5$, $[\alpha]_{15}^{16} - 8.9^{\circ}$ in water, and a difructose, $C_{12}H_{22}O_{11}$, decomp. 198°, $[\alpha]_{15}^{16} - 25.5^{\circ}$ in water. Exhaustive methylation of fructose anhydride by the method of Haworth and Learner (A., 1928, 510) affords hexamethyldifructose anhydride, b. p. 150°/0·1 mm., $n_{\rm p}$ 1·4738, $[\alpha]_{15}^{16} + 31.1^{\circ}$ in chloroform, hydrolysed to a trimethylfructose, yielding a phenylosazone identical



$$\begin{array}{c} \begin{array}{c} OH \cdot CH \cdot CH (OH) \\ CH \end{array} \\ \hline \\ CH_2 \cdot OH \end{array} \\ \hline \\ CH_2 \cdot OH \end{array} \\ \begin{array}{c} CH_2 \cdot O \\ (IL.) \end{array} \\ \begin{array}{c} CH_2 \cdot O \\ OH \end{array} \\ \hline \\ OH OH \\ H \end{array} \\ \begin{array}{c} OH OH \\ H \end{array} \\ \hline \\ H W_{BEN} \end{array}$$

Constitution of highly polymerised substances. XIII. H. STAUDINGER (Ber., 1928, 61, [B], 2427— 2431).—A theorotical paper in which the structure of cellulose and caoutchoue is discussed in the light of the author's observations on polyoxymethylenes. Deductions as to the size of the molecule cannot be made from the size of the elementary cell, since the same structural principle can be repeated in a long molecule and thus a molecule may extend through many elementary cells. The soluble polyoxymethylene diacetates and dimethyl others, as well as the insoluble, highly polymerised polyoxymethylenes, have small elementary cells. The most convincing evidence of the highly polymerised nature of cellulose lies in the assumption that it is built on the same principle as the polyoxymethylenes. H. WREN.

Cellulose. K. H. MEYER and H. MARK (Ber., 1928, 61, [B], 2432—2436).—A reply to Hess and Trogus (A., 1928, 1225). A protest is raised against the manner in which the authors have applied röntgenographic methods to the elucidation of the cellulose problem. H. WREN.

Sulphuric esters of carbohydrates. E. GEBAUER-FÜLNEGG, W. H. STEVENS, and E. KRUG (Monatsh., 1928, 50, 324-327).-When cotton is treated with chlorosulphonic acid in the cold and kept for 24 hrs., hygroscopic crystals of chloroglucose tetrasulphate separate (cf. Claesson, A., 1879, 1033). If the reaction mixture is slowly added to acetic anhydride, a-penta-acetyl-d-glucose may be separated by treatment with brine or sodium acetate solution. The same product is obtained from dextrose by the same treatment. If, however, the reaction mixture from cotton or dextrose is added to acetyl chloride or bromide, *β*-acetochloroglucose is obtained, identified by conversion into penta-acetyl-d-glucose. Acetyl iodide is decomposed in this reaction. If the reaction between cotton and chlorosulphonic acid is stopped after 2 or 5 hrs., small quantities of octa-acetylcellobiose or tetra-acetylglucose, respectively, can be R. K. CALLOW. separated.

Compounds of hexamethylenetetramine with silver and other metal salts and the influence of anionic volume on the capacity for association by the central positive ion. P. RAY and J. DASGUPTA (J. Indian Chem. Soc., 1928, 5, 519–525). —Complex compounds of hexamethylenetetramine with the following silver salts are prepared in ammoniacal solution [in the following formulæ $B=(CH_2)_6N_4$]: 3AgCN,B; 2AgCNO,B; 2AgCNS,B; $AgClO_4,B$; Ag_2CrO_4,B ; $4Ag_2Cr_2O_7,5B,4H_2O$; $Ag_2MOO_4,2B,2H_2O$; $Ag_2WO_4,2B,H_2O$; $2Ag_2SO_4,3B,6H_2O$; $4Ag_2SO_4,5B,13H_2O$, and $AgSeO_4,2B,12H_2O$. The

compounds 3CuCN,2B and 3Cd(CN)2,B have also been prepared. The substances are usually readily soluble in ammonia and are decomposed by mineral acids, yielding formaldehyde, and by alkali hydroxides giving the metal oxide. When heated they decompose with charring and give characteristic amine odours. In the above silver salt complexes increase in anionic volume is accompanied by an increased capacity of association of neutral molecules by the silver cation. In the silver halide-hexamethylenetetramine complexes the capacity of silver for association diminishes in the order F, I, Br, Cl, an anomaly similar to that observed by Ephraim (A., 1918, ii, 313) for the corresponding ammines. Since cadmium and silver have almost the same atomic volume, the composition of the complexes is similar, but the results are not strictly comparable, as cadmium is bivalent. The smaller atomic volume of copper causes an increase in the associating power.

Silver tellurate, borate, iodate, phosphate, arsenite, and arsenate do not form compounds with hexamethylenetetramine, probably because of the insolubility of these salts, whilst silver sulphite, benzoate, and salicylate give indefinite crystalline substances.

H. BURTON.

Molecular compound between glycine anhydride and silver nitrate. T. ASAHINA (Z. physiol. Chem., 1928, 179, 83—87).—A molecular compound, $NO_3Ag < \binom{C_4H_6O_2N_2}{C_4H_6O_2N_2} > AgNO_3$, incipient decomp. 195°, is obtained when glycine anhydride and silver nitrate are mixed in concentrated aqueous solution. J. H. BIRKINSHAW.

Substituted butyrolactams. S. S. G. SIRCAR (J. Indian Chem. Soc., 1928, 5, 549—554).—Substituted glutaric anhydrides are converted by ammonia and sodium hydroxide into the corresponding sodium glutaramates, which, after treatment with potassium hypobromite and subsequent acidification,

afford the butyrolactams NH·CH₂·CRR'·CH₂·CO in 15—45% yield. These lactams are precipitated from aqueous solution by tannic and phosphotungstic acids, lead and mercuric acetates, and Meyer's and Dragendorff's reagents. With 3 : 5-dinitrobenzoyl chloride in alkaline solution they give deep violet colorations. The following are described : cyclohexanespirobutyrolactam, b. p. 180—181°/13 mm., m. p. 98° (benzoyl derivative, m. p. 138°; nitroso-derivative, m. p. 82°; mercurichloride, m. p. 158—160°); cyclopentanespirobutyrolactam, b. p. 164°/16 mm., m. p. 75° (benzoyl derivative, m. p. 70—71°; nitroso-derivative, m. p. 51—52°; mercurichloride, m. p. 135°); $\beta\beta$ -dimethylbutyrolactam, b. p. 146—147°/12 mm., m. p. 65—66° (benzoyl derivative, m. p. 69°; nitroso-derivative, m. p. 45°); β-methyl-β-ethylbutyrolactam, b. p. 150–152°/13 mm., m. p. 74–75°; ββ-diethylbutyrolactam, b. p. 163°/12 mm., m. p. 76–77° (mercurichloride, m. p. 130°); β-ethylbutyrolactam, b. p. 117–118°/13 mm., and β-methylbutyrolactam, b. p. 116°/15 mm. The lactam ring is more stable to alkali than the lactone, imide, or paraconic acid rings. H. BURTON.

Product from β -alanine ester of high mol. wt., composed of β -alanyl groups united by linkings of amide character. E. ABDERHALDEN and F. REICH (Z. physiol. Chem., 1928, 178, 169—172).— β -Alanine methyl ester, when kept for a few days, yielded a white, amorphous *solid*, insoluble in ether, decomp. 310°, reacting alkaline in aqueous solution. The ratio of amino-nitrogen to total nitrogen was 1:10, but the mol. wt. determined by depression of the f. p. of acetic acid corresponded with the condensation of only 5 molecules. Hydrolysis by boiling 25% aqueous sulphuric acid gave a quantitative yield of β -alanine. R. K. CALLOW.

Identity of the two possible isomeric methyl β -methyl- $\alpha\gamma$ -dicyanoglutaconates. ethvl URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 261-265).-Proof of the identity of the sodium compounds obtained by either condensation (A., 1928, 1356) is obtained by converting each specimen into the crystalline silver derivative by the action of aqueous silver nitrate and examination of their refractive indices. X-Ray spectra of either specimen obtained by the Debye-Scherrer method with the Ka molybdenum line are identical, the most intense line corresponding with a lattice distance 3.56 Å. Either specimen, or one obtained by mixed crystallisation of the two, gives the same refractive indices, elongation occurring in the direction of the optical elasticity axis X, n_1 (the refractive index for the faster wave) being equal to α , the value of α_D^{ay} being 1.503 ± 0.001 , and the zone of elongation being negative. Similar results were obtained with the silver derivative of dimethyl β-methyl-ay-dicyanoglutaconate, whilst the silver derivative of the diethyl ester elongates in the direction of the optical elasticity axis Z, the zone being positive and $\alpha_D^{27} = 1.580$. The results do not decide between the constitutions

C(CN)(CO₂Et):CMe·CNa(CN)·CO₂Me and

 $C(CN)(CO_2Me)$:CMe·CNa(CN)·CO₂Et, but the fact that the presence of a β -methyl group causes no change in the course of the condensation favours the mechanism given previously (*loc. cit.*).

Methyl ethoxyethylidenecyanoacetate, m. p. 76-77°, is described. J. W. BAKER.

Action of multivalent alcohols and phenols on arsenic compounds, especially arsenoacetic acid. B. ENGLUND (Svensk Kem. Tidskr., 1928, 40, 278— 285; cf. A., 1928, 1364).—Arsenious acid dissolves in warm ethylene glycol and in solutions of pentaerythritol in glacial acetic acid or pyridine, but no definite chemical compounds could be prepared from these solutions. The action of arsenoacetic acid on some forty organic hydroxy-compounds has been investigated by the following method, which is based on the slight solubility of the acid in glacial acetic acid and the ready solubility of the substance

together with arsenoacetic acid is introduced into a glass tube, and a known volume of acetic acid (containing about 1% of water) added. The tube is sealed and placed in a thermostat at 25°, where it is kept in rotation. After 24 hrs. 2 c.c. of the liquid are withdrawn and the dissolved arsenic is determined with 0.05N-potassium bromate solution. The extent to which interaction has taken place can be ascertained from the formula $L=(v-v_0)/80\div 1000g/MV$, in which v and $v_0 =$ final and initial titration in c.c., g =weight of substance, V = volume of acetic acid, and M =mol. wt. of substances. Where the compound produced contains 1 mol. of hydroxy-compound to one atom of arsenic, L has a maximum value of 1. If 2 mols. of hydroxy-compound are combined with one atom of arsenic, its maximum is 0.5. The value of L is practically constant over a wide range of concentrations, but in cases where L is greater than 0.4 it diminishes with increasing concentration. A marked effect takes place in the case of substances containing two hydroxy-groups on adjacent carbon atoms, compounds with a five-membered ring being formed. ay-Glycols and m- and p-dihydroxybenzene derivatives give a much less marked effect, showing the tendency to form six- and seven-membered rings to be relatively small. Stereoisomerides exhibit a marked difference in reactivity, and the insertion of substituted groups in the substance under investigation also has a pronounced effect. The equilibrium constants of a number of these reactions have also been determined, but although the results were satisfactory the method is laborious, and the values obtained are affected by factors which have little influence on the value of L. The method as described is accordingly recommended for use in determining the configuration of polyhydroxy-compounds, as it requires only simple apparatus, and it is easy to determine if a reaction has taken place, L then giving a H. F. HARWOOD. measure of its relative extent.

Iron cacodylate and the determination of cacodylic acid. O. J. NOSKOWA and V. A. TERE-CHINA (Arch. Pharm., 1928, 266, 599-602).-Pure ferric cacodylate was obtained by treating dialysed ferric hydroxide with six equivalents of cacodylic acid, evaporating to dryness at 50°, and extracting unchanged acid with chloroform. Numerous attempts to prepare this compound in a more direct way afforded only basic salts. Arsenic was determined satisfactorily by the method described by Rupp and Siebler (B., 1924, 614) after conversion into arsenic trisulphide and arsenic acid. Cacodylic acid is not removed quantitatively from toxicological specimens by extraction with chloroform-alcohol mixtures.

S. COFFEY.

Organic salts of telluric acid. F. R. GREEN-BAUM (Amer. J. Pharm., 1928, 100, 630-635).-The following salts of telluric acid are described : hexamethylenetetramine, $(CH_2)_6N_4, H_2TcO_4, 4H_2O$; c amide, $CON_2H_4, H_2TeO_4, 0.5H_2O$; thiocarbamide, carb-

 $CSN_2H_4, 4H_2TeO_4$; piperazine, $C_4H_{10}N_2, 2H_2TeO_4, 4H_2O$. The first two salts are soluble in water, the others in alkali only. H. BURTON.

Nomenclature of parent ring systems. A. M. PATTERSON (J. Amer. Chem. Soc., 1928, 50, 3074--

3087; cf. A., 1925, i, 824).-Existing systems of nomenclature are reviewed and the general principles involved in the framing of a logical and comprehensive system are discussed. Additional methods of naming the more complicated ring systems are proposed, for details of which the original should be consulted. H. E. F. NOTTON.

Highly-polymerised compounds. XIV. Constitution of dicyclopentadienes. H. STAUDINGER (Annalen, 1928, 467, 73-75).-A theoretical introduction (polemical against Diels and Alder, A., 1928, J. W. BAKER. 1018) to the following abstract.

Constitution of dicyclopentadienes. F. BERGEL and E. WIDMANN (Annalen, 1928, 476, 76-91).--Evidence is adduced which is considered to render untenable the structures suggested by Diels and Alder (A., 1928, 1018) for dicyclopentadiene derivatives, and to confirm the 1:2-addition structures suggested by Staudinger (A., 1926, 719). The interconversion of the two isomeric acids,

CH2---CH·CH·CO2H

CH₂·CH₂·CH·CH·CH₂·CO₂H ^(I), m. p. 200° (decomp.), and (II), m. p. 133.5°, obtained by the oxidation of ketotetrahydrodicyclopentadiene and dihydrodicyclopentadiene glycol respectively with nitric acid (Wieland and Bergel, A., 1926, 56), has been investig-ated by the method of Hückel and Goth (A., 1925, i, 402). Diazomethane converts I into its dimethyl ester, m. p. 72.5-73°, which by hydrolysis with methyl-alcoholic sodium methoxide yields a product, m. p. 170°, from which light petroleum (b. p. 90-115°) extracts an acid identical with II, leaving an acid, m. p. 178°, the methyl ester, b. p. 120°/15 mm., of which yields only resinous acids by a repetition of the hydrolysis. When similarly treated, II (best prepared in 70-80% yield by oxidation of dihydro-dicyclopentadiene with a slight excess of potassium permanganate in acetone) yields an oily dimethyl ester, b. p. 134°/13 mm., which with sodium methoxide yields only an unidentified substance, m. p. 110°. Oxidation of ketotetrahydrodicyclopentadiene with potassium permanganate in aqueous-alkaline suspension, instead of with nitric acid, yields an acid, m. p. 232° (not identical with I or II), the dimethyl ester, m. p. 77.5-78°, of which by hydrolytic rearrangement yields the acid of m. p. 178°. Mild hydration by boiling with very dilute hydrochloric acid converts tetrahydrodicyclopentadiene dioxide into the hygroscopic, syrupy glycol,

ÇH(OH)·CH2·CH·CH·CH2·CHOH (III), and keto-ĊH(OH)----ĊH·ĊH----ĊH·OH tetrahydrodicyclopentadiene oxide, m. p. 115° (obtained by oxidation of ketotetrahydrodicyclopentadiene with perbenzoic acid in chloroform), into the glycol, $CH(OH) \cdot CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH_2$ (1V). Oxidation of CH(OH) ----- $CH \cdot CH$ ----- COthese products and their parent substances under various conditions yields amorphous acids the composition of which agrees moderately well with that

of the expected tetracarboxylic acid. Catalytic reduction (platinum oxide in chloroform) of the monoand di-cyclopentadienebenzoquinones V and VI (Diels and others, loc. cit.; ef. Albrecht, A., 1906, i,





by heating above its m. p. the formulæ proposed by Diels are rejected and the structures given above suggested. J. W. BAKER.

X-Ray investigation of polymerised cyclopentadienes. J. HENGSTENBERG (Annalen, 1928, 467, 91-94).—Debye-Scherrer diagrams of tri-, tetra-, and poly-cyclopentadienes have been obtained and the distances between the planes for about 9 lines are tabulated. In every case the distance between the strongest reflecting planes is the same $(5\cdot3$ Å.). The largest values for tri- and tetra-cyclopentadienes are 7.7 and 10.5 Å., respectively, the difference, 2.8 Å., being the size of the cyclopentadiene ring without double linkings, whence the value 2.45 Å. is obtained for each of the other rings. By sublimation of tetracyclopentadiene small (0.1 mm.) laminæ are obtained from which by X-ray and optical examination it is deduced that the crystal is orthogonal and either hexagonal or pseudohexagonal. With an assumed unit cell and the known density, 1.23 g./c.c., it is found that the unit cell contains 2 molecules. Thus, although the tri-, tetra-, and poly-cyclopentadienes have different lattices, the molecules are all the same size (2.8 A.) in one direction, in agreement with the structures suggested by Staudinger. J. W. BAKER.

Chromium powder in organic synthesis. S. N. CHAKRABARTY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 513—518).—A 42% yield of diphenylmethane is obtained when a mixture of benzene, benzyl chloride, and chromium powder is heated for 3—4 hrs. The chromium powder can be used in typical Ullmann and Friedel-Crafts reactions, but only with reactive chloro-compounds. It cannot be employed in the Reformatsky reaction, and it has no effect on bromo- or iodo-compounds. Freshlypowdered chromium is more reactive than an old specimen, but reactivation is effected to a certain extent by heating it in a current of pure, dry hydrogen to a red heat. H. BURTON.

Titanium tetrachloride in organic synthesis. G. L. STADNIKOV and L. J. KASCHTANOV (J. Russ. Phys. Chem. Soc., 1927, 60, 1117—1122).—Benzene does not react with titanium tetrachloride even at the b. p., but reacts with others and esters, both aliphatic and aromatic. With benzyl ethyl ether, diphenylmethane, m. p. $25-26^{\circ}$, b. p. $259-261^{\circ}$, *p*-dibenzylbenzene, m. p. $85-86^{\circ}$, and *m*-dibenzylbenzene, m. p. $58-59^{\circ}$, were obtained. Oxidation with chromic anhydride yielded the corresponding diketones, m. p. $159 \cdot 5-160^{\circ}$ and 99° . Benzyl chloride gave the same products, the reactions going to completion in both cases. With benzoylchloride and subsequent treatment with alkali, a quantitative yield of benzoic acid only was obtained, the benzene distilling over unchanged. If thiophen was added, however, a yield of benzothiophenone, m. p. $55-56^{\circ}$ (oxime, m. p. $90-91^{\circ}$), was obtained. Diisoamyl ether did not react, whilst isoamyl acetate and isoamyl benzoate were hydrolysed to a slight extent. M. ZVEGINTZOV.

Benzene theory. H. LOEWEN (Z. Elektrochem., 1928, 34, 760—768).—Theoretical. It is considered that the most satisfactory benzene model is one in which six tetrahedra are grouped round a point in a plane, so that the apices of the tetrahedra lie alternately above and below the plane. This model will not explain the facts of enantiomorphism, but in all other respects is held to be in excellent agreement with the physical and chemical properties of benzene and the aromatic compounds. L. L. BIRCUMSHAW.

3: 4-Dichloronitrobenzene. L. MCMASTER and A. C. MAGILL (J. Amer. Chem. Soc., 1928, 50, 3038-3041).-3: 4-Dichloronitrobenzene (cf. Beilstein and Kurbatow, A., 1875, 450) is transformed by heating from 15° to 25° from a solid, m. p. 43° , to a liquid modification, equilibrium mixtures of the two forms being present at intermediate temperatures. It is converted by alcoholic potassium hydroxide into 3:3':4:4'-tetrachloroazoxybenzene and a little 2-chloro-4-nitrophenol and 3: 4-dichloroaniline. With sodium alkoxides in the boiling alcohols it yields the following ethers of 2-chloro-4-nitrophenol : ethyl, m. p. 142°; isopropyl, m. p. 128°, and n-butyl, m. p. 136°, which have been converted by reduction, diazotisation, and coupling with β -naphthol into red or purple dyes. H. E. F. NOTTON.

Constitution of the *m*-xylenesulphonic acids. J. POLLAK and F. VON MEISSNER (Monatsh., 1928, 50, 237—250).—Previous work on the *m*-xylenesulphonic acids is critically reviewed. In combination with the work now described, the results lead to the conclusion that the disulphonic acid (chloride, m. p. varying from 128° to 131°; amide, m. p. 248— 249°) obtained by direct sulphonation of *m*-xylene is the 4 : 6-disulphonic acid, whilst the disulphonic acid with a liquid chloride (amide, m. p. 223—224°) which accompanies the former in small quantity in the preparation by certain indirect methods is the 2 : 4-disulphonic acid. The recognition of the true 2 : 4-disulphonic acid has been obscured by its ready transformation during the preparation of the chloride into *m*-xylene-4 : 6-disulphonyl chloride.

The constitution of m-xylene-4: 6-disulphonic acid obtained by Wischin (A., 1891, 73) and, as the chloride, by Pollak and Lustig (A., 1924, i, 30) directly from m-xylene, is proved by its preparation from 6-amino-m-xylene-4-sulphonic acid by way of the diazo-compound (Pollak and Lustig, *loc. cit.*; Holleman and Choufoer, A., 1924, i, 1071) and also by the work of Pollak and Schadler (A., 1918, i, 497) and of Pollak and Rudich (A., 1923, i, 27). It is now also confirmed by the formation of 4: 6-dibromo-mxylene in small quantity by treatment of the acid with bromine in aqueous solution at 60°, and by the failure to brominate the chloride. When m-xylene-4:6-disulphonyl chloride was treated with bromine in ether at the ordinary temperature, the substance was recovered unchanged, accompanied only by a little 4:6-dibromo-m-xylene-2-sulphonyl chloride, formed possibly by displacement and migration of the sulphonic acid group, or, more probably, derived from *m*-xylene-2-sulphonyl chloride present as an impurity. Wischin's proof (loc. cit.) of the constitution by conversion into 2:4-dichloro- and 2:4-dihydroxy-m-xylene is vitiated by the drastic nature of the reactions. The preparation of the same acid by Pfannenstill (Diss., Lund, 1894) from both m-xylene-2- and m-xylene-4-sulphonic acid is to be explained by migration of the sulphonic acid group in the former case. The possibility of such a migration, already demonstrated by Moody (Proc. C.S., 1888, 77), is now confirmed by the separation of m-xylene-4-sulphonamide, m. p. 136-137°, as a byproduct in the preparation of m-xylene-2-sulphonamide, m. p. 112-113°, through the chloride, from the 2-sulphonic acid, even when the latter has been regenerated from the purified amide. m-Xylene-2sulphonic acid, of the constitution of which there is no doubt (cf. Moody, loc. cit.), was prepared by debromination of 4: 6-dibromo-m-xylene-2-sulphonic acid (Jacobsen and Weinberg, A., 1879, 61). It was also separated from the mother-liquors of the 4-sulphonic acid prepared by sulphonation of m-xylene by concentrated sulphuric acid at the ordinary temperature (Pollak and Lustig, loc. cit.). Further, Pfannenstill's liquid "2:5-disulphonyl chloride" (obtained solid, m. p. 85°, with difficulty) must be the 2:4-derivative, whilst his conclusion that the disulphonic acid which he prepared by way of the 6-amino-4-sulphonic acid was a new acid appears to be erroneous, since his supposed two series of compounds correspond closely in their properties, and he observed no mixed m. p. Wischin's preparation of a disulphonic acid by sulphonation of 6-bromo-mxylene and debromination was examined. 6-Bromom-xylene-2: 4-disulphonic acid yielded 6-bromo-mxylene (characterised as the 4-sulphonyl chloride) when heated with hydrochloric acid at 150°, and, therefore, no migration has occurred in the first reaction. Debromination yielded a material which gave a mixture of solid 4: 6- and liquid 2: 4-disulphonyl chlorides, which were separated and converted into the amides. m-Xylene-2: 4-disulphonyl chloride was prepared in best yield by treatment of sodium m-xylene-2-sulphonate with chlorosulphonic acid at 80-90° for 4 hrs., and elimination of the 4:6-derivative by crystallisation from ether. Reaction at 150° yielded the 4:6-derivative only. The 2:4-disulphonyl chloride yielded an amide, m. p. 223-224°, and its constitution was proved by converting it into 2:4-dibromo-m-xylene by bromination of the acid in aqueous solution at 70-80°. The occurrence of migration during preparation of the chloride was confirmed by treating the acid obtained from the

pure 2:4-disulphonamide with phosphorus pentachloride. Fractionation of the product yielded the 4:6-disulphonyl chloride. R. K. CALLOW.

So-called "liquid distyrene." R. STOERMER and H. KOOTZ (Ber., 1928, 61, [B], 2330—2336).— Benzylacetone, b. p. 235—236°, conveniently prepared by reduction of styryl methyl ketone by hydrogen in presence of palladised calcium carbonate, is converted by magnesium phenyl bromide into $\alpha\gamma$ -diphenyl-n-butan- γ -ol, b. p. 180—190°/12 mm., converted by boiling 20% sulphuric acid into $\alpha\gamma$ -diphenyl- Δ^{β} -butene, b. p. 169—170°/12 mm., $d_4^{\alpha\gamma}$ 6 1·0149 [nitrosochloride, m. p. about 126° (decomp.)]. The hydrocarbon is transformed by ozonisation into acetophenone and phenylacetaldehyde; with bromine it vigorously evolves hydrogen bromide, leaving only non-crystalline products. It is not isomerised by exposure to the light of a mercury-vapour lamp.

Treatment of a preserved specimen of "liquid distyrene" which had yielded two dibromides, m. p. 102° and 129°, respectively (Stoermer and Thier, A., 1926, 160), yielded acetophenone and phenylacetaldehyde, showing that the double linking had become displaced from the α - to the β -position. The supposition that the change is due to traces of sulphuric acid not removed from the product is in harmony with the observation that protracted treatment of cinnamic acid with boiling, moderately dilute sulphuric acid gives a similar hydrocarbon which, like the preserved specimen, does not give a solid dibromide, preserved specimen, does not give a solid dibromide, but vigorously evolves hydrogen bromide when treated with bromine. The same isomerisation is observed when pure "distyrene" (which yields a crystalline bromide), dissolved in carbon disulphide containing a trace of iodine, is exposed to sunlight. The pure distyrene is transformed by ozonisation into benzoic acid and β -phenylpropaldehyde and is therefore an diphenyl $\Delta \alpha$ but are Careful bromin therefore $\alpha\gamma$ -diphenyl- Δ^{α} -butene. Careful bromin-ation of the latter hydrocarbon affords a new dibromide, C₁₈H₁₆Br₂, m. p. 79°, in addition to the dibromides, m. p. 102° and 129°, described previously. Since aβ-dibromo-ay-diphenylbutane contains three asymmetric carbon atoms, its existence in four racemic forms is to be presumed, but only indications of the fourth isomeride are observed. The dibromide, m. p. 102°, is separated by crystallisation from light petroleum (instead of alcohol) into the dibromide, m. p. 129°, and a new *dibromide*, m. p. 122°, so that the compound of m. p. 102° should be deleted from the literature. Debromination of the three dibromides with zine affords in each case an unsaturated hydrocarbon of constant b. p. which is ozonised to benzaldehyde and β-phenylpropaldehyde and yields all three dibromides with bromine without evolution of hydrogen bromide. It appears that previous investigators have invariably used a distyrene contaminated with $\alpha\gamma$ -diphenyl- Δ^{β} -butene. Pure distyrene is colourless and non-fluorescent.

H. WREN.

Action of hydrogen iodide on tetraphenylbutinenediol. J. SALRIND and A. KRUGLOV (Ber., 1928, 61, [B], 2306–2312; cf. A., 1926, 1121).— $\alpha \alpha \delta \delta$ -Tetraphenyl- $\Delta \beta$ -butinene- $\alpha \delta$ -diol is converted by hot aqueous hydriodic acid (10–12%) mainly into

at 100-120° gives, in addition to monobenzylnaphthalenes (Roux, A., 1888, 1305; Dziewoński and Dziecielewski, A., 1928, 405), a viscous liquid from which have been isolated by fractional distillation 1 : 8-dibenzylnaphthalene (I), m. p. 146.5° (cf. Boguski, A., 1906, i, 825), " β "-dibenzylnaphthalene, m. p. 88° (*picrate*, m. p. 107°), and " γ "-dibenzylnaphthalene, m. p. 132°. Benzyl chloride and 1-benzylnaphthalene in presence of aluminium chloride at 100-120° give 15% of I, oxidised by boiling dilute nitric acid to 1:8-dibenzoylnaphthalene, m. p. 189-190° (bis-phenylhydrazone, m. p. 270-271°). Nitration of I in acetic acid solution at 80-90° with a mixture of nitric acid $(d \ 1.52)$ and sulphuric acid monohydrate gives the 4(?)-nitro-derivative, m. p. 141°, whilst sulphonation with chlorosulphonic acid in nitrobenzene solution at 100-110° affords 1:8-dibenzylnaphthalene-4(?)-sulphonic acid (sodium salt). When the initial reaction is carried out with an excess of naphthalene in presence of aluminium chloride a considerable amount of 2:2'-dinaphthyl is obtained. H. BURTON.

Phenyl-a- and -\beta-acenaphthylmethanes (5and β-benzylacenaphthenes). K. Dziewoński and K. LEONHARD (Bull. Acad. Polonaise, 1928, A, 99-110).-Benzyl chloride and acenaphthene react in presence of molten zinc chloride (cf. A., 1904, i, 390; 1926, 70), yielding 40% of 5-benzylacenaphthene (I), m. p. 110-111°, together with some β -(3 or 4)benzylacenaphthene (II), b. p. 260-265°/20 mm., m. p. 45-46° (dipicrate, m. p. 101-102°). Oxidation of I with sodium dichromate in boiling acetic acid solution gives 5-benzylacenaphthenequinone, m. p. 170° (monophenylhydrazone, m. p. 177-178°), together with 5-benzoylacenaphthenequinone, m. p. 199°, and small amounts of 4-benzyl- and 4-benzoyl-naphthalic acids (methyl esters, m. p. 120-121° and 130°, respectively). When the oxidation is carried out first at 40-50°, and then at 100°, a mixture of 5:5'-dibenzyl-, m. p. 318-320°, and 5:5'-dibenzoyl-diacendione (annexed formula), m. p. 305°, is produced. Nitration of I with 30% nitric



Nitration of I with 30% nitric acid at 25-30° affords 6-nitro-5-benzylacenaphthene, m. p. 144°, whilst pyrogenic decomposition 2 gives 5-benzylacenaphthylene, m. p.

104—105°. Oxidation of II with sodium dichromate in boiling acetic acid solution furnishes a *benzoylnaphthalic anhydride*, m. p. 199—200° (*phenylhydrazone*, m. p. 248°).

4-Benzoylnaphthalic anhydride (*phenylhydrazone*, m. p. 260°) condenses with resorcinol in presence of zinc chloride at 190°, forming 4-*benzoylnaphthfluor*escein, m. p. 160°. 4-*Benzylnaphthalic anhydride phenylhydrazone* has m. p. 236°. H. BURTON.

Perylene and its derivatives. XVII. A. ZINKE, A. DADIEU, K. FUNKE, and K. PONGRATZ (Monatsh., 1928, 50, 77—86).—If the products of chlorination of perylene, $C_{20}H_{11}Cl_9$ and $C_{20}H_9Cl_7$, previously described (A., 1928, 282) actually had those compositions, then reduction with amalgamated zinc and hydrochloric acid would be expected to yield monoand tri-chloroperylenes, respectively, since the nuclear halogen of 3 : 9-dichloroperylene is unaffected by this

the corresponding iodo-oxide, $3 \cdot iodo-2 : 2 : 5 : 5 \cdot tetra$ $phenyl-2 : 5 \cdot dihydrofuran, m. p. 139—140°, which$ does not contain a hydroxyl group and is oxidisedby permanganate in acetone to benzophenone, carbon $dioxide, and benzilic acid. In addition, <math>\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene, m. p. 235°, is obtained in small amount; the hydrocarbon is the main product when the glycol or furan is treated with a saturated solution of hydrogen iodide in water or acetic acid at 0°. It is oxidised to benzophenone and carbon dioxide and reduced to $\alpha\alpha\delta\delta$ -tetraphenyl-*n*-butane (cf. Brand, A., 1921, i, 783). Under more drastic conditions, the glycol, furan, or hydrocarbon is transformed into 1:10:10-triphenylbenzofulvene,

 $C_6H_4 < C(:CPh_2) > CH, m. p. 204-205^{\circ}$ (cf. Brand, loc. cit.), oxidised to benzophenone and o-benzoylbenzoic acid, and reduced in presence of spongy platinum to 1-phenyl-3-diphenylmethyldihydroindene, m. p. 135° (probably accompanied by a second form, m. p. 107°). Production of the fulvene is frequently accompanied by that of $\alpha\alpha\delta\delta$ -tetraphenyl- Δ^{ey} -butadiene. H. WREN.

1-Chloronaphthalene. III. Sulphonation. P. FERRERO and G. BOLLINGER (Helv. Chim. Acta, 1928, 11, 1144-1151).-A detailed investigation has been made of the sulphonation of 1-chloronaphthalene by concentrated sulphuric acid at 20-160°. 1-Chloronaphthalene-4-sulphonic acid is formed in all cases with a maximum yield of 70% at 56°, using 2 parts of concentrated acid and a small amount of sulphuric monohydrate. No acid 1-chloronaphthalene-5sulphonic acid was isolated in any experiment (cf. Armstrong and Wynne, Proc. C.S., 1890, 86), but at 160° some 1-chloronaphthalene-6-sulphonic acid was produced. In the experiments at 20-100° a small amount of an impure, apparently new chloronaphthalenesulphonic acid was isolated from the concentrated mother-liquors as its potassium salt. With chlorosulphonic acid at 30° 1-chloronaphthalene-4-sulphonyl chloride, m. p. 94°, is obtained (cf. Armstrong and Williamson, *ibid.*, 1886, 233; 1887, 145). Numerous salts of 1-chloronaphthalene-4- and

Numerous salts of 1-chloronaphthalene-4- and -5-sulphonic acids have been prepared, and the solubilities in water at 18° and 98° determined for the sodium, potassium, calcium, barium, and lead salt. H. BURTON.

Electrochemical oxidation of α -methylnaphthalene. F. FICHTER and S. HERSZBEIN (Helv. Chim. Acta, 1928, 11, 1264—1267).—Oxidation of 1-methylnaphthalene in presence of acetone and dilute sulphuric acid at a lead anode at 20° and a current density of 0.018 amp./cm.² gives, in addition to unchanged material (38.7%), resinous products (36.6%) and crystalline material (10.5%). This last fraction when crystallised from acetone affords 4 : 4'-dimethyl-1 : 1'. dinaphthyl, m. p. 147°, which on nitration yields a mixture of dinitro-derivatives and on bromination gives a dibromo-derivative, m. p. 243°.

H. BURTON.

peri-Dibenzylnaphthalene and two isomerides. K. DZIEWONSKI and J. MOSZEW (Bull. Acad. Polonaise, 1928, A, 283-291).—The action of benzyl chloride on naphthalene in presence of zinc chloride treatment. Reduction of the product $C_{20}H_{11}Cl_9$ yielded, however, a product which changed in composition on repeated recrystallisation, and was shown, by examination of the absorption spectrum, to consist of a mixture of perylene and 3 : 9-dichloroperylene, and the product $C_{20}H_{11}Cl_9$ is, therefore, probably a mixture of the compounds $C_{20}H_{12}Cl_{10}$ and $C_{20}H_{10}Cl_8$. The product $C_{20}H_9Cl_7$ yielded 3 : 9-dichloroperylene when reduced, and is, similarly, a mixture of the compounds $C_{20}H_8Cl_9$ and $C_{20}H_{10}Cl_6$.

The products of bromination of perylene (cf. A., 1925, i, 383) were further investigated. An attempt to prepare 3:10-dicyanoperylene from the impure 3:10-dibromoperylene was unsuccessful. Treatment of the product from the mother-liquors of the dibromocompounds with cuprous cyanide in quinoline yielded impure tricyanoperylene, converted into perylenetricarboxylic acid (sodium and pyridinium salts), the silver salt of which yielded with ethyl iodide the triethyl ester, m. p. 252° after sintering. Analogously to 3:9-dicyanoperylene (Pongratz, A., 1928, 177), tricyanoperylene yielded with hot concentrated sulphuric acid deep red crystals of 9:10-anhydrodicarboxyperylene-4-sulphon-3-carboxylimide.

R. K. CALLOW. Fluosilicates of organic bases. C. A. JACOBSON and H. A. H. PRAY (J. Amer. Chem. Soc., 1928, 50, 3055-3058).—Aniline and fluosilicic acid in alcohol yield aniline fluosilicate, (NH₂Ph)₂H₂SiF₆, which, when heated, sublimes and decomposes liberating silicon tetrafluoride. The characteristically crystalline methylaniline, o-toluidine, m-toluidine, and p-toluidine fluosilicates are prepared similarly.

H. E. F. NOTTON.

Chlorination of anilides. V. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFIELD and B. JONES.—See this vol., 34.

Nitration of o-bromoacetanilide. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 3092-3093).— Contrary to the statement of Franzen and Engel (A., 1921, i, 713), it is found that both mononitration products of o-bromoacetanilide are soluble in aqueousalcoholic potassium hydroxide; the 2-bromo-4-nitroacetanilide is, however, more easily hydrolysed and 2-bromo-4-nitroaniline separates on keeping. Treatment of the filtrate with glacial acetic acid gave 2-bromo-6-nitroacetanilide, from which 2-bromo-6nitroaniline, m. p. 74-75°, is obtained by hydrolysis with alcoholic hydrochloric acid. 2-Bromo-4-nitroaniline yields 2-bromo-4-nitroacetanilide, m. p. 132-133°, with acetyl chloride and acetic acid (cf. Chattaway, Orton, and Evans, A., 1901, i, 23; Körner, Atti R. Accad. Lincei, 1914, 22, i, 825). A. I. VOGEL.

Pentanitroaniline. B. FLÜRSCHEIM and E. L. HOLMES (J.C.S., 1928, 3041-3046).—Nitration of 3:5-dinitroaniline or of 3:5-dinitroacetanilide with a mixture of sulphuric and nitric acids yields *pentanitroaniline* containing 1 mol. of benzene of crystallisation, which is lost on exposure in a vacuum at the ordinary temperature to give *pentanitroaniline*, m. p. 192° (decomp.). The latter reacts with aqueous sodium acetate and acetone or with saturated sodium carbonate solution forming 2:4:6-trinitro-5-amino-

resorcinol, m. p. 236–237° (decomp.), which affords 2:4:6-trinitrophloroglucinol, m. p. 167°, with aqueous potassium hydroxide, whilst methyl and ethyl alcohol yield, respectively, 2:4:6-trinitro-5-aminoresorcinol dimethyl, m. p. 127.5°, and diethyl ether, m. p. 127.25–127.75°. With aqueous ammonia pentanitroaniline yields 2:4:6-trinitro-1:3:5-triaminobenzene, m. p. above 300°. A tetranitrodiacetamidophenol, $C_{10}H_{17}O_{11}N_5$, m. p. 147–147.5°, was produced on acetylation with acetic anhydride and a little sulphuric acid. These reactions prove that all the nitro-groups are in the nucleus. Tetranitroaniline is converted into tetranitroacetanilide, m. p. 169°, on acetylation under similar conditions. A. I. VOGEL.

Interaction of chlorosulphonic acid with substituted cyanoacetamides. K. G. NAIK and M. B. AMIN (J. Indian Chem. Soc., 1928, 5, 579-583).-When cyanoacetanilide is treated with chlorosulphonic acid in presence of salicylide-chloroform (Anschütz, A., 1893, i, 121), cyanoacetanilide-aa-disulphonic acid (+4H₂O), CN·C(SO₃H)₂·CO·NHPh, (I), is produced. Cyanoacet-p-toluidide- $(2H_2O)$, -o-toluidide- $(2H_2O)$, -m-toluidide- $(2H_2O)$, - α -naphthylamide- (H_2O) , - β naphthylamide- (H2O), -benzylamide- (2H2O), and -xylidide- (2H2O), -aa-disulphonic acids are prepared similarly. These compounds have no definite m. p. but char at about 260-280°. Treatment of I with bromine causes replacement of both sulphonic acid groups by the halogen. Cyanoacetamide does not react with chlorosulphonic acid, and the rate of sulphonation of the substituted cyanoacetamides appears to depend on the electronegative character of the groups attached to the methylene carbon H. BURTON. atom.

Absorption spectra of thiocarbamides. Constitution of thiocarbamide. H. RIVIER and J. BOREL (Helv. Chim. Acta, 1928, 11, 1219-1228).-Absorption spectra of 0.1-0.0001M aqueous and alcoholic solutions of thiocarbamide, trimethyl-, s- and iso-tetramethyl-, s-diphenyldimethyl-, isodiphenyldimethyl-, b. p. 175°/0.5 mm., m. p. 30° (picrate, m. p. 131°; from methyl iodide and methylthiocarbanilide), s-tetraphenyl-, isotetraphenyl-thiocarbamides, m. p. 70° (lit. 185°), and s- and iso-pentamethylthiobiurets have been measured between 232 and 580 µµ. The s-derivatives show more marked absorption than the iso-derivatives, but the curves for thiocarbamide, trimethyl- and isotetramethylthiocarbamides are almost identical. It is concluded that thiocarbamide does not contain the C.S group, and Werner's internal salt formula is favoured. It is possible that thiocarbamide exists in a different form in solution from that in the crystal (cf. Demény and Nitta, A., 1928, 819). H. BURTON.

Preparation and rearrangement of methylbenzhydryldichloroamine. A. McN. NEFF (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 141—149).—Hydrolysis of the product of heating methylbenzhydryldichloroamine with soda-lime at 200° afforded ammonia, aniline, and benzophenone, but not methylamine. Rearrangement experiments carried out below 150° indicate that the phenyl group is more easily removed from the CMePh₂- radical than the methyl group. An explanation is offered. CHEMICAL ABSTRACTS.

Preparation, rearrangement, and reduction of β -methylbenzhydrylhydroxylamine. M. E. MAVER (Abstr. Theses Univ. Chicago Sci. Ser., 1925— 1926 (1928), 4, 111—116).—Methylbenzylhydrylhydroxylamine, m. p. 112—113° (hydrochloride, m. p. 196°; chloroplatinate, decomp. 165°; benzoyl derivative, m. p. 183°), when heated with soda-lime at 230—250°, followed by hydrolysis, affords benzophenone and methylamine. It is concluded that only the methyl group migrated, a result which is not in accord with Neff's views (preceding abstract).

CHEMICAL ABSTRACTS. Rearrangement of stereoisomeric hydrazones. J. XANTHOPOULOS (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 195—201).—Isomeric p-bromobenzophenonehydrazones, α , m. p. 166—167°, β , m. p. 102·5—103·5°, were separated by means of chloroform and petroleum. The ketazine was obtained as by-product. Isomeric p-chlorobenzophenonehydrazones, α , m. p. 154—155°, β , m. p. 105— 106°, were separated by means of methyl alcohol, which dissolves the latter. The rearrangement of the four compounds when heated with zinc chloride was studied quantitatively; differences are due to the structural influence of the stereoisomerides. Two reactions are involved: CRR':N·NH₂=CR;N+ NH₂R'; CRR':N·NH₂=CR':N+NH₂R.

CHEMICAL ABSTRACTS. Substitution products of azobenzene. J. BURNS, H. MCCOMBIE, and H. A. SCARBOROUGH Substitution products (J.C.S., 1928, 2928-2936) .-- Nitration of 4-methylazobenzene, m. p. 72° (this and all other azobenzenes described in this paper were prepared by the condensation of nitrosobenzene with the appropriate amine), gives 4'-nitro-4-methylazobenzene, m. p. 183°; 3-methylazobenzene, b. p. 165°/15 mm., m. p. 18°, gives 4:4'-dinitro-3-methylazobenzene, m. p. 183°; and 2-methylazobenzene, b. p. 180°/20 mm., yields 4:4'-dinitro-2-methylazobenzene, m. p. 220°. Bromin-ation of 4-methylazobenzene yields 4'-bromo-4-methylazobenzene, m. p. 152°, and 3-methylazobenzene affords 4-bromo-3-methylazobenzene, m. p. 69°, but 2-methylazobenzene yields a substance, $C_{13}H_9NBr_3$ (?), m. p. 210°, which is not an azo-derivative. Nitration, chlorination, and bromination of 4-chloroazobenzene, m. p. 92°, yield respectively 4-chloro-4'-nitroazo-benzene, m. p. 169°, 4:4'-dichloroazobenzene, m. p. 188° (lit. 184°), and 4-chloro-4'-bromoazobenzene, m. p. 195°, whilst nitration and bromination of 3-chloroazobenzene, m. p. 68°, give 3-chloro-4'-nitroazobenzenc, m. p. 129°, and 3-chloro-4'-bromoazobenzene, m. p. 128°. 4-Methoxyazobenzene, m. p. 64°, when chlorinated, gives 3: 5-dichloro-4-methoxyazobenzene, m. p. 98°, whilst regulated bromination led to 3-bromo-4-methoxyazobenzene, m. p. 78°, and 3:4': 5-tribromo-4-methoxyazobenzene, m. p. 130°; nitration yielded 3: 4'-dinitro-4-methoxyazobenzene, m. p. 190°. Chlorination of 4-acetamidoazobenzene, m. p. 144°, gave 3-chloro-4-acetamidoazobenzene, m. p. 134° (3-chloro-4-aminoazobenzene, m. p. 99.5°), but attempts to introduce other substituents into the molecule failed. Bromination of 4-aminoazobenzene gave 3:5-dibromo-4-aminoazobenzene, m. p. 168°, but iodination and nitration were unsuccessful. The following are described: 4-bromomethylazobenzene, m. p. 115°, 4:4'-dichloroazoxybenzene, m. p. 157°; 2-bromo-4nitroanisole, m. p. 108°; 3:5-dichloro-4-hydroxyazobenzene, m. p. 116°; 2-chlorobenzidine, m. p. 113°; 3:5-dibromoazobenzene, m. p. 104°; 3:5-dibromohydrazobenzene, m. p. 114°; 2:6-dibromobenzidine, m. p. 185°. A. I. VOGEL.

Coupling reactions. J. POLLAK and E. GEBAUER-FÜLNEGG (Monatsh., 1928, 50, 310—323).—Previous work on the coupling of diazonium compounds with o-substituted phenols, particularly 1-substituted β -naphthols, is reviewed.

[With W. SPECHT and K. WINTER.]-Contrary to the statement of Wahl and Lantz (A., 1923, i, 209) and of Rowe and collaborators (A., 1926, 625), the coupling of diazotised p-nitroaniline with 1-bromoor 1-chloro-\$-naphthol does not immediately produce Para-red by displacement of the halogen atom. The substances formed are brown in colour and contain 85-90% of the amount of halogen calculated for the formula C₁₆H₁₀O₃N₂X (X=Br or Cl). The substances may be formed on cotton by the usual method, and the brown shades produced are stable except to alkali. The substances are decomposed when recrystallisation is attempted, and Para-red is prob-ably separated ultimately. Similar results are obtained with 1 : 6-dibromo- β -naphthol (on cotton only), 1-bromo-2-hydroxy-3-naphthoic acid, and 1-bromo-2-hydroxy-3-naphthanilide, m. p. 164° (prepared by bromination of 2-hydroxy-3-naphthanilide in acetic acid). The constitution of these products is uncertain, but it is possible that both diazo-oxides and β -naphthaquinone derivatives (Rowe, loc. cit.) are formed. 1-Nitro-β-naphthol yields an unstable product which decomposes at the ordinary temperature. No coupling takes place with nitroso- β -naphthol. 1-Methyl- β -naphthol couples readily (cf. Rowe, *loc.* 2:2' - Dihydroxy - 1:1' - dinaphthylmethane cit.). couples slowly with diazotised o-nitroaniline on cotton, giving a shade different from Para-red. In this and other cases the "abnormal" product of coupling seems to be stabilised on the fibre.

[With R. MICHEL and P. POLLAK.]—Diazotised amines couple with thiol derivatives to form unstable diazo-sulphides, e.g., $NO_2 \cdot C_6H_4 \cdot N: N \cdot S \cdot R$, exclusively. These substances lose their diazo-nitrogen completely on attempting to recrystallise them, but are stabilised on the fibre. The *diazo-sulphides* obtained by coupling diazotised *o*-nitroaniline, aniline, and sulphanilic acid with dithioresorcinol, and diazotised *p*-nitroaniline with 2: 4-dithiolphenol, 4: 6-dithiol-*m*-cresol, 2-thiolnaphthalene, and 1: 5-dithiolnaphthalene are described.

[With P. POLLAK and F. BECKER.]—1:5-Dithiolnaphthalene, m. p. 119° (Braun and Ebert, A., 1892, 1471, give 103°), is prepared by reduction of naphthalene-1:5-disulphonyl chloride by zinc dust and sulphuric acid, and separated by steam-distillation. The acetyl derivative, m. p. 187—189°, is obtained directly or by heating the disulphonyl chloride with zinc dust, acetic acid, acetic anhydride, and sodium acetate. The dibenzoyl derivative, m. p. 232°, and the *dimethyl ether*, m. p. 150°, are described. R. K. CALLOW.

Compounds of arylenediamines [with zinc chloride etc.]. IMPERIAL CHEM. INDUSTRIES and A. RILEY.—See B., 1928, 886.

Alkaline fusion of anthracenemonosulphonic acids. P. FERRERO and A. CONZETTI (Helv. Chim. Acta, 1928, 11, 1152—1159).—Anthracene- α - and - β sulphonic acids are obtained in 85% yield by reducing the anthraquinonesulphonic acids with zinc dust and ammonia. α -Anthrol is best obtained by fusing an alkali anthracenesulphonate with 3 parts of potassium hydroxide at 270° for 3 hrs. in a silver crucible (90% yield), or with 1 part of potassium or sodium hydroxides and 2 parts of water at 230° or 240° in an autoclave for 7 or 10 hrs., respectively. Optimum yields of β -anthrol are obtained with 3 parts of potassium or sodium hydroxides and 3 parts of water at 270° or 290° for 4 or 4.5 hrs. in an autoclave (95% yield), respectively. H. BURTON.

Organic acids and bases in non-aqueous solutions. IV. Phenols and amines. F. HÖLZL [with P. B. FIRCKS and M. MUCHITSCH] (Monatsh., 1928, 50, 291-309; cf. A., 1926, 1206; 1927, 310, 558).—The behaviour of (a) phenol, (b) pyrocatechol, (c) resorcinol, and (d) quinol towards organic bases in absolute alcoholic solution has been examined by conductivity measurements at 25° as in the previous investigations.

All compounds formed are largely dissociated by the action of the solvent, and, whilst the formation of a compound is easily shown, the ratios of the components are frequently determined with difficulty. The occurrence of maximum values of κ and of $\Delta = \kappa - (\kappa_s + \kappa_\beta - \kappa_\alpha)$ (where $\kappa, \kappa_s, \kappa_\beta$, and κ_α are, respectively, the conductivities of the mixture, phenol, base, and alcohol) must be interpreted with due regard to the greater effect of the more highly dissociated basic component in repressing dissociation of the compound by the solvent, so that maxima corresponding with a compound tend to be displaced towards the basic side.

The compounds formed with (a), (b), (c), and (d)are as follows (A=1 mol. of phenol, B=1 mol. of base): ammonia: with (a), A_2B ; with (b), (c), and (d), AB; ethylamine: with (b), (c), and (d), AB; diethylamine: with (a), A_2B ; with (b), (c), and (d), AB; trimethylamine: with (a), A_2B ; with (b), AB; with (c) and (d), A_2B ; ethylenediamine : with (a), A_2B ; with (b), AB; with (c) and (d), A_2B ; benzylamine: with (a), (b), (c), and (d), AB; aniline: with (a), (b), (c), and (d), AB; p-toluidine: with (b), none; with (d), AB; o- and m-phenylenediamine : with (a), (b), (c), and (d), none; p-phenylenediamine: with (a), none; with (b), (c), and (d), AB. The occurrence of other, more highly dissociated, compounds may be assumed in many cases. The exceptional behaviour of trimethylamine with resorcinol and quinol is analogous to the behaviour with dicarboxylic acids. R. K. CALLOW.

Phenol- and cresol-sulphonyl chlorides. E. RIESZ, F. BERNDT, and G. HITSCHMANN (Monatsh., 1928, 50, 328-334).—The phenol- and cresol-sulphonyl chlorides previously prepared (Pollak, Gebauer-Fülnegg, and Riesz, A., 1926, 514) have been converted into sulphonanilides and, by the action of phosphorus pentachloride and a trace of phosphoryl chloride at $120-140^{\circ}$, into the corresponding chlorobenzene- and chlorotoluene-sulphonyl chlorides, with the exception of *p*-cresol-3:5-disulphonyl chloride, which reacts anomalously. Additional proof of the constitution of the phenol- and cresol-sulphonyl chlorides is thus obtained, and, in particular, the alternative formula for the trisulphonyl chlorides, in which the third group is attached to oxygen, already disproved by the preparation of trithiol derivatives (Pollak and Riesz, this vol., 60), is finally ruled out.

Phenol-2: 4-disulphonyl chloride yields the -disulphonanilide, m. p. 205°, and chlorobenzene-2: 4disulphonyl chloride. Phenol-2: 4: 6-trisulphonyl chloride yields the trisulphonanilide, m. p. 247°, and chlorobenzene-2: 4: 6-trisulphonyl chloride (cf. Davies and Wood, A., 1928, 746). o-Cresol-3: 5-disulphonyl chloride yields the disulphonanilide, m. p. 154°, and 2-chlorotoluene-3: 5-disulphonyl chloride, m. p. 78° [disulphonanilide, m. p. 183° (Wynne and Bruce, J.C.S., 1898, 73, 731, give 85° and 183°)]. m-Cresol-4: 6-disulphonyl chloride yields the disulphonanilide, m. p. 185°, and 3-chlorotoluene-4: 6disulphonyl chloride, m. p. 125°. m-Cresol-2: 4: 6trisulphonyl chloride, m. p. 125°. m-Cresol-2: 4: 6trisulphonyl chloride yields the trisulphonanilide, m. p. 235°, and 3-chlorotoluene-2: 4: 6-trisulphonyl chloride, m. p. 161°. Tolylene-3: 4-sulphonylide 6: 6'-disulphonyl chloride yields, with ammonium carbonate and ammonia, the disulphonamide, decomp. 300°, whilst when heated with aniline the sulphonylide ring is opened to give m-cresol-4: 6-disulphonylide ring is opened to give m-cresol-4: 6-disulphonylide ring is opened to give m-cresol-4: 6-disulphonanilide. p-Cresol-3: 5-disulphonyl chloride yields the disulphonanilide, m. p. 129° (Anschütz and Cürten, A., 1927, 1183, give 231°; cf. following abstract), and, with phosphorus pentachloride, (?) 3: 4: 5-trichlorobenzylidene chloride, m. p. 196°, which isomerised on keeping to esopentachlorotoluene, m. p. 218°. R. K. CALLOW.

Constitution of cresoldisulphonyl chlorides. E. RIESZ and F. PILPEL (Monatsh., 1928, 50, 335-340).-The constitutions of the cresoldisulphonyl chlorides previously described (Pollak, Gebauer-Fülnegg, and Riesz, A., 1926, 514; cf. preceding abstract) have now been verified. When o-cresol-3:5-disulphonyl chloride is hydrolysed by heating with 30% alcohol and heated with 2N-nitric acid, 3:5-dinitro-o-cresol is obtained. m-Cresol-4:6-disulphonyl chloride under the same conditions yields . 2:4:6-trinitro-m-cresol, but nitration with fuming nitric acid gives 2-nitro-m-cresol-4: 6-disulphonyl chloride, m. p. 183° [disulphonanilide, m. p. 212-215° (decomp.)], converted by heating with hydrochloric acid at 160° into 2-nitro-m-cresol, b. p. 60-68°/0.5 mm., m. p. 36°. Nitration in the 2-position is explicable only on the assumption that the sulphonyl chloride groups are initially in positions 4 and 6. p-Cresol-3: 5-disulphonyl chloride yields on hydrolysis the disulphonic acid, m. p. 115° (Anschütz and Cürten, A., 1927, 1183), converted by successive treatment with acetic anhydride and phosphorus

pentachloride into acetyl-*p*-cresol-3: 5-disulphonyl chloride, m. p. 121°, and m. p. 116° when mixed with the substance prepared by the method of Anschütz and Hodenius (A., 1918, i, 425) and Anschütz and Cürten (loc. cit.). The same acetate is obtained directly from *p*-cresol-3: 5-disulphonyl chloride. When heated with aniline it yields *p*-cresol-3: 5-disulphonanilide, m. p. 129° (cf. preceding abstract) (acetyl derivative, m. p. 105—110°). The constitution of *p*-cresol-3: 5-disulphonyl chloride is sufficiently proved by its conversion into 3: 5-dinitro-*p*-cresol by the usual method, and the m. p. 231° observed by Anschütz and Cürten for the disulphonanilide is unexplained. R. K. CALLOW.

Oxidation products of 4:4'-dichloro-2:2'-dinitrodiphenyl sulphide and disulphide. E. RIESZ [with A. LORENZ, C. MYSCHALOV, and O. STRAKOSCH] (Monatsh., 1928, 50, 263-268).-Oxidation of 4:4'-dichloro-2:2'-dinitrodiphenyl sulphide (Beilstein and Kurbatow, A., 1879, 230) by fuming nitric acid at 150° yielded the sulphoxide, m. p. 236°. Further oxidation of the sulphoxide by the same method yielded the sulphone, m. p. 176° , identical with the by-product of oxidation of 4:4'-dichloro-2: 2'-dinitrodiphenyl disulphide obtained by Blanksma (A., 1901, i, 460). The low m. p. of the sulphone and its decomposition by alcoholic alkali are anomalous. Treatment of the sulphide with chlorine in chloroform or acetic acid yielded the sulphoxide. Whilst treatment of the disulphide with chlorine in chloroform yields 4-chloro-2-nitro-1-chlorothiolbenz-ene (Zincke, A., 1918, i, 537), in acetic acid 4-chloro-2-nitrophenylsulphonyl chloride (sulphonanilide, 2-intropnenyisulphonyl chloride (sulphonanilide, m. p. 138°; sulphonamide, m. p. 164°) was obtained. The reaction of hydrogeless The reaction of hydrazobenzene with the sulphonyl chloride in equimolecular proportions yielded benzidine hydrochloride, azobenzene, 4-chloro-2-nitrobenz-enesulphinic acid, m. p. 108° (lit. 127°), and un-changed sulphonyl chloride. The intermediate formation of a compound of the type NR'(SO₂R)·NHR' is assumed in this and the analogous reaction with 4-chloro-2-nitro-1-chlorothiolbenzene (Gebauer-Fülnegg and Riesz, A., 1928, 168). R. K. CALLOW.

cycloHexanediols. I. cis- and trans-Quinitols. Separation and properties. L. PALFRAY and B. ROTHSTEIN (Bull. Soc. chim., 1928, [iv], 43, 1122-1131).-Separation of the cis- and trans-quinitols with a mixture of acetone and butyl alcohol gives unsatisfactory results, but separation is readily effected with acetone alone (cf. Willstätter and Lessing, A., 1901, i, 265) using a centrifuge, the trans-isomeride separating first. In acetone at 16° the solubility of the trans-isomeride is 1.91 g. per 100 c.c., of the cisisomeride, 5.61; in commercial acetone, containing 3% of water, the corresponding values at 17.5° are 2.76 and 5.91. In either case the ratio of the solubilities varies inversely with the temperature and accordingly separation is more efficient at low temperatures. trans-Quinitol has m. p. 139° (cf. Baeyer, A., 1894, i, 174), and its phenylurethane, m. p. 262°; cis-quinitol has m. p. 102° (cis-phenylurethane, m. p. 188°). Crystallographic measurements are recorded for the four compounds. Mixtures of the quinitols containing 0-64% of the trans-isomeride have m. p. between

99.4° and 102°, and such mixtures can be approximately analysed by separation with acetone and m.-p. determinations on the three fractions, referred to the fusion curve. In this way quinitol prepared by Senderens and Aboulenc's method (A., 1922, i, 136) at 133° is found to contain 48-50% of *trans*-isomeride and 53-55% at 200°, temperature thus only slightly affecting the proportion of *trans*-isomeride. It is probable therefore that the quinitol, m. p. 102°, obtained by Sabatier and Mailhe (A., 1908, i, 529) was not the pure *cis*-isomeride but a mixture rich in the *trans*-form. R. BRIGHTMAN.

Aromatic allyl and propenyl compounds. II. Geometrical isomerism of isosafrole. H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1928, 47, 1027—1036).—The $cis(\alpha)$ -isosafrole obtained by the action of alcoholic potassium hydroxide on safrole (Nagai, A., 1921, i, 857; cf. Hoering and Baum, A., 1909, i, 788) is shown to be a mixture of safrole (43%) and $trans(\beta)$ -isosafrole. The safrole is determined through its mercuriacetate compound, or the mixture is analysed by the authors' iodine addition method (A., 1928, 999). H. BURTON.

Hydroxythiophenols. I. J. POLLAK and E. RIESZ (Monatsh., 1928, 50, 251-262).—Thiol derivatives of the three cresols and of resorcinol have been prepared by reduction of the corresponding sulphonyl chlorides (A., 1926, 514, 832).

[With R. FEIKS.]-o-Cresol-3: 5-disulphonyl chloride is reduced in acetone solution with zinc and 50% sulphuric acid, and the product, 3: 5-dithiol-o-cresol, m. p. 51°, separated by steam-distillation. The triacetyl derivative, an oil, is prepared by combined reduction and acetylation of the disulphonyl chloride by the action of zinc, acetic anhydride, sodium acetate, and acetic acid. The tribenzoyl derivative, m. p. 96° and dipicryl derivative, decomp. on heating, were also prepared. The latter yields a phenoxthene derivative with alcoholic potassium hydroxide. m-Cresol-4:6-disulphonyl chloride yields, similarly, 4:6-dithiol-m-cresol, m. p. 69° (derivatives : triacetyl, m. p. 56°; tribenzoyl, m. p. 120°; dipicryl, decomp. when heated). In this case treatment of the dipicryl derivative with alcoholic potassium hydroxide yields 2:4:2':4' - tetranitro - 7:7' - dimethyldibenzophenox thene-6 : 6'-disulphide (I), reduced by sodium sulphide



and alkali to a vat which dyes cotton a reddishbrown. *m*-Cresol-2:4:6-trisulphonyl chloride yields 2:4:6-trithiol-m-cresol, m. p. $35-36^{\circ}$ (tetra-acetyl derivative, m. p. 76°).

[With F. PILPEL.] — $p \cdot \text{Cresol} \cdot 3:5 \cdot \text{disulphonyl}$ chloride yields $3:5 \cdot \text{dithiol-p-cresol}$, m. p. 48° (derivatives: triacetyl, m. p. 98° ; tribenzoyl, m. p. 138° ; dipicryl, decomp. 109° ; trimethyl ether, m. p. 77° ; phenoxthene disulphide). By condensation with sodium monochloroacetate, $3:5 \cdot \text{di}(\text{carboxymethyl-thiol})$ -p-cresol, m. p. 139° , was prepared.

[With W. FRANKFURTHER.]—Resorcinol-4: 6-disulphonyl chloride yields 4: 6-dithioresorcinol as an oil, sparingly volatile in steam, isolated as the *lead* salt, $C_6H_4O_9S_2Pb$ [derivatives: tetramethyl ether, m. p. 83-86° (cf. A., 1915, i, 529); tetra-acetyl, m. p. 136-138°; di(carboxymethyl), m. p. 174; tetracarbethoxy-, m. p. 81°; dipicryl, decomp. on heating:



phenoxthene derivative (II), decomp. above 280°). Resorcinol-2:4:6-trisulphonyl chloride yields the very readily oxidised 2:4:6-trithiolresorcinol, isolated as the lead salt, $(C_6H_3O_2S_3)_2Pb_3$ (penta-acetyl derivative, m. p. 105—110°). R. K. CALLOW.

Manufacture of phenylthioglycollic acids containing halogen and alkyl groups in the nucleus. I. G. FARBENIND. A.-G.—See B., 1928, 921.

Mechanism of Salkovsky's colour reaction with cholesterol. V. J. NIKOLAEV and S. A. KRASTELEVSKAJA (J. Russ. Phys. Chem. Soc., 1928, 60, 1211—1216).—Cholesterol in chloroform solution gives with sulphuric acid an orange or red colour, depending on the concentration. When a solution of cholesterol in dry chloroform solution is treated with sulphuric acid and evaporated in a vacuum, ruby-red crystals of cholesterol sulphate, m. p. 160°. are obtained. The m.-p. diagrams of the system cholesterol-sulphuric acid also indicated the formation of an equimolecular compound, m. p. 160°. The colour reaction is due to the undissociated red cholesterol sulphate; moisture causes first dissociation into colourless ions, followed by hydrolysis, with fading of the colour, which returns on drying.

M. ZVEGINTZOV.

Yeast ergosterol. III. F. REINDEL (Annalen, 1928, 466, 131—147). [With H. WASENEGGER.]— Oxidation of α -ergostenol (A., 1928, 295) in acetic acid solution at 70° with chromic oxide gives α -ergostenone (I), m. p. 131—133°, $[\alpha]_p$ +38.8° in chloroform [phenylhydrazone, m. p. 127—128° (decomp.); oxime; ketazine, m. p. 225° (decomp.); benzylidene derivative, m. p. 162°], together with a small amount of a neutral compound, C₂₆H₄₂O₃, m. p. 219—221°. Catalytic reduction of I regenerates α -ergostenol [benzoyl derivative, m. p. 118—120° (cf. A., 1927, 241)], indicating that the ethylenic linking in I is not $\alpha\beta$ - to the keto-group. When a chloroform solution of I is treated with hydrogen chloride, β -ergostenone, m. p. 149—151°, $[\alpha]_p$ +37·1° in chloroform (oxime, m. p. 214—216°), is produced. This ketone does not give a benzylidene derivative, suggesting that isomerisation is of the type ·CO·CH₂·C:CH· —> ·CO·CH·C·CH₂·.

[With A. DETZEL.]—Oxidation of allo- α -ergostanol in acetic acid solution at 90° with chromic oxide gives, in addition to allo- α -ergostanone (34%), an acid, C₂₅H₄₄(CO₂H)₂, m. p. 217—219°, $[\alpha]_{\rm p}$ +22·8° in chloroform (26%: methyl ester, m. p. 81—83°), which when heated at 260—265° yields a cyclic ketone, C₂₆H₄₄O, m. p. 125—126°, $[\alpha]_{\rm p}$ +107·7° in chloroform (oxime, m. p. 215—216°). Catalytic reduction of allo- α -ergostanone gives allo- α -ergostanol together with an isomeric sterol. m. p. 206—207°, $[\alpha]_{\rm p}$ +4·04°

in chloroform, not precipitable by digitonin, and having no antirachitic action even when irradiated. The *acetate*. m. p. $144-145^{\circ}$, of this new sterol is not identical with *allo-a*-ergostanyl acetate, m. p. $144-145^{\circ}$.

145°. [With A. FRÖHLICH.]—When a solution of ergosterol in hexahydrotoluene is shaken with potassium permanganate solution at the ordinary temperature, a small amount of an acid, b. p. 187°, resembling *n*-valeric acid, and a neutral compound (II), $C_{26}H_{42|07|40|}O_4$, m. p. 199—201°, $[\alpha]_D -24\cdot4°$ in chloroform (diacetate, m. p. 148—152°, $[\alpha]_D +5\cdot46°$ in chloroform), are produced. This compound contains three active hydrogen atoms, and when its di *p*-nitrobenzoate, m. p. 197° (decomp.), is hydrolysed with 5% alcoholic potassium hydroxide a compound (III), $C_{26}H_{40(38)}O_3$, m. p. 217—218°, is obtained. Catalytic reduction of II yields a compound, $C_{26}H_{44(42)}O_3$, m. p. 235—238° [di-p-nitrobenzoate, m. p. 242° (decomp.)], formed by absorption of 3 mols. of hydrogen and subsequent climination of water. When III is reduced catalytically 4 mols. of hydrogen are absorbed, and a substance, m. p.

131–132°, results. Analogous oxidation of ergosteryl acetate gives the substance, $C_{27}H_{41}O_4Ac$, m. p. 174–175°.

H. BURTON.

p-Methoxycinnamyl alcohol. P. KARRER (Helv. Chim. Acta, 1928, **11**, 1209).—The alcohol has m. p. 79—80° (cf. A., 1922, i, 825). H. BURTON.

Thiophenols. XII. Triphenylmethane series. K. BRAND and H. PABST (J. pr. Chem., 1928, [ii], 120, 199-213).-The synthesis of various 2-methoxy-5-chlorotriphenylcarbinols has been effected and the stability of their salts compared with that of the corresponding 2-methoxy-, 2-thiol-, and their 5-chloroderivatives. 4-Chloro-o-anisidine is converted by the appropriate Sandmeyer reaction into 4-chloro-2-bromoanisole (I), m. p. 29–30°, b. p. 127–130°/12 mm., d_4^{30} 1.6170, n_D^{201} 1.58592 (yield 65%), and 4-chloro-2-cyanoanisole, m. p. 99° (yield 65%), and hydroxyile is hydrolysed by dilute alcoholic potassium hydroxide to 5-chloro-2-methoxybenzoic acid, the methyl ester (II), b. p. 235-240°, of which is also obtained by the action of methyl sulphate on 5-chlorosalicylic acid. By the action of magnesium 5-chloroo-anisyl bromide (from I) on benzophenone is obtained 5-chloro-2-methoxytriphenylcarbinol, m. p. 124° (yield 50-60%), which is converted by zinc dust and acetic acid or alcohol and anhydrous hydrogen chloride into 5-chloro-2-methoxytriphenylmethane, m. p. 120°. The action of the same Grignard reagent on ethyl benzoate furnishes 5:5'-dichloro-2:2'-dimethoxytriphenylcarbinol, m. p. 190° (yield 60-70%), similarly reduced to 5:5'-dichloro-2:2'-dimethoxytriphenylmethane, m. p. 144-145°, whilst from II is obtained 5:5':5''-trichloro-2:2':2''-trimethoxytriphenylcarbinol, m. p. 165°, converted into the corre-sponding methane, m. p. 212°. The colours of these carbinols and of the corresponding 2-methoxy-. 2-methylthiol, and their 5-chloro-derivatives in a mixture of acetic and sulphuric acids and in liquid sulphur dioxide are tabulated, and the stability of the various carbonium sulphates and perchlorates is

determined by the method of Bacyer and Villiger (A., 1902, i, 769). The stability of the 2-methoxytriphenylcarbonium salts to hydrolysis is greater, but that of the 5-chloro-2-methoxy-derivatives is less, than that of the parent triphenylcarbonium salts. In general the introduction of a methoxy- (and, to a smaller extent, a methylthiol) group in the 2-position increases the stability, whilst the presence of chlorine in the 5-positions decreases it to a value less than that of the unsubstituted derivatives themselves, with the exception that the 5:5'-dichloro-2:2'-dimethoxycompound has the lowest and the 5:5':5"-trichloro-2:2': 2''-trimethoxy-compound the greatest stability of this group of derivatives (cf. Brand and Groebe, A., 1925, i, 397). J. W. BAKER.

Preparation of compounds of the type of malachite-green and of phenolphthalein by means of the Grignard reaction. J. S. CHAMBER-LAIN and M. F. DULL (J. Amer. Chem. Soc., 1928, 50, 3088—3092).—Michler's ketone and magnesium p-dimethylaminophenyl bromide (cf. Baeyer and Villiger, A., 1903, i, 811; Sachs and Ehrlich, A., 1904, i, 196) yield pp'p'' - hexamethyltriaminotriphenylcarbinol (crystal-violet). Magnesium p-carboxyphenyl bromide was obtained in sufficient quantity to form with Michler's ketone a trace of pp'-tetramethyldiaminop''-carboxytriphenylcarbinol (chrome-green). Benzoylbenzoic acid and 2 mols. of magnesium phenyl bromide afford diphenylphthalide (cf. Ostersetzer, A., 1913, i, 729). H. E. F. NOTTON.

Constitution of isocampholic acid. II. J. VON BRAUN and A. HEYMONS (Ber., 1928, 61, [B], 2276— 2280).—The constitution assigned previously (A., 1928, 753) is confirmed. Ethyl isocampholate is reduced by sodium and alcohol to β -2:2:3-trimethylcyclopentylethyl alcohol,

13 mm., d_4^{20} 0.9046, n_1^{20} 1.4591, from which β -2 : 2 : 3-trimethyloyolopentylethyl bromide, b. p. 102°/12 mm., and $trimethyl - \beta - \overline{2}: 2: 3$ -trimethylcyclopentylethylammonium bromide, decomp. 277° (corresponding chloroplatinate, decomp. 244°), are successively derived. The bromide is transformed by silver oxide into the corresponding hydroxide, converted by distillation after addition of 3-4 mols. of potassium hydroxide into a mixture of dimethyl- 3-2:2:3-trimethyloyclopentylethylamine, b.p. 94-95°/14 mm. (picrate, m. p. 100-111°; hydro-chloride, m. p. 226°), and 2:2:3-trimethylcyclopentylethylene, b. p. 155-156°, d4 0.8024, np 1.4439. Ozonisation of the hydrocarbon and subsequent decomposition of the ozonide with zinc dust and water gives norisocampholic acid (2:2:3-trimethylcyclopentanecarboxylic acid), b. p. about 130°/12 mm., (chloride, b. p. about 85°/13 mm.; ethylamide, m. p. 68-69°), and 2:2:3-trimethylcyclopentane-1-alde*hyde*, b. p. $75-77^{\circ}/13 \text{ mm.}, d_4^{18} 0.9158, n_D^{20} 1.4486$ (semicarbazone, m. p. 188°; non-crystalline oxime).

H. WREN. o-Sulphinobenzoic acid. W. B. PRICE and S. SMILES (J.C.S., 1928, 2858-2863).—When dry chlorine is passed into a mixture of carbon tetrachloride and o-thiolbenzoic acid until the latter is dissolved, an unstable *dichloride* of o-sulphinobenzoic acid,

 $C_6H_4 < \frac{SCl_2}{CO} > 0$ (I), m. p. 62°, is formed, which when decomposed with ice gives a 70% yield of o-sulphinobenzoic acid, m. p. 126° (ef. Gattermann, A., 1899, i, 516; Davis and Smiles, J.C.S., 1910, 97, 1290). Treatment of I with p-nitrobenzyl alcohol affords p-nitrobenzyl o-carboxybenzenesulphinate, m. p. 121°; o-carboxyphenyl-p-nitrobenzylsulphone, m. p. 226°, is obtained by boiling equimolecular proportions of potassium o-sulphinobenzoate and p-nitrobenzyl bromide. The p-nitrobenzyl ester of o-carboxyphenylp-nitrobenzylsulphone, m. p. 190°, was produced with 2 mols. of p-nitrobenzyl bromide, and gave 3-keto-2-p-nilrophenyl-2: 3-dihydrothionaphthen 1:1-dioxide, m. p. 186°, when boiled with alcoholic sodium hydroxide followed by treatment with dilute sulphuric acid. The p-nitrobenzyl ester of m-carboxyphenyl-p-nitrobenzylsulphone, prepared in a similar manner, has m. p. 203°. The interaction of ethyl chloroacetate and potassium o-sulphinobenzoate led 3-keto-2-carbethoxy-2:3-dihydrothionaphthen to 1:1-dioxide, identical with the "anhydro"-derivative obtained by Feist (A., 1926, 74; cf. Arndt, Kirsch, and Nachtwey, ibid., 843) from the reaction between fuming sulphuric acid and ethyl benzoylacetate. The dichloride I reacts with solutions of phenols (2 mols.) in carbon tetrachloride or in dry ether with the formation of hydroxy-derivatives of o-carboxydiphenyl sulphide in good yield; thus phenol gave 2-carboxy-4'-hydroxydiphenyl disulphide, m. p. 193°: resorcinol yielded 2-carboxy-2': 4'-dihydroxydiphenyl disulphide, m. p. 190° [interaction in equimolecular proportions gave bis-2'-carboxyphenylthiol-2: 4-dihydroxybenzene,

 $C_6H_2(OH)_2(S \cdot C_6H_4 \cdot CO_2H)_2$, m. p. 272°], and β -naphthol furnished o-carboxyphenyl 2-hydroxy- α -naphthyl sulphide, m. p. 237°. A. I. VOGEL.

p-Cymene. XI. *p*-Cymyl-2-carbithionic acid. A. S. WHEELER and C. L. THOMAS (J. Amer. Chem. Soc., 1928, **50**, 3106—3109).—The Grignard reagent from 2-bromo-*p*-cymene (Bogert and Tuttle, A., 1916, i, 601) yields with carbon disulphide at -10° red, oily *p-cymyl-2-carbithionic acid* (yellow zinc salt, m. p. 92°; methyl ester, b. p. 167—168°/8 mm.; ethyl ester, b. p. 141—142°/3 mm.) (cf. Houben, A., 1906, i, 847). Complex, amorphous, yellow zinc, m. p. 196° (decomp.), copper, m. p. 75° (decomp.), mercuric, m. p. above 300°, and cadmium, m. p. 125° (decomp.), salts of the type $C_{10}H_{13}$ ·CS₂·M·OAc are formed from the acid and metallic acetates. With phenylhydrazine the acid gives a colourless substance, m. p. 112°, and with phosphorus pentachloride a *liquid*, b. p. 141°/8 mm. H. E. F. NOTTON.

Liquid crystals of stereoisomeric cinnamic acids. R. STOERMER and F. WODARG (Ber., 1928, 61, [B], 2323—2330).—In extension of the observation that trans-p-methoxycinnamic acid has liquidcrystalline properties which are not shared by the corresponding allo-acid (Stoermer, A., 1911, i, 295), it is found that the stable, linear forms of p-alkoxycinnamic acids give enantiotropic crystalline-liquid phases which do not occur with the angular, labile forms. Extreme lengthening of the alkyl chain causes disappearance of this property, as does also its branching. The esters, amides, anisidides, and p-toluidides of the liquidcrystalline alkoxycinnamic acids do not exhibit enantiotropic phases, but liquid-crystalline esters are obtained by esterification with anisoleazophenol even in the case of the labile acids.

The following substances are described : the p-anisidide, m. p. 184°, p-toluidide, m. p. 161°, and p-anisoleazophenyl ester, m. p. 162° and about 320°, of p-anisoleazophengi ester, in. p. 102 and about 320, of p-methoxycinnamic acid; p-anisoleazophenyl p-meth-oxyallocinnamate, m. p. 157.5° and 301°; p-ethoxy-benzaldehydesemicarbazone, m. p. 202° (decomp.); p-ethoxycinnamic acid, m. p. 190° and 196° (methyl ester, m. p. 68-69°; ethyl ester, m. p. 36°; amide, m. p. 195°; p-anisolde, m. p. 179°; p-toluidide, m. p. 164°: p-anisoleazophenel p. ethometizmenade, m. p. 164°; p-anisoleazophenyl p-ethoxycinnamate, m. p. 178° and about 317°; p-ethoxyallocinnamic acid, m. p. 86°, its chloride (prepared by means of phosphorus pentachloride in presence of ether) and amide, m. p. 118°; p-anisoleazophenyl p-ethoxyallocinnamate, m. p. 172° and about 300°; p-propoxybenzaldehyde, b. p. 268°, and its semicarbazone, m. p. 178-179° (decomp.); p-propoxycinnamic acid, m. p. 166° and 182° (methyl ester, m. p. 65°; ethyl ester, m. p. 37°; amide, m. p. 188—189°; p-anisidide, m. p. 161°; p-toluidide, m. p. 166—167°); p-propozyallocinnamic acid, m. p. 90-91°, and its amide, m. p. 115°; p-butoxybenzaldehyde, b. p. 285°; p-n-butoxycinnamic acid, m. p. 154° and 185-186° (methyl ester, m. p. 77°; ethyl ester, m. p. 38°; amide, m. p. 184°; p-anisidide, m. p. 148°; p-toluidide, m. p. 146—147°); p-anisoleazophenyl p-n-butoxycinnamate, m. p. 177° and about 320°; p-n-butoxyallocinnamic acid, m. p. 74° (amide, m. p. 110°; p-anisidide, m. p. 114°; p-anisoleazophenyl ester, m. p. 138° and about 300°); p-isobutoxybenz-aldebude b p. 258°: p-isobutoxycinnamic acid m. p. aldehyde, b. p. 258°; p-isobutoxycinnamic acid, m. p. 159°; p-benzyloxybenzaldehyde, m. p. 72°, which is not suitable for Perkin's reaction; methyl p-benzyloxycinnamate (from methyl p-hydroxycinnamate, benzyl bromide, and potassium hydroxide) and p-benzyloxycinnamic acid, m. p. 199°; p-cetyloxybenzaldehyde, m. p. 19° (phenylhydrazone, m. p. 89°); p-cetyloxy-cinnamic acid, m. p. 200—202° (decomp.); p-anisole-azophenyl benzoate, m. p. 161° and 173°. H. WREN.

Theory of the Perkin synthesis. Mechanism of the reaction. P. KALNIN (Helv. Chim. Acta, 1928, 11, 977-1003).-When a mixture of benzaldehyde (1 mol.), acetic anhydride (1 mol.), and pyridine (optimum 0.67 mol.) is heated at 180° for 32 hrs. a 5.4% yield of cinnamic acid is obtained. If the anhydride is replaced by sodium acetate the yield is nil. When a stronger tertiary base is used in place of pyridine, the yield increases with the strength of the base and the maximum yield is obtained with a smaller mol. proportion of bases. Thus, benzyldiethylamine gives 6.87% of acid, whilst triethylamine affords 29.27% using 0.33 mol. of base. The action of the base is to cause enolisation of the anhydride. The mechanism of the Perkin reaction is explained in five stages: (1) enolisation of the anhydride by sodium acetate, (2) addition of benzaldehyde to the enol, (3) further enolisation of the intermediate benzoyl derivative. (4) elimination of acetic acid from the enol additive product, (5) rearrangement of the intermediate compound lowing evidence is advanced to substantiate the mechanism. (1) Acetic anhydride reacts in the enol form with sodium, since decomposition of the resulting product with dilute acetic acid gives appreciable amounts of acetone. The yield of unsaturated acid is greater with increased ability of the anhydride used to exist in enol form. Thus, the firmly-bound methyl and phenyl groups in propionic and phenylacetic anhydrides activate the methylene hydrogen atom, resulting finally in correspondingly larger amounts of condensation products. (2) Small amounts of cinnamic acid are obtained with sodium as condensing agent at 180°, or from benzylideneaniline and acetic anhydride in presence of potassium carbonate. Addition to the double linking occurs thus : $\cdot CH_2:C(OH) \cdot + Ph \cdot CHO \longrightarrow CH_2Bz \cdot CH(OH) \cdot, be-$

····CPh:CH·CH(OH)·O··· to cinnamic acid. The fol-

 $CH_2.C(OH)$ + Ph CHO \longrightarrow CH_2BZ CH(OH), because of the strong valency requirement of the phenyl group (cf. Scheibler and Friese, A., 1925, i, 1417). (3) Most benzoyl derivatives of similar constitution to the intermediate exist in enol forms (K. H. Meyer, A., 1912, i, 940). (4) When the Perkin reaction is carried out in presence of a relatively large amount of acetic acid the yield of cinnamic acid is almost nil.

When sodium or potassium acetate is repeated by sodium or potassium carbonates, sodium or potassium phosphates, and potassium sulphite, 20.4-58.9%yields of cinnamic acid are obtained.

The results of Meyer and Beer (A., 1913, i, 617; cf. Michael, A., 1901, i, 358), and the condensation of o-chlorobenzaldehyde with potassium acetate at 240°, are explained by assuming the intermediate production of acetic anhydride during the experiment (cf. Campardou and Séon, A., 1928, 393). H. BURTON.

Preparation of dimethyl phenylethylmalonate. T. W. RAY (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 151—156).—An attempt to prepare dimethyl phenylethylmalonate from propylbenzene failed because this on attempted α-dibromination afforded an unsaturated compound, probably γ -phenyl- $\Delta\beta$ -propylene. In an attempt to prepare it from phenyl ethyl ketone, treatment of this substance with hydrogen chloride and cyanide afforded methylatropic acid, m. p. 134—136°. Attempted preparation from benzyl cyanide failed because methyl α-bromo-α-phenylbutyrate, decomp. 95—100°/2 mm., with potassium cyanide gave very little methyl α-cyano-α-phenylbutyrate b. p. 120—130°/0·1 mm. Ethyl α-cyano-α-phenylbutyrate has b. p. 100—140°/ 0·2 mm. CHEMICAL ABSTRACTS.

Addition of halogens to unsaturated acids and esters. II. Addition of "bromine chloride" to phenylpropiolic acid. N. W. HANSON and T. C. JAMES (J.C.S., 1928, 2979–2985; cf. A., 1928, 1004).—An equimolecular mixture of bromine and chlorine dissolved in carbon tetrachloride ("bromine chloride" solution) reacts in the dark with phenylpropiolic acid in carbon tetrachloride solution at 0° to give a mixture of two *chlorobromocinnamic acids* which were separated by means of light petroleum into two forms, m. p. 129° (plates) and 112° (needles), respectively. These two forms are considered to be geometrical isomerides, since (a) exposure of a chloroform solution of the less fusible acid mixed with a

little bromine gave almost entirely the more fusible acid, and (b) the more fusible form is unaffected by such treatment (cf. Roser and Haselhoff, A., 1888, 1314; Stoermer and Heymann, A., 1913, i, 618). When the compound of m. p. 112° is treated with cold concentrated sulphuric acid 3-chloro-2-bromo-1-ketoindene (I), m. p. 105° [anilido-derivative, m. p. 170°; piperidyl derivative, m. p. 117° (decomp.); oxime, m. p. 194°; mixed m. p. with 2-chloro-3-bromo-1-ketoindene, m. p. 105°, 65-100°; the oxime of 2-chloro-3-bromo-1-ketoindene has m. p. 184° (decomp.); cf. Roser and Haselhoff, loc. cit.], is formed, whilst the isomeride, m. p. 127°, is unaffected by this treatment : indeed I may be conveniently prepared from the product of interaction of phenylpropiolic acid and " bromine chloride," since the indone was readily separable from the residual acid by dissolving in hot light petroleum. This establishes the compound of m. p. 112° as the cis- and that of m. p. 127° as the transisomeride. "Bromine chloride" reacts much more rapidly with phenylpropiolic acid than either bromine or chlorine, the reaction being of the bimolecular type without an inhibition period (cf. A., 1928, 1004). The action of bromine and chlorine dissolved in carbon tetrach bride with the cis-forms of β-chloro-α-bromo-, $\alpha\beta$ -dibromo-, and $\alpha\beta$ -dichloro-cinnamic acids was studied in the manner described by Williams and James (A., 1928, 412). With bromine, the amount of halogen which disappeared was extremely small even after several weeks. With chlorine, aβ-dichlorocinnamic acid formed an additive product, aaββ-tetrachloro-\$-phenylpropionic acid, m. p. 130°; aB-dibromocinnamic acid led to some replacement of the bromine by chlorine but to no recognisable product, whilst β-chloro-α-bromocinnamic acid gave mainly αββ-trichloro-α-bromo-β-phenylpropionic acid, m. p. 127°, together with a small quantity of $\alpha\alpha\beta\beta$ -tetrachloro-\$-phenylpropionic acid (produced by partial replacement of bromine by chlorine). A. I. VOGEL.

Reactions of nitroso-derivatives with unsaturated compounds. VI. Catalytic action of nitroso-derivatives on o-nitro-substituted [aryl]acetylenes; behaviour of p-nitrosoanisole. L. ALESSANDRI (Gazzetta, 1928, 58, 551-560).-Owing to the complexity of the reaction between nitrosobenzene and o-nitrophenylacetylene (A., 1927, 572), the reactions of the former with o-nitrophenylpropiolic acid, which might be expected to behave more simply, have been examined. Since, however, this acid readily loses carbon dioxide, it gives the same products as does o-nitrophenylacetylene, viz., isatin, N-hydroxyisatin, and a trace of α -isatinoxime N-phenyl ether, together with azoxybenzene and unchanged acid. Ethyl o-nitrophenylpropiolate is converted by nitrosobenzene into ethyl isatogenate; similar changes have been observed under the influence of sulphuric acid or of pyridine; nitrosobenzene (which remains unaltered) gives a greater yield than these, with also a colourless secondary product, m. p. 121°. Methyl o-nitrophenylpropiolate similarly isomerises to methyl isatogenate and a substance, m. p. 139°. These colourless by-products have the same percentage composition as the initial materials, and are produced whether these are treated with nitrosobenzene or with p-nitrosoanisole; it must therefore be assumed that these latter substances have only a catalytic action.

p-Nitrosoanisole acts on safrole, ethyl phenylpropiolate, or tolane in a similar manner to nitrosobenzene. E. W. WIGNALL.

Ring fission in the cyclopropane series. XIV. R. STOERMER and F. SCHENCK [with H. BUSCHMANN] (Ber., 1928, 61, [B], 2312-2323; cf. A., 1928, 174).— The requisite 2-phenyl-3-hydroxybenzylcyclopropane-1-carboxylic acids are obtained from γ -truxillic acid (cf. loc. cit.) or from ε -truxillic acid through ε -truxillamic acid and 3^c-amino-2^c-4^t-diphenylcyclobutane-1^c-carboxylic acid, which is transformed by ethereal nitrosyl bromide into the lactone IIb (R = CHPh·OH), to-



gether with diphenylbutadiene. The lactone is converted into the corresponding acid, oxidised to the ketonic acid II (R=Bz), m. p. 174—175° (semicarbazone, m. p. 194—195°; methyl ester, m. p. 93°). The ketonic acid, like the stereoisomeric acids I, II, and III (loc. cit.), is converted by catalytic hydrogenation into α -phenacyl- β -phenylpropionic acid.

The hydroxy-acid IIb is converted by hydrogen chloride in cold ether into γ -phenyl- α - α' -chlorobenzyl- Δ^{β} -butenoic acid, m. p. 155—156°, converted by sodium hydroxide into benzaldehyde, diphenylbutadiene, and regenerated hydroxy-acid and by aluminium amalgam into γ -phenyl- α -benzyl- Δ^{β} -butenoic acid; the methyl ester, m. p. 98—99°, is described. Hydrogen chloride, like hydrogen bromide, is therefore added at the carbon atoms 2 and 3 of the cyclopropane ring. Fission of the ring by glacial acetic and sulphuric acids occurs in a precisely similar manner, giving γ -phenyl- α - α' -acetoxybenzyl- Δ^{β} -butenoic acid,

CHPh:CH+CH(CO₂H)·CHPh·OAc. Since the acid contains two asymmetric carbon atoms it can exist in two racemic modifications (each of which may give two *cis-trans*-isomerides). The hydroxy-acids IIa, IIb, and IIIa give an acid, m. p. 152—152·5° (methyl ester, m. p. 87°), whereas the hydroxy-acid Ia yields an isomeric acid, m. p. 152—154° (methyl ester, m. p. 92—92·5°). The methyl ester of the hydroxy-acid Ia gives both esters simultaneously. The difference of the two unsaturated acids is caused by the arrangement of the groups around the asymmetric carbon atoms, since it persists in the products of their hydrogenation, the γ -phenyl- α - α' -hydroxybenzyl-n-butyric acids [isomeride I (from acid of m. p. 152—152·5°), m. p. 112—113° (methyl ester, m. p. 62—62·5°; noncrystalline acetyl derivative, and its methyl ester, m. p. of 50—51°); isomeride II (from acid of m. p. 152—154°), m. p. 93-94.5° (methyl ester, m. p. 64-64.5°; methyl ester of acetyl derivative, m. p. 69-70°)]. The methyl esters are oxidised to the same methyl α -benzoyly-phenyl-n-butyrate, converted by hydrolysis into αδ-diphenylbutan-α-one, m. p. 56—57° (oxime, m. p. 101—102°; semicarbazone, m. p. 126·5—127·5°), obtained directly by oxidation of the corresponding acids. The syntheses of the ketone by addition of benzaldehyde to an ethereal solution of magnesium y-phenyl-n-propyl bromide with subsequent oxidation of the ad-diphenylbutan-a-ol, m. p. 45-46°, or directly by addition of the Grignard reagent to the aldehyde, is recorded. The identity of the non-crystalline methyl a-benzoyl-y-phenyl-n-butyrates from the different hydroxy-acids is further established by the conversion of each preparation by means of semicarbazide into 3-phenyl-4-3-phenylethyl-5-pyrazolone-1-carboxylamide, m. p. 131.5-132.5°. The fission of the cyclopropane ring between the carbon atoms 2 and 3 in the production of the γ -phenyl- α - α' -acetoxybenzyl- Δ^{β} -butenoic acids is established by the production of ad-diphenylbutadiene and the formation of aβ-dibenzylidenepropionic acid by the hydrolysis of the methyl esters. The position of the o-acetyl group follows from the conversion of the free acetylated acids by boiling sodium carbonate into phenylisocrotonic acid, benzaldehyde, and acetic acid. The isomeric γ -phenyl- α - α' -hydroxybenzyl-n-butyric acids are transformed by 75% sulphuric acid into 1-phenyl-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid, m. p. 150-151°

Addition of formic acid takes places in the same manner as that of acetic acid. The hydroxy-acids IIb and IIa give a formyl product, m. p. 160° (methyl ester, m. p. 96°), whereas the methyl ester of the hydroxy-acid Ia yields mainly an isomeric methyl ester, m. p. 93-94°.

The results thus obtained appear to justify the previous assumption that, after contraction of the ring, the carboxyl and phenyl groups remain on the same side of the ring as in the truxillic and truxinic H. WREN. acids.

Condensation of chloral with anisic acid, with p-nitroanisole, and with 2:6-dichloroquinol. F. D. CHATTAWAY and F. CALVET (J.C.S., 1928, 2913-2918; cf. A., 1927, 458, 967).-Anisic acid condenses with chloral in the presence of a large excess of concentrated sulphuric acid at the ordinary temperature, forming 5-carboxy-2-methoxy-1-BBB-trichloroa-hydroxyethylbenzene (I), m. p. 198-199°; if the condensation be prolonged (8 days) or if dry hydrogen chloride be passed into a solution of I in concentrated sulphuric acid, 5-carboxy-2-methoxy-1- $\alpha\beta\beta\beta$ -tetrachloro-ethylbenzene, m. p. 247–249°, is formed, whereas if I be heated with concentrated sulphuric acid 4-methoxyisophthalaldehydic acid, m. p. 244-245° (2:4-dichlorophenylhydrazone, m. p. 303-305° [decomp.]), is obtained. The constitution of I was established by oxidation with alkaline potassium permanganate to a mixture of 5-carboxy-2-methoxyphenylglyoxylic acid, m.p.254-255° (phenylhydrazone, m.p.231° [decomp.]), and 4-methoxyisophthalic acid, m. p. 275-276°. p-Nitroanisole condenses similarly with chloral in the presence of concentrated sulphuric acid at the ordinary temperature, giving 5-nitro-2-methoxy-1-αβββ-tetrachloroethylbenzene, m. p. 131-132°, which was converted into aββ-trichloro-5-nitro-2-methoxystyrene, m. p. 94-95°, when boiled with alcoholic potassium hydroxide, and into 5-nitro-2-methoxybenzoic acid, m. p. 161°, when oxidised with potassium permanganate in acctone solution. 2:6-Dichloroquinol condenses readily with 2 mols. of chloral in the presence of a large excess of concentrated sulphuric acid, forming



5:7-dichloro-6-hydroxy-2:4--O·CH·CCl₃ bistrichloromethyl-1 : 3-benzdioxin (II), m. p. 114-115°, which gave an acetyl derivative, m. p. 179-180°, and 5:7-dichloro-6-hydroxy-2 : 4 - bisdi-

chloromethylene-1: 3-benzdioxin, m. p. 137-138°, when boiled with alcoholic potassium hydroxide.

A. I. VOGEL.

Dependence of rotatory power on chemical constitution. XXXIII. Resolution of dl-m-carboxyphenyl ethyl sulphoxide and of dl-m-carboxyphenylethylsulphine - p - toluenesulphonylimine. J. HOLLOWAY, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 3000-3006).-m-Ethylthiolbenzoic acid, m. p. 99-100°, prepared from m-thiolbenzoic acid and ethyl p-tolucnesulphonate, gave dl-m-carboxyphenyl ethyl sulphoxide, m. p. 104-106°, when oxidised with nitrie acid. The 1-brucine salt, m. p. 125-126°, [a]²⁵/₅₄₆₁+69° in chloroform, was decomposed with aqueous sodium hydroxide to d-m-carboxyphenyl ethyl sulphoxide, m. p. 71°, $[\alpha]_{491}^{29}$ +236° in chloroform. A table of specific rotatory powers of this substance in various solvents for different wave-lengths is given; they are all greater than those of d-m-carboxyphenyl methyl sulphoxide (Clarke and others, A., 1927, 243). The quinidine salt, m. p. 198—199°, $[\alpha]_{461}$ +102° in chloroform, when decomposed gave 1-m-carboxyphenyl ethyl sulphoxide, [a]²³₅₄₆₁ -232° in chloroform. m-Carb-oxyphenylethylsulphone, m. p. 162-164°, prepared by oxidation of m-methylthiolbenzoic acid or d-mcarboxyphenyl ethyl sulphoxide with hydrogen peroxide, and also m-carboxyphenyl ethyl sulphide dibromide, m. p. 102° , prepared from *m*-ethylthiol-benzoic acid and bromine in carbon disulphide solution, are optically inactive.

"Chloramine-T" and m-ethylthiolbenzoic acid react, yielding dl-m-carboxyphenylethylsulphine-p-toluenesulphonylimine, m. p. 149°, giving a brucine salt, m. p. 161°, $[\alpha]_{3401}^{20}$ – 157° in ethyl alcohol; decom-position of the latter with hydrochloric acid yielded 1 - m - carboxyphenylethylsulphine - p -toluenesulphonyl imine, (I) m. p. 149–150°, $[\alpha]_{349}^{25}$ –368° in ethyl alcohol. The d + dl-sulphilimine isolated from the mother-liquors of I gave the pure d-m-carboxyphenylethylsulphine-p-toluenesulphonylimine, m. p. 150-151°, $[\alpha]_{\text{s4c1}}^{25}$ +373° in ethyl alcohol, through the strychnine d-salt, m. p. 174° (decomp.), $[\alpha]_{\text{s4c1}}^{23}$ +152° in ethyl alcohol, and a slightly less pure compound, m. p. 149–150°, $[\alpha]_{5461}^{25}$ +364° in ethyl alcohol, through the cinchonidine salt, m. p. 198–199°, $[\alpha]_{3461}^{20}$ + 50° in chloroform. The rotatory dispersion is less complex than that exhibited in the corresponding solvents by the sulphoxide; the sulphilimine exhibits simple rotatory dispersion in ethyl-alcoholic solution. The l+dl-sulphilimine is converted into a mixture of p-toluenesulphonamide, m-carboxyphenyl ethyl sulphide, and dl-m-carboxyphenyl ethyl sulphoxide when hydrolysed with hydrochloric acid, whilst the dl-sulphilimine gives p-toluenesulphonamide and m-carboxyphenylethylsulphone with hydrogen peroxide. These results provide further evidence for the existence of semipolar double linkings (cf. Harrison and others, A., 1926, 1031). A. I. VOGEL.

So-called "fluoreneoxalic ester." R. KUHN and E. LEVY (Ber., 1928, 61, [B], 2240-2248).-Ethyl fluoreneoxalate has the enolic structure and hence must be regarded as ethyl a-hydroxy-\beta-diphenyleneacrylate. Methyl α-hydroxy-β-diphenyleneacrylate, m. p. 117.5°, is prepared in 65% yield by condensing fluorene with methyl oxalate in presence of methylalcoholic potassium methoxide. It is converted by ozone into fluorenone and methyl oxalate and by hydrogenation in presence of platinum oxide into methyl α -hydroxy- β -diphenylenepropionate. With alkaline hypoiodite it yields 9-iodofluorene. It affords fluorenone-p-nitrophenylhydrazone, m. p. 209°, with p-nitrophenyldiazonium hydrate. It is converted by diazomethane and *p*-nitrobenzoyl chloride into the corresponding methyl ether, $C_{17}H_{14}O_{31}$, m. p. 60°, and p-nitrobenzoate, $C_{23}H_{15}O_6N$, m. p. 255°. As ketone, it is transformed by bromine in glacial acetic acid into methyl 3-bromo-3-diphenylenepyruvate, m. p. Methyl a-oximino-\$-diphenylenepropionate, 94·5°. m. p. 190°, is described. When methyl α -hydroxy- β diphenyleneacrylate is titrated with bromine by Meyer's method, results varying from 75 to 95% of enol are obtained owing to the unusually slow reaction between the bromoketone and hydriodic acid. At the end of 1-2 hrs. after addition of β -naphthol and potassium iodide, an enol content of 100% is indicated if the crystalline ester is covered with bromine dissolved in glacial acetic acid. If solutions of the ester in glacial acetic acid are employed which have been preserved for about 20 hrs., titration shows 58.8% of enol. H. WREN.

Syntheses with radiant energy. II. Photosynthesis of $\alpha\beta\beta$ -triphenyl-lactic acid. R. DE FAZI.—See A., 1928, 1341.

Colour on the basis of molecular strain. VI. Effect of sulphur on colour. A. N. DEY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 639-641).-When sulphur replaces oxygen in a series of dyes the colour is deepened, presumably because of the greater loading effect of the sulphur atom. A similar increase of colour is to be expected when carbon is replaced by sulphur, and to test this hypothesis a series of dyes has been prepared from thiodiglycollic acid analogous to those obtained from glutaric acid (Dutt and Thorpe, A., 1925, i, 140; Dutt, A., 1926, 830). Resorcinol condenses with thiodiglycollic acid in presence of a small amount of concentrated sulphuric acid at 150°, vielding resorcinolthiodiglycollein, not melted at 310°. Similar condensations using phloroglucinol, phenol, m-diethylaminophenol, and *m*-phenylenediamine afford phloroglucinolthiodiglycollein, phenolthiodiglycollein, m. p. 129°, tetraethylthiodiglycollylrhodamine, m. p. 172-173°, and 2:7-diaminothiodiglycollylacridine, m. p. 241°, respectively. These compounds have deeper colours than the corresponding glutaric acid derivatives. H. BURTON.

Succinic acid derivatives from acylphenylacetonitrile. G. HELLER, H. HERRMANN, and G. SPIELMEYER (J. pr. Chem., 1928, [ii], 120, 193-198). -Oxidation of a-acetylphenylacetonitrile (anil, m. p. 102-103°; phenylhydrazone, m. p. 114°) with sodium nitrite and acetic acid at 0° for 24 hrs. yields aa'-diacetyl-aa'-diphenylsuccinodinitrile, m. p. 173-174°, together with isomeric and other substances which could not be purified. The same product is obtained when absolute nitric acid diluted with 2 parts of acetic acid at 0° or nitric acid (d 1.36) at the ordinary temperature (accompanied, in this case, with 30% of p-nitrobenzoic acid) is used as oxidising agent, or by the action of iodine and sodium methoxide on the original nitrile. Similarly, oxidation of a-benzoylphenylacetonitrile either with nitrous acid at 0°, 20% hydrogen peroxide in acetic acid solution, or sodium methoxide and iodine, yields aa'-dibenzoyl-aa'-diphenylsuccinodinitrile, m. p. 207°, which is converted by treatment with concentrated sulphuric acid for 2 months into aa'-dibenzoyl-aa'-diphenylsuccinic anhydride, m. p. 243°. J. W. BAKER.

Mellitic acid. E. LURIA (Quim. e Ind., 1928, 5, 35-38; Chem. Zentr., 1928, i, 2501).—The neutral metallic mellitates (*uranyl*, $+12H_2O$; *cerium*, $+9H_2O$; *cadmium*; *lithium*, $+9H_2O$) crystallise with $3nH_2O$, where n=0 to 8, in accordance with the tribasicity of the acid towards methyl-orange, and other properties. Evaporation of a solution containing mellitic acid and hydrazine gives compounds I and (subsequently) II:



A. A. ELDRIDGE.

Manufacture of cyclic ketones [from naphthalene etc. and maleic anhydride]. I. G. FARBENIND. A.-G.—See B., 1928, 887, 922.

Manufacture of compounds of the perylene series [perylenecarboxylic acids]. I. G. FARBEN-IND. A.-G.—See B., 1928, 921.

Intermediate compounds and azo dyes therefrom [aminohydroxyarylsulphonecarboxylic acids]. BRIT. DYESTUFFS CORP. and M. MENDOZA. —See B., 1928, 887, 921.

Tautomerism of o-nitrobenzaldehyde. II. Reply to H. Gilman, R. Fothergill, and F. Arndt. I. TANASESCU (Bull. Soc. chim., 1928, [iv], 43, 1117— 1122).—In reply to Gilman and Fothergill's criticism (A., 1928, 64) of the theory previously advanced (A., 1928, 178) to account for the tautomerism of o-nitrobenzaldehyde, the author points out that the hypothesis is not based exclusively on the presence of a mobile hydrogen atom and that such mobile hydrogen atoms have been observed in other nitro- and nitroso-benzene derivatives. The formation of unsaturated hydrocarbons by the action of magnesium organohalides is readily attributed to the reducing powers of the latter compounds. With magnesium methyl iodide methane only was formed. In reply to Arndt (A., 1928, 759) it is asserted that photochemical reasons render the dynamic equilibrium (I) very probable in the case of o-nitrotriphenylmethane. If the oxygen atom remains attached to nitrogen there results the o-quinonoid derivative (II)



already described (A., 1927, 139), whilst if the oxygen atom comes within the sphere of attraction of the carbon atom the o-nitrosocarbinol (III) (loc. cit.) results. The fact that p-nitrobenzaldehyde is slightly soluble in alkali is attributed to the formation of hydrates, which is an insufficient explanation of the much greater solubility of the o-isomeride. Although o-nitroacetophenone cannot react in a tautomeric form, the formation of C-methylanthranil on reduction may be preceded by the formation of the intermediate phase $C_6H_4 < CMe_{NO} > 0$: in the case of o-nitrobenzaldehyde a corresponding structure (OH for Me) gives a ready interpretation of the reaction with aromatic hydrocarbons in presence of sulphuric acid.

R. BRIGHTMAN. "Oxidising " action of alkalis. I. G. Lock (Ber., 1928, 61, [B], 2234—2240).—The potassium salt of salicylaldehyde reacts quantitatively with potassium hydroxide at 105—110°, giving potassium salicylate and hydrogen. The presence of moisture is not necessary, but advantageous, since it depresses the temperature of reaction by facilitating the form-ation of an intimate mixture. The reaction is not preceded by a Cannizzaro change, since the potassium compound of salicyl alcohol does not react with potassium hydroxide under these conditions. Sodium and lithium hydroxides behave similarly to the potassium compound but require a higher temperature. Barium hydroxide, dehydrated at 120°, also effects the change; the absence of "oxidising action" is not a specific property of the alkaline-earth hydroxides but merely a consequence of their use in aqueous solution. Sodamide does not react with the potassium derivative of salicylaldehyde. The "oxidising" action of potassium hydroxide cannot be ascribed to dissociation of water, since it may occur at a relatively low temperature and with anhydrous materials. It must be regarded as a dehydrogenation with replacement of the typical hydrogen atom of the aldehydic . H. WREN. group by the OK radical.

1:2-Dialkylcyclopentane derivatives. F. H. CASE and E. E. REID (J. Amer. Chem. Soc., 1928, 50, 3062-3065).-The 2-methyl, b. p. 106-107°/17 mm. (all b. p. corr.) (semicarbazone, m. p. 152-153°), 2-ethyl (I), b. p. 100°/7 mm., d²⁵ 1.0310 (semicarbazone, m. p. 148-149°), and 2-isopropyl derivatives of ethyl cyclopentanone-2-carboxylate have been obtained from

the sodio-derivative (cf. Rysselberge, A., 1926, 1238) and the appropriate alkyl iodide in boiling benzene or xylene. The ester I is hydrolysed by dilute sulphuric acid to 2-ethylcyclopentanone, b. p. 160-161°/755 mm., d_4^{35} 0.9260 (cf. Best and Thorpe, J.C.S., 1909, 95, 713). This is converted in poor yield by magnesium n-propyl bromide into 2-ethyl-1-propylcyclopentan-1-ol, b. p. 115-116°/42 mm., d²⁵ 0.8949, and by magnesium ethyl bromide into 1: 2-diethylcyclopentan-1-ol, b. p. $101 - 102^{\circ}/46 \text{ mm.}, d_{4}^{23} 0.9041$, the iodide of which yields with zinc dust mainly a 1 : 2-diethylcyclopentene, b. p. 147-149°/761 mm., d²³ 0.8136 (cf. Kijner, A., 1911, i, H. E. F. NOTTON. 967).

Alkylation of hydroxymethylenecyclohexanones. H. K. SEN and K. MONDAL (J. Indian Chem. Soc., 1928, 5, 609-630).-When the sodium salts of hydroxymethylenecyclohexanones are treated with alkyl iodides O-ethers are not produced, but C-alkylation occurs, and after hydrolysis of the intermediate products (when isolated) 2-alkylcyclohexanones are obtained. The intermediate product is a reducing agent and is postulated as a 2-alkylcyclohexanone-2aldehyde. Thus, when 2-hydroxymethylenecyclohexanone is treated with sodium in benzene and then heated at 100° with methyl iodide, the resulting product is a liquid, b. p. 130-150°/45 mm. (slight decomp.), hydrolysed by cold, dilute sodium hydroxide to 2-methylcyclohexanone. With sodium ethoxide at 100° under pressure, no intermediate is isolated. 2-Methyl-6-hydroxymethylenecyclohexanone gives 2 : 6-dimethylcyclohexanone (oxime, m. p. 118°; semicarbazone, m. p. 193-194°) in benzene or ether solution, but in presence of alcohol a small amount of the monomethyl derivative is also formed. From the requisite alkylhydroxymethylenecyclohexanones and alkyl iodides the following substituted cyclohexanones were prepared : 2-ethyl-; 2:5-dimethyl- (oxime, m. p. 96°); 6-benzyl-2-methyl- (impure semicarbazone, m. p. 140° after sintering at 132°); 2:3:4-trimethyl-(semicarbazone, m. p. 212°). 3-Methyl-6-hydroxymethylenecyclohexanone and isopropyl iodide yield a mixture of 3-methylcyclohexanone and menthone. The action of acetyl chloride on the sodium salt of hydroxymethylenecyclohexanone is to form the corresponding O-acetate (semicarbazone, m. p. 182-184°). Similarly, 2- and 4-methyl-6-hydroxymethylenecyclohexanone benzoates (semicarbazones, m. p. 175° and 183—184°, respectively) are prepared using benzoyl chloride. Alkylation of hydroxymethyleneacetophenone gives impure O-ethers.

Determinations of the amounts of enol form present in 2-hydroxymethylene-, 2-, 3-, and 4-methyl-6hydroxymethylene-cyclohexanones, hydroxymethylenecamphor, and hydroxymethyleneacetotoluone by K. H. Meyer's titration method shows that the percentage of enol falls considerably when an alcoholic solution is kept for some time. In benzene or ether the reverse change takes place. Since these hydroxymethylene derivatives can exist in the aldehyde form the sodium compounds are postulated as >CNa·CHO. H. BURTON.

Carbon rings. XIII. Oxidation of thirteento seventeen-membered monocyclic ketones with Caro's acid to fourteen- to eighteen-ring lactones.

L. RUZICKA and M. STOLL (Helv. Chim. Acta, 1928, 11, 1159-1173) .- Oxidation of exaltone (cyclopentadecanone) in light petroleum solution at 30-35° with Caro's acid gives a mixture of cyclopentadecanone peroxide (I), m. p. 179–180°, ξ -hydroxypentadecoic acid (II), m. p. 82–82.5°, ξ -hydroxypentadecoic acid lactone (exaltolide) (III), b. p. 171-174°/14 mm., m. p. 31–32°, $d_4^{i_1}$ 0.9383, $n_{\rm P}^{i_1}$ 1.4633, etholide, $\dot{\rm C}_{30}{\rm H}_{58}{\rm O}_5$, m. p. 75–77°, formed by loss of 1 mol. of water from 2 mols. of II, and resinous products. If the oxidation is carried out at 50° or 65° no peroxide is produced. In acctic acid solution at 20-40° similar mixtures are also formed. Hydrolysis of III with cold 5% sodium hydroxide solution and subsequent oxidation with chromic oxide and acetic acid yields tridecane-av-dicarboxylic acid. Reduction of J with zinc dust and acetic acid or treatment with warm 90% sulphuric acid regenerates exaltone. Similar oxidation of cyclotridecanone furnishes the lactone, b. p. 147-148°/14 mm., m. p. 25-26°, d³³/₄ 0.9590, n³³/_D 1.4649, of μ-hydroxytridecoic acid, m. p. 77-78°. From cyclotetradecanone the lactone, b. p. 164-165°/16 mm., m. p. 27-28°, d⁴³ 0.9528, n⁴⁹_D 1.4644, of v-hydroxytetradecoic acid, m. p. 93-95°, is obtained. o-Hydroxyhexadecoic acid lactone, b. p. 188°/15 mm., m. p. 33-34°, d4 0.9348, $n_{\rm p}^{39}$ 1.4644, from cyclohexadecanone, is the pure dihydroambrettolide of Kerschbaum (A., 1927, 541). Dihydrocivetone yields the lactone, m. p. 40-41°, d_4^{i5} 0.9231, n_p^{46} 1.4615, of π -hydroxyheptadecoic acid, m. p. 84-85°, oxidised further to pentadecane-ao-dicarboxylic acid.

The lactones described show a fairly regular increase of m. p. with increase of carbon atoms, but a corresponding decrease in the values of d. The hydroxyacids show an alternation in the m. p., the oddnumbered acids being the more fusible. The lactones have pronounced odours. H. BURTON.

Carbon rings. XIV. Ketones with nineteen-, twentyone-, and twentynine-membered rings. L. RUZICKA, M. STOLL, and H. SCHINZ (Helv. Chim. Acta, 1928, 11, 1174-1180).-Distillation of the thorium salt of octadecane-as-dicarboxylic acid, m. p. 124-125° (prepared by electrolysis of ethyl hydrogen nonane-al-dicarboxylate and subsequent hydrolysis), gives 2.5% of cyclononadecanone, m. p. 72° (semicarbazone, m. p. 184°), oxidised by chromic oxide and acetic acid to heptadecane-ap-dicarboxylic acid. From yttrium eicosane-au-dicarboxylate 3.8% of cycloheneicosanone, b. p. 176-177°/0.3 mm., m. p. 45–46°, $d_4^{s_2}$ 0.8746, $n_D^{s_2}$ 1.4617 (semicarbazone, m. p. 177–178°), is obtained. The benzylidene derivative of this ketone is oxidised to nonadecane-at-dicarboxylic acid. cycloNonacosanone, m. p. 45-47°, d4 (supercooled) 0.8802, n_D 1.4702 (semicarbazone, m. p. 152-154°), is prepared from the yttrium salt of octacosane-1: 28-dicarboxylic acid, obtained by electrolysing methyl hydrogen tetradecane-az-dicarboxylate, m. p. 65-67°. Methyl hydrogen decane-akdicarboxylate has m. p. 39-41°. H. BURTON.

Ionone. F. HERNÁNDEZ, J. JAUMÁ, and L. VERDERAU (Quim. e Ind., 1927, 4, 301–309; Chem. Zentr., 1928, i, 1954).—Descriptive. The b.-p. curves of α - and β -ionone between 3 and 19 mm. are given. A. A. ELDRIDGE.

Acylation of diazomethane. Formation of chloroacetophenone from benzoyl chloride. W. BRADLEY and G. SCHWARZENBACH (J.C.S., 1928, 2904-2912; cf. Dale and Nierenstein, A., 1927, 564; Arndt and Eistert, A., 1928, 739; Bradley and Robinson, A., 1928, 759, 1009).-The interaction between an acid chloride (1 mol.) and an ethereal solution of diazomethane (2 mols.) led primarily to a diazoketone: $R \cdot COCl + CH_2N_2 = R \cdot CO \cdot CHN_2 + HCl (a); CH_2N_2 +$ $HCl=CH_3Cl+N_2$ (b), small quantities of the chloroketone being produced from the diazoketone by a side reaction: $\mathbf{R} \cdot \mathbf{CO} \cdot \mathbf{CHN}_2 + \mathbf{HCl} = \mathbf{R} \cdot \mathbf{CO} \cdot \mathbf{CH}_2 \mathbf{Cl} + \mathbf{N}_2$ (c). Nierenstein's claim (A., 1928, 739) that the chloroketones are obtained in good yield, e.g., w-chloroacetophenone 72%, by adding the diazomethane to the acid chloride could not be confirmed. The course of the reaction between benzoyl chloride and diazomethane under various experimental conditions is interpreted as follows: when benzoyl chloride is in excess, (a) is the primary reaction and (c) occurs to a small extent: rapid mixing or mixing during 25 min. of equimolecular quantitics in ether dried over phosphoric oxide or calcium chloride gives about 50% of ω -diazoacetophenone and 10-13% of ω -chloroacetophenone.

Phenylacetyl chloride and diazomethane gave an oily diazomethyl ketone, which yielded benzyl p-nitrobenzoyloxymethyl ketone, m. p. 120°, when treated with p-nitrobenzoic acid in acetone. p-Nitrobenzoyl chloride and diazomethane react, giving ω -diazo-p-nitroacetophenone, m. p. 116—117°, which was converted into p-nitro-w-acetoxyacetophenone, m. p. 121-122°, when heated in glacial acetic acid solution (Dale and Nierenstein, A., 1927, 564, describe p-nitro- ω -acetoxyacetophenone, m. p. 132°). The interaction between the chloride of o-diacetylprotocatechuic acid, m. p. 48-50° (Malkin and Nierenstein, A., 1928, 646, give m. p. 55°), and diazomethane yielded ω -diazo-3:4-diacetoxyacetophenone, m. p. 76-77°, which furnished ω -3:4-triacetoxyacetophenone, m. p. 92-93°, when heated with glacial acetic acid at $65-70^{\circ}$ and ω -chloro-3: 4-diacetoxyacetophenone, m. p. 107.5—108°, when treated with hydrogen chloride in dry ether (cf. Voswinckel, A., 1910, i, 42, m. p. 110°; Malkin and Nierenstein, loc. cit., m. p. 94°). Cinnamoyl chloride and diazomethane react to give a diazocompound, m. p. 77-78°, which is probably the pyrazoline related to styryl diazomethyl ketone.

A. I. VOGEL.

Aromatic hydroxymethylene ketones and their derivatives. E. BENARY (Ber., 1928, 61, [B], 2252—2255; cf. A., 1926, 500; 1927, 573).—Nuclearsubstituted hydroxymethylene ketones are converted by ammonium acetate and glacial acetic acid into imino-compounds, basic substances being produced, at the most, in traces. p-Bromophenyl β -hydroxyyinyl ketone, m. p. 71—72° (copper salt, decomp. about 268°; anilide, m. p. 178°), is prepared from p-bromoacetophenone, ethyl formate, and sodium in the presence of ether. It is converted by phenylhydrazine into 1-phenyl-5(3)-p-bromophenylpyrazole, m. p. 127°, and by ammonium acetate and glacial acetic acid into di- β -p-bromobenzoylvinylamine, C₁₈H₁₃O₂NBr₂, m. p. 217°. p-Chlorophenyl β -hydroxyvinyl ketone, m. p. 48—49°, similarly yields an anilide, m. p. 163—164°, di- β -p-chlorobenzoylvinylamine, m. p. 204°, and 1-phenyl5(3)-p-chlorophenylpyrazole, m. p. 118°. m-Nitrophenyl β -hydroxyvinyl ketone, m. p. 85°, its anilide, m. p. 151° after darkening, and di- β -m-nitrobenzoylvinylamine, m. p. 215—216°, are described. m-Cyanophenyl β -hydroxyvinyl ketone, m. p. 103—104°, yields di- β -m-cyanobenzoylvinylamine, m. p. 165°. Di- β -ptoluoylvinylamine, m. p. 155—156°, and di- β -pmethoxybenzoylvinylamine, m. p. 188—189°, are prepared from p-tolyl β -hydroxyvinyl ketone and p-methoxyphenyl β -hydroxyvinyl ketone, respectively. H. WREN.

Stereoisomeric bromoketimines. H. D. YOUNG (Abstr. Theses Univ. Chicago Sei. Ser., 1925— 1926 (1928), 4, 203—207).—Of the six bromoketimines prepared : CRR'.NH+HOBr=CRR'.NBr+H₂O, only *p*-chlorobenzophenonebromoimine (α -form m. p. 109°, β -form m. p. 85°) and *p*-bromobenzophenonebromoimine (α -form m. p. 104°, β -form m. p. 80°, third form m. p. 102—103°) were obtained in stereoisomeric forms. Bromoimines of benzophenone, m. p. 41°, *p*-methoxybenzophenone, m. p. 95°, β -naphthophenone, m. p. 102°, and *p*-chloro-*p*methoxybenzophenone, m. p. 77.5°, are described. CHEMICAL ABSTRACTS.

Isomerism of styryl methyl ketones. J. PASCUAL (Anal. Fis. Quim., 1928, 26, 222).—An isomeride of isobenzylidenedeoxybenzoin, m. p. 78— 79°, is obtained from β -bromobenzylideneoxybenzoin by treatment with potassium acetate and acetic acid and extraction with ether. The new substance, which is white, gradually changes to the yellow isomeride (cf. A., 1925, i, 144). H. F. GILLBE.

Interaction of ethyl acetoacetate with distyryl ketones. IV. Selective addition to unsymmetrical chlorodistyryl ketones. I. M. HEILBRON and R. HILL (J.C.S., 1928, 2863-2870; cf. A., 1927, 565) .- Interaction of styryl methyl ketone with o-chlorobenzaldehyde in the presence of 0.01 mol. of aqueous sodium hydroxide led to 2-chloro-B-hydroxy-Bphenylethyl styryl ketone, m. p. 79-80°, which with acetic anhydride gave 2-chlorodistyryl ketone, m. p. 82-83°; the latter could be obtained directly by increasing the alkali concentration to 0.03 mol. 3-Chlorodistyryl ketone, m. p. 108-109°, was similarly 4-Chloro-β-hydroxy-β-phenylethyl styryl prepared. ketone has m. p. 108-109°. Condensation of 2-chlorostyryl methyl ketone with m-chlorobenzaldehyde in the presence of dry hydrogen chloride at 0° gave 2:3'-dichlorodistyryl ketone, m. p. 67-68°; 2:4'-di-chlorodistyryl ketone, m. p. 109°, and 3:4'-dichloro-distyryl ketone, m. p. 134° (3-chlorostyryl methyl ketone, b. p. 171°/20 mm., m. p. 28-29°, from m-chlorobenzaldehyde and acetone in the presence of aqueous sodium hydroxide), were prepared similarly. All the above distyryl ketones condense readily with ethyl acetoacetate in the presence of alcoholic sodium ethoxide. Thus, 2-chlorodistyryl ketone yielded ethyl 3-phenyl-5-o-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carb-oxylate, (I), m. p. 137° [also obtained by warming ethyl $(\gamma$ -keto- α -phenyl- ϵ -2-chlorophenyl- Δ^{δ} -pentenyl) acetoacetate, m. p. 112°, produced by condensation of the ketone and ethyl acetoacetate in the presence of piperidine, with alcoholic sodium ethoxide], and ethyl 3-phenyl-5-0-chlorostyryl- Δ^4 -cyclohexen-1-one-2-carboxylate (?)

(II), m. p. 107°, both of which gave o-chlorobenzoic acid when oxidised with potassium permanganate in acetone solution. When treated with sulphuric and acetic acids I afforded 3-phenyl-5-o-chlorostyryl-D5cyclohexen-1-one, m. p. 142°, whilst II gave 3-phenyl-5-0-5-chlorostyryl-∆4-cyclohexen-1-one(?), m. p. 136-137°. 4-Chlorodistyryl ketone condenses similarly to give ethyl 3-phenyl-5-p-chlorostyryl-25-cyclohexen-1-one-2carboxylate, m. p. 124-125° (oxidised to p-chlorobenzoic acid). Ethyl 3-o-chlorophenyl-5-m-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate has m. p. 108-109° and yields m-chlorobenzoic acid, and ethyl 3-o-chlorophenyl-5-p-chlorostyryl- Δ^5 -cyclohexen - 1 - one-2-carboxylate, m. p. 143°, affords p-chlorobenzoic acid on oxidation. 3:4'-Dichlorodistyryl ketone gives ethyl 3-m-chlorophenyl-5-p-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate, m. p. 122° (p-chlorobenzoic acid on oxidation). The mechanism of the reaction is discussed and an explanation of the results based on electronic conceptions is given. 2-Chlorostyryl methyl ketone condenses with m-chlorobenzaldehyde in the presence of aqueous sodium hydroxide with the formation of 2:2'-dichlorodistyryl ketone, m. p. A. I. VOGEL. 124°.

Phloracetophenone monomethyl ether and the so-called "hydroxypæonol." A. SONN (Ber., 1928, 61, [B], 2300—2302).—The constitutions assigned previously (A., 1925, i, 1267) to 2:6-di-hydroxy-4-methoxyacetophenone, m. p. 136—137°, and 4:6-dihydroxy-2-methoxyacetophenone, m. p. 205-207°, are confirmed. Both compounds are converted by diazomethane into 2-hydroxy-4:6-dimethoxyacetophenone, which is transformed by ethyl iodide and potassium hydroxide into 4:6-dimethoxy-2-ethoxyacetophenone, m. p. 69-70°. This substance is also derived from the compound, m. p. 136-137°, by the successive action of diazoethane (giving 2-hydroxy-4-methoxy-6-ethoxyacetophenone, m. p. 133-134°) and methyl iodide and potassium hydroxide, whereas the isomeric ether, m. p. 205—207°, is transformed successively into 2-hydroxy-6-ethoxy-4-methoxyaceto-phenone, m. p. 56—57°, and 2 : 6-dimethoxy-4-ethoxy-acetophenone, m. p. 81—82°. The "hydroxypæonol" of Bennie, Cocke, and Finlemen (LOS) 1000 the of Rennie, Cooke, and Finlayson (J.C.S., 1920, 117, 338) and of Finlayson (B., 1927, 27) cannot be a monomethyl ether of phloracetophenone, since its m. p. is too low and the monoethers are not volatile with steam; it is probably the dimethyl ether. H. WREN.

Tautomerism of phloracetophenone and related substances. A. SONN and K. WINZER (Ber., 1928, 61, [B], 2303—2306).—Phloracetophenone, its 2- and 4-monomethyl ethers, its dimethyl ether, diand tri-acetyltriketohexamethylene, phloroglucinol and its trimethyl ether, resorcinol, and dimethyldihydroresorcinol have been titrated with bromine in methyl alcohol and chloroform according to Meyer's method. The behaviour of phloracetophenone is best

expressed by the constitution C(OH)·CH:C·OH CH-CO-CHAC

Ethyl 4-hydroxy-2: 6-diethoxybenzoate, m. p. 180-181°, 4-methoxy-2: 6-diethoxybenzoic acid, m. p. 166° (decomp.) (methyl ester, m. p. 95°), and methyl 2-hydroxy-4-methoxy-6-ethoxybenzoate, m. p. 97-98°, are described. H. WREN. Constitution of a new hydroxybenzfluorenone. H. E. FIERZ-DAVID and G. JACCARD (Helv. Chim. Acta, 1928, **11**, 1042—1047).—Condensation of α -naphthyl methyl ether with benzoyl chloride in presence of carbon disulphide and aluminium chloride gives phenyl α -4-methoxynaphthyl ketone, m. p. 82—83°, which when heated with 6 parts of dry aluminium chloride at 100—145° affords 85% of 5-hydroxychrysofluorenone (I), m. p. 305°,



145° affords 85% of 5-hydroxychrysofluorenone (I), m. p. 305°, and 2% of 2-hydroxybenzanthrone (Perkin, J.C.S., 1922, **121**, 478, 917). The hydroxybenzanthrone described by Scholl and Seer (A., 1913, i, 56) is therefore I. Zinc dust distillation of I gives chryso-

fluorene, m. p. 188° (cf. Graebe, A., 1905, i, 83). β -Naphthyl methyl ether and benzoyl chloride yield mainly phenyl α -2-methoxynaphthyl ketone (25%) of the methoxyl group is hydrolysed), which in turn gives 4-hydroxybenzanthrone. 1:5-Dimethoxy-4:8dibenzoylnaphthalene, m. p. 356—358°, does not yield a benzanthrone derivative when heated with aluminium chloride. H. BURTON.

Derivatives of hydroxyaminomethylanthraquinones and dihydroxydianthraquinonylethylenes. H. DE DIESBACH and P. GUBSER [with R. DE LANDERSET and H. LEMPEN] (Helv. Chim. Acta, 1928, 11, 1098—1125).—2-Hydroxyanthraquinone reacts with N-methyloltrichloroacetamide (cf. Einhorn, A., 1906, i, 245) in cold concentrated sulphuric acid, yielding 2-hydroxy-1-trichloroacetamidomethylanthraquinone (I), m. p. 215° (decomp.), hydrolysed by boiling 10% sodium hydroxide solution in an atmosphere of hydrogen to 2-hydroxy-1: 9(N)-isopyrroleanthrone (II)



(annexed formula) (cf. Scholl, A., 1927, 675) (benzoyl derivative). This compound is decomposed by boiling with solvents, and dissolves in sulphuric acid and alkalis giving red solutions. One of the methylene hydrogen atoms

is very labile (cf. Scholl, loc. cit.). When II is boiled with acetic acid, preferably in absence of air, s-di-(a-2-hydroxyanthraquinonyl)ethylene glycol (tetrabenzoyl derivative $+12H_2O$) is formed, oxidised to 2-hydroxyanthraquinone-1-carboxylic acid, m. p. 237° with loss of carbon dioxide. Oxidation of I or II with gaseous oxygen in alkaline solution, or with nitrous acid after previous hydrolysis, gives s-di-(a-2-hydroxyanthraquinonyl)ethylene (III) (dibenzoyl derivative +3H₂O), also oxidised to 2-hydroxyanthraquinone-1-carboxylic acid. N-Methylolbenzamide and N-methylolphthalimide yield similarly 2-hydroxy-1-benzamidomethyl., m. p. 250° (decomp.), and 2-hydroxy-1-phthalimidomethyl-anthraquinone (IV), m. p. 265° (decomp.), respectively. Accompanying IV is some 2-hydroxy-1-anthraquinonylmethylphthalamic acid, which loses water at 190°, forming IV. When IV is treated with hot sodium hydroxide solution and then acidified, the phthalate of 2-hydroxy-1-aminomethylanthraquinone (dibenzoyl derivative, m. p. 196°) is produced, which when boiled with acetic acid furnishes the acetate. When the above phthalate is heated with acetic acid at 170° s-di-(a-2-hydroxyanthraquinonyl)ethylenediamine (tetra-

benzoyl derivative) is formed. This is converted by boiling with nitrobenzene into III. 1-Hydroxyanthraquinone and the three N-methylol compounds yield 1-hydroxy-4-trichloroacetamidomethyl-, m. p. 197° a mixture of 1-hydroxy-4-benzamidomethyl-, m. p. 208° (decomp.), and -2: 4-di(benzamidomethyl)-, m. p. 276° (decomp.), and a mixture of 1-hydroxy-2: 4-di(phthalimidomethyl)-, m. p. 295°, and -2: 4-di(phthalamidomethyl)-anthraquinones, m. p. about 178°, respectively. 1-Hydroxy-2-methylanthraquinone affords 1-hydroxy-2-methyl-4-trichloroacetamidomethyl- (V), m. p. 239°, and -4-phthalimidomethyl-anthraquinone (VI), m. p. 285°. Hydrolysis of V with 10% sodium hydroxide solution in an atmosphere of hydrogen gives 4-hydroxy-3-methyl-1:9(N)-isopyrroleanthrone, more stable than II but oxidised in alkaline solution by gaseous oxygen to s-di(x-4-hydroxy-3-methylanthraquinonyl)ethylene (VII). Hydrolysis of VI affords the phthalate of 1-hydroxy-2-methyl-4-aminomethylanthraquinone, which with acetic acid at 170° gives s-di-(a-4-hydroxy-3-methylanthraquinonyl)ethylenediamine, converted by boiling nitrobenzene into VII. 2-Hydroxy-3-methyl-1-trichloroacetamidomethyl- and -1-phthalimidomethylanthraquinones have m. p. 227° and 244°, respectively.

2-Hydroxy-1-trichloroacetamidomethylanthraquinone-3-carboxylic acid, decomp. 260° (-1-phthalimidomethyl derivative, m. p. 290°), is hydrolysed by sodium hydroxide solution to an unstable acid (2-hydroxyisopyrroleanthrone-3-carboxylic acid?) which readily loses nitrogen, furnishing s-di-(α -2-hydroxy-3-carboxyanthraquinonyl)ethylene oxide. Oxidation of the unstable acid with nitrous acid gives s-di-(α -2-hydroxy-3-carboxyanthraquinonyl)ethylene. Both these compounds are oxidised by potassium permanganate or hydrogen peroxide to 2-hydroxyanthraquinone-1:3dicarboxylic acid, decomp. about 250°.

2:3 - Dihydroxy - 1:4 - di(trichloroacetamidomethyl)anthraquinone, m. p. 253° [-1:4-di(phthalimidomethyl) derivative, m. p. 272°], is converted by warm 10% sodium hydroxide solution into β -amino- $\alpha\beta$ -bis-(α -2:3-dihydroxy-4-aminomethylanthraquinonyl)ethyl alcohol isolated as its dihydrochloride.

Anthrarufin reacts with N-methylolphthalimide, yielding 1: 5-dihydroxy-4(?)-phthalimidomethylanthraquinone, decomp. 230°, but with N-methyloltrichloroacetamide 1: 5-dihydroxy-2: 4: 6: 8-tetra(trichloroacetamidomethyl)anthraquinone, decomp. about 275°, is produced. Similarly, chrysazin gives 1: 8-dihydroxy-2: 4: 5: 7-tetra(phthalimidomethyl)-, -2: 4: 5: 7tetra(trichloroacetamidomethyl)-, decomp. 260°, and -2: 4: 5-tri(benzamidomethyl)-anthraquinones, decomp. about 250°, respectively. H. BURTON.

Munjistin. I. P. C. MITTER and A. K. SEN (J. Indian Chem. Soc., 1928, 5, 631-638).--Munjistin (Stenhouse, Annalen, 1864, 130, 325; Schunk and Römer, A., 1877, ii, 788), probably 1:3-dihydroxyanthraquinone-2-carboxylic acid, should be formed by oxidation of rubiadin (A., 1928, 763). A further attempt has been made to prepare rubiadin in order to test the above hypothesis. When o-cresol and phthalic anhydride are condensed in presence of aluminium chloride (cf. Bentley and others, J.C.S., 1907, 91, 1631; Ullmann, A., 1920, i, 53), a mixture of o-2'-hydroxy-3'-methylbenzoylbenzoic acid, m. p. 196°, and o-4'-hydroxy-3'-methylbenzoylbenzoic acid (I), m. p. 223°, is obtained. When I is heated with concentrated sulphuric acid on the water-bath, 2-hydroxy-1-methylanthraquinone, m. p. 211-212° (acetyl derivative, m. p. 125°), is produced (cf. Bentley, loc. cit.). Oxidation of this with alkaline potassium ferricyanide gives an ill-defined acid product. o-4'-Methoxy-3'-methylbenzoylbenzoic acid, m. p. 176°, is converted by heating with sulphuric acid at 155° into a mixture of 2-hydroxy-3-methylanthraquinone (II), m. p. 299° (acetyl derivative, m. p. 176°), and its methyl ether, m. p. 184°. Zinc dust distillation of II affords 2-methylanthracene, thus establishing the constitution. When II is heated with potassium hydroxide at 200-205°, 3-methylalizarin, m. p. 245-246° (acetyl derivative, m. p. 262°), is formed, and this is oxidised by manganese dioxide and concentrated sulphuric acid to 3-methylpurpurin, m. p. 234° (acetyl derivative, m. p. 287°). It was not possible to reduce 3-methylpurpurin to rubiadin by alkaline stannous chloride. Oxidation of munjistin gives no definite H. BURTON. product.

Cannizzaro's reaction in pinacolin and benzil transformations. B. L. VANZETTI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1298—1301; Chem. Zentr., 1928, i, 2823—2824).—A neutral, reddishbrown oil obtained in the preparation of veratrilic acid from veratril and potassium hydroxide is believed to be a tetramethoxyanthraquinone. A. A. ELDRIDGE.

Orcein-like dyes. II. F. HENRICH and W. HEROLD (Ber., 1928, 61, [B], 2343-2349; cf. A., 1928, 632) .- p-Amino-m-cresol is oxidised by silver oxide in dry ether to toluquinonemonimine, m. p. 59°, which may be preserved for a considerable period, particularly in the dark. Amino-orcinol, in ether or benzene, does not appear to be affected by silver oxide. 6-Amino-5-methoxy-m-cresol is readily transformed into the corresponding quinoneimine, m. p. 111° (hydrochloride, nitrate, sulphate, picrate), which gradually gives a blue, indophenol-like coloration with alkaline solutions of phenol, immediately with those of resorcinol, orcinol, or cresorcinol. Similarly, 2-amino-5-methoxy-m-cresol yields the corresponding quinone-monimine, m. p. 61°. The orcein-like dye, obtained previously (loc. cit.) by oxidation of an alcoholic solution of amino-orcinol with air, can be separated into a part soluble and a portion almost insoluble in alcohol. The insoluble portion does not yield aminoorcinol when treated with stannous chloride and hydrochloric acid, but this is obtained from the part H. WREN. soluble in alcohol.

Derivatives of dibenzanthronyl. K. ZAHN and P. OCHWAT, Assrs. to GRASSELLI DYESTUFF CORP.— See B., 1928, 808.

Manufacture of α-anthraquinonyl ketones. I. G. FARBENIND. A.-G.—See B., 1928, 887.

Manufacture of benzanthrones and intermediate products. I. G. FARBENIND. A.-G.—Sce B., 1928, 922.

Manufacture of derivatives of pyrazolanthrone. I. G. FARBENIND. A.-G.—See B., 1928, 922.

Formula of digitoxin. A. WINDAUS and G. STEIN (Ber., 1928, 61, [B], 2436-2440).-New

analyses of digitoxin and many of its derivatives indicate the formula $C_{41}H_{64}O_{13}$ for the substance and its hydrolysis to 1 mol. of digitoxigenin, $C_{23}H_{34}O_4$, and 3 mols. of digitoxose. Digitoxigenin is a simply unsaturated, dihydroxy-lactone containing a system of four carbocyclic rings. One of the two hydroxyl groups is secondary and readily acetylated; the other is tertiary and is readuly eliminated as water by combination with a neighbouring hydrogen atom. The following revised data are recorded (cf. Cloetta, A., 1921, i, 39; Windaus and Freese, A., 1926, 153): digitoxigenin, $C_{23}H_{34}O_4$, m. p. 250°, $[\alpha]_{17}^{17} + 19\cdot1°$ in methyl alcohol; acetyldigitoxigenin, $C_{25}H_{36}O_5$, m. p. 217°; anhydrodigitoxigenin, $C_{23}H_{32}O_3$, m. p. 193°, $[\alpha]_{15}^{18} - 4.68^{\circ}$ in methyl alcohol; tetrahydroanhydrodigitoxigenin, $C_{23}H_{36}O_3$, m. p. 167—168°, $[\alpha]_{15}^{18} + 24.60^{\circ}$ in methyl alcohol; tetrahydroanhydrodigitoxigenone, $C_{23}H_{24}O_3$, m. p. 245°, $[\alpha]_{15}^{18}$ +37.3° in chloroform, converted by Clemmensen's method into the lactone, $C_{23}H_{36}O_2$, m. p. 185°, $[\alpha]_{1}^{16} + 33 \cdot 7^{\circ}$ in chloroform; the lactonedicarboxylic acid, $C_{23}H_{34}O_6$, has m. p. 296°, and its dimethyl ester, $C_{25}H_{38}O_6$, m. p. 128°. Further study of the isomerisation of digitoxigenin by alkali hydroxide considered in conjunction with the observations of Jacobs and Gustus (A., 1928, 1120) permits the identification of the following arrangements :



New or revised data are given for the following compounds: *iso*digitoxigenin, m. p. 272° (acetyl derivative, m. p. 243°); digitoxigenone, m. p. 200°, $[\alpha]_{15}^{16}$ +33·3° in chloroform; *iso*digitoxigenone, m. p. 264°, $[\alpha]_{15}^{16}$ +19·5° in chloroform. H. WREN.

Amyrins. I. Dehydrogenation of amyrin. O. BRUNNER (Monatsh., 1928, 50, 284—290).—Since the isomerism of the amyrins probably disappears on dehydrogenation, the investigation was carried out with the mixture of the two isomerides. When heated with sulphur a violent reaction took place with foaming and carbonisation, but dehydrogenation occurred smoothly by heating with palladised animal charcoal (cf. Diels and Gädke, A., 1925, i, 1062) at 290° for 100 hrs. and finally at 320° for 24 hrs. The product was extracted with ether and fractionated. The fraction of b. p. 120—150°/12 mm. yielded the picrate, m. p. 131—132°, of an oily hydrocarbon (C, 91.43; H, 9.20%; mol. wt. 179). The fraction of b. p. 150—190°/12 mm. yielded the picrate of a hydrocarbon, m. p. 87° (C, 90.97; H, 10.36%; mol. wt. 197). The higher-boiling fractions yielded no crystalline compound. R. K. CALLOW.

Osmotic experiments with caoutchouc solutions. H. KROEPELIN and W. BRUMSHAGEN (Ber., 1928, 61, [B], 2441-2443).—Measurements of the osmotic pressure of benzene solutions of sol caoutchouc obtained from crêpe rubber extracted with acetone at concentrations of 10—20 g. per litre give results for the micellar weight of the same order of magnitude as those of Meyer and Mark (A., 1928, 1252). H. WREN.

Effect of silent electric discharge on caoutchouc and decalin. P. FROMANDI (Kolloidchem. Beihefte, 1928, 27, 189-222).-When the silent electrical discharge acts on decahydronaphthalene, hydrogen is eliminated and this process is followed by condensation of the resulting unsaturated molecules. The exact course of the reaction depends on the atmosphere in which the experiment is conducted; thus, the unsaturated compound forms an ozonide in an atmosphere of oxygen, and in a nitrogen atmosphere an entry of nitrogen into the molecule takes place. The experiments on caoutchouc were carried out in decahydronaphthalene as solvent. Natural caoutchouc passes into a cyclic isomeride under the influence of the silent electric discharge. Meanwhile, the iodine value, viscosity, softening point, and mol. wt. are lowered. Synthetic isoprene caoutchouc, which from its iodine value already appears to have a cyclic structure, behaves similarly, with the exception that in the first stages of the process the charge is in the reverse direction. This latter fact seems to suggest that the physical and chemical properties of synthetic caoutchouc may be made to resemble those of the natural material. The effect of ultra-violet light is not similar to that of the silent electric discharge in the above cases. E. S. HEDGES.

Structure of terpin hydrate. A. S. GINZBERG and M. S. ESCHMANN (J. Russ. Phys. Chem. Soc., 1928, 60, 1165—1171).—It is concluded that terpin hydrate does not possess the open-chain structure ascribed to it by Tiemann. Oxidation with potassium permanganate yielded only acids, without any trace of aldehyde or ketone, such as might have been expected had a primary carbinol group been present. Metallic sodium gave only terpin and sodium hydroxide in equivalent amounts. The determination of the number of hydroxyl groups by the Tschugaev-Zerevitinov method (with magnesium alkyl halides) showed conclusively that two hydroxyl groups and one molecule of water of crystallisation were present. This was further confirmed by the formation in the cold of s-diphenylcarbamide with phenylcarbimide, instead of a phenylcarbamate. The absence of a primary alcohol grouping was further demonstrated by the negative action of benzoyl chloride, methyl sulphate, or Nessler's reagent. Terpin hydrate, accordingly, is concluded to be, like many tertiary M. ZVEGINTZOV. alcohols, a crystallohydrate.

Nopinene ozonide. G. BRUS and G. PEYRES-BLAUQUES (Compt. rend., 1928, 187, 984–986).— When nopinene is ozonised in chloroform solution at 0° and the solvent is evaporated, the ozonide, $C_{10}H_{16}O_3$, is obtained as a viscous liquid, which slowly and partly crystallises at 0°. This when hydrolysed by acid or alkali furnishes hydrogen peroxide, formaldehyde, nopinone, and a crystalline substance, m. p. 125–126°,

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possibly the lactone,

As the yield of nopinone (characterised by the formation of a compound $C_{18}H_{29}OCl_3$, m. p. 145—146°, by the action of hydrogen chloride in alcoholic solution) is 50%, the present is the best method of preparation. Determination of the formaldehyde obtained furnishes an accurate determination of nopinene (cf. Dupont and Brus, A., 1923, i, 934); the sample used was found to contain 93% of a substance containing the CH₂: grouping.

E. W. WIGNALL. Configuration of tervalent nitrogen. M. FRÉREJACQUE (Compt. rend., 1928, 187, 894-896).-Various amines have been condensed with camphora-sulphonyl chloride, m. p. 88° (amide, m. p. 143°, [a]₅₄₆₁ +94° in water; cf. A., 1926, 1251), and thus are obtained the camphorsulphonyl derivatives of aniline, m. p. 124°, $[\alpha]_{5461}$ -42·5° (alcohol); o-toluidine, m. p. 117°, $[\alpha]_{5461}$ -49·5° (alcohol); p-toluidine, m. p. 197°, $[\alpha]_{5461}$ -52·5° (alcohol); p-toluidine, m. p. 197°, $[\alpha]_{5461}$ -52·5° (alcohol); and ethylaniline, m. p. 89°, $[\alpha]_{5461}$ -68° (benzene). In neutral solvents these derivatives are strongly lævorotatory, whilst the sulphonic acid, its methyl ester, amide, and chloride are dextrorotatory, but in alkaline solution the anilides are dextrorotatory, this being explained by the conversion of the camphor portion of the molecule into the enol form. The rotation of the anilides increases proportionately to the amount of alcoholic potassium hydroxide added until an equimolecular proportion has been added and then remains constant. All attempts to isolate enantiomorphous forms of these compounds of tervalent nitrogen were unsuccessful, the rotation remaining unchanged after fusion for several hours, or after reprecipitation by acids from their solutions in dilute alkalis. J. W. BAKER.

Compounds of camphor with amines. E. ROMAGNOLI (Annali Chim. Appl., 1928, 18, 465–468; cf. Saccardi and Romagnoli, A., 1927, 1196)— Camphor-2-aminodimethylphenylisopyrazolone,

 $\begin{array}{c} \mathrm{CH}_2 \cdot \mathrm{CMe} \cdot \mathrm{CH}_2 \\ | & \mathrm{CMe}_2 | \\ \mathrm{CH}_2 \cdot \mathrm{CH} - \mathrm{CN} \cdot \mathrm{C} \\ \end{array} \\ \begin{array}{c} \mathrm{CH}_2 \cdot \mathrm{CH} - \mathrm{CN} \cdot \mathrm{C} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \mathrm{NPh} \\ \mathrm{NMe} \end{array}$

m. p. 194°, prepared from pernitrosocamphor and aminoantipyrine, is readily split into the component molecules by hydrochloric acid, and forms with hydroferrocyanic acid an additive *compound*, charring at about 160°, T. H. POPE.

Constituents of campherol. M. ISHIDATE (J. Pharm. Soc. Japan, 1928, No. 555, 410–415; cf. A., 1928, 526).—By repeated fractional crystallisation from light petroleum, *d*-campherol is separated into 5-hydroxycamphor, m. p. 217–218°, $[\alpha]_D^{\infty}$ +41·3° (acetyl derivative, b. p. 159–160°/27 mm., $[\alpha]_D^{\infty}$ +24·8°; semicarbazone, m. p. 233–235°), and 3-hydroxycamphor, m. p. 193–195°, $[\alpha]^{\circ}$ +15·2° (semicarbazone, m. p. 183–184°). K. ISHIMURA.

Synthesis of tetrahydrofurylpropylamine. R. TAKAMOTO and T. HIROHASHI (J. Pharm. Soc. Japan, 1928, No. 555, 446—450).— β -2-Furylacraldoxime is reduced with sodium amalgam to γ -2-furylpropylamine, b. p. 172·5—173°/754 mm., 34—35°/20 mm. (platinum double salt, m. p. 179—180°; picrate, m. p. 165—166°; picrolonate, m. p. 231—232°), which
is converted by hydrogen and platinum into γ -2-tetrahydrofurylpropylamine, b. p. 186—187°/754 mm., 46—47°/20 mm. (platinum double salt, m. p. 171— 172°; picrate, m. p. 136—137°; picrolonate, m. p. 176—177°). K. ISHIMURA.

αα'-Disubstituted-αα'-dihydro-ββ'aaand benzofurans. F. SEIDEL (Ber., 1928, 61, [B], 2267-2276).-2:2-Diphenyl-1:2-diphenyl-1:2-dihydroisobenzfuran, described by Guyot and Catel (A., 1905, i, 226, 540; 1906, i, 761; 1907, i, 76), and o-benzoyldiphenylmethane are completely independent compounds which cannot be transformed into one another. Phthalide is converted by magnesium phenyl bromide in ether into o-hydroxymethyltriphenylcarbinol, m. p. 159°, transformed by boiling hydrochloric and acetic acids into 2:2-diphenyl-1:2-dihydroisobenzfuran, m. p. 95°, which does not react with phenyl- or benzoyl-hydrazine or p-nitroaniline and is not reduced by zinc and acetic acid, hydriodic acid, tin and hydrochloric acid, sodium amalgam, or sodium. It is oxidised by potassium dichromate in acetic acid to diphenylphthalide, m. p. 115-116°. Boiling, dilute nitric acid transforms it into the ether,

 $(C_6H_4 < CPh_2O)_2O$, m. p. 259—260°, oxidised by potassium dichromate and acetic acid to diphenylphthalide and converted by hydrochloric acid and ethyl alcohol at 135° into 1-ethoxy-2:2-diphenyl-1:2-dihydroisobenzfuran, m. p. 97°. Addition of a solution of phenylphthalide in benzene to ethereal magnesium phenyl bromide affords 1-hydroxy-1:2-diphenyl-1:2-dihydroisobenzfuran, reduced by sodium amalgam and methyl alcohol to 1:2-diphenyl-1:2-dihydroisobenzfuran, m. p. 93—95°, which does not react with hydrazine or 2:4-dinitrophenylhydrazine and is oxidised by nitric acid to o-dibenzoyl-

benzene, m. p. 148°. o-Benzoyldiphenylmethane, b. p. 220—225°/15—17 mm., m. p. 47—50° (phenylhydrazone, m. p. 139°), prepared from o-cyanodiphenylmethane and magnesium phenyl bromide, is oxidised by nitric acid to o-dibenzoylbenzene. o-Aminobenzyl chloride hydrochloride is converted by benzene in the presence of aluminium chloride into o-aminodiphenylmethane hydrochloride, m. p. 180°, from which o-iododiphenylmethane, b. p. 175—180°/14—17 mm., is derived. H. WREN.

7-Hydroxy-6-methoxycoumarin and its glucoside. E. GLASER [with M. SCHNECK] (Arch. Pharm., 266, 573-582).-Partial methylation of 1928, æsculetin (7:6-dihydroxycoumarin) with methyl iodide affords a-methylæsculetin, m. p. 184° (Tiemann and Will, A., 1883, i, 199), which is shown to be 6-hydroxy-7-methoxycoumarin. Methyl sulphate and potassium hydroxide in methyl-alcoholic solution, however, furnish 7-hydroxy-6-methoxycoumarin, yellow, m. p. 199°, in 75% yield, identical with β -methylæsculetin, scapoletin, gelsemic acid, and chrysotropic acid, for which the following colour reactions are described : ferric chloride, green; potassium permanganate, dark green, turning indigoblue with dilute sulphuric acid; boiling concentrated hydrogen sulphite solution followed by ferric chloride, blue, changing to red on addition of ammonia solution.

Its solutions in alkali or alcohol fluoresce more strongly than those of æsculetin. Condensation of acetobromoglucose with β-methylæsculetin (7-hydroxy-6methoxycoumarin) in presence of alkali gives 6-methoxy-7-coumarinyl tetra-acetylglucoside, m. p. $104-105^{\circ}$, $[\alpha]_{D}^{15}$ -39° in methyl alcohol. This is a β-glucoside according to the emulsin test, and is hydrolysed by absolute methyl-alcoholic ammonia to 6-methoxy-7-coumarinyl β-glucoside, m. p. 127-128°, $\left[\alpha\right]_{0}^{12}$ -37.5° in water. The parent glucoside and, incidentally, also methylæsculin give a clear green coloration with ferric chloride, whilst the tetraacetate remains colourless in the cold but becomes red on boiling. Colour reactions with potassium permanganate and nitric acid are similar in both cases. The fluorescence of these substances in acid solution has been studied: methylæsculetin>æsculetin> S. COFFEY. methylæsculin.

New synthesis of coumarin derivatives. R. WEISS and E. MERKSAMMER (Monatsh., 1928, 50, 115-122).-The reaction previously described (Weiss and Woidich, A., 1927, 250), in which resacctophenone is condensed with ethyl ethoxyacetoacetate by heating with alcoholic sodium ethoxide, has been further investigated, and the product is now found to be 7-hydroxy-3: 6-diacetylcoumarin. The reaction affords a new general synthesis of coumarin derivatives. Proof of this interpretation is given by the reaction of resorcinol with ethyl ethoxyacetoacetate to yield 7-hydroxy-3-acetylcoumarin, m. p. 236°, identical with the product obtained by Knoevenagel's method by the condensation of resorcylaldehyde with ethyl acetoacetate. It yields a p-bromobenzoyl derivative, m. p. 212-214°, and reacts with hydrazine hydrate to give resorcylaldazine (+H₂O), m. p. above 300° (cf. Knöpfer, A., 1909, i, 188).

7-Hydroxy-3: 6-diacetylcoumarin is accompanied by a substance, $C_{16}H_{14}O_6$, m. p. 192—197°, in small amount. The substance previously described as 2-resorcyl-5-benzoyl-1: 4-pyrone is actually 7-hydroxy-3-benzoyl-6-acetylcoumarin. The following compounds, prepared by the same method, are described: 7-hydroxy-3: 6-diacetyl-5-methylcoumarin, m. p. 211— 212° (from orcacetophenone); 7-hydroxy-6-benzoyl-3acetylcoumarin, m. p. 215—217° (from 2: 4-dihydroxybenzophenone); 7: 8-dihydroxy-3-acetylcoumarin, m. p. 254—255° (from pyrogallol). Methyl methoxyacetoacetate, also used in these reactions, was obtained crystalline, m. p. 56—58°. R. K. CALLOW.

Production of thiophen by the interaction of acetylene and carbon disulphide. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1928, 2857—2858).—Thiophen obtained from acetylene and sulphur (cf. Peel and Robinson, A., 1928, 1112) is produced probably by a direct reaction of acetylene with sulphur, and not by a secondary reaction between acetylene and carbon disulphide. Thiophen is produced in quantity by the latter reaction only when temperatures considerably higher than those required with sulphur are used. Acetylene saturated with carbon disulphide vapour was passed through a tube packed with broken porous pot and heated electrically. At 350° a trace of thiophen

appeared; at 700° maximum formation occurred, the condensate containing 10% by volume of thiophen and 10% of hydrocarbons. R. J. W. LE FEVRE.

Primary tar oils [thiophens]. R. WEISSGERBER. -See B., 1928, 917.

Alkylation and acylation of thiophen in presence of tin tetrachloride. G. STADNIKOV and I. GOLDFARB (Ber., 1928, 61, [B], 2341-2342; cf. A., 1928, 427).-The yields of acylated thiophens obtained by the action of acid chlorides on thiophen in presence of tin tetrachloride depend considerably on the solvent employed. The yield of acetylthiophen increases from 50-58% to 96% when petroleum, b. p. 120-140°, is replaced by benzene. Benzoylthiophen. m. p. 55°, is prepared in 92% yield in presence of benzene. Benzhydryl ethyl ether, thiophen, and stannic chloride in carbon disulphide afford diphenylthienylmethane, m. p. 65°, and dibenzhydrylthiophen, m. p. 85-85.5° (oxidised by chromic acid to benzophenone). H. WREN.

Thiophenols. Formation of rings containing sulphur. C. FINZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1312—1314; Chem. Zentr., 1928, i, 2178).—The formation of thioresorcinol-o-benzoic acid, dithioxanthone, dithioxanthhydrol, thio-resorcinoldipropionic acid, dithiochromanone, ketodihydrothiazinethiopropionic acid, thioresorcinol-Bphenylpropionic acid, and dithioflavanone is described.

A. A. ELDRIDGE. Derivatives of isatin. A new example of isomerism. N. J. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1179-1190).-The condensation of sodio-isatin with ethyl chloroacetate and chloromalonate and with ethylene dibromide was investigated. Sodio-isatin and ethyl chloroacetate gave a good yield of ethyl isatin-N-acetate, m. p. 114°, which could be hydrolysed only with extreme difficulty by aqueous hydrogen iodide, with partial reduction,



to give a compound, m. p. 219-220°, of the annexed formula.

With ethyl chloromalonate.

 $N \cdot CH_2 \cdot CO_2 H$ sodio - isatin yielded diethyl isatin-N-malonate, m. p. 82°. Interaction of sodio-isatin with ethylene dibromide was very slow, the final products being isatin N-ethyl bromide, m. p. 130°, and ethylenedi-isatin, m. p. 190°. Further condensation of isatin N-ethyl bromide with ethyl sodiomalonate yielded a mixture of unidentified products together with *n*-propylaniline. When ethylenedi-isatin was distilled with lime, an oil containing aniline and quinoline was obtained. The quinoline was separated from aniline by means of silver nitrate, which formed with it a compound, m. p. 128°, from which the silver can be removed by ammonium sulphate. M. ZVEGINTZOV.

Synthesis of carboline derivatives. G. TATSUI (J. Pharm. Soc. Japan, 1928, No. 555, 453-459).β-(3-Indolyl)ethylamine reacts with paraldehyde, yielding tetrahydroharman, m. p. 179-180° [hydrochloride, m. p. 265° (decomp.); benzoyl derivative, m. p. 168-169°], which with ethyl sodiomalonate at 110120° gives tetrahydroharmanmalonate, m. p. 134 135°, thus :



Tetrahydroharmanmalonic acid loses carbon dioxide at 155°, giving acetyltetrahydroharman.

K. ISHIMURA. Acridone derivatives. R. WEISS (Monatsh., 1928, 50, 109-114).-An account is given of unsuccessful attempts to synthesise a heterocyclic analogue of trimethylenetriphenylmethane triketone (Weiss and Korezyn, A., 1925, i, 560) derived from triphenylamine.

[With L. KATZ.]-3-Nitro-4-methylbenzophenone, m. p. 130-132°, was prepared from 2-nitro-p-toluoyl chloride and benzene by the Friedel-Crafts reaction. The 3-amino-derivative, m. p. 108-110°, obtained by reduction with stannous chloride, yielded with o-chlorobenzoic acid by the Ullmann reaction N-(5'benzoyl-o-tolyl)anthranilic acid (+0.5H2O), m. p. 190-192° (methyl ester, m. p. 95-100°). Condensation of o-chlorobenzoic acid with 2-amino-p-toluic acid hydrochloride yielded 2-methyldiphenylamine-5: 2'-dicarboxylic acid [N-(5-carboxy-o-tolyl)anthranilic acid], m. p. 257° (decomp.). Attempts to prepare acridone derivatives from either of these anthranilic acids were unsuccessful.

[With W. HANDL and J. L. MELZER.]-Condensation of o-iodotoluene with N-o-tolylanthranilic acid yielded NN-di-o-tolylanthranilic acid, m. p. 206-209°. When heated with concentrated sulphuric acid it yielded N-o-tolyl-4-methylacridone, m. p. 197-199°. Similarly, N-phenyl-N-o-tolylanthranilic acid, m. p. 166-168°, yielded a mixture, m. p. 180-195°, of N-o-tolyl- and N-phenyl-4-methyl-acridones. Attempts to oxidise the methyl groups of the anthranilic acids or to bring about further ring-closure in the acridones were unsuccessful. R. K. CALLOW.

Pyridine and quinoline derivatives. III. New synthesis of 2-aminonicotinic acid and its behaviour with nitric acid. C. RATH and G. PRANGE (Annalen, 1928, 467, 1-10).-2: 5-Diaminopyridine (obtained by electrolytic reduction of 5-nitro-2-aminopyridine) is converted (yield 50%) by the Sandmeyer reaction into 5-cyano-2-aminopyridine, b. p. 240-250°/15 mm., m. p. 163-164°, which is hydrolysed to 2-aminopyridine-5-carboxylic acid $+2H_2O$ (I), decomp. 312° [*nitrate*, m. p. 242° (decomp.)]. This is converted by the action of a mixture of sulphuric and nitric (d 1.35) acids not, as Marckwald (A., 1894, i, 381) states, into the nitrate, but into 2-nitroaminopyridine-5-carboxylic acid (II), decomp. explosively 233° (sodium salt), which is reduced by tin and hydrochloric acid to I, and, also contrary to Marckwald (loc. cit.), is converted by 10% sodium hydroxide into the disodium salt of 3-nitro-2-hydroxypyridine-5-carboxylic acid, m. p. 277°

(decomp.); the free acid is converted by the action of iodine, potassium hydroxide, and sodium hydrogen carbonate at 150-160° into 5-iodo-3-nitro-2-hydroxypyridine. If I is nitrated under Tschitschibabin's conditions (cf. A., 1915, i, 591) and the whole reaction mixture subsequently heated to 100°, the main product is 2-hydroxypyridine-5-carboxylic acid, converted by iodine and sodium hydrogen carbonate into J. W. BAKER. 3:5-di-iodo-5-hydroxypyridine.

quinoline-2-aldehyde. Dyes derived from A. N. DEY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 535-537) .- Condensation of quinoline-2-aldehyde with dimethylaniline in presence of zinc chloride, and subsequent oxidation of the product formed with manganese or lead dioxide, affords pp'-tetramethyldiaminodiphenyl-\$-quinolinylcarbinol, m. p. 196-198°. The corresponding tetraethyldiamino-, m. p. 144-145° dibenzyldimethyldiamino-, m. p. 172-174°, and dibenzyldiethyldiamino-derivatives, m. p. 252-254°, are obtained from diethyl-, benzylmethyl-, and benzylethyl-aniline, respectively. If 2-methylquinoline tribromide is used instead of the aldehyde the carbinols can be obtained directly. The dyes described are green or blue-green and are devoid of H. BURTON. photosensitising properties.

Derivatives of diketopiperazine. Synthesis of o- and m-tyrosine. H. UEDA (J. Biochem. Japan, 1928, 8, 397–407).—3:6-Di-(o-acetoxybenzylidene)-2:5-diketopiperazine, obtained by condensation of glycine anhydride with salicylaldehyde, was diacetylated and reduced to o-tyrosine anhydride. Condensation of glycine anhydride with o-methoxybenzaldehyde afforded 3:6-di-(o-methoxybenzylidene)-2:5-diketopiperazine, or with m-hydroxybenzaldehyde, the corresponding m-compound. The latter, on deacetylation and reduction, gave *m*-tyrosine anhydride. Reduction before hydrolysis produced CHEMICAL ABSTRACTS. the amino-acids.

Pyrazole derivatives of the type of diketopiperazine. K. von Auwers and E. CAUER (Ber., 1928, 61, [B], 2402-2411).-Pyrazolecarboxylic acids generally lose carbon dioxide when heated above their m. p. and pass into the corresponding pyrazoles, but in certain cases amorphous products of high m. p. are formed in greater or smaller amount. These substances are also produced by attempts to acylate certain pyrazolecarboxylic acids. They are doubtless diketopiperazine derivatives of the type

CH < CH:C+CO+N-N > CH. Introduction of an acyl

group into an aliphatic a-amino-acid scarcely affects the behaviour of the compound when heated. If an acid residue is attached to one of the nitrogen atoms of a pyrazolecarboxylic acid, the tendency to lose carbon dioxide when heated may be greatly or completely repressed. The approximate yields of diketopiperazine and acylpyrazole obtained when the various acids are heated are given in parentheses : N-carbethoxy-4-methylpyrazole-3-carboxylic acid (20%, 80%); N-o-nitrobenzoyl-4-methylpyrazole-3-carboxylic acid (60%, 40%); *N-o*-nitrobenzoyl-5-methyl-pyrazole-3-carboxylic acid (90%, 10%); *N*-acetyl-5-methylpyrazole-3-carboxylic acid (100%, 0%);

N-acetyl-4-bromo-5-methylpyrazole-3-carboxylic acid (100%, 0%); N-carbethoxy-4:5-dimethylpyrazole-3carboxylic acid (50%, 50%); N-acetyl-4-phenyl-pyrazole-3-carboxylic acid (100%, 0%). The pro-duction of diketopiperazines by the acylation of pyrazolecarboxylic acid does not depend greatly on the mode of operation (heating with acyl chloride or treatment in pyridine), but the influence of the structure of the pyrazole and nature of the acyl chloride is very marked. The yields of diketopiperazine and acyl derivative obtained by the two processes are given below : pyrazole-3-carboxylic acid and o-nitrobenzoyl chloride (little, much, 50%, 50%); 4-methylpyrazole-3-carboxylic acid with ethyl chloroformate (0%, 100%), acetyl chloride (0%, 100%, 0%, 100%), 0%, 100%) or *o*-nitrobenzoyl chloride (0%, 100%, 5%, 95%); 5-methylpyrazole-3-carboxylic acid with acetyl chloride (5%, 95%, 10%, 90%), or o-nitro-benzoyl chloride (95%, 5%, 100%, 0%); 4:5-dimethylpyrazole-3-carboxylic acid with ethyl chloroformate (--, 80%), with acetyl chloride (10%, 90%) or o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); 4-chloro-5-methylpyrazole-3-carboxylic acid with o-nitrobenzoyl chloride (100%, 0%); 4-bromo-5methylpyrazole-3-carboxylic acid with acetyl chloride (10%, 90%) or *o*-nitrobenzoyl chloride (100%, 0%, 100%, 0%); 4-phenylpyrazole-3-carboxylic acid with acetyl chloride (0% 100%) or o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); 4-phenylpyrazole-3-carb-oxylic acid with o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); tetrahydroindazole-3-carboxylic acid with o-nitrobenzoyl chloride (0%, 100%). Thionyl chloride is the most suitable acid chloride for the transformation of pyrazolecarboxylic acids into diketopiperazines. Glycine and o - nitrobenzoyl chloride react vigorously at 135° without giving a piperazine derivative, but the acid is not affected by thionyl chloride. Boiling acetic anhydride, which converts a-amino-acids into diketopiperazines, mainly acetylates pyrazolecarboxylic acids. Whereas esters of a-amino-acids are usually converted more or less readily into diketopiperazines at the ordinary temperature, pyrazolecarboxylic esters are stable under these conditions but lose carbon dioxide when heated without production of anhydrised compounds.

The following compounds appear to be new : N-onitrobenzoylpyrazole-3(5)-carboxylic acid, m. p. 195-196°; ethyl N-chloroacetyl-5-methylpyrazole-3-carboxylate, m. p. 127.5-129.5°; 3-methyl-5-ethylpyrazole, b. p. 118°/12 mm. (picrate, m. p. 137.5-139°; an isomeric picrate, m. p. 126-128°, is described); 3(5)-propylpyrazole, m. p. 117°/13 mm. (picrate, m. p. 150–152°); diketopiperazine, $C_{12}H_{12}O_2N_4$. m. p. 285–286°, from 4 :5-dimethylpyrazole-3-carboxylic acid and o-nitrobenzoyl chloride; N-acetyl-4-phenylpyrazole-3-carboxylic acid, m. p. 162.5-164.5° (decomp.).

H. WREN.

Relative tenacity of alkyl groups towards nitrogen. K. VON AUWERS and W. MAUSS (Ber., 1928, 61, [B], 2411-2420; cf. A., 1925, i, 1100; 1928, 306).-Thermal decomposition of the iodides of NN'-dialkylbenziminazoles, (C₆H₄< $\frac{NR}{NR'}$ >CH)X,

requires somewhat protracted heating at an elevated temperature and yields a considerable proportion of

resinous matter, whilst the decomposition products are mixed with unchanged original material. The compounds are therefore not so suitable as the indazolium salts for the comparison of the tenacities of alkyl groups. Nevertheless such tenacity is found to increase in the order methyl, ethyl, propyl, and to diminish with benzyl. With simple iminazoles (cf. Sarasin, A., 1923, i, 710), von Braun's rule is followed by the methylethyl and methylpropyl but not by the ethylbutyl and propylbutyl derivatives. The ethylpropyl compound behaves unexpectedly by yielding ethyliminazole. Somewhat similar irregularities are observed with tetra-alkylammonium salts, so that it appears that the thermal decomposition of quaternary salts can be applied to the constitution of tenacity series only in very definite circumstances.

The following compounds are described: 1:3-diethylbenziminazolium iodide, m. p. 225-227°, and the corresponding picrate, m. p. 254-257°; 1-ethylbenziminazole, b. p. 160-162°/12 mm. (picrate, m. p. 219°); 1-methyl-3-ethylbenziminazolium iodide, m. p. 192-193°; 1-benzylbenziminazole, m. p. 115-115·5° (picrate, m. p. 161-163°); 1-methyl-3-benzylbenziminazolium iodide, m. p. 158°; 1:3-dipropylbenziminazolium iodide, m. p. 202-203°; 1-propylbenziminazole, b. p. 170-172°/14 mm. (picrate, m. p. 204-206°); 1-ethyl-3-propylbenziminazolium iodide, m. p. 172°; 1-benzyl-3-ethylbenziminazolium iodide, m. p. 173·5-174·5°; 1-n-butyliminazole, b. p. 114-116°/12 mm. (picrate, m. p. 79·5-81·5°); 1-ethyl-3-butyliminazolium iodide; 1-propyl-3-butyliminazolium iodide.

Triethylpropylammonium iodide, m. p. 255—256°, decomposes at 260—270° into ethyl iodide and diethylpropylamine. Ethyltripropylammonium iodide affords propyl iodide and ethyldipropylamine. Diethyldipropylammonium iodide, m. p. 238—240°, gives ethyl and propyl iodides and diethylpropylamine and ethyldipropylamine. H. WREN.

Preparation of histidine. F. CHEMNITIUS (Pharm. Zentr., 1928, 69, 741-742).-Ox blood is hydrolysed with boiling hydrochloric acid (d 1.19) and the product distilled in a vacuum at 50°. The syrupy residue is neutralised with 0.1N-sodium hydroxide and sodium carbonate without allowing the temperature to rise, filtered, and heated with 0.2Nsodium hydroxide until all the ammonia is expelled. After filtering off small quantities of leucine and tyrosine which separate, histidine is precipitated as its double mercurichloride by alternate addition of a hot solution of mercuric chloride and a cold solution of sodium carbonate so that the reaction mixture remains alkaline. The precipitate, purified by reprecipitation with sodium carbonate from its solution in dilute hydrochloric acid, is decomposed by hydrogen sulphide, and the filtrate concentrated to yield histidine hydrochloride, which may be purified by crystallisation from 60% alcohol or by conversion into the picrate. J. W. BAKER.

Synthesis of methyl 2:4-dihydroxybenz-1:10-naphthyridine-3-carboxylate. G. KELLER and E. STRANG (Monatsh., 1928, 50, 144-148).-Quinoline-2:3-dicarboxylic acid (cf. A., 1928, 1024) was converted into the anhydride, m. p. 223° (cf. Konopnicki and Sucharda, A., 1928, 73), by heating with acetic anhydride. Treatment of the anhydride with ammonia in benzene solution yielded the amorphous quinoline-2-carboxylamide-3-carboxylic acid, sintering at 175°, m. p. 189—190°, which, by the action of sodium hypobromite, yielded 2-aminoquinoline-3-carboxylic acid, m. p. 290—292° (decomp.), from



H which 2-aminoquinoline was obtained by distillation. Methyl CO₂Me 2-aminoquinoline-3-carboxylate, m. p. 140-141°, ethyl malonate, and sodium ethoxide when heated at 145-150° gave

methyl 2: 4-dihydroxybenz-1: 10-naphthyridine-3-carboxylate (annexed formula), m. p. 240°, gelatinous from alcohol. R. K. CALLOW.

Manufacture of derivatives of pyrazolanthrone and of vat dyes. I. G. FARBENIND.—See B., 1928, 922, 923.

Red quinoline dye of Besthorn. H. WIELAND, O. HETTCHE, and T. HOSHINO (Ber., 1928, 61, [B], 2371—2381; cf. A., 1904, i, 527; 1905, i, 612).—The dye obtained by Besthorn by heating quinoline-2-carboxylic acid with acetic anhydride or from quinoline-2-carboxyl chloride and quinoline is readily hydrogenated in the presence of Adams' platinum catalyst to the compound C19H18ON2, m. p. 155°, which is readily re-converted into the dye. It is isomerised by boiling methyl-alcoholic potassium hydroxide to the β -compound, $C_{19}H_{18}ON_2$, m. p. 133—134°, reconverted by lead peroxide into the dye. Either the α - or β -form of the hydro-compound is transformed by 20% hydrochloric acid at 150° into a mixture of dihydrocarbostyril, m. p. 163-164°, 1:2:3:4tetrahydroquinoline, quinoline, and 1:2:3:4-tetrahydroquinoline-2-carboxylic acid (isolated as the hydrochloride dihydrate, m. p. 115-125°, decomp. 200°), and a yellow resin probably containing poly-merised dihydroquinoline. The non-appearance of tetrahydrocarbostyril is due, probably, to its instability. The results are interpreted as giving confirmation to the constitution I of the hydrocompound and to formula II for the dye :



The following observations are recorded as results of unsuccessful attempts to synthesise the hydroderivative. Quinoline-2-carboxyl chloride condenses with tetrahydroquinoline to 2-quinolyl 1-tetrahydroquinolyl ketone, m. p. 115-116° (hydrochloride, m. p. 160-162°), which could not be hydrogenated or oxidised directly to Besthorn's dye. 1:2:3:4-Tetrahydroquinoline-2-carboxylic acid, m. p. 112-113° (hydrochloride, m. p. 115-120° with loss of water of crystallisation, m. p. [anhyd.] 200° [decomp.]; methyl ester, b. p. 180°/15 mm., and its hydrochloride, m. p. 191°; nitroso-derivative, decomp. 132°), is prepared by hydrogenation of quinoline-2-carboxylic acid in glacial acetic acid in presence of Adams' platinum catalyst. Hydrogenation of the methyl ester with

palladium-black affords methyl di-4:4'-tetrahydroquinolyl-2: 2'-dicarboxylate, m. p. 175-176°, in addition to the simple ester, but this complication is not observed when the Adams catalyst is employed. The acid hydrochloride is converted by ethyl chloroformate in weakly alkaline solution into 1-carbethoxy-1:2:3:4-tetrahydroquinoline-2-carboxylic acid, m. p. 96-97°, converted by hot thionyl chloride into the corresponding anhydride, m. p. 155-156°. 1:2:3:4-Tetrahydroquinoline-2-carboxylic acid hydrochloride is transformed by acetic anhydride in pyridine into 1-acetyl-1:2:3:4-tetrahydroquinoline-2-carboxylic acid, m. p. 175—176°, and by benzoyl chloride and sodium hydroxide into 1-benzoyl-1:2:3:4-tetrahydroquinol-ine-2-carboxylic acid, m. p. 187—188° (decomp.), which with thionyl chloride yields a labile compound containing sulphur and ultimately decomposing into quinoline-2-carboxyl chloride and sulphur.

H. WREN.

Triphenylmethane compounds with linked benzene nuclei. IV. Preparation of an iminophenyleneacridine derivative; dependence of colour on the nature of the atoms completing the ring. R. WEISS and J. L. KATZ (Monatsh., 1928, 50, 225-230).-N-(5'-Anilino-o-tolyl)anthranilic acid, m. p. 190-193°, was obtained when o-chloro-benzoic acid was heated with 3-amino-4-methyldiphenylamine in amyl alcohol in presence of potassium carbonate and copper powder. When heated with zinc chloride in acetic acid, it yielded 1-anilino-4-methylacridone, m. p. 140-160° (+AcOH or +EtOH),



NH Me which was converted by heating with phosphoryl chloride or zine chloride into methyliminophenyleneacridine (1), dark blue crystals, m. p. above 355°, yielding a blue solution in hydrochloric N acid. Coeramidonine derivatives (in which NH is replaced by CO) are reddish-brown and fluorescent. In the course of attempts to synthesise com-

pounds of this class by other methods, 5-nitro-2methyldiphenylamine-2'-carboxylic acid, m. p. 220-221° (methyl ester, m. p. 152-155°), was prepared by an Ullmann reaction from 4-nitro-o-toluidine and o-chlorobenzoic acid. Closure of the ring could not be effected, only amorphous products being obtained. When reduced by stannous chloride, carbon dioxide was lost simultaneously, yielding 5-amino-2-methyldiphenylamine, m. p. 89-91°. R. K. CALLOW.

New synthesis of benztriazole derivatives. S. N. CHAKRABARTY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 555-559).-o-Nitrobenzeneazophenol is reduced by alcoholic ammonium sulphide to 2-4'-hydroxyphenyl-1:2:3-benztriazole,

C₆H₄ N·C₆H₄·OH, m. p. 231°, oriented by oxid-

ation with alkaline potassium permanganate, when triazoledicarboxylic acid (Bladin, A., 1893, i, 375) is produced. The following 2-substituted-1:2:3-benztriazoles have been prepared : 4'-methoxyphenyl-, m. p. 138°; 2': 4'-dihydroxyphenyl-, m. p. 191°; 4'-hydroxynaphthyl-, m. p. 201°; 2'-hydroxynaphthyl-, m. p. 119°; 4'-hydroxy-3'-carboxyphenyl-, m. p. 300°; 4'-hydroxy-3'-carboxynaphthyl-, m. p. 189°; 3'-hydr-

oxy-4'-carboxyphenyl-, m. p. 109°; 2':3':4'-trihydroxy-6'-carboxyphenyl-, m. p. 191°; 4'-hydroxy-3'-aldehydophenyl-, m. p. 132°; 4'-aminophenyl-, m. p. 135°, and 4'-dimethylaminophenyl-, m. p. 187°. Reduction of 4-benzeneazo-m-nitroaniline gives 5-amino-2-phenyl-1:2:3-benztriazole, m. p. 182°. 5-Amino-2-4'-sulphophenyl-, 5-amino-2-naphthyl-, m. p. 169°, and 5-amino-2-β-naphthyl-1 : 2 : 3-benztriazole, m. p. 114°, are prepared similarly.

It is suggested that the introduction of a group into one of the benzene nuclei in o-nitroazobenzene (reduced normally to the o-amino-derivative) causes the two rings to move nearer to each other in space. The intermediate reduction product, o-hydroxylaminohydrazobenzene, can then eliminate water, and subsequently loses hydrogen forming the benz-H. BURTON. triazole.

II. E. P. isoOxazole ψ -bases and salts. KOHLER and N. K. RICHTMYER (J. Amer. Chem. Soc., 1928, 50, 3092-3106).-Further evidence is adduced for the structures previously ascribed (A., 1928, 652) to the ψ - and anhydro-bases derived from fully substituted isooxazolinium salts. The additive product from 3:4:5-triphenylisooxazole and ethyl sulphate is converted by ferric chloride and hydrochloric acid into 3:4:5-triphenyl-2-ethylisooxazolinium ferrichloride, m. p. 165-167°. This is not attacked by ozone, but with permanganate it gives acetaldehyde, benzoic acid, and benzil. It is reduced by Grignard reagents to ethyl-\$-benzoyl-\$\alpha\$-diphenylvinylamine, m. p. 118-119°, the constitution of which is confirmed by its synthesis from the substance CPhBz:CPh·N:CH2 (I) (loc. cit.) and magnesium methyl iodide. The ferrichloride affords with aqueous sodium hydrogen carbonate a solution of the isooxazolinium hydroxide, which readily isomerises to the 4-base (II), 5-hydroxy-3:4:5-triphenyl-2-ethylisooxazoline, m. p. 120° (decomp.) with rapid heating. This forms with methyl alcohol 5-methoxy-3:4:5-triphenyl-2-ethylisooxazoline (III), m. p. 100°, with acids, the corresponding 3:4:5-triphenyl-2-ethylisooxazolinium salts, and with sodium in dry ether, a yellow sodio-derivative. 3:4:5-Triphenyl-2-ethylisooxazolinium chloride and sodium cyanide yield 5-cyano-3:4:5-triphenyl-2-ethylisooxazoline (IV), m. p. 89°, which, unlike the isooxazolinium salts, is oxidisable by ozone.

When II, III, and IV are heated above their m. p. they lose water, methyl alcohol, and hydrogen cyanide, respectively, forming the anhydro-base, CPhBz:CPh·N:CHMe, m. p. 112°. In presence of traces of bases this gives with methyl alcohol yellow a-methoxyethyl-\$-benzoyl-x\$-diphenylvinylamine, m. p. 140°, with hydrogen cyanide, α -cyanoethyl- β -benzoyl- $\alpha\beta$ -diphenylvinylamine, m. p. 130°, which is hydrolysed by concentrated hydrochloric acid to dibenzoylphenylmethane and alanine, and with magnesium methyl iodide, yellow isopropyl- β -benzoyl- $\alpha\beta$ -diphenylvinyl-amine, m. p. 115°, which yields isopropylamine hydro-chloride on hydrolysis. The anhydro-base is hydrolysed by traces of acid in the air to β -benzoyl- $\alpha\beta$ -diphenylvinylamine, m. p. 162°, the ozonide of which is hydrolysed to benzil and benzamide. On one occasion a (? stereo-)isomeric amine, m. p. 208°, was obtained from the base I. Both isomerides are hydrolysed by acid to dibenzoylphenylmethane, but the former reacts with 2 mols. and the latter with 1 mol. of Grignard reagent. The former is also formed from magnesium phenyl bromide and either 3:4:5-triphenyl*iso*oxazole or benzoylphenylacetonitrile (cf. Claisen, A., 1926, 406).

α-Nitrostilbene and p-bromophenylnitromethane in methyl alcohol are converted by sodium methoxide into a mixture of isooxazoles, which was ethylated and treated with ferric chloride. Pure 3: 4-diphenyl-5-bromophenyl-2-ethylisooxazolinium ferrichloride, m. p. 172-174° (greenish-yellow and brown modifications), obtained by recrystallisation of the product, was identified by decomposition of the corresponding chloride at 170° to 3:4-diphenyl-5-bromophenyliso-oxazole, m. p. 172—173°. This is ozonised to β -benzilmonoxime p-bromobenzoate, m. p. 145-146°, which is formed from p-bromobenzoyl chloride and β -benzilmonoxime in pyridine. With alkali, the ferrichloride yields 5-hydroxy-3:4-diphenyl-5-p-bromophenyl-2-ethylisooxazoline, m. p. 105° (decomp.), which is ozonised to p-bromobenzil, m. p. 89-90°, and benzoic acid. This decomposition establishes the constitutions ascribed to these ψ -bases, the tautomeric open-chain formulæ, such as CPhBz:CPh·NEt·OH, being rendered improbable by the differences in colour between the isomeric derivatives of the ψ - and anhydro-bases. β -p-Bromo-benzoyl- $\alpha\beta$ -diphenylvinylamine, m. p. 172°, and its ethylidene derivative, m. p. 102°, are also described. H. E. F. NOTTON.

Curtius' decomposition of acid azides. H. LINDEMANN (Helv. Chim. Acta, 1928, 11, 1027— 1028).—The author objects to the term "modified Curtius reaction" (Naegeli and Stefanovitsch, A., 1928, 881) for the preparation of azides from acid chlorides and sodium azide. Examples using this method are quoted, namely, the formation of 2-chloro-3: 5-dinitro-p-toluidine, m. p. 173° (from the corresponding toluoyl chloride and sodium azide, with subsequent action of hot 50% acetic acid), and the conversion of indoxazen-3-carboxylazide into 3-aminoindoxazen, m. p. 110°. H. BURTON.

Amino-3-hydroxy-1: 4-benzisooxazines. G. NEWBERY and M. A. PHILLIPS (J.C.S., 1928, 3046— 3050).—The synthesis of three remaining amino-3-hydroxy-1: 4-benzisooxazines is described. 3-Nitro-2-aminophenol, obtained by nitration of ON-diacetylo-aminophenol, gave, with chloroacetyl chloride, 3-nitro-2-chloroacetamidophenol, m. p. 153—154°. This, when treated with 2N-sodium hydroxide, yielded 5-nitro-3-hydroxy-1: 4-benzisooxazine, m. p. 115—116°, which by reduction with iron and water led to 5-amino-3-hydroxy-1: 4-benzisooxazine, m. p. 236° (hydrochloride; acetyl derivative, m. p. 255°; derived triazole, m. p. 204°).

Reduction of 2:4-dinitrophenoxyacetic acid (iron and dilute hydrochloric acid) gave 6-amino-3-hydroxy-1:4-benzisooxazine, (I), m. p. 300° (decomp.) [acetyl derivative, m. p. 298—299° (bath at 240°)]. 4-Nitro-2-aminophenol gave 4-nitro-2-chloroacetamidophenol, m. p. 245° (decomp.), which led to 6-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 233—234°. 4-Acetamidophenoxyacetic acid when nitrated formed 2-nitro4-acetamidophenoxyacetic acid, m. p. 205-206°, which when treated with tin and hydrochloric acid gave I. 5-Nitro-2-chloroacetamidophenol, m. p. 233° (decomp.), yielded 7-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 232°, and 7-amino-3-hydroxy-1:4-benzisooxazine, m. p. 220° [hydrochloride, m. p. 275-278° (decomp.); acetyl derivative, m. p. 250°]. Dc-arsenication of 3:5-dinitro-4-hydroxyphenylarsinic acid gave 2:6dinitrophenol, from which 6-nitro-2-aminophenol (acetyl derivative, monohydrate, m. p. 102-103°, anhydrous, m. p. 122°) was obtained. 6-Nitro-2-chloroacetamidophenol had m. p. 126° and formed, successively, 8-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 255°, and 8-amino-3-hydroxy-1:4-benzisooxazine, m. p. 180° [hydrochloride, m. p. 272° (decomp.); acetyl derivative, m. p. 257°]. R. J. W. LE FÈVRE.

X. Mobility of the Aminobenzthiazoles. 1-amino-3-methylbenzthiazole system. R. F. HUNTER and E. R. STYLES (J.C.S., 1928, 3019-3027).—The mobility of 1-amino-3-methylbenzthiazole is established by application of the symmetry test (Ingold and Piggott, ibid., 1922, 121, 2381) and also the substitution test (ibid., 1923, 123, 1470). 1-Acetamido-3-methylbenzthiazole, (I), m. p. 258° [from stable acetyl-o-tolylthiocarbamide by conversion into a tetrabromide, m. p. 140° (decomp.), followed by reduction with sulphurous acid], and 1-imino-2-acetyl-3-methyl-1: 2-dihydrobenzthiazole, m. p. 170° [obtained by the action of bromine on labile acetyl-o-tolylthiocarbamide (at higher temperatures the tetrabromide derived from stable acetyl-o-tolylthiocarbamide is formed) to a tribromide, m. p. 173° (decomp.), and treatment of this with sulphurous acid followed by ammonia], gave (tautomeric) 1-amino-3-methylbenz-thiazole when hydrolysed. The compound I with bromine gives a hexabromide, m. p. 255-258° (decomp.). Bromine converts o-tolylthiocarbamide into 1-amino-3-methylbenzthiazole dibromide hydrobromide, m. p. 129° (decomp. and efferv.), which by treatment with (1) ethyl alcohol gives 5-bromo-1-amino-3-methylbenzthiazole hydrobromide, m. p. 280-290° (with charring); (2) sulphurous acid, gives 1-amino-3-methylbenzthiazole; (3) air, gives 1-amino-3-methylbenzthiazole hydrobromide, m. p. 220°. 1-Amino-3-methylbenzthiazole tetrabromide has m. p. 302°.

Methylation of 1-amino-3-methylbenzthiazole by means of methyl iodide gives a mixture of 1-methylamino-3-methylbenzthiazole and 1-imino-2:3-dimethyl-1:2-dihydrobenzthiazole. These are synthesised as follows : s-o-tolylmethylthiocarbamide, m. p. 161°, gives with bromine either a tetrabromide, m. p. 75° (decomp.), or a tribromide, m. p. 113°, both of which give 1-methylamino-3-methylbenzthiazole, m. p. 130° (acetyl derivative, m. p. 133°), by reduction with sulphurous acid; the bromo-compound from as-o-tolylmethylthiocarbamide yields, when treated with sulphurous acid, 1-imino-2:3-dimethyl-1:2-dihydrobenzthiazole, m. p. 86° (acetyl derivative, m. p. 147°). 5-Bromo-1-amino-3-methylbenzthiazole gives a dibromide hydrobromide, m. p. above 250°, leading to 5-bromo-1-amino-3-methylbenzthiazole. The following are prepared by the usual methods : 5-bromo-1-amino-3-methylbenzthiazole, m. p. 212° (dibromide hydrobromide, m. p. above 250°); s-o-tolyl-n-propylthiocarbamide, m. p. 66°; 1-n-propylamino-3-methylbenzthiazole tetrabromide, m. p. 71° (efferv. at 130°); 1-n-propylamino-3-methylbenzthiazole, m. p. 62° [hydrobromide, m. p. 179° (decomp.); acetyl derivative, m. p. 61°], (?)-bromo-1-n-propylamino-3-methylbenzthiazole hydrobromide, m. p. 259°; s-5-bromo-0-tolyl-n-propylthiocarbamide, m. p. 79°; 5-bromo-1-n-propylamino-3methylbenzthiazole, m. p. 82°; s-0-tolyl-n-heptylthiocarbamide, m. p. 98° (hexabromide, m. p. 53°); 1-n-heptylamino-3-methylbenzthiazole, m. p. 57° (acetyl derivative, m. p. 73°); (?)-bromo-1-n-heptylamino-3-methylbenzthiazole hydrobromide, m. p. 220°; s-5-bromo-0-tolyl-n-heptylthiocarbamide, m. p. 71°, and 5-bromo-1-n-heptylamino-3-methylbenzthiazole, m. p. 75°.

R. J. W. LE FEVRE.

Benzidine rearrangement in heterocyclic P. K. Bose and B. K. SEN (J. series. II. Indian Chem. Soc., 1928, 5, 643-655).-Phenacyl bromide and 1-o-tolylthiosemicarbazide, m. p. 163-164° (from o-tolylhydrazine, potassium thiocyanate, and alcoholic hydrogen chloride), react in alcohol, forming 2-o-tolylhydrazino-4-phenylthiazole, m. p. 175-180° (decomp.; acetyl derivative, m. p. 152°), which is oxidised by alcoholic ferric chloride to 2-o-tolueneazo-4-phenylthiazole, m. p. 110°, and converted by boiling dilute hydrochloric acid by a benzidine rearrangement (cf. A., 1928, 188) into 2-amino-4-phenyl-5-p-amino-m-tolylthiazole, m. p. 165° [hydrochloride, m. p. 197°; picrate, m. p. 227° (decomp.); diacetyl derivative, m. p. 182°; chloroplatinate, not melted at 300°]. 2-o-Tolylhydrazino-4-p-tolylthiazole, m. p. 179° (decomp.; acetyl derivative, m. p. 160-161°; azo-derivative, m. p. 148°), gives similarly 2-amino-4-p-tolyl-5-p-amino-m-tolylthiazole, m. p. 181° [hydrochloride, m. p. 278° (decomp.); diacetyl deriv-ative, m. p. 208°; picrate, m. p. 201° (decomp.); chloroplatinate]. 2-0-Tolyl-4-methylthiazole, m. p. 162° (decomp. ; acetyl derivative, m. p. 96°), affords 2-amino-5-p-amino-m-tolyl-4-methylthiazole, m. p. 144° [hydrochloride, m. p. 261° (decomp.); picrate, m. p. 247° after decomp. at 200°; diacetyl derivative, m. p. 266°; chloroplatinate]. From 1-m-tolylthiosemicarbazide, m. p. 134-135°, and the appropriate halogeno-ketone there were prepared 2-m-tolylhydrazino-4phenyl-, m. p. 188° (decomp.; acetyl derivative, m. p. 145°), -4-p-tolyl-, m. p. 191° (decomp.; acetyl derivative, m. p. 121°), and -4-methyl-thiazole, m. p. 135° (decomp.; acetyl derivative, m. p. 119°), which are converted into 2-amino-4-phenyl-5-p-amino-o-tolyl-, m. p. 135° [hydrochloride, m. p. 265-270° (decomp.); picrate, m. p. 215° (decomp.); diacetyl derivative, m. p. 235°], 2-amino-4-p-tolyl-5-p-amino-o-tolyl-, m. p. 175° [hydrochloride, m. p. 247° (decomp.); picrate, m. p. 202° (decomp.); diacetyl derivative, m. p. 236°], and 2-amino-5-p-amino-o-tolyl-4-methyl-thiazole, m. p. 157° [hydrochloride, m. p. 263° (decomp.); picrate, m. p. 212° (decomp.); diacetyl derivative, m. p. 236°], respectively.

p-Tolylthiosemicarbazide, m. p. 174° (lit. 150°), and phenacyl bromide afford 3-p-toluidino-2-imino-4phenyl-2: 3-dihydrothiazole, m. p. 193° (decomp.; acetyl derivative, m. p. 147°), hydrolysed by hydrochloric acid to the corresponding 2-keto-derivative, m. p. 210—211°. The analogous -2-imino-4-methyl derivative, m. p. 168—169° (p-tolylthiocarbimide derivative, m. p. 143°), affords the corresponding 2-keto-compound, m. p. 177°. 3-p-Toluidino-2-imino-4-p-tolyl-2: 3-dihydrothiazole (acetyl derivative, m. p. 155°; p-tolylthiocarbimide derivative, m. p. 152°) has m. p. 184° (decomp.). 2-Benzeneazo-4-phenyl-, m. p. 117°, -4-p-tolyl-, m. p. 161°, and -4-methyl-thiazole, m. p. 120°, are prepared by oxidising the corresponding phenylhydrazino-derivatives (loc. cit.) with ferrie chloride.

The rearrangements now and previously described support the view that a system of conjugated double linkings must be present in the heterocyclic ring (Fargher and Pyman, J.C.S., 1919, **115**, 222) before isomerisations can occur. H. BURTON.

Microchemical reactions of homatropine. M. WAGENAAR (Pharm. Weekblad, 1928, 65, 1213— 1216).—The crystal forms and optical properties of the precipitates obtained by addition of gold chloride, picrolonic acid, picric acid, iodine, and bromine solutions are described. The bromine test will detect 2 mg. in 20 c.c. of solution, the iodine test 5 mg. in 25 c.c. S. I. LEVY.

Determination of the absorbing capacity of the ergot alkaloids in the ultra-violet and a practical application. A. HARMSMA (Pharm. Weekblad, 1928, 65, 1114—1134).—The absorption spectra of ergotin, ergotoxin, ergotamine, and ergotaminin have been mapped for wave-lengths from 360 to 260 $\mu\mu$. The maximum in each case is at 316 $\mu\mu$. Quantitative spectrum determinations of the alkaloid content of *Secale cornutum* agreed well with chemical determinations carried out by the Keller–Fromme method. Similar determinations on extracts prepared in various ways also showed good agreement with the chemical determinations. Physiological methods of examination are discussed, and some results given. S. I. LEVY.

Synthesis of oxydehydrocorydaline. J. B. KOEPFLI and W. H. PERKIN, jun. (J.C.S., 1928, 2989—3000).—A literature review suggests that corydaline is preferably represented by II rather than by I (Dobbie and Lauder, *ibid.*, 1902, 81, 148).



The synthesis of oxydehydrocorydaline described supports this conclusion. β -Veratrylcrotonic acid, m. p. 138—140° (from ethyl bromoacetate and zinc by dehydration of ethyl β -veratryl- β -hydroxybutyrate giving ethyl β -veratrylcrotonate, b. p. 195—196°/ 10 mm.), was reduced by sodium amalgam to β -veratrylbutyric acid, m. p. 84—85° (monohydrate, m. p. 60—61°, with loss of 1H₂O at 100°), which, when treated with sulphuric acid yielded 5:6-dimethoxy-3-methyl-1-hydrindone, m. p. 90—91° [oxime, m. p. 128—129°; isonitroso-derivative, m. p. 225—226° (decomp.)], and when brominated in acetic acid gave 6-bromo- β -veratrylbutyric acid, m. p. 106—107°. This

acid readily gave with sulphuric acid 4-bromo-6:7-dimethoxy-3-methyl-1-hydrindone, m. p. 82-83°, the isonitroso-derivative, m. p. 217° (decomp.), of which underwent the Beckmann transformation with toluenep-sulphonyl chloride, giving 6-bromo-2-carboxy-3:4-dimethoxy-a-phenylpropionitrile. This by hydrolysis led to 6-bromo-3: 4-dimethoxy-a-methylhomophthalic acid (anhydride, m. p. 128-129°). Debromination by sodium amalgam gave 3:4-dimethoxy-a-methylhomophthalic acid; the anhydride, m. p. 131–133°, of this acid combined with β -veratrylethylamine to give N-β-veratrylethyl-3: 4-dimethoxya-methylhomophthalamic acid, the methyl ester of which lost water when treated with phosphoryl chloride giving 6:7:3':4'-tetramethoxy-9-methyl-2'-carbomethoxy-3: 4-dihydroprotopapaverine, m. p. 136-137° (with previous softening), which when heated eliminated methyl alcohol giving oxydehydrocorydaline, m. p. 235-236° (lit. 228-228.5°).

An acid, m. p. 90–95°, is described as probably a stereoisomeride of β -veratrylcrotonic acid.

R. J. W. LE FEVRE. Constitution of laurotetanine. E. SPATH and F. STRAUHAL (Ber., 1928, 61, [B], 2395-2402; cf. Greshoff, A., 1891, 334; Filippo, A., 1899, i, 312; Gorter, A., 1921, i, 587).-Methylation of laurotetanine in alcohol-ether yields an amorphous product which mainly retains the secondary character of the nitrogen atom. It is divided by treatment with acetic anhydride at the ordinary temperature into N-acetyl-laurotetanine O-methyl ether, $C_{22}H_{25}O_5N$, m. p. 188–189°, and a tertiary base identical with glaucine. Gorter's isoglaucine (loc. cit.) is therefore a mixture of laurotetanine O-methyl ether and glaucine, and laurotetanine must possess the ring system of the latter substance. Oxidation of laurotetanine affords 4:5-dimethoxybenzene-1:2:3 -tricarboxylic acid, which passes at 260° into carbon dioxide and m-hemipinic



NH Anhydride. The annexed formula is therefore suggested for laurotetanine. The presence of the phenanthrene nucleus is established by transformation of the alkaloid into benzene - 1 : 2 : 3 : 4 - tetra carboxylic acid; for this

purpose glaucine methiodide is transformed into the corresponding methochloride, which is successively reduced by sodium amalgam and oxidised by nitric acid. Laurotetanine is converted by treatment with diazoethane and oxidation of the ethyl ether with potassium permanganate into 4-methoxy-5-ethoxybenzene-1:2-dicarboxylic acid, identified as the anhydride and ethylimide. Attempts to convert laurotetanine into corydaldine were unsuccessful. Glaucine is not appreciably affected by treatment with tin and hydrochloric acid and laurotetanine does not suffer electrolytic reduction at a lead cathode; it may therefore be assumed that the pyridine nucleus is tetrahydrogenated. The accumulated data do not permit a decision as to the positions of the hydroxyl and methoxyl groups indicated in the formula.

1-Keto - 5:6 - dimethoxy - 1:2:3:4 - tetrahydroiso-

quinoline, m. p. 154—155°, is obtained by the action of phosphoric oxide in toluene on carbethoxy- β -2:3-dimethoxyphenylethylamine. H. WREN.

Constitution of laurotetanine. G. BARGER and R. SILBERSCHMIDT (J.C.S., 1928, 2919-2927).-A study of the products obtained by exhaustive methylation (Hofmann) has shown that, contrary to the opinions of Gorter (A., 1921, i, 587), the N-methyl methyl ether of laurotetanine (Gorter's isoglaucine) and glaucine are identical; therefore laurotetanine has the constitution suggested for it independently by Späth and Strauhal (preceding abstract). Hydrated laurotetanine (m. p. 124-134°; lit. 125°, 134°) gave, by methylation with diazomethane followed by addition of methyl iodide, dimethyl-laurotetanine methiodide, m. p. 210°. Treatment of this with alcoholic potassium hydroxide and subsequent acidification gave dimethyl-laurotetaninemethine hydriodide, m. p. 265°. The free methine was an uncrystallisable oil, but dimethyl-laurotetaninemethine methiodide (obtained from the components in ethereal solution) had m. p. 276°. The last compound, when heated with methyl-alcoholic potassium hydroxide, gave trimethylamine (isolated as the chloroplatinate) and 2:3:5:6-tetramethoxy-8-vinylphenanthrene, m. p. 142°, which was oxidised by cold neutral permanganate 2:3:5:6-tetramethoxyphenanthrene-8-carboxylic to acid, m. p. 215°.

Attempts are described to decide between the two formulæ by exhaustive methylation of laurotetanine ethyl ether and comparison of the products with two synthetic ethoxytrimethoxyethylphenanthrenes. Both laurotetanine and glaucine gave a vinylphenanthrene and phenanthrenecarboxylic acid; attempts to decarboxylate the acid were unsuccessful. 2:3:5:6-Tetramethoxy-8-ethylphenanthrene was therefore prepared by reduction of the vinyl compound with hydrogen-palladium chloride-gum arabic.

3:4-Dimethoxyethylbenzene, b. p. 110-112°/9 mm. (obtained by the reduction of 3:4-dimethoxyvinylbenzene or of acetoveratrone, the latter being the better method), gave by Gattermann's reaction 3:4-dimethoxy-6-ethylbenzaldehyde, b. p. 150-159°/ 9 mm., m. p. 28-30° (semicarbazone, m. p. 197-199°). Oxidation by alkaline permanganate gave 3:4-dimethoxy-6-ethylbenzoic acid, m. p. 138°. The above aldehyde condensed with hippuric acid under the conditions of a Perkin reaction to give the azlactone of 3:4-dimethoxy-6-ethylbenzylidenehippuric acid, m. p. 155° (hydrolysis with dilute potassium hydroxide gave the free acid, m. p. 212°), which, by boiling with 30% potassium hydroxide yielded 3:4-dimethoxy-6-ethylphenylpyruvic acid, m. p. 181°. Oxidation of this by alkaline hydrogen peroxide led to 3:4-dimethoxy-6-ethylphenylacelic acid, m. p. 67°, the potassium salt of which condensed with 6-nitro-3:4-dimethoxybenzaldehyde, giving α -3:4-dimethoxy-6-ethylphenyl - β - 6 - nitro - 3 : 4 - dimethoxyphenyl-acrylic acid, m. p. 208° (previous sintering at 203°), which by ammoniacal ferrous hydroxide reduction gave the corresponding amine, m. p. 192°. This was treated with nitrous acid and the resulting crude 2:3:5:6-tetramethoxy-8-ethylphenanthrene-9-carboxylic acid decarboxylated to 2:3:5:6-tetramethoxy-8-ethylphenanthrene identical with the corresponding compound obtained from laurotetanine.

6-Nitro - 3 - methoxy - 4 - ethoxybenzaldehyde (nitrovanillin ethyl ether) has m. p. 159—160°. Improved methods for the methylation of vanillin and guaiacol are described. R. J. W. LE FÈVRE.

Morphine alkaloids. VI. Thebaizone and other products of ozonolysis. H. WIELAND and L. F. SMALL (Annalen, 1928, 467, 17–52).— α -Thebaizone (hydriodide, m. p. 185–187°; hydrochloride), obtained by the ozonolysis of thebaine (Pschorr and Einbeck, A., 1907, i, 958), has formula I if the Schöpf-



Robinson formula for thebaine (cf. A., 1927, 472) is accepted. It is converted by bromine in dilute hydrochloric acid, and subsequent treatment with alkali, into bromothebaizone, m. p. 147°, the bromine probably entering ring I, and by 30% hydrogen peroxide in acetic acid into thebaizonedicarboxylic acid, m. p. 189-190° (decomp.), the ester group being hydrolysed. Hydrolysis with cold 0.33N-barium hydroxide yields the aldehyde acid, thebaizonic acid, decomp. 235°, but concentrated hydrochloric acid at 95-98° gives rise to the hydrochloride, m. p. 210° (decomp.) (also obtained by the action of excess of N-hydrochloric acid on thebaizonic acid), of hydroxydihydrothebaizonic acid (A), decomp. 230-240°, the free acid being liberated by the action of methyl-alcoholic sodium methoxide, whilst thallium hydroxide yields a different substance, decomp. 231-235°, containing an additional mol. of water and yielding a different hydrochloride, decomp. 260°. Catalytic reduction of a-thebaizone with platinum oxide in methyl alcohol opens the



oxygen bridge, leaving the 8:14 double linking unattacked, and yields the phenolic derivative dihydrothebaizone, m. p. 140° (indefinite) [methiodide, m. p. 239-240° (decomp.); acetyl derivative of methiodide, m. p. 250° (decomp.)]. Reduction of a-thebaizone with aluminium amalgam in moist ether (and, in poor yield, with zinc and hydrochloric acid) yields deoxythebaizone (B), m. p. 147° (decomp.) (hydrochloride), which retains the oxygen bridge but has no aldehydic properties, and is reduced catalytically after hydrolysis with N-hydrochloric acid, to dihydrodeoxythebaizonic acid (C), m. p. 163-165° (decomp.), isolated as its hydrochloride, m. p. 236-237° (decomp.). The Hofmann degradation of the methiodides of these various compounds has been investigated. The methiodide, m. p. 163° (decomp.), of A eliminates only

methyl alcohol, the product again treated with methyl iodide yielding the original methiodide; α -thebaizone methiodide, decomp. 250—255°, yields de-N-methylthebaizonic acid (D), amorphous [methiodide, decomp. 250—255°; hydrochloride, m. p. 270° (decomp.)]; the methiodide, m. p. 175—177°, of dehydrodeoxythebaizone similarly yields de-N-methyldihydrodeoxythebaizonic acid (E), m. p. 195—197° (decomp.) (methiodide, m. p. 156—158°). When C is heated with methyl iodide



at 100° it yields a substance, C₃₇H₄₅O₈N₂I,H₂O, m. p. 217-218° (decomp.), which by decomposition with thallium hydroxide and further treatment with methyl iodide yields the simple methiodide, m. p. 167-168° (decomp.). By short heating at 200° α -thebaizone is converted into β -thebaizone, m. p. 151° (probably stereisomeric about the 8:14 double linking), which yields the same deoxythebaizone by reduction with aluminium amalgam, but by reactions by reduction when applied to the α -compound it yields hydroxydihydro- β -thebaizonic acid, m. p. 230° (decomp.) (hydrochloride, decomp. 260°); ethyl hydrogen β -thebaizonedicarb-oxylate decomposes at 220° (the ester group is less readily hydrolysed than in the a-compound). Ozonolysis of dihydrothebaine in hydrochloric acid yields isodihydrothebaizonic acid (F), m. p. 248-249° (decomp.) [hydrochloride; methiodide, m. p. 179-180° (decomp.); reduced with hydrogen and platinum oxide in water to the tetrahydro-acid, m. p. 230-235° (decomp.)], and isodihydrothebaizone, m. p. 103-105° [methiodide, m. p. 147-148° (decomp.)]. Ozonolysis of chlorocodide yields chlorocodizone (G), m. p. 104° [hydrochloride, m. p. 212° (decomp.); oily methiodide], which is reduced by zinc and acetic acid to deoxy-codizone, m. p. 161° [hydrochloride, m. p. 223-224° (decomp.)]. The action of hot methyl-alcoholic



potassium hydroxide on chlorocodizone for 15 min. yields anhydrocodizone (H), m. p. 110°. Longer treatment (1 hr.) yields two nitrogen-free substances, $C_{15}H_{12}O_4$, m. p. 88° and 159°, for which the structures





Robinson formula for thebaine, similar revision being necessary to Freund's formulæ for phenyldihydrothebaine methyl ether and O-methylthebainone, neither of which reacts with ozone.

J. W. BAKER.

Strychnine and brucine. VII. Constitution of the alkaloids discussed in relation to the hypothesis that dinitrostrychol is an *iso*quinoline derivative. R. C. FAWCETT, W. H. PERKIN, jun, and R. ROBINSON (J.C.S., 1928, 3082—3092).—Under the conditions for the formation of dinitrostrycholcarboxylic acid from strychnine, methylstrychnine gives another *substance* (or *substances*) with the alternative formulæ I, II, or III, whence it becomes evident that the *b* (more basic) nitrogen of strychnine is not situated in that portion of the molecule which is broken up during oxidation, but is actually the heterocyclic nitrogen of dinitrostrycholcarboxylic acid.



The logical consequences of this view are discussed, and a formula, IV (where, however, the possibility of bridged rings is left open), which satisfactorily explains the known reactions of strychnine is advanced. R. J. W. LE FÈVRE.

Strychnos alkaloids. XLVII. Behaviour of derivatives of Hanssen's acid, C19H22OcN2, particularly when oxidised by bromine or mercuric oxide. H. LEUCHS, K. BENDER, and W. WEGENER (Ber., 1928, 61, [B], 2349-2358; cf. A., 1887, 505; 1922, i, 1052; 1925, i, 1314).-The free acid, C19H22O8N2, obtained by the action of bromine and hydrobromic acid on Hanssen's acid, and its sulphate, C₁₉H₂₂O₈N₂,H₂SO₄, are described. Treatment of its hydrobromide with methyl alcohol and hydrogen chloride gives the dimethyl ester, C12H26O8N2, m. p. 225-227° (decomp.) [anhydrous nitrate], and the monomethyl ester nitrate. The monosilver salt has been prepared. The acid yields a monoxime and monosemicarbazone, C20H25O8N5 (nitrate; hydrochloride). The previous assumption of the presence of two ketonic groups is rendered improbable. The original change appears thus to consist of the addition of two hydroxyl groups at the C=C linking reducible by sodium amalgam and the conversion of the (nondemonstrable) >CH-OH group of brucine and cacotheline into >CO. The acid C19H22O8N2 is

oxidised by yellow mercuric oxide suspended in water to the acid $C_{19}H_{22}O_9N_2, 2H_2O$ [hydrobromide (+3H₂O); hydrochloride]. Reduction of the acid $C_{19}H_{22}O_8N_2$ by sodium amalgam affords the compound, $C_{19}H_{24}O_8N_2$, isolated as the nitrate or hydrobromide; the latter substance is oxidised by mercuric oxide to the hydrobromide, $C_{19}H_{22}O_9N_2$, HBr. The free, reduced Hanssen acid, $C_{19}H_{24}O_6N_2$, yields a silver salt from which the methylbetaine, $C_{20}H_{26}O_6N_2$, MeOH, methobromide, $C_{20}H_{27}O_6N_2Br$, and methiodide, $C_{20}H_{27}O_6N_2I$, are obtained. The methobromide is transformed by silver carbonate and water into the betaine. The dihydrazide, $C_{19}H_{28}O_4N_6$, m. p. 265—268° (decomp.), of the acid $C_{19}H_{24}O_6N_2$ has been prepared. The trihydrated and anhydrous hydrobromide; nitrate). The hydrobromide of the acid $C_{19}H_{26}O_9N_2$ is oxidised by yellow mercuric oxide to the substance $C_{19}H_{24}O_9N_2$ (hydrobromide; nitrate; hydrochloride). H. WREN.

Helleborus group. VII. Constituents of the roots of Helleborus niger and H. viridis; new alkaloids from H. viridis. O. KELLER [with W. SCHÖBEL] (Arch. Pharm., 1928, 266, 545-572; cf. A., 1927, 799).—Previous investigators are not agreed as to the composition of the two glucosides helleborin and helleborein. The two substances, m. p. 269° and 270°, respectively, previously isolated by Keller, are identical with helleborin, to which the formula $C_{28}H_{36}O_6$ is now ascribed. The benzene extract from the roots of H. viridis acidified with aluminium sulphate solution affords helleborin, 1% of fat, brown colouring matters, resin, and a pungent oil volatile in steam, but no alkaloids. The latter, which are present to the extent of 0.1-0.2%, are obtained by repeating the extraction after basifying the roots with ammonia, the following substances being isolated, chiefly by means of their different solubilities in ether : celliamin, $C_{21}H_{35}O_2N$, readily soluble, m. p. 127—131° after sintering at 115°; sprintillamin, $C_{28}H_{45}O_4N$, moderately soluble, m. p. 228—229° (methiodide, m. p. 251-252°; sparingly soluble hydrochloride, m. p. 287-288°); sprintillin, C₂₅H₄₁O₃N, sparingly soluble, m. p. 141-142° after sintering at 132° (hydrochloride, m. p. 278-279°). All the above compounds are nonglucosidic tertiary bases, containing no methoxyl groups, but sprintillamin has one methyl group attached to nitrogen. A fourth, very feebly basic alkaloid, C₂₅H₄₃O₆N, m. p. 267-268° after darkening at 210°, is described. In addition to the above the roots of *H. viridis* contain sucrose. The roots of *H.* niger are free from alkaloids. Celliamin, sprintillamin, and sprintillin have a characteristic action on the heart. S. COFFEY.

Unsymmetrical arseno-compounds from p-arsinoanilinoethyl alcohol and p-arsinoanilinoacetamide. C. S. PALMER and E. B. KESTER (J. Amer. Chem. Soc., 1928, 50, 3109—3119; cf. A., 1924, i, 109).—Water-soluble, unsymmetrical derivatives of 4-carbamylmethylaminoarsenobenzene and 4- β -hydroxyethylaminoarsenobenzene have been prepared by reducing equimolecular mixtures of one of the above arsinic acids with another suitably substituted arsinic acid by means of stannous chloride or hypophosphorous acid and potassium iodide at 5-10°. It is shown that reduction takes place first to the two symmetrical arsenobenzenes, which then rearrange. The following *derivatives* of 4'- β -hydroxyethylaminoarsenobenzene are described: 4-amino-(dihydrochloride; N - methylenesulphoxylic acid); 4 - hydroxy- (hydrochloride); 3 - amino - 4 - hydroxy- (dihydrochloride; N-methylenesulphoxylic acid); 4-carboxymethylamino-(dihydrochloride) and 4-carboxymethoxy-; also the following derivatives of 4'-carbamylmethylaminoarsenobenzene: 4-amino-[dihydrochloride; di-(N-methylenesulphoxylic acid)]; 4-hydroxy- (hydrochloride); 3-amino-4-hydroxy- (dihydrochloride; N-methylenesulphoxylic acid); and 4-carboxymethoxy-. Equal mols. of p-arsinoanilinoacetic acid and p-arsinoanilinoacetamide are reduced by stannous chloride to 4-carboxymethylamino-4'-carbamylmethylaminoarsenobenzene dihydrochloride and by hypophosphorous acid at the ordinary temperature to 4-carboxymethylamino-4' - carbamylmethylaminotetra - arsenobenzene dihydrochloride. Other arsenobenzenes prepared include 4 - carboxymethylamino - 4' - hydroxy-, hydrochloride; 3-amino-4-hydroxy-4'-carboxymethoxy-; 3:4'-diaminodihydrochloride; and 4-amino-4'-4-hvdroxy-, hydroxy-, hydrochloride; but the 3-amino-4-hydroxyhydrochloride could not be obtained in a similar way from a mixture of phenylarsinic and 3-amino-4hydroxyphenylarsinic acids, only the symmetrical arseno-derivatives being formed.

H. E. F. NOTTON.

Pyridine and quinoline derivatives. IV. Pyridine-3-arsinic acid. A. BINZ, C. RATH, and J. GANTE (Annalen, 1928, 467, 11-16).-The difficulty encountered in the preparation of pyridine-3-arsinic acid (A., 1927, 890) has been overcome by using 5-aminopyridines with a negative substituent in the 2-position, which is readily eliminated after conversion into the arsinic acid. 2-Chloropyridine-5-arsinic acid (loc. cit.) is converted by heating with hydrazine hydrate in aqueous solution for 3.5 hrs. into 2-hydrazinopyridine-5-arsinic acid (I), not melting below 240° (p-nitrobenzylidene derivative, reduced to p-aminobenzylidene derivative), which by condensation with ethyl acetoacetate and heating the product in toluene, yields 1-(2'-pyridyl)-3-methyl-5-pyrazolone-CMo=N

5'-arsinic acid,

CH₂·CO N AsO₃H₂. Oxidation

of I with hydrogen peroxide and 5% hydrochloric acid yields (10-12%) pyridine-3-arsinic acid, m. p. 112-113° (copper salt), from which are obtained 3-pyridyldichloroarsine, decomp. 137°, 3-pyridylarsenious oxide, decomp. 187°, and 3-pyridylarsine, decomp. 102°, and, by reduction with hypophosphorous acid before isolation, 3: 3'-arsenopyridine. J. W. BAKER.

Heterocyclic arsenic compounds. II. Derivatives of 1:4-benzisooxazine. G. NEWBERY, M. A. PHILLIPS, and R. W. E. STICKINGS (J.C.S., 1928, 3051-3073).-3-Hydroxy-1:4-benzisooxazine-5-arsinic acid, m. p. 245-248° (decomp.) (calcium, barium, and mignesium salts), was prepared from 2-nitro-3-carbethoxyaminophenylarsinic acid. 3 - Acetamido - 4 hydroxyphenylarsinic acid with chloroacetic acid gave 2-acetamidophenoxyacetic acid, m. p. above 280° (magnesium salt); 2 - acetamidophenoxyacetamide-4-arsinic acid, m. p. 236° (decomp.) (magnesium salt), was prepared similarly, and was reduced by sulphurous and hydrochloric acids in presence of potassium iodide to 2-nitrophenoxyacetic acid 4-dichloroarsine. Reduction of the corresponding arsinic acid gave impure 3-hydroxy-1:4-benzisooxazine-4-dichloroarsine, which dissolved in sodium hydroxide to give 3-hydroxy-1:4-benzisooxazine 6-arsenoxide. 3-Hydroxy-1:4-benzisooxazine 6-arsenoxide. 3-Hydroxy-1:4-benzisooxazine-6-arsinic acid was reduced by hyposulphite to 3:3'-dihydroxy-6:6'-arseno-1:4benzisooxazine.

Nitration of 3-hydroxy-1:4-benzisooxazine-6arsinic acid gave about equal yields of 5-nitro-3hydroxy-1: 4-benzisooxazine-6-arsinic acid (calcium, barium, magnesium, and monoammonium salts) and 7-nitro-3-hydroxy-1: 4-benzisooxazine-6-arsinic acid. Ferrous hydroxide reduced the former to 5-amino-3hydroxy-1: 4-benzisooxazine-6-arsinic acid, m. p. above 300° [calcium, barium, magnesium, and sodium salts; acetyl derivative; corresponding triazole, m. p. 247° (decomp.), and its calcium, barium, and magnesium salts], which underwent de-arsenication when boiled with hydrochloric acid to 5-amino-3-hydroxy-1:4benzisooxazine hydrochloride, whilst the latter was reduced by ferrous hydroxide (or dextrose and alkali) 7-amino-3-hydroxy-1: 4-benzisooxazine-6-arsinic to acid, m. p. 258-260° (decomp.) (barium, calcium, and magnesium salts; acetyl derivative, m. p. 275°; urethane), de-arsenication of which gave 7-amino-3-3:7-Dihydroxy-1:4hydroxy-1: 4-benzisooxazine. benzisooxazine-6-arsinic acid, m. p. above 300° (barium, calcium, and magnesium salts), was obtained from 5-amino-2: 4-dihydroxyphenylarsinic acid by chloroacetylation in alkaline solution.

The following compounds are also described : 8-nitro-3-hydroxy-1: 4-benzisooxazine-6-arsinic acid, 3-nitro-5-chloroacetamido-4-hydroxyphenylarsinic acid, m. p. 200° (decomp.) (magnesium salt), 8-nitro-3-hydroxy-1: 4-benzisooxazine-6-arsinic acid, decomp. 320° (calcium and magnesium salts), 2:6-diacet-amidophenoxyacetic acid 4-arsinic acid, m. p. 212° (decomp.) (magnesium salt), 8-amino-3-hydroxy-1: 4-pbenzisooxazine-6-arsinic acid, m. p. above 300° (barium calcium, and magnesium salts), 8-amino-3-hydroxy-1:4 - benzisooxazine - 6 - hydroxychloroarsine hydro-8-amino - 3 - hydroxy - 1 : 4 - benzisooxazine chloride, 6-arsenoxide hydrochloride, 8:8'-diamino-3:3'-dihydroxy-6: 6'-arseno-1: 4-benzisooxazine, 8-acetamido-3-hydroxy-1: 4-benzisooxazine-6-arsinic acid, m. p. 275-280° (decomp.) (barium and magnesium salts), 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-dichloroarsine (corresponding arsenoxide), 8:8'-diacetamido-3 : 3'-dihydroxy-6 : 6'-arseno-1 : 4-benzisooxazine, 3-hydroxy-1: 4-benzisooxazine-6-arsinic acid 8-glycineamide (corresponding arsenic acid), 8-glycylamino-3hydroxy-1: 4-benzisooxazine-6-arsinic acid, 8-chloro-3hydroxy-1: 4-benzisooxazine-6-arsinic acid, m. p. above 280° (magnesium salt), 3-hydroxy-8-methyl-1:4-benzisooxazine-6-arsinic acid, 3:3'-diacetamido-4:4'-dihydroxy - 5 : 5' - dimethylarsenobenzene, 3 - hydroxy - 8methyl-1: 4-benzisooxazine-6-arsenic acid, 3: 3'-dihydroxy-8: 8'-dimethyl-6: 6'-arseno-1: 4-benzisooxazine, 8-3-hydroxyethylamino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, 3-hydroxy-8-carboxy-1: 4-benz-

isooxazine-6-arsinic acid, 3-nitro-4-hydroxy-5-carboxyphenylarsinic acid [monohydrate, m. p. 282-284° (decomp.); magnesium, barium, and calcium salts], 3-amino-4-hydroxy-5-carboxyphenylarsinic acid, m. p. above 300° (calcium, barium, magnesium, mono- and di-sodium salts), 3-acetamido-4-hydroxy-5-carboxyphenylarsinic acid, m. p. 250-254° (decomp.) (magnesium and calcium salts), 3-hydroxy-8-carboxy-1:4-benzisooxazine-6-arsinic acid, m. p. 300-305° (decomp.), 3-hydroxy-2-methyl-1: 4-benzisooxazine-6arsinic acid, m. p. above 300° (calcium and magnesium salts), 3-hydroxy-2-ethyl-1: 4-benzisooxazine-6-arsinic acid, m. p. above 280° (magnesium salt), 8-acetamido-3hydroxy-2-methyl-1: 4-benzisooxazine-6-arsinic acid, decomp. 265° (magnesium salt), 8-acetamido-3-hydroxy-2-ethyl-1: 4-benzisooxazine-6-arsinic acid, 3-w-chlorocarbethoxyamino-4-hydroxyphenylarsinic acid, m. p. 209° (decomp.) (magnesium salt), 2:3-dihydro-1:4benzisooxazine-6-arsinic acid, m. p. above 300° (magnesium salt), 2:3-dihydro-1:4-benzisooxazine-6-arsenoxide, 6:6'-arseno-(2:3-dihydro-1:4-benziso-oxazine), $3 \cdot \omega$ -chlorocarbethoxyamino-5-acetamido-4hydroxyphenylarsinic acid, m. p. 189° (decomp.) (magnesium salt), 3:3'-di- $(\beta$ -hydroxyethylamino)-5:5'diacetamido-4:4'-dihydroxyarsenobenzene, 3-hydroxy-1: 4-benzisooxazine-8-arsinic acid, m. p. 298° (decomp.) (magnesium, calcium, barium, and sodium salts), 6-amino-3-hydroxy-1: 4-benzisooxazine-8-arsinic acid, m. p. above 300° (barium, calcium, and magnesium salts), 6-acetamido-3-hydroxy-1:4-benzisooxazine-8arsinic acid, m. p. above 300° (magnesium salt), and 6:6'-diacetamido-3:3'-dihydroxy-8:8'-arseno-1:4-R. J. W. LE FEVRE. benzisooxazine.

Heterocyclic arsenic compounds. III. Derivatives of 4-amino-3-hydroxyphenylarsinic acid. I. E. BALABAN (J.C.S., 1928, 3066-3073) .---The preparation of the following arsenicals from 4-amino-3-hydroxyphenylarsinic acid (cf. Brit. J. Venereal Dis., 1927, 3, 1) is described : 3-hydroxy-1: 4-benzisooxazine-7-arsinic acid (calcium, magnesium, and barium salts), 8-nitro-3-hydroxy-1: 4-benzisooxazine-7-arsinic acid, decomp. 280°, 6(?)-nitro-3-hydroxy-1: 4-benzisooxazine-7-arsinic acid, decomp. 280° (magnesium, calcium, and barium salts), 8-amino-3hydroxy-1: 4-benzisooxazine-7-arsinic acid (hydrate 0.75H₂O; barium, calcium, and magnesium salts), 8-acetamido-3-hydroxy-1:4-benzisooxazine-7-arsinic acid (magnesium and calcium salts), 2-nitro-4-w-hydroxyacetamido-3-hydroxyphenylarsinic acid, efferv. 210°, 2-amino-4-w-hydroxyacetamido-3-hydroxyphenylarsinic acid (magnesium, calcium, and barium salts), 4-w-hydroxyacetamido-2-acetamido-3-hydroxyphenylarsinic acid, S-acetamido-3-hydroxy-1:4-benzisooxazine-5-arsinic acid (magnesium and calcium salts), 8-amino-3-hydroxy-1:4-benzisooxazine, m. p. 180° (hydrochloride, chars at 270° and decomp. about 300°, efferv.; acetyl derivative, m. p. 257°), 8-amino-3-hydroxy-1:4-benzisooxazine-5-arsinic acid (hydrate 0.5H2O; magnesium, calcium, and barium salts), benzoxazolone-5-arsinic acid (magnesium salt), 5-nitro-4-amino-3-hydroxy-phenylarsinic acid (hydrate $1H_2O$; calcium salt), 6-nitrobenzoxazolone-5-arsinic acid (magnesium and barium salts), 6-aminobenzoxazolone-5-arsinic acid (hydrate 1H₂O; barium, calcium, and magnesium salts),

6-acetamidobenzoxazolone-5-arsinic acid (magnesium and calcium salts), 6-acetamidobenzoxazolone-3-arsinic acid (magnesium, calcium, and barium salts). R. J. W. LE FÈVRE.

Organo-selenium compounds. M. TAKAMATSU (J. Pharm. Soc. Japan, 1928, No. 555, 450–453).— Phenol gives with selenious acid selenophenol (dihydroxydiphenyl selenide), $Se(C_6H_4 \cdot OH)_2$ (cf. Michaelis and Kunckell, A., 1898, i, 136), and similarly phenoxyacetic acid gives diphenoxyacetic acid selenoxide (dianisylselenoxide- $\omega\omega'$ -dicarboxylic acid), $SeO(C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H)_2$, decomp. 210°.

K. ISHIMURA. Mercuration of neutral-red and its sulphonic acid. I. M. LEVINE (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 105—110).—The following compounds were prepared (the constitutions indicated being doubtful): 2:5-Diacetoxymercurineutral-red acetate; 2:5-dichloromercuri-neutral-red chloride; neutral-red-2-sulphonic acid (mercury salt); sodium 5-hydroxymercuri-neutral-red-2-sulphonate. CHEMICAL ABSTRACTS.

Chromium triphenyl, chromium tetraphenyl, and thallium diethyl. F. HEIN and E. MARKERT (Ber., 1928, 61, [B], 2255-2267; cf. A., 1926, 534).-Chromium triphenyl is prepared as a brownish-yellow, friable powder by the electrolysis of chromium triphenyl iodide dissolved in liquid ammonia at a platinum cathode or by mixing solutions of the iodide and sodium in liquid ammonia. The electrolytic product invariably contains ammonia either adsorbed or chemically combined. The compound is unstable, readily losing diphenyl. By suitable treatment with alcohol and water it is converted quantitatively into chromium triphenyl hydroxide. The metal in chromium triphenyl cannot normally be tervalent, since it passes readily into chromium triphenyl hydroxide, in which it is quadrivalent. It is assumed that the operative valency electrons are derived from groups other than the usual and that the 4_{11} electron ("potassium electron"; cf. Hund, A., 1925, ii, 912) is not involved and thus causes the similarity of chromium triphenyl to the alkali metals as shown by its ready conversion into a base. The same hypothesis is applicable to chromium tetraphenyl and its transformation into chromium tetraphenyl hydroxide. Electrolysis of chromium pentaphenyl hydroxide in liquid ammonia affords chromium tetraphenyl identical with the product derived from the tetraphenyl iodide. Solutions of chromium tetraphenyl in pyridine are stable when shielded from light and preserved in an atmosphere of nitrogen and the substance is unimolecular at concentrations 0.062-0.086N, according to the results of Rast's capillary method. The similarity of chromium tetraphenyl to the tetra-alkylammonium radicals, indicated by the ready transition into strong bases, is not paralleled by any power of yielding amalgams or of formation of blue solutions in liquid ammonia. Measurements of the decomposition tension and the cathodic polarisation potential of chromium tetraphenyl hydroxide in methyl alcohol do not indicate metallic properties of the radical. Chromium tetraphenyl is deposited on the mercury as a compact precipitate which shows no tendency to penetrate into the metal and does not

possess the characteristic metallic conductivity. The cathodic potential curve shows no similarity to that of metals. The ion, CrPh_4' , does not therefore appear to be formed during the transformation of chromium tetraphenyl into the corresponding hydroxide and the change is expressed : $\operatorname{CrPh}_4 + \operatorname{HOH} \longrightarrow \operatorname{CrPh}_4 \operatorname{H·OH}$ or $\operatorname{CrPh}_4 + \operatorname{H'} \longrightarrow \operatorname{CrPh}_4 \operatorname{H'}$. Hydrogen is not evolved but remains attached to the basic molecule. Superficially, the chromium tetraphenyl radical may be regarded as a basic anhydride analogous to ammonia, but the properties of the CrPh_4 group are not markedly influenced by the addition of hydrogen and the reaction with water is irreversible.

Electrolysis of thallium diethyl hydroxide or iodide in liquid ammonia or methyl alcohol at platinum or mercury cathodes gives only thallium at temperatures down to -70° . H. WREN.

Aspartic and glutamic acids in various proteins. D. B. JONES and O. MOELLER (J. Biol. Chem., 1928, 79, 429-441).—Figures are given for the content of aspartic and glutamic acids of various proteins, the determinations being made by direct isolation of the amino-acids by the method of Foreman (A., 1914, ii, 826) except that barium salts were utilised instead of calcium salts. The percentages of these acids found were in all cases greater than those recorded in the literature, the difference being especially marked in the case of aspartic acid. C. R. HARINGTON.

Alkaline decomposition of cystine. J. C. ANDREWS (J. Biol. Chem., 1928, 80, 191-210) .-The yield of sulphide obtained on keeping cystine in cold 4N-sodium hydroxide is increased by the presence of lead and by exclusion of oxygen; the result is due to the fact that accumulation of sulphide in solution leads to some reduction of the cystine to cysteine. The speed of racemisation of cystine in alkaline solution is greater than the speed of decomposition, although here again fictitiously large results are obtained for the change in optical rotation, owing to formation of cysteine. The rate of liberation of sulphide from cystine depends on the concentration of alkali. The speed of deamination of cystine is greatly increased by the presence of lead, an effect which is apparently specific for this metal, since it is not exhibited by other metals (e.g., copper and zinc) which form insoluble sulphides ; deamination proceeds at the same rate whatever be the degree of racemis-C. R. HARINGTON. ation of the cystine.

Cystine content of proteins. Y. TERUUCHI and L. OKABE (J. Biochem. Japan, 1928, 8, 459-467).— A modification of Okuda's method gave the following results : serum-albumin 1.58, egg-white, 2.01, serumglobulin 1.64, fibrin 1.48, beef 0.66, chicken 0.64, salmon 0.58, edestin 1.13, legumin 0.90, gliadin 2.19, zein 0.58, globin 0.61, gelatin 0.04, human hair 14.26, horse hair 11.07, wool 9.12, casein 0.33.

CHEMICAL ABSTRACTS.

[Structure of silk fibroin.] R. O. HERZOG (Ber., 1928, 61, [B], 243).—The author's treatment of silk fibroin with resorcinol at 120° was limited to 30 min., not 30 hrs. as stated by Meyer and Mark (A., 1928, 1229). H. WREN.

Carbon and hydrogen determinations using a metal tube. S. AVERY (Ind. Eng. Chem., 1928,

20, 1232—1234).—A copper tube protected by an outer nickel tube held in place by friction is suitable for organic combustions. The copper tube projects beyond the nickel tube, at each end of which water jackets are soldered to protect the stoppers. The progress of the combustion can be followed by counting gas bubbles. C. IRWIN.

Elementary organic analysis. A. WAHL and J. P. SISLEY (Bull. Soc. chim., 1928, [iv], 43, 1279—1282).—See A., 1928, 909.

Determination of nitrogen in nitro-compounds by reduction with stannous chloride and subsequent titration. G. WALLERIUS (Tekn. Tidsskr., 1928, 58, Kemi, 33-35; Chem. Zentr., 1928, ii, 372).-Colver and Prideaux's method (A., 1917, ii, 340, 512) is improved. The stannous chloride solution is prepared by dissolving 130-140 g. of the dihydrate in a mixture of 200 g. of water and 880 g. of hydrochloric acid (d 1.19), filtering, and keeping in an atmosphere of carbon dioxide; its titre falls 0.5% per week. The nitro-compound (0.02 g.-equiv.) is boiled under reflux for 20 min. with 20 c.c. of the N-stannous chloride solution, decomposition of particles being avoided by the use of asbestos sheet. The mixture is rapidly cooled, starch solution added, and the liquid titrated with 0.1N-iodine solution. Nitro-compounds which are volatile in steam must first be sulphonated by means of fuming sulphuric acid. A. A. ELDRIDGE.

Volumetric determination of reducing sugars. R. BIAZZO (Annali Chim. Appl., 1928, 18, 447-453).-The difficulty of determining cuprous oxide formed by the action of a small quantity of a reducing sugar on Fehling's solution may be overcome by allowing the oxide to react with silver oxide in ammoniacal solution and determining the amount of metallic silver produced. After the sugar solution has been boiled for 2 min. with 10 c.c. of Fehling's solution diluted to 50 c.c. with water, the flask is closed by a rubber stopper traversed by a cylindrical separating funnel charged with 15 c.c. of a solution containing 220 g. of ammonium sulphate and 300 c.c. of concentrated ammonia solution per litre. After a short time, almost the whole of this solution is run into the flask and the tap of the funnel is then closed. The flask is shaken until the cuprous oxide is completely dissolved, and 10 c.c. of 3.5% silver nitrate solution are introduced ; air is then admitted to the flask, which is left in the dark for some time. The silver is then washed by decantation, the filter-paper being afterwards returned to the flask and the silver dissolved in nitric acid and determined by titration with thiocyanate. Using 10.84, 21.79, 32.53, 43.62, and 51.50 mg. of invertsugar, the above procedure gave 11.14, 21.16, 31.93, 42.33, and 50.68 mg.

Methylene-blue forms a convenient indicator in the determination of reducing sugars by Ionescu and Vargolici's method (A., 1921, ii, 283). T. H. POPE.

Polarimetric determination of small amounts of dextrose. C. LUNDSGAARD and others.—See this vol., 91.

Determination of aniline by Lehmann's method. A. V. PAMFILOV and V. E. KISSELEVA.— See B., 1928, 885. Jaffé's reaction for creatinine. V. Isolation of the red compound. I. GREENWALD (J. Biol. Chem., 1928, 80, 103—106; cf. A., 1928, 744).—A hot solution of picric acid (2 mols.) was treated with creatinine (1 mol.) and, after cooling, with excess of sodium hydroxide, the solution was filtered and poured into 10 vols. of alcohol, yielding a precipitate of a red substance, $C_4H_7ON_3, C_6H_3O_7N_3, 2NaOH$. On treatment with dilute acetic acid this yielded creatinine picrate, whilst, when dissolved in water in presence of sodium picrate, it gave immediately the red colour of Jaffé's reaction equivalent to its content of

C. R. HARINGTON.

Colorimetric microdetermination of furfuraldehyde. K.SUMINOKURA and Z.NAKAHARA (Trans. Totteri Soc. Agric. Sci., 1928, I, 158—159).—Xylidine in presence of acetic acid gives with furfuraldehyde a red colour stronger and more stable than the corresponding colour with aniline. The colour with xylidine has the added advantage of being specific for furfuraldehyde, and enables accurate determinations of the latter to be made in aqueous or ethereal solution. B. W. ANDERSON.

Detection of colouring matter by separation [of fluid layers]. J. J. HOFMAN (Pharm. Weekblad, 1928, 65, 1190—1198).—The method consists in adding 5 c.c. of the aqueous liquid containing the colouring matter to mixtures of (a) 5 c.c. each of ethyl and benzyl alcohols, (b) 5 c.c. each of ethyl and amyl alcohols, and (c) 10 c.c. of acetone and 1 c.c. of benzene, and then causing separation into two layers by adding

enthelixer oxide in anniopiaçal solution

5 c.c. of water. Tables are given showing the colorations of the two layers for a large number of natural and synthetic colouring materials when water, dilute hydrochloric acid, dilute sodium hydroxide solution, and solutions of sodium hydrogen sulphite and hydrogen peroxide are added to cause separation. The method may be used to identify an unknown colouring material, and also to detect the presence of synthetic colouring matter in foods, essences, etc. S. I. LEVY.

Detection of gallic acid and tannin. S. A. CELSI (Rev. Centr. Est. Farm. Bioquim., 1928, 16, 642—650; Chem. Zentr., 1928, i, 2850).—Gallic acid, tannin, etc., which yield pyrogallol when heated, are detected by the production of a cherry-red colour when a trace of the latter in concentrated acetic acid is heated with a few drops of formaldehyde solution and concentrated hydrochloric acid.

A. A. ELDRIDGE.

Reactions of colchicine. L. EKKERT' (Pharm. Zentr., 1928, 69, 662—663).—Colchicine gives a yellow colour with concentrated sulphuric acid and when heated the solution changes colour through goldenyellow, saffron-yellow, brownish-red, blood-red to deep garnet-red. A yellow colour is also formed by colchicine and dilute sulphuric acid, dilute and concentrated hydrochloric acid, dilute nitric acid, acetic acid, and hot phosphoric and lactic acids. A mixture of 0.01 g. of colchicine, 0.003—0.005 g. of tartaric acid, and 1 c.c. of concentrated sulphuric acid on heating becomes green and if either salicylic or citric acid be used instead of tartaric acid a garnet-red solution is formed. E. H. SHARPLES.

solution leads to some reduction of

Biochemistry.

Gas tensions in tissues affected by local temperatures. H. C. BAZETT and L. SRIBYATTA (Amer. J. Physiol., 1928, 86, 565—577).—Carbon dioxide tension is under normal conditions lower in the subcutaneous tissue than in alveolar air. The high oxygen saturation of blood at lower temperatures is dependent on a failure of the tissues to utilise oxygen rather than on the physical effects of temperature on hæmoglobin dissociation. B. A. EAGLES.

Mode of combination of carbon dioxide in the blood. K. HAYASI, Y. NISIMURA, and M. OKUYAMA (J. Biophysics, 1927, 2, 293-303).— Samples of oxalated goat's blood have been equilibrated with carbon dioxide at a definite pressure and the quantities of carbon dioxide contained in the plasma and in the whole blood have been determined separately as well as the $p_{\rm H}$ of the whole blood. At the same carbon dioxide tension the corpuscles take up more carbon dioxide than does the plasma. The results are at variance with the view that carbon dioxide in the plasma exists only as free carbon dioxide or hydrogen carbonate, but suggest that a part of it exists in an unknown form.

W. O. KERMACK.

Production of carbon monoxide by the oxidation of dextrose in alkaline solution by oxygen or air. Biological consequences of this reaction. M. NICLOUX (Bull. Soc. Chim. biol., 1928, 10, 1135— 1163).—When a solution of dextrose (0.25 g.) in 0.1Npotassium hydroxide (50 c.c.) is shaken with oxygen (50 c.c.) or an equivalent amount of air at 84° , carbon monoxide (1.62 c.c.) and dioxide (5.13 c.c.) are liberated. Carbon monoxide is not liberated in the absence of oxygen, but an excess of oxygen tends to diminish the amount formed. Sodium and lithium hydroxides act in a similar way and barium and calcium hydroxides and sodium carbonate more slowly; sodium hydrogen carbonate is without action. Lævulose, galactose, lactose, and maltose behave similarly to dextrose; sucrose yields carbon monoxide only subsequent to its inversion by the alkali.

Carbon monoxide is found in the blood of mammals, birds, and fish; dog's blood contains about 1.5 c.c. per litre. The amount present in the blood is too great to be accounted for by the small amount possibly existing in the atmosphere (Gautier, A., 1900, ii, 720) and it is therefore suggested that it arises from oxidation of the sugars in the blood-stream.

G. A. C. GOUGH.

Correlation between oxygen capacity and the total hærnoglobin content. E. BAUER, K. LAWROWSKY, and E. SKUJIN (Z. ges. exp. Med., 1927, 58, 586-595; Chem. Zentr., 1928, i, 3086).—A

creatinine.

large hæmoglobin content corresponds in man with a small degree of oxygen saturation.

A. A. ELDRIDGE. Hydrogen-ion equilibrium in the blood. III. Temperature effect on the amphoteric property of oxyhæmoglobin. S. KATO (J. Biophysics, 1927, 2, 243-249) .- When blood-serum and defibrinated blood from the same animal are equilibrated at 18° at a carbon dioxide tension of 51.6 mm. the $p_{\rm H}$ of the two fluids is 6.97. At higher tensions of carbon dioxide at this temperature the $p_{\rm H}$ of the serum is below that of the defibrinated blood, whilst at lower carbon dioxide tensions the $p_{\rm H}$ of the defibrinated blood is less than that of the serum. The oxyhæmoglobin therefore acts as a buffer at any p_{π} other than 6.97, which is therefore the isoelectric point of oxyhæmoglobin at 18°. By the use of the same method the isoelectric point of oxyhæmoglobin is found to be 6.82 at 25°, 6.75 at 30°, whilst at 37° the isoelectric point was not attained at a carbon dioxide tension of 200 mm. These results have been confirmed by experiments on cataphoresis of oxyhæmoglobin at various hydrogen-ion concentrations. By this method the isoelectric point of oxyhæmoglobin at 37° was found to be 6.57. W. O. KERMACK.

Spectrophotometric studies on oxyhæmoglobin. E. KEVE (Biochem. Z., 1928, 201, 439— 453).—Determinations of the extinction coefficient ε and of the constant A, where c (concentration)= $A\varepsilon$, were carried out on various samples of crystallised oxyhæmoglobin from the horse and dog. The ratio $\varepsilon_{541\cdot6-533\cdot1}/\varepsilon_{565\cdot8-555\cdot9}$ has the value $1\cdot61-1\cdot62$ for once-crystallised oxyhæmoglobin; further crystallisation lowers the value eventually to $1\cdot55$. For oncecrystallised horse oxyhæmoglobin $A_{541\cdot6-533\cdot1}=1\cdot16$, $A_{565\cdot8-555\cdot9}=1\cdot88$. In the spectrophotometric determination of the hæmoglobin content of blood, the value as determined from the values for ε and A may differ by 3%. J. H. BIRKINSHAW.

Hæmochromogen. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1928, 12, 273-288).-Hæmochromogens contain reduced hæm combined with a nitrogenous base, a reversible equilibrium existing between the hæmochromogen on the one hand and its constituents on the other. One of the two compounds formed by reduced ham with cyanide 18 a typical hæmochromogen to which the name cyanohæmochromogen has been given. This compound probably contains one cyano-group per mol. of hæm. The hæmochromogen formed from hæmoglobin is a compound of denatured globin and reduced hæm, 1 mol. of denatured globin (M 16,700) being able to convert 10 mols. of reduced hæm into hæmochromogen. Edestin and zein are less efficient as bases in the formation of hæmochromogen than is denatured globin. W. O. KERMACK.

Conversion of blood pigment into bile pigment. —F. SCHWERDTEL (Biochem. Z., 1928, 201, 435— 438; cf. Pollak, A., 1928, 1270).—The substance $C_{16}H_{16}O_4N_4$ was prepared in crystalline form from quinone (1 mol.) and pyrocatechol (2 mols.) by the action of ammonia. It had m. p. 194—195° and corresponded in all respects with the product obtained by Pollak (loc. cit.) from pyrocatechol and hæmin. Pollak's product is therefore not of pyrrole nature. J. H. BIRKINSHAW.

Differentiation of the labile iron of blood by means of its reaction with carbon monoxide and oxygen. G. BARKAN and E. BERGER (Arch. exp. Path. Pharm., 1928, 136, 278-299; cf. A., 1928, 537).-Saturation of blood with carbon monoxide or complete reduction with hydrogen prevents the separation by acid of 65% of the total labile iron. This action is partly reversible in the former case and completely in the latter by reoxygenation. Application of a distribution equation for the reaction of this labile iron with carbon monoxide and oxygen yields a distribution constant one fourth to one tenth of that for hæmoglobin. The remainder of the labile iron (35%) can be separated by acid after saturation of blood with carbon monoxide or complete reduction with hydrogen. Hydrocyanic acid is without action on the labile iron of blood. This action of carbon monoxide on part of the labile iron shows itself in the case of the blood of living rabbits. H. R. ING.

Blood-cell metabolism. I. Effect of methylene-blue and other dyes on the oxygen consumption of mammalian and avian erythrocytes. G. A. HARROP and E. S. G. BARRON (J. Exp. Med., 1928, 48, 207—223).—The respiratory metabolism of non-nucleated mammalian erythrocytes is greatly increased by the addition of methylene-blue and certain other dyes; the effect on avian blood is less marked. The rôle of an oxygen-carrier is ascribed to the dye. CHEMICAL ABSTRACTS.

Permeability of membranes. VI. Mensuration of the dried collodion membrane (calculation of dimensions and relations to certain biological membranes). A. A. WEECH and L. MICHAELIS (J. Gen. Physiol., 1928, 12, 221-230).— Measurements are given of the arca, thickness, density, and water content of collodion membranes used in experiments previously described (A., 1927, 727). The results are discussed in relation to the behaviour of certain membranes of animal origin and in particular to the membrane of the red blood-corpuscle. W. O. KERMACK.

Colloidal osmotic pressure of the blood fluid. I. Conditions which influence the colloidal osmotic pressure of the blood-serum. II. Restitution of the blood fluid after hæmorrhage. K. HIROTA (J. Biochem. Japan, 1928, 9, 71-85, 87-102).-I. When the colloidal osmotic pressure of blood-serum is measured by the use of a collodion membrane, the results obtained depend on the nature of the aqueous solution against which the serum is equilibrated, being reduced with increasing concentration of the salts in this liquid and with increasing acidity. When isotonic salt solutions are used, higher results are obtained with potassium chloride and ammonium chloride and lower results with disodium hydrogen phosphate, potassium sulphate, magnesium chloride, calcium chloride, and potassium dihydrogen phosphate than with sodium chloride. Serum shows the same colloidal osmotic pressure as does plasma from the same blood.

II. In rabbits bled up to 30% of their blood-volume,

fluid passes into the blood-stream and at the same time the colloidal osmotic pressure is almost but not quite maintained. The liver plays an important part in regulating the process. The conditions favouring rapid restoration of the blood-volume are low bloodpressure and high colloidal osmotic pressure in the blood. The results support Bayliss and Starling's theory of lymph production. W. O. KERMACK.

Importance of the membrane in the measurement of the osmotic pressure of plasma-protein. A. NITSCHKE (Z. ges. exp. Med., 1928, 59, 298—302; Chem. Zentr., 1928, i, 3099).—The osmotic pressure of serum-protein towards isotonic Ringer's solution is higher with a collodion membrane or a parchment membrane coated internally with collodion than with a parchment membrane, uncoated or coated externally with collodion. An explanation is offered.

A. A. ELDRIDGE.

Colorimetric determination of serum-proteins by means of phenol reagent. H. WU and S. M. LING (Chinese J. Physiol., 1928, 2, 399-402).—It is suggested that the standard for use in Wu's method (A., 1922, ii, 406) should be made by the addition of 50 c.c. 0·1N-sodium carbonate and 200 c.c. 95% alcohol to 250 c.e. of an approximately 0·5% solution of dialysed egg-albumin, the actual concentration of the protein being determined by Kjeldahl's method. F. C. HAPPOLD.

Protein spreading as method for determination of serum-albumin and -globulin. E. GORTER and F. GRENDEL (Biochem. Z., 1928, 201, 391—411).— The general principles of the spreading of proteins on water are discussed. In maximum spreading (on 0.1N-acid or -alkali) the linked amino-acids which form the protein molecule assume an approximately horizontal position. A second maximum occurs at the isoelectric point due to the free amino- and carboxyl groups. On 0.001N-acid or alkali the spreading is much less; the cause of this is uncertain.

A method is described for the determination of albumin and globulin in serum, using the principle of spreading on 0.1N-hydrochloric acid. The proteins were separated by precipitation of the globulin with half-saturated ammonium sulphate. A number of determinations were made on the sera of man and various animals and compared with gravimetric data. In a micro-method for the determination of globulin and albumin, the globulin and total protein are determined and the albumin by difference.

J. H. BIRKINSHAW. Examination of sera of mountain-dwellers by electrodialysis. A. Tóth (Biochem. Z., 1928, 201, 412—423).—Globulin and albumin determinations were made on the sera of animals and man living at high and low altitudes. Rats showed a lower globulin content at high than at low altitude. In the case of the guinea-pig, rabbit, and man there was no marked difference. Repeated removal of blood from rabbits led to a diminution of the globulin content of the serum. J. H. BIRKINSHAW.

Micro-determination of the ether-soluble organic acids in blood. S. L. ÖRSKOV (Biochem. Z., 1928, 201, 22-33).—The rocking extraction method of Widmark, used for urine (A., 1928, 96), is adapted

as a micro-method and is successfully applied to the determination of the organic acids of 0.1-0.2 c.c. of human and rabbit's blood and of added benzoic acid. P. W. CLUTTERBUCK.

Cholesterol ester content of blood-serum and plasma. Cholesterol esterase in animal tissues. Hypercholesterolæmia of fasting. Effect of age on cholesterol of blood-serum. R. E. SHOPE (J. Biol. Chem., 1928, 80, 125-126, 127-132, 133-140, 141-148).-Blood-serum contains a higher proportion of cholesterol in the form of esters than does plasma. An enzyme capable of hydrolysing cholesteryl esters is widely distributed throughout animal tissues; the action of this enzyme probably accounts for the low cholesteryl ester content of post-mortem blood. The hypercholesterolæmia of fasting is relieved equally by the administration of any one primary foodstuff or of a mixed diet; exclusive feeding with fat for 48 hrs. causes no increase in blood-cholesterol. The cholesterol content of the blood increases from birth during the early life of the animal and slowly decreases again in old age; cholesteryl esters are absent from the blood at birth and appear when the increase in C. R. HARINGTON. total cholesterol begins.

Solvent action of normal and pathological human serum on cholesterol. M. LÖPER, A. LEMAIRE, and A. LESURE (Compt. rend. Soc. Biol., 1928, 98, 101—103; Chem. Zentr., 1928, i, 3086).— The solvent action of serum on cholesterol is not dependent on the cholesterol content, the flocculation, or the cholesterol skin-reaction, although this is usually negative when the cholesterololysis is increased.

A. A. ELDRIDGE.

Colorimetric determination of lipin-phosphorus in blood. S. L. LEIBOFF (J. Biol. Chem., 1928, 80, 211-214).—Blood is poured into a mixture of alcohol and ether, an aliquot portion of the filtrate is evaporated, and the residue incinerated with sulphuric acid and hydrogen peroxide; phosphate is then determined by the author's method (A., 1928, 1391). C. R. HARINGTON.

Relationship between phosphoric acid and glycolysis in blood. W. A. ENGELHARDT and A. E. BRAUNSTEIN (Biochem. Z., 1928, 201, 48-65). —Two opposed and independent processes contribute to the phosphoric acid balance of blood *in vitro*, first, a separation of inorganic phosphorus from organic compounds, and second, the processes directly related to glycolysis in which phosphoric acid becomes combined, the former, in distinction to the latter, being insensitive to the action of ions and to the displacement of p_{π} . The inorganic phosphorus content of rabbit's defibrinated blood does not change on keeping in a thermostat at 37°, but increases considerably on dilution with isotonic saline, the increase being greater the greater is the dilution. If diluted with anisotonic saline, the increase is greater the more strongly hyper- or hypo-tonic is the saline. Addition of a series of chlorides showed that univalent cations do not exert any specific effect on the amount of inorganic phosphorus formed, but calcium ions caused a greater increase than the univalent ions. Dilution with isotonic solutions of salts of monobasic acids showed that different anions cause different increases of

inorganic phosphorus, the following being arranged in order of the intensity of their action : I, NO_3 , CNS <Br<Cl<F. Erythrocytes contain both the substrate from which inorganic phosphorus is derived and the phosphatase necessary to release it, but serum contains only the enzyme. If in place of whole blood washed red cells or serum to which has been added a boiled suspension of corpuscles are used, a constant increase of inorganic phosphorus occurs which is independent of dilution and of the action of different ions and of displacement of $p_{\rm H}$. The difference between the two sets of experiments is due to the fact that in the latter glycolysis cannot occur. When washed cells are suspended in Ringer's solution containing dextrose, a glycolysing system is again obtained and the increase of inorganic phosphate is greatly decreased in comparison with controls of the same cells in Ringer's solution without dextrose, whilst the effect of ions becomes similar to that in whole blood. All the factors which, with a glycolysing system, bring about an increase of inorganic phosphorus inhibit glycolysis to the same extent. Addition of arsenate either to whole blood or to the cells-dextrose system causes an even greater increase of inorganic phosphorus than addition of sodium fluoride (cf. A., 1928, 1269). P. W. CLUTTERBUCK.

Nature of the sugar combined with protein of blood-plasma. Z. DISCHE (Biochem. Z., 1928, 201, 74-86).—The total carbohydrate of horse blood-plasma is about 0.3%, of which 0.08-0.11% exists as free sugar, and the rest, which is combined with protein (cf. Glassmann, A., 1926, 192, 1169), consists of about equal amounts of *d*-mannose and a non-fermenting sugar resembling glucosamine. Mannose was isolated by autoclaving the dialysed plasma with 3% sulphuric acid at 120°, precipitating the protein decomposition products with phosphotungstic acid, and identifying as the phenylhydrazone.

P. W. CLUTTERBUCK. Total sugar of blood and urine. II. Hydrolysable sugar of blood. M. R. EVERETT and F. SHEPPARD (J. Biol. Chem., 1928, 80, 255-268).--Hydrolysis with sulphuric acid does not increase the nitrogenous reducing substances in protein-free bloodfiltrates, nor does it affect the reducing power of solutions of dextrose; technical errors are also excluded, so that the real existence of hydrolysable sugar (A., 1927, 1102) is confirmed. This substance is present also in plasma, but to a smaller extent than in corpuscles; it is not removed by treatment with yeast, and it is for the most part resistant to alkaline hydrolysis. It is present in increased amount in leucemic blood, and may consist, in part, of glycogen. C. R. HARINGTON.

Variations of the results of sugar determinations in relation to dilution of the blood after the mercurial proteinisation of blood. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, 10, 1164—1178).—The more dilute the blood the greater is the apparent sugar content after deproteinisation by mercuric sulphate or chloride. The plasma and, to a greater extent, the corpuscles are both subject to this effect, which is not due to the acidity of the mercuric salts, since deproteinisation with tungstic acid gives figures for the "immediately reducing" sugar independent of dilution. The effect is not produced after the action of yeast. The facts may be explained by supposing that the mercuric salt combines with an unknown blood-constituent, thus setting free at certain dilutions a reducing substance, probably a carbohydrate. G. A. C. GOUGH.

Oscillations of blood-sugar values within brief periods and the blood-sugar curve on uniform ingestion of dextrose. O. J. NIELSEN (Biochem. J., 1928, 22, 1490-1498).-A number of determinations of the blood-sugar in fasting individuals at complete rest made at intervals of 1-5 min. for a period of $\frac{1}{2}$ —2 hrs. did not divulge the previously described oscillations of the blood-sugar curve. In normal individuals an almost horizontal curve was found, in insulin- and diet-treated diabetics a rising curve, in diabetics treated with diet only a falling curve, and in a diet-treated diabetic with advanced kidney insufficiency a horizontal curve. There were no oscillations in the blood-sugar in non-diabetics after ingestion of dextrose or in diabetics at different times of the day after ingestion of food or administration of insulin. No uniform blood-sugar curves were obtained on different days after ingestion of the same amount of dextrose with a plentiful and fairly uniform mixed diet. On the other hand, the amount of dextrose eliminated in the urine in 2 hrs. was the same each day. In one case uniform blood-sugar after ingestion of dextrose on three different days was obtained in a patient receiving during this time the same amount of food, salts, and liquid.

S. S. ZILVA.

Micro-determination of the water-content of blood. L. BRACALONI (Arch. Farm. sperim., 1928, 46, 115—118).—Modifications in Bang's method are suggested. T. H. POPE.

Ultra-violet absorption spectra of uric acid and of the ultra-filtrate of serum. F. C. SMITH (Biochem. J., 1928, 22, 1499-1503).-Uric acid when dissolved in water shows two sharp bands in the ultraviolet absorption spectrum; when dissolved in sodium carbonate only one band is obtained. The values for the concentration of uric acid in serum obtained from the spectroscopical examination are in very fair agreement with those obtained by chemical methods. The absorption spectrum of uric acid present in the ultra-filtrate of blood-serum is similar to that of uric acid dissolved in water or in the buffer solution and not to that of the acid dissolved in carbonate. A blood-filtrate from a pathological case showed marked general absorption. S. S. ZILVA.

Theory of blood coagulation. E. WALD-SCHMIDT-LEITZ, P. STADLER, and F. STEIGERWALDT (Naturwiss., 1928, 16, 1027).—The capability of a substance to be decomposed by trypsin-kinase is connected with its power of inhibiting blood-clotting. The conclusion is reached that blood-clotting is a proteolytic process and thrombin a proteolytic enzyme. Of the proteolytic enzymes examined, trypsin-kinase alone is able to hasten blood-clotting. It is probable that thrombin is related to trypsin-kinase, if not identical with it. J. H. BIRKINSHAW. Imitation of organic forms by means of albumin and hydrofluoric acid. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], 8, 15-19).—An extension of previous work (cf. A., 1928, 913).

Microscopical tests for glutathione in cells. P. JOYET-LAVERGNE (Compt. rend. Soc. Biol., 1928, 98, 658—660; Chem. Zentr., 1928, i, 2946).—The red colour-reaction with sodium nitroprusside solution given by reduced glutathione in fresh tissue is rendered more sensitive by placing the material in a 10% sodium cyanide or saturated aqueous sodium sulphite solution for 10 min. Sodium sulphate and trichloroacetic acid solutions exercise a similar effect.

A. A. ELDRIDGE.

Membrane of the egg of Voluta brasiliana as dialyser. A. H. ROFFO and L. M. CORREA (Bol. Inst. Med. Exp., 1927, No. 16, 5 pp.; Chem. Zentr., 1928, ii, 364).—The membrane of the egg of Voluta brasiliana, a La Plata mollusc, is insoluble in water, but soluble in acetic acid and concentrated alkalis. It contains 2.45% of ash, traces of carbohydrate, and no lipins. Its properties resemble those of keratin. The membrane is suitable for ultra-filtration.

A. A. ELDRIDGE.

Chemistry of brain. II. Phosphatides of the normal human brain soluble in light petroleum. K. SINGER and O. DEUTSCHBERGER. III. Phosphatides of the brain, soluble in light petroleum, in progressive paralysis and marasmus. K. SINGER (Biochem. Z., 1928, 198, 328-339, 340-349).-II. The total light petroleum extract of human adult brain (per g. moist weight) is constant, but the amount extractable from different slices varies irregularly. The nitrogen distribution of these extracts is the same as that obtained for horse brain (A., 1927, 371) with the exception of the galactoside-nitrogen, which is much smaller. The foetal brain contains only a small amount of substance extractable by light petroleum, the nitrogen content of which, however, is 1.5-2 times that of the extracts of adult brain. As development proceeds, the total light petroleum extract increases and the amount of nitrogen decreases, the decrease being initially rapid and later more gradual. III. The amount of the light petroleum extract of brain in five cases of progressive paralysis is increased and the nitrogen content is decreased, in comparison with the normal. The choline-nitrogen is decreased to one third of the normal, the amino-nitrogen is slightly decreased, and only traces of galactosidenitrogen are detectable. The ratio total aminonitrogen : choline-nitrogen is 3.1:1 instead of the normal value 1.4:1. This decrease in lecithin is not, however, specific for progressive paralysis. P. W. CLUTTERBUCK.

Combination of the protein of brain with alkaloids and organic bases. A. PETRUNKINA and M. PETRUNKIN (Biochem. Z., 1928, 201, 185– 189).—Alkaloids (strychnine, morphine, cocaine, and quinine) and guanidine combine with the denatured protein of brain only when the $p_{\rm H}$ is higher than 4 (cf. A., 1928, 190). P. W. CLUTTERBUCK.

Physical chemistry of the epidermis. H. SCHADE and A. MARCHIONINI (Arch. Dermat. Syph., 1928, 154, 690-716; Chem. Zentr., 1928, ii, 7172).—The $p_{\rm H}$ of the epidermis is between 1.78 and 5.17, the average value being 3.78; the values vary at different points. Perspiration is associated with an increase of acidity; wounding or restricted evaporation is attended by an alkaline reaction.

A. A. ELDRIDGE.

Cholesterol in tissues. E. N. CHAMBERLAIN (J. Physiol., 1928, 66, 249—261).—Tables are given showing the cholesterol content of the suprarcnals, spleen, brain, liver, kidneys, lungs, muscle, and blood in normal rabbits. Cholesterol injected intravenously causes a large increase in the cholesterol content of the spleen. It is suggested that the spleen may be concerned normally in maintaining the blood-cholesterol at a fixed value by continually removing small excesses. B. A. EAGLES.

Cholesterol of protoplasm. I. Ox-heart. G. PFEIFFER (Biochem. Z., 1928, 201, 424-434).—The isolation of the total cholesterol of heart tissue by extraction with solvents was found not to give quantitative results. The best method was the hydrolysis of the tissue with 2% sodium hydroxide solution followed by ether extraction according to Fex's method (A., 1920, i, 697). The ether extract was fractionally crystallised after a digitonin precipitation of cholesterol and oxycholesterol. The saponification of the cholesteryl esters with 5% metallic sodium in absolute alcohol required 24-30 hrs. The bound cholesterol was 34% of the total cholesterol. J. H. BIRKINSHAW.

Distribution of potassium in the animal organism. A. LEULIER, L. VELLUZ, and H. GRIFFON (Compt. rend., 1928, 187, 957—959).— The potassium contents, determined by a modification of the cobaltinitrite method, of the small intestine, heart, and leg muscle of the guinea-pig are 1.84, 2.02, and 2.31%, respectively (average for dry tissue). The amounts vary very little from animal to animal.

G. A. C. GOUGH.

Composition of the enamel of teeth. A. BERNARDI (Annali Chim. Appl., 1928, 18, 454-460). Analyses of the dental enamel of cattle gave : For animals of 2—5 years, (1) soluble ash, 99.87; Ca, 32.74; Mg, 2.50%; (2) soluble ash, 99.87; Ca, 37.28; Mg, 2.42; PO₄, 52.44; Cl, 0.33%. For animals of 7—10 years or older, (1) soluble ash, 99.81; Ca, 40.89; Mg, 0.40%; (2) soluble ash, 99.63; Ca, 41.54; Mg, 0.89; PO₄, 52.05; Cl, 0.25%. In two of a number of cases traces of fluorine were detected.

T. H. POPE.

Determination of silica in tissues. E. J. KING (J. Biol. Chem., 1928, 80, 25—31).—The dried tissue is incinerated with nitric acid in presence of boric acid, the ash is extracted with sodium hydroxide, and the solution almost neutralised with sulphuric acid; phosphates are precipitated with magnesia mixture, the filtrate is treated with molybdic acid, and the ,yellow colour of the silicomolybdic acid formed is compared with a picric acid standard. Figures are given for the silica content of various tissues. C. R. HARINGTON.

Is ozone a normal constituent of cod-liver oil? J. A. DE LOUREIRO (Compt. rend. Soc. Biol., 1928, 97, 879-880; Chem. Zentr., 1928, ii, 301).-Ozone was detected in all crude oils examined; it is considered to originate from autoxidation, and not to be an original constituent. A. A. ELDRIDGE.

Arsenic in fish. E. SADOLIN (Biochem. Z., 1928, 201, 323-331).—The arsenic of fish occurs principally in the fat-soluble compounds. The arsenic compounds appear to be acidic, since they are extracted by a weakly alkaline solution along with the fatty acids.

The concentration of arsenic is higher in the liver of fish than in muscular tissue. The oil extracted from tissue contains more arsenic than the tissue itself. The arsenic content of fish bears no relation to their oil content. J. H. BIRKINSHAW.

Biochemistry of mixed human saliva. I. Dextrose content. D. ENTIN and A. A. SCHMIDT (Deut. Monatsschr. Zahnheilkunde, 1927, 710—712; Chem. Zentr., 1928, i, 2955).—The Hagedorn-Jensen method is not applicable to saliva. Dextrose and fermenting substances are absent from fasting mixed human saliva. The quantity of substances which reduce thiocyanate (average 9.7 mg.-%) is fairly constant for the individual. A. A. ELDRIDGE.

Chemical mechanism of hydrochloric acid secretion. I. Electrolyte variations in human gastric juice. H. A. BULGER, C. M. STROUD, and M. L. HEIDEMAN. II. Blood passing through the stomach of dogs. H. A. BULGER, D. ALLEN, and L. B. HARRISON (J. Clin. Invest., 1928, 5, 547— 560, 561—571).—Acid secretion is accompanied by little change in the chlorine concentration of blood, although the total base falls proportionally to the increase in acid. The concentration of phosphate in gastric contents is usually greater than in serum. As blood flows through a secreting portion of a dog's stomach, the total base increases, whilst the chlorine is little changed. CHEMICAL ABSTRACTS.

Composition of human milk. M. BELL (J. Biol. Chem., 1928, 80, 239-247).—Figures are given for the composition of human milk at various stages of lactation; in general the ash and protein content decreased and the lactose and fat increased with the time after delivery. The volume of milk was increased by increase in the carbohydrate of the diet, and decreased by supplementing the fat; in neither case was the composition of the milk significantly affected. C. R. HARINGTON.

Effect of heat on certain constituents of milk. Adult utilisation of heated milk. K. DAUM (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925—1926, 4, 423— 430). CHEMICAL ABSTRACTS.

Polarimetric determination of small amounts of dextrose. C. LUNDSGAARD, C. N. J. GRAM, S. A. HOLBØLL, and E. RUD (Biochem. Z., 1928, 201, 341— 352).—A comprehensive series of polarimetric determinations of dextrose on solutions of unknown composition was carried out by three observers. Three different polarimeters were used. The results indicate that when the amount of dextrose is small a considerable percentage error is encountered. In 95% of the cases this did not exceed the absolute value of 0.020%of dextrose. Previous determinations of dextrose in biological fluids employing the polarimetric method and conclusions therefrom need confirmation.

J. H. BIRKINSHAW.

Optical activity of cerebrospinal fluids. C. N. J. GRAM, O. J. NIELSEN, and E. RUD (Biochem. Z., 1928, 201, 353-368).-Polarimetric determinations of dextrose in samples of cerebrospinal fluid were carried out under special precautions (see preceding abstract). The values were consistently lower than the figures obtained by copper reduction. After precipitation of proteins with lead acetate the polarimetric value coincided with the reduction value. After partial removal of the sugar by dialysis, negative rotations were obtained which again became positive on precipitation of protein. No evidence for a "con-densation product" of sugar and protein was found; the rotation observed is merely the sum of the rotations due to dextrose and protein. An increase in the rotation after two days as observed in some cases must be ascribed to changes in the protein.

J. H. BIRKINSHAW.

Determination of hexamethylenetetramine in cerebrospinal fluid. E. BERTEL (Biochem. Z., 1928, 201, 13—14).—The acidified fluid is distilled in steam and the formaldehyde in the distillate is determined by adding standard iodine and sodium hydroxide, acidifying after 30 min., and titrating with standard thiosulphate. P. W. CLUTTERBUCK.

Analysis of colouring matter of urine. VI. M. WEISS (Biochem. Z., 1928, 201, 337—340).—A new spectrometer is described which may also be used as a colorimeter. J. H. BIRKINSHAW.

Renal excretion of chlorides and water. A. R. FEE (J. Pharm. Exp. Ther., 1928, 34, 305–316).— Anæsthetics and narcotics inhibit the water diuresis following the absorption of water from the intestine. The physical theories of renal excretion are not sufficient to explain this effect. A disturbance of a mechanism involving the pituitary body is indicated. B. A. EAGLES.

Study of physiological condition and function by biological analysis of the urine. I. Diagnosis of pregnancy. C. FUNK and H. R. OLIVIER (J. Pharm. Chim., 1928, [viii], 8, 449-453).—A method for the diagnosis of pregnancy, based on the presence of folliculin in the urine, is described. The results confirm those of Aschheim and Zondek (Klin. Woch., 1928, 5, 8). From the sixth week, folliculin is detectable in quantities of 30-50 c.c. of urine, but in normal females it cannot be detected in 1400 c.c. of urine. The method appears to be more specific than that depending on the demonstration in the urine of the hormone of the posterior lobe of the pituitary gland. E. H. SHARPLES.

Fat metabolism of cancer patients. K. KLAUS (Biochem. Z., 1928, 201, 286—291).—The total cholesterol in the blood-serum of 9 women patients was below normal; the fatty acids were normal except in advanced cases. The percentage of cholesterol in the unsaponifiable fraction varied around 56%; the lipæmic coefficient (cholesterol/fatty acids) was about 0.5. J. H. BIRKINSHAW.

Oxidation of fats etc. and metabolism in normal health and diabetes. C. C. PALIT and N. R. DHAR.—See this vol., 48. Supposed effect of tumour extracts on glycolysis. J. BROOKS and M. JOWETT (Biochem. J., 1928, 22, 1413—1416).—Saline extracts of malignant tumours have no effect on the anaërobic glycolysis of normal rat tissue. Washing tissues with a suitable Ringer's solution does not affect their glycolysis (cf. Waterman, A., 1924, i, 137; Brit. J. Exp. Path., 1925, 6, 300). S. S. ZILVA.

Ammonium chloride acidosis and diabetic acidosis. F. MAINZER and A. JOFFE (Z. ges. exp. Med., 1928, 59, 492—508; Chem. Zentr., 1928, i, 3085—3086).—Ammonium chloride acidosis is generally followed by alkalosis, conditioned by reduction of the chlorine content and a retarded increase of carbon dioxide. Abolition of diabetic acidosis by insulin treatment is also accompanied by alkalosis and fall in chlorine content. A. A. ELDRIDGE.

Gastric lipase in various stomach diseases. K. ANDO (Nagaya J. Med. Sci., 1927, 2, 103—108).— The lipase, determined by Ogawa's modification of Michaelis and Rona's tributyrin method, was not decreased in hyperacidity ($p_{\rm H}$ 1·1—1·5, determined by Michaelis' indicator method) and gastric ulcer ($p_{\rm H}$ 1·2), whilst in anacidity, gastric cancer, and other diseases with $p_{\rm H}$ above normal it was considerably lowered. Chemical Abstracts.

Metabolism in hepatic disease. I. Carbohydrate metabolism. A. OPPENHEIMER (Z. klin. Med., 1928, 107, 467-475; Chem. Zentr., 1928, i, 3087).—The lactic acid value is not higher (13 mg.-%) than normally or in other chronic disease. Administration of sugar does not increase the blood-lactic acid. A. A. ELDRIDGE.

Cholesterol and its esters in the blood in hepatic disease. A. ADLER and H. LEMMEL (Deut. Arch. klin. Med., 1928, 158, 173–213; Chem. Zentr., 1928, ii, 165).—Normal human blood contains 150-200 mg.-% of total cholesterol (determined by Bloor's method), of which 50-70% is present as ester. When the flow of bile to the intestine is prevented, e.g., by tumour or calculus, the cholesterol value markedly rises, except when an inflammatory process is present. Values in pathological conditions are recorded. A. A. ELDRIDGE.

Cutaneous and venous blood-sugar curves. I. Normal individuals after insulin, and with liver disease. M. FRIEDENSON, M. K. Rosen-BAUM, E. J. THALHEIMER, and J. P. PETERS (J. Biol. Chem., 1928, 80, 269-288).-In the post-absorptive state in normal individuals little difference was found between the cutaneous (arterial) and venous bloodsugar, although the former was usually greater; after ingestion of 50 g. of dextrose the difference became more marked at the time of maximum hyperglycæmia. After a dose of insulin, in a fasting normal individual, the difference generally remained positive, although in one instance it became negative during the period of recovery. In cases of hepatic disease, the pronounced hyperglycæmia resulting from ingestion of 50 g. of dextrose was accompanied by a definitely positive arterio-venous difference in the blood-sugar. C. R. HARINGTON.

Human insulin hypoglycæmia. III. Behaviour of the protein fractions of the blood, the bilirubin, blood-concentration, and bloodcoagulation, particularly in hepatic disease. O. KLEIN and M. KMENT (Z. Klin. Med., 1928, 107, 476-487; Chem. Zentr., 1928, i, 3085).—The blood coagulation-time and the bilirubin value were reduced, the total protein, the fibrinogen, the serum-protein, and the blood-concentration were increased. A. A. ELDRIDGE.

Inflammation and condition of irritation and stimulation. I. Gas metabolism. II. Sugar metabolism. F. BRICKER (Arch. exp. Path. Pharm., 1928, 137, 329—338, 339—342).—Determinations have been made of the oxygen, carbon dioxide, and dextrose content of the venous blood in the two ears of a rabbit, one of which had been irritated by the application of xylene or hot water, or by mechanical stimulation. W. O. KERMACK.

Plasma proteins in leprosy. M. H. NEILL and M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 1—20).—Normal values for plasma are: fibrin, 0.33, albumin 5.23, globulin 2.29%; values obtained in leprosy varied with the condition of the patients, the total protein being about normal, the fibrin increased, and the albumin: globulin ratio lowered. CHEMICAL ABSTRACTS.

Lipase in the blood-serum of lepers. M. H. NELL and M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 21—27).—In general, normal values were obtained; low values were associated with acute exacerbation, advanced pulmonary tuberculosis, and liver diseases. Injection of chaulmoogric ester did not increase the blood-lipase.

CHEMICAL ABSTRACTS.

Toxic action of diastase and cell injury. K. BOSHAMER (Klin. Woch., 1928, 7, 978–980; Chem. Zentr., 1928, ii, 169).—Cells of an injured organism are further injured by diastase. Severe injury by diastase in presence of decomposition products of the pancreas indicates that it is a cause of death in pancreatic necrosis. A. A. ELDRIDGE.

Biochemistry of scurvy. A. ABRAHAM (Klin. Woch., 1928, 7, 353—355; Chem. Zentr., 1928, i, 2960).—Reduced osmotic resistance of the red bloodcorpuscles, hypocholesterolæmia, reduction of serumcalcium, increase of serum-potassium, and retarded increase of blood-sugar after administration of dextrose (with protracted course of the blood-sugar curve) were observed. A. A. ELDRIDGE.

Metabolism in scurvy. II. Nitrogen absorption and retention of guinea-pigs. H. L. SHIPP and S. S. ZILVA (Biochem J., 1928, 22, 1449—1460).— There are no indications of a disturbed absorption or retention of nitrogen during the early stages of the development of scurvy in growing guinea-pigs. The nitrogen balance becomes negative only when the intake of food is diminished as a consequence of the disease. Although the results obtained were not concordant, it is unlikely that the C/N ratio of the urine of young guinea-pigs is disturbed by the onset of scurvy. S. S. ZILVA. Rickets in rats. VIII. Rickets and tetany. A. T. SHOHL and F. C. BING (Amer. J. Physiol., 1928, 86, 633-638).—Rachitic rats cured by irradiation or by the addition of cod-liver oil to the diet show a lessened irritability, whilst those cured by the addition of phosphate show an increased irritability of the neuro-muscular system. The rats cured of rickets by the addition of phosphate exhibited definite symptoms of tetany. B. A. EAGLES.

Irradiated ergosterol in parathyroid tetany. J. C. BROUGHER (Amer. J. Physiol., 1928, 86, 538— 541).—Irradiated ergosterol given with milk to parathyroidectomised dogs prevents the development of violent tetany. B. A. EAGLES.

Effect of irradiation on the blood chemistry in tuberculosis. K. C. SPENCE (Brit. J. Actinother., 1928, 3, 148—149).—The effect of irradiation with a mercury-vapour lamp on (1) the clinical condition of the patient and (2) the calcium, phosphate, and cholesterol content of the blood has been studied. In ten out of twelve cases irradiation resulted in an increase in the cholesterol content and an improved clinical condition. F. C. HAPPOLD.

Lipoid phosphorus-cholesterol ratio before and after feeding irradiated eggs to tuberculous patients. D. F. MCRAE and T. INGVALDSEN (Amer. Rev. Tuberculosis, 1928, **17**, 520—521).—No changes of the ratio in the plasma were observed.

CHEMICAL ABSTRACTS.

Serum-calcium. II. Experimental tuberculosis—intraperitoneal inoculation. III. Experimental tuberculosis—subcutaneous inoculation. J. C. HOYLE (J. Pharm. Exp. Ther., 1928, 34, 259—276, 317—324).—II. Rabbits inoculated intraperitoneally with bovine tuberculosis show changes in their serum-calcium which vary with the course of the disease.

III. In rabbits inoculated subcutaneously with bovine tuberculosis the serum-calcium rises during the formation of the local lesion. On ulceration of the lesion it falls, later returning to normal with improvement in the condition of the ulcer. There is no fall in the serum-calcium in the final weeks of the disease, as is the case following intraperitoneal inoculations. B. A. EAGLES.

Diffusion of oxygen and lactic acid through tissues. A. V. HILL (Proc. Roy. Soc., 1928, B, 104, 39—96).—Particular problems in diffusion are studied mathematically, and the results are applied to diffusion processes in the living organism and in experimental physiology with particular reference to the diffusion of oxygen, lactic acid, and carbon dioxide. W. O. KERMACK.

Iron metabolism. V. HENRIQUES and H. ROLAND (Biochem. Z., 1928, 201, 479-485).—The iron excreted in urine of normal and of diseased men in 24 hrs. amounts to 0.08-0.32 mg.; after daily intravenous injection of iron salts the value may increase to 13.5 mg. in the dog. The iron excretion in bile is inconsiderable, about 0.2 mg. daily in the dog. Daily intravenous injection of ferrous lactate causes no increase. J. H. BIRKINSHAW. Lactic acid metabolism of the central nervous system. I. H. JUNGMANN (Biochem. Z., 1928, 201, 259—268).—Lactic acid was determined in the spinal chord of the frog and toad. The average content in the surviving marrow in salt solution was 0.14%; this is gradually given up to the solution. The lactic acid increases to some extent in oxygen and considerably in nitrogen; the lactic acid formed in presence of nitrogen is not removed by oxygen. Stimulation causes a diminution of lactic acid in oxygen, but has no influence in nitrogen.

J. H. BIRKINSHAW.

Artificial elevation of lipin content of central nervous system. I. M. SEREJSKI (Biochem. Z., 1928, 201, 292—297).—Brain-lipins, whether derived from the ox or dog, when administered subcutaneously or orally to dogs, led to an increase in the lipin content of the brain.

J. H. BIRKINSHAW.

Liver-glycogen and muscle training. Y. WAKABAYASHI (Z. physiol. Chem., 1928, 179, 79– 82).—The liver-glycogen of untrained rats determined after moderate exercise was practically nil. Trained rats showed only a small decrease.

J. H. BIRKINSHAW.

Inorganic phosphorus of frog muscle in relation to lactacidogen and phosphagen. G. M. BASTEDO and L. IRVING (Amer. J. Physiol., 1928, 86, 505—519).—In the contraction of isolated frog muscles phosphagen is broken down and acid-soluble inorganic phosphorus is liberated. During the period in which a muscle is approaching fatigue there is a decrease in acid-soluble phosphorus. This decrease is due to the production of an acid-stable compound, presumably "lactacidogen," from the liberated inorganic phosphorus. The decomposition of phosphagen and synthesis of lactacidogen in muscle are independent processes. The compounds may be considered to be in indirect relationship, however, since both are in equilibrium with inorganic phosphorus. B. A. EAGLES.

Fission of lactacidogen in muscular con-traction. G. EMBDEN and H. JOST (Z. physiol. Chem., 1928, 179, 24-40).-A method of determination of inorganic phosphoric acid, lactacidogenhexose, and lactacidogen-phosphoric acid is described. A previous series of determinations on the frog's gastrocnemius is repeated, since the earlier figures showing change in inorganic phosphoric acid cannot be used as a measure of lactacidogen hydrolysis in view of Lohmann's discovery of the enzymic conversion of pyro- into ortho-phosphoric acid in striped muscle. The general conclusion that at the moment of contraction a quickly reversible lactacidogen hydrolysis takes place in which the orthophosphoric acid greatly exceeds the lactic acid is confirmed. The quantity of lactacidogen preformed in muscle is much less than was thought previously.

J. H. BIRKINSHAW.

Creatine-phosphoric acid of muscle. A. PAL-LADIN, A. KUDRJAVZEVA, and E. SAVRON (Z. physiol. Chem., 1928, 179, 9–23).—Poisoning of rabbits with phosphorus and tetrahydro- β -naphthylamine produced in general an increase in the creatine, creatinephosphoric acid and percentage of creatine bound to phosphoric acid, and a diminution of the lactacidogen of red and white muscle. Although the changes in red and white muscle were mostly in the same direction, the quantitative effects were diverse in the two cases. J. H. BIRKINSHAW.

Influence of sympathetic innervation on the phosphate and creatinine contents of striated mammalian muscle. W. SCIMID (Biochem. Z., 1928, 201, 125—147).—The jaw muscles of white rats on the side from which the sympathetic influence had been removed showed a 10% decrease of organic phosphate compared with the muscle of the normal side, but the creatinine contents of the two sides were identical. P. W. CLUTTERBUCK.

Lactic acid and glycogen content of kidney cortex. J. T. IRVING (Biochem. J., 1928, 22, 1508— 1513).—The production of lactic acid in excised kidney cortex is rapid. The glycogen content under the same conditions, on the other hand, changes little. The origin of the bulk of the acid is unknown. It is probable that the glycogen figures obtained are contributed to a larger extent by substances other than glycogen. S. S. ZILVA.

"Acetone body" formation and the chemical affinity of oxygen for carbohydrate and fatty acid. D. M. ERVIN (J. Lab. Clin. Med., 1927, 12, 1059-1065).—An explanation is independent of the theory of dextrose oxidation.

CHEMICAL ABSTRACTS.

Decomposition of acetoacetic and β -hydroxybutyric acids in muscle. I. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1928, 201, 464–472).— When dog's extremities and calf's tongue are perfused with blood to which β -hydroxybutyric acid is added, this shows a decrease of 45—75% and 13—40%, respectively, but no oxidation to acetoacetic acid is observed. About 80% of added acetoacetic acid disappears; part of this, 18—20% in dog's extremities, 29—67.5% in calf's tongue, is recovered from the bone and muscle as β -hydroxybutyric acid.

J. H. BIRKINSHAW. Decomposition of acetoacetic acid and β -hydroxybutyric acid in the organs of the phloridzinised dog. I. SNAPPER, A. GRÜNBAUM, and C. MENDES DE LEON (Biochem. Z., 1928, 201, 473— 478).—The kidneys and the extremities of the phloridizin-diabetic dog are able to break down keto-bodies. This activity seems to be unaffected by phloridzin-acidosis, which therefore is characterised by an increased production and not by a diminished breakdown of keto-compounds. J. H. BIRKINSHAW.

Regulation of metabolism. X. Glycogen in adipose tissue and the possibility of conversion of fat into carbohydrate. E. WERTHEIMER (Pflüger's Archiv, 1928, 219, 190-201; Chem. Zentr., 1928, ii, 368).--With dogs, but not with rabbits or guinea-pigs, after hunger followed by feeding with carbohydrate, glycogen is present in the adipose tissue. With rats, after hunger followed by feeding with cooked rice, or white bread, milk, and dextrose, glycogen is present in the subcutaneous and abdominal fat. On administration during feeding of toxic doses of insulin the deposition of glycogen is small. The fat of frogs in October and November contains glycogen. With dogs deficient in carbohydrate by hunger and treatment with phloridzin, after cessation of acidosis, a conversion of fat into carbohydrate appears to take place in the liver.

A. A. ELDRIDGE.

Lactose metabolism of women. O. WATKINS (J. Biol. Chem., 1928, 80, 33-66).-Lactose was determined in urine by preliminary determination of total sugar by the method of Folin and Berglund (A., 1922, ii, 400), followed by a similar determination on a sample of the urine previously subjected to yeast fermentation. Normal men, and women in the intermenstrual period, tolerate 10 g. of lactose by mouth without excretion of the sugar in the urine. During menstruation the woman's tolerance for lactose may be raised to as much as 20 g.; during pregnancy the tolerance is also raised, whilst in lactation it is normal. In the later stages of pregnancy lactose is excreted in constant small amounts; this excretion rises immediately before delivery and then falls for a few days; at this point it rises again very markedly and then fluctuates until, at the end of a month, it becomes almost constant at a low level. C. R. HARINGTON.

Variations in some of the constituents of the blood throughout the menstrual cycle in normal women. H. G. CLOSE and A. A. OSMAN (Biochem. J., 1928, 22, 1544—1547).—In healthy adult females there is a slight decrease in the serum-hydrogen carbonate and corresponding slight increase in the serum-chloride during the menstrual flow. The serum-calcium and serum-urea show no significant change at this time. S. S. ZILVA.

Arginine metabolism. **K**. FELIX, II. H. MÜLLER, and K. DIRR (Z. physiol. Chem., 1928, 178, 192-201) .- Of several arginine compounds substituted in the α -amino-group, d- α -monobenzoylarginine was the only one resolved by arginase. Esterification hindered but did not prevent the action. The d- α -monobenzoylarginine was prepared by a Schotten-Baumann reaction; the mixture being maintained at about neutrality, it decomposes at 298° (uncorr.). The hydrochloride has $[\alpha]_D^{20} - 8 \cdot 1^\circ$. The optimum $p_{\rm H}$ for arginase action on the benzoyl derivative is 7. J. H. BIRKINSHAW.

Availability of ergothioneine in supplementing diets deficient in histidine. B. A. EAGLES and G. J. Cox (J. Biol. Chem., 1928, 80, 249-254).--Ergothioneine is unable to replace histidine in the diet of rats. C. R. HARINGTON.

Diet deficient in tyrosine. H. D. LIGHTBODY and M. B. KENYON (J. Biol. Chem., 1928, 80, 149-153).—Rats showed normal growth on diets containing as little as 0.0397% of tyrosine. C. R. HARINGTON.

Animal calorimetry. XXXVII. Specific dynamic action of glycine in normal and adrenalectomised dogs. F. NORD and H. J. DEUEL, jun. (J. Biol. Chem., 1928, 80, 115—124).—After both oral and intravenous administration, glycine exercises a specific dynamic action in adrenalectomised dogs which is only slightly less than that produced in normal animals. C. R. HARINGTON.

Nutritive properties of gelatin. R. W. JACK-SON, B. E. SOMMER, and W. C. ROSE (J. Biol. Chem., 1928, 80, 167-186).-Diets containing gelatin as the sole protein remain unsatisfactory for rats when supplemented with tyrosine, tryptophan, and cystine, or even with the 11 amino-acids in which gelatin is somewhat deficient. The results were not improved by preliminary hydrolysis of the protein, and are therefore not to be ascribed to failure of digestion. When gelatin forms as much as 35% of the diet it seems to produce an unfavourable effect per se, since nephritis was observed in many of the animals, and an inhibition of the growth of rats on a caseinogencarbohydrate diet was produced by substitution of this amount of gelatin for part of the carbohydrate.

C. R. HARINGTON.

Soya-bean meal in the human dietary. V. DUCCHESCHI (Arch. fisiol., 1928, 25, 428-468; Chem. Zentr., 1928, ii, 115) .- Experiments in vivo and in vitro indicate a high digestive value.

A. A. ELDRIDGE.

Nitrogen, calcium, and phosphorus metabolism in infants fed on soya-bean "milk." E. TSO, M. YEE, and T. CHEN (Chinese J. Physiol., 1928, 2, 409-414).-An infant fed for 4-5 day periods on a daily ration of soya bean "milk" (720 g.), sucrose (72 g.), and orange juice (4 g.) showed satisfactory nitrogen absorption and retention. The calcium and phosphorus absorption appeared to be inadequate. The addition of cod-liver oil (10-15 g.), calcium lactate (0.6 g.), and cabbage soup (100 g.) greatly increased the calcium and phosphorus F. C. HAPPOLD. retention in a second case.

Effect of variation of potassium and chlorine in a wheat ration. J. L. ST. JOHN (J. Agric. Res., 1928, 37, 55-64) .- Rations containing added potassium do not maintain partly grown rats. There is no evidence that potassium is capable of replacing sodium in the ration. The addition of chlorine did not affect this conclusion. The actual amounts of sodium and potassium present seem to be of more importance than the ratio of the two elements.

H. J. G. HINES.

Interpretation of nutritional experiments. C. NEWCOMB (Indian J. Med. Res., 1928, 16, 537-543).-The variability of the weights of rats under experimental conditions has been examined statistically and coefficients of weight variation have been obtained. Tables are given for finding the minimum significant differences between the mean weight of W. O. KERMACK. groups of rats.

Formation and fate of urea in the dog, and the relation between urea formation and the retention of amino-acid substances and ammonia in the liver. E. S. LONDON, N. KOTSCHNEV, A. CHOLOPOV, T. S. ABASCHIDZE, and A. K. ALEX-ANDRY (Pflüger's Archiv, 1928, 219, 238-245; Chem. Zentr., 1928, i, 2962-2963).-The continuous excretion of urea from the liver into the blood-stream takes place 2.5 times as rapidly during digestion as during starvation. Besides the kidneys, the intestinal The pancreas wall removes urea from the blood. produces smaller quantities of urea. Its formation in the liver cannot be ascribed simply to protein

derivatives. The production of urea is increased by alanine, cysteine, and ammonium carbonate, and arrested by arginine and tyrosine.

A. A. ELDRIDGE.

Kidney function. Relationships between action of carhamide, diuresis, and mineral metabolism. R. E. MARK (Arch. exp. Path. Pharm., 1928, 137, 143-167).—Whereas in normal animals, after administration of carbamide, the ratio of carbamide to potassium in the urine is fairly constant, in renal insufficiency (removal of one kidney and partial suppression of the blood supply of the other) an increased excretion of potassium sets in 1-2 hrs. after giving carbamide, decreasing to small values after 8-10 hrs. Carbamide fed to normal animals causes an immediate diuresis, but in animals with defective kidney function diuresis is much E. BOYLAND. delayed.

Excretion of choline in urine. P. KLEE and S. PETROPULIADES (Arch. exp. Path. Pharm., 1928, 137, 129-142).-Choline is estimated physiologically. After acetylation the acetylcholine is compared with standard solutions in its effect on the isolated frog heart. Normal men excrete 5-50 mg. of choline per day. The amount is increased by exercise, ingestion of lecithin, by subcutaneous or rectal administration of choline chloride, and by tissue-wasting diseases. E. BOYLAND.

Changes in the nuclear-plasmic ratio of vertebrate poikilotherms during hunger. A. DMO-CHOWSKI (Biochem. J., 1928, 22, 1548-1554).-In inanition the nuclear-plasmic ratio is practically constant for frogs (Rana esculenta). In the case of axolotls (Amblystoma) it rises by 15% after 5 months of hunger and falls to 15% below normal after 11 months of hunger. The ratio of trout after 80 days of hunger rises by 30% for fry and 49% for 2-year-olds. This rise in the nuclear-plasmic ratio is transient, values obtained for the final stages of hunger being subnormal. A short period of restitution does not reduce the nuclear-plasmic ratio of trout to its normal value, but it does so after a prolonged period of restitution. The results obtained with trout support the assumption of the existence of reserve S. S. ZILVA. protein.

Changes in the nuclear-plasmic ratio of mammals during hunger. A. DMOCHOWSKI (Biochem. J., 1928, 22, 1555-1561).-The purine-nitrogen content of rabbit skeletal muscle has an average value of 104.6 mg. per 100 g., varying from 85 to 119 mg. The mean value of the nuclear-plasmic ratio is 28.55×10^{-3} . The former and latter values remain constant throughout the duration of inanition. The purine-nitrogen content of rabbit liver varies from 149.5 mg. per 100 g. in fed animals to 162.1 mg. in inanition. The mean nuclear-plasmic ratio is respectively 50.9 and 48.4×10^{-3} before and after starvation. More than 50% of the purines of muscletissue can be extracted by water. Results similar to the above were obtained with muscle from which the extranuclear purine substances had been removed S. S. ZILVA. by extraction with water.

Hunger and the potassium and calcium ion content of blood-serum. B. A. SCHAZILLO and

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D. C. KONSTANTINOVSKAYA (Biochem. Z., 1928, 201, 318—322).—Hunger influences the ratio of potassium to calcium ions in the blood-serum of dogs. The potassium varies within normal physiological limits, but the calcium decreases when symptoms of irritability and paralysis appear. J. H. BIRKINSHAW.

Influence of active iron oxide ("siderac") on metabolism. A. A. GOLDBLOOM (Z. ges. exp. Med., 1928, 59, 514—530; Chem. Zentr., 1928, i, 2960).— The urinary C: N quotient was in general increased; the nitrogen balance became more positive.

A. A. ELDRIDGE. Action of lachrymal fluid on cholesterolæmia and glycæmia. D. MICHAIL and P. VANCEA (Compt. rend. Soc. Biol., 1928, 98, 64—65; Chem. Zentr., 1928, i, 3085).—Injection of lachrymal fluid into dogs causes a continuous, progressive, and longcontinued hypercholesterolæmia, as well as a hypoglycæmia. A. A. ELDRIDGE.

Aminoazotoluene, aminoazotolueneazo - β naphthol, and tolueneazoacetotoluidide as cicatrising agents. E. JUSTIN-MUELLER (J. Pharm. Chim., 1928, [viii], 8, 441—449).—The behaviour of these compounds in mineral oil suspension or solution when shaken with water and with ovalbumin or blood-albumin solutions has been examined. Emulsions of varying degrees of stability are formed, and from their appearance after filtering through paper and after keeping a method is developed for testing the cicatrising power. The results compare favourably with clinical experience. The action of the substances appears to be one of peptisation.

E. H. SHARPLES. Relationship between chemical constitution and pharmacological action of local anæsthetics. I. Novocaine, tutocaine, cocaine, and psicaine. K. TOMINAGA and I. HAYASHI (Nagoya J. Med. Sci., 1927, 2, 6—10).—Quantitative differences were observed in the anæsthetic action of six stereoisomerides of cocaine. The four drugs show no remarkable difference in physical properties; pharmacologically, cocaine and psicaine are very similar, whilst tutocaine is weaker. In toxicity, psicaine is intermediate between tutocaine and novocaine. CHEMICAL ABSTRACTS.

Rôle of calcium in narcosis and stimulation of decorticated and completely decerebrated animals. H. FISCHER (Arch. exp. Path. Pharm., 1928, 138, 169—189).—During sleep or narcosis in dogs intact or deprived of the cerebral cortex a decrease in the calcium content of the citrated plasma takes place, whilst stimulation of the brain results in an increase. In the case of completely decerebrated animals no alteration in the plasma-calcium occurs as the result of narcosis or stimulation. The potassium content of the blood-plasma varies in an opposite sense to the calcium content. W. O. KERMACK.

Fixation of suspensoids [in the body] by anæsthetics and narcotics. G. SPAGNOL (Arch. exp. Path. Pharm., 1928, 137, 250—256).—Colloidal suspensions of lead and mercury sulphides and many dyes can be fixed in tissues, in which they are not usually precipitated, by the application of anæsthetics, such as chloroform, or narcotics, such as the urethanes, to the skin. Only electro-negatively charged colloids are precipitated in this way. E. BOYLAND.

Action of colloidal sulphur (sulphosol) on the blood-sugar of experimental animals and of man. G. BUCCIARDI (Arch. Farm. sperim., 1928, 49, 90—96, 97—114).—In the guinea-pig, rabbit, dog, and sheep, small doses of colloidal sulphur produce slight hyperglycæmia, followed by slight hypoglycæmia. The dose necessary to induce these reactions varies slightly in animals of the same, and widely in animals of different, species, the order of diminishing sensitiveness being : sheep, dog, rabbit, guinea-pig. When administered orally to man, sulphosol is uncertain in its effect and may cause slight increases or decreases in the amount of the bloodsugar; hyperglycæmia followed by hypoglycæmia was not observed in man. T. H. Pore.

Effect of alcohol and of anæsthetics on sugar utilisation. W. E. BURGE and D. J. VERDA (J. Pharm. Exp. Ther., 1928, 34, 299—303).—Alcohols were introduced into sugar solutions in which gold fish had been placed and sugar determinations were carried out at intervals on portions of the solutions. Methyl and ethyl alcohol markedly increased the rate of sugar utilisation, whilst chloroform and ether produced a significant decrease. B. A. EAGLES.

Action of alcohol on blood-sugar. J. GAVRILA and T. SPARCHEZ (Compt. rend. Soc. Biol., 1928, 98, 65-66; Chem. Zentr., 1928, i, 3085).—Alcohol slightly reduces the blood-sugar of normal man; the reduction in diabetes is thrice as great.

A. A. ELDRIDGE.

Influence of ethyl alcohol on the excretion of purine substances. L. LA GRUTTA (Riv. Patol. Sperim., 1927, 2, No. 3, 185—196; Chem. Zentr., 1928, ii, 71).—Large doses of ethyl alcohol cause an increase in the destruction of proteins and nucleins, and hence an increase in the amount of their decomposition products in the urine. Moderate and small doses reduce the excretion of total and purine nitrogen and of phosphorus. Immediately after the ingestion of moderate or large doses of alcohol a temporary disturbance of the ratio urea-nitrogen/purinenitrogen is observed. A. A. ELDRIDGE.

Blood-sugar after peptone injection in the dog. W. W. BRANDES and J. P. SIMONDS (Amer. J. Physiol., 1928, 86, 618-622).—At the height of peptone shock the sugar content of the blood from the hepatic vein is increased, but there is a hypoglycæmia in the peripheral venous blood. There is an increased glycogenolysis in the liver, but so little blood leaves the liver that a hypoglycæmia of the general circulation results. B. A. EAGLES,

Hypoglycæmic action of *Phaseolus* preparations. O. GESSNER and K. SIEBERT (Münch. med. Woch., 1928, 75, 853-855; Chem. Zentr., 1928, ii, 169).—The preparations caused a fall in blood-sugar on peroral administration; dextrose- or adrenalinehyperglycæmia was reduced and abbreviated.

A. A. ELDRIDGE.

Physiological effects of two poisons of the adrenaline series : β -hydroxy- β -(4-hydroxy-

phenyl)-N-methylethylamine, and the corresponding ketone. O. EHRISMANN and G. MALOFF (Arch. exp. Path. Pharm., 1928, 136, 172-184).-The former of these two compounds is very similar in its physiological effects to adrenaline. The effects of the ketone depend to some extent on the dosage; some of them are similar to those of adrenaline, others quite the opposite. Both substances are much less powerful than adrenaline. W. MCCARTNEY.

Mechanism of the action of ephedrine and the difference between the activities of its isomerides. O. SCHAUMANN (Arch. exp. Path. Pharm., 1928, 138, 208-218).-Ephedrine acts on the blood-pressure by rendering the vessels more sensitive to adrenaline. *l*-Ephedrine is very much more active W. O. KERMACK. than *d*-ephedrine.

Assays of Chinese ephedrine. C. T. FENG and B. E. READ (Chinese J. Physiol., 1928, 2, 337-344).-The separated male and female flowers of Ephedra equisetina and E. sinica have been analysed for ephedrine and ψ -ephedrine. The seasonal variation in content has been studied. In the flowering season there is a higher alkaloidal content in the male plants than in the female (13-17% difference), but after the fruiting season the two contents are practically identical. The root, berries, and seeds of E. equisetina contain no alkaloid, the nodes contain 32% of the alkaloidal content of the internodes and a greater proportion of *u*-ephedrine. Samples collected in winter gave only 53% of the ephedrine content of mature samples collected in October.

F. C. HAPPOLD.

Comparative study of ephedrine, racemic ephedrine, and ψ -ephedrine. C. PAK and B. E. READ (Chinese J. Physiol., 1928, 2, 435-458).-The approximate ratios of the pressor actions of the three isomerides, in doses of 0.5-1.0 mg. per kg. body-weight, are ephedrine : ephetonine : 4-ephedrine as 1:0.7:0.5. A diminished efficiency in the pressor action of the three isomerides was observed with repeated injection, but differences in the maximal rise of blood-pressure, following such repeated injections, were not so great where the dogs were vagotomised and atropinised. Continued perfusion of the peripheral blood vessels of the toad with 0.2% ephedrine-Ringer solution caused an initial vasoconstriction, but vasodilation occurs after prolonged perfusion. The isomerides exerted a mutually immunising effect on the pressor action and lowered one another's activity; e.g., the action of ψ -ephedrine was abolished by previous injection of ephedrine. This immunising effect was more strongly marked in the case of ephedrine after previous injection of ψ -ephedrine or vice versa, than in the case of ephetonine after previous F. C. HAPPOLD. injection of ephedrine.

Ephedrine and blood-sugar. I. I. NITZESCU (Compt. rend. Soc. Biol., 1928, 98, 55-57; Chem. Zentr., 1928, i, 3085) .- Injection of ephedrine into dogs (not starving) causes slight hyperglycæmia, the duration of which is somewhat extended by simultaneous injection of dextrose. A. A. ELDRIDGE.

Action of ergotamine and adrenaline on the residual nitrogen content of fluid perfusing

isolated organs. G. A. MEDNIKIANZ (Arch. exp. Path. Pharm., 1928, 136, 370-380).-When isolated testicles of cats and rabbits are perfused by Ringer-Locke's solution a gradual decline in the residual nitrogen content occurs. The addition of adrenaline (dilution 1 in 10⁶) to the perfusing solution produces a marked increase in the amount of nitrogen. Ergotamine (dilution 1 in 105) produces a fall and the previous action of ergotamine destroys the effect of H. R. ING. adrenaline.

Influence of ergotamine on the blood-sugar. Z. CZEZOWSKA and J. GOERTZ (Compt. rend. Soc. Biol., 1928, 98, 148-150; Chem. Zentr., 1928, i, 3085).-In normal and diabetic man ergotamine considerably reduces alimentary hyperglycamia.

A. A. ELDRIDGE.

Effect of substances of the quinine group on the enzymic functions of the organism. X. Influence of quinine on the dynamics of protein exchange and on oxido-reduction processes. I. A. SMORODINCEV (Biochem. Z., 1928, 201, 66-73) .- Quinine restricts the breakdown of protein and the oxidation processes of the organism. P. W. CLUTTERBUCK.

Influence of arsenic and antimony compounds on enzymic functions of the organism. V. Cause of inhibitory influence of arsenites and arsenates on salivary amylase. I. A. SMORODIN-CEV and E. A. ILJIN (Biochem. Z., 1928, 201, 34– 47).—In well-buffered solutions of $p_{\rm H}$ 6.8 sodium arsenate has no effect on the action of salivary amylase, the previously observed inhibition being due to change of $p_{\rm H}$, but with arsenites, in addition to change of $p_{\rm H}$, the arsenic itself appears to take part in the inhibition (cf. A., 1927, 792). P. W. CLUTTERBUCK.

Action of cyanide on the living cell. M. S. RESNITSCHENKO (Biochem. Z., 1928, 201, 110-124).-With very small concentrations of cyanide in the first stages of poisoning respiration of eggs of Ascaris megalocephala is increased due to the alkaline nature of the cyanide, the specific respiratory inhibition, due to the cyanide group itself, being P. W. CLUTTERBUCK. obtained later.

Effect of magnesium sulphate or lactose on blood volume in normal, beri-beri, and fasting pigeons. O. W. BARLOW and M. S. BISKIND (Amer. J. Physiol., 1928, 86, 594-598).-There is a diminution of the red cell count as well as total blood-volume in fasting or beri-beri pigeons. The anti-anæmic effect of magnesium sulphate or lactose during the course of the inanition is not due to concentration of the blood but to interference with the destruction B. A. EAGLES. of blood.

Pharmacology of lead. III. Distribution of lead between blood and tissue after intravenous injection. B. BEHRENS and G. ANTON (Arch. exp. Path. Pharm., 1928, 137, 305-310).-Lead chloride injected into a jugular vein of a guinea-pig rapidly disappears from the blood until an equilibrium is attained in which most of the lead chloride is taken W. O. KERMACK. up by the tissues.

Pharmacology of lead. IV. Mechanism of lead poisoning of fishes. B. BEHRENS (Arch. exp.

Path. Pharm., 1928, 137, 311—314).—Fish poisoned by lead salts dissolved in the water in which they are immersed show the greatest concentration of lead in the gills, but small quantities are also found in the other organs and in the musculature. The toxic action of the lead appears to be exerted mainly if not entirely through its presence in the gills.

W. O. KERMACK.

Diuretic action of organic mercury compounds. B. VON ISSEKUTZ and F. VON VÉGH (Arch. exp. Path. Pharm., 1928, 138, 245-255).--The toxicities and diuretic activities of certain organic mercury compounds have been determined on rats. Diuretic action associated with low toxicity occurs with certain derivatives of camphoric acid.

W. O. KERMACK.

Histochemical detection of mercury in organs. E. CHRISTELLER and R. SAMMARTINO (Z. ges. exp. Med., 1928, 60, 11—33; Chem. Zentr., 1928, i, 2975). —Mercury is deposited chiefly in the kidneys, liver, and lungs. Small quantities are found in the large intestine, spleen, pancreas, heart, and central nervous system. The distribution of mercury shortly after injection is described, and details are given of a modification of Almkvist's method for its detection. A. A. ELDRIDGE.

Toxicity of thallium sulphate. J. C. MUNCH (J. Amer. Pharm. Assoc., 1928, 17, 1086—1093).— Thallium is a certain, but not a rapid, poison for rats and it is cumulative in action. The minimum lethal dose when fed to rats or intravenously injected into rabbits is 25 mg. of thallium per kg. body-weight. Previous work on the toxicity of thallium is discussed. E. H. SHARPLES.

Formation from histidine by ultra-violet irradiation of a substance which lowers bloodpressure and stimulates the intestine. F. ELLINGER (Arch. exp. Path. Pharm., 1928, 136, 129-157).—Histidine hydrochloride in 1% solution when irradiated with a quartz mercury-vapour lamp yields small amounts of a decomposition product, which is isolated by the method used for extracting histamine. Within certain limits the formation of this product is unaffected by the $p_{\rm H}$ of its solutions or by the duration of the irradiation, and photocatalysts do not accelerate the process of its formation. Light of wave-lengths 297 and 302 µµ causes irradiated solutions to lose their activity. Unirradiated serum from rabbits, horses, or pigs and also unirradiated skin from guinea-pigs contain considerable amounts of histamine-like substances. Extracts of unirradiated guinea-pig skin are never more active than those from the irradiated skin. W. MCCARTNEY.

Alterations in the blood determined by X-ray therapy. C. STARNOTTI (Arch. Farm. sperim., 1928, 46, 49—89).—The alterations in the blood produced by X-ray therapy are slight, particularly in relation to those of the secondary irradiation to which X-ray operators are subject, and consist in mild leucocytosis; with excessive treatment, however, the opposite effect may result. The hæmoglobin and red corpuscles remain uninfluenced and the physico-chemical properties are unchanged. The results obtained with 20 patients show that these effects appear immediately after the application of the rays, but the period after which the maximum effect is reached, and also the duration of the effect, vary in different cases.

T. H. POPE. Viscosity changes produced in egg-albumin by X-rays. J. A. V. FAIRBROTHER (Brit. J. Radiol., 1928, [ii], 1, 121-125).—The viscosity of egg-albumin suffers a permanent decrease (up to 40%) by a dose of 211,500 e of Mo-K radiation. At the coagulation

temperature, 61°, setting is delayed. CHEMICAL ABSTRACTS.

How many respiratory enzymes are there? O. WARBURG (Biochem. Z., 1928, 201, 486–488).— For oxygen transport nature employs hæmoglobin, but all hæmoglobins are not identical and other means of transport, e.g., hæmocyanin, exist. As for the transport of oxygen, so for respiration, nature makes use for the greater part of one mechanism only. Other enzymes of respiration do exist, however.

J. H. BIRKINSHAW.

Reduction of the disulphide group by enzyme systems. K. A. C. ELLIOTT (Biochem. J., 1928, 22, 1410—1412).—Neither dithiodiglycollic acid nor glutathione is reduced by succinoxidase and succinic acid. Neither leucomethylene-blue nor hypoxanthine with xanthine-oxidase reduces the S·S-group even in the presence of muscle residue. S. S. ZILVA.

Preparation of succinodehydrogenase free from fumarase. N. ALWALL (Skand. Arch. Physiol., 1928, 54, 1-5; Chem. Abstr., 1928, ii, 60).—The fumarase present in succinodehydrogenase prepared from muscle is decomposed by heating the mixture at 50° for 30 min. The activity of the succinodehydrogenase is thereby only weakened.

A. A. ELDRIDGE.

Enzymic oxidation of oxalic acid by seeds. Constitution of oxalic acid. T. THUNBERG (Skand, Arch. Physiol., 1928, 54, 6—16; Chem. Zentr., 1928, ii, 31—33).—By the use of powder and extracts of seeds of *Malva crispa*, *Citrus aurantium* var. *dulcis*, and *Prunus communis* the action of oxalate in increasing the ability to decolorise methylene-blue in a vacuum was demonstrated. The behaviour of potassium oxalate as a hydrogen donator, forming potassium hydrogen carbonate, is discussed. A. A. ELDRIDGE.

Function of peroxidase systems and the chemistry of the adrenal cortex. New carbohydrate derivatives. A. SZENT-GYÖRGYI (Biochem. J., 1928, 22, 1387-1409).-The isolation of a highly reactive hexuronic anhydride, isomeric with glycuronic anhydride, m. p. 175–189°, $[\alpha]_D^{\infty}$ +24°, from the adrenal cortex, from oranges, and from cabbages is described. The method is based on the precipitation of the substance with lead acetate and on the purification by reprecipitation with this reagent and with light petroleum from methyl alcohol-ether solution. The hexuronic acid is of biological significance. In its distribution in nature it is closely connected with peroxidase. Its oxidation by hydrogen peroxide in the plant, which is reversible, is catalysed by peroxidase and unless a sufficiency of peroxide is added the peroxidase reaction may be masked by its presence. Molecular oxygen oxidises the acid irreversibly with the formation of a new carboxyl group. This autoxidation is catalysed by copper but not by iron and manganese. Cyanide inhibits the oxidation. Mild oxidising agents effect a reversible oxidation with loss of two atoms of hydrogen. The oxidation of the hexuronic acid by peroxide and peroxidase is catalysed in plant juices by phenols. In the absence of these substances it is not oxidised by indophenoloxidase of animal tissue. Pigment formation in vitro can be inhibited by concentrations of 1:0.00025 of the acid. It reduces hæmatin compounds slowly. Oxidised hexuronic acid is reduced by animal tissues. The dehydrogenases of the type of the Schardinger enzyme and the succinodehydrase are unable to reduce the oxidised hexuronic acid. The oxidised substance is reduced by the glutathione system. Glutathione and fixed thiol groups strongly reduce the oxidised acid. The author suggests the following scheme of oxidation in the plant : H_2O_2 + peroxidase \rightarrow phenol \rightarrow hexuronic acid \rightarrow other oxidation systems.

S. S. ZILVA.

Enzymic condensation of formaldehyde to sugar. II. J. BODNAR (Biochem. Z., 1928, 201, 281-285).—Both the pulped and the dried leaves of *Tropæolum* are able to convert formaldehyde but not acetaldehyde into sugar. Boiling destroys this power. J. H. BIRKINSHAW.

Lipases. I. Organ-lipases and the inhibition of lipase action by poisons. K. GYOTOKU (Proc. Imp. Acad. Tokyo, 1928, 4, 503—504).—Serum- and liver-lipases are more sensitive to atoxyl than are other lipases. An atoxyl-sensitive lipase on purification becomes atoxyl-refractory. Sodium fluoride has a poisonous action on lipases. A poisoned lipase cannot be regenerated by dialysis. B. A. EAGLES.

Lipases. II. Determination of lipase in duodenal contents. III. Lipases and proteins. IV. Separation of lipase into two fractions. K. GVOTOKU and S. TERASHIMA (Proc. Imp. Acad. Tokyo, 1928, 4, 505, 506—507, 508—509).—II. 'The duodenal contents are appropriately diluted with a solution of equal parts of glycerol and 1% ammonium phosphate. The resultant lipase solution is very stable. The tributyrin method of Rona and Michaelis is used.

III. The lipases of blood-serum, pancreatic and gastric juices are always found with the proteins precipitated by 60% saturation with ammonium sulphate.

IV. The addition of quinine to gastric or pancreatic lipases yields two fractions, each of which alone is inactive, but a mixture of the two constituents has a strong lipolytic action. B. A. EAGLES.

Ricinus lipase. I. (A) Hydrolysis of esters and of beeswax. (B) Hydrolysis of carbohydrates. A. PIUTTI and E. DE' CONNO (Annali Chim. appl., 1928, 18, 468—478).—An industrial preparation hydrolyses, not only glycerides, but also, almost quantitatively, other esters, and to some extent sucrose and starch. T. H. POPE.

Biochemical synthesis and hydrolysis of glycerides. L. VELLUZ (Bull. Soc. Chim. biol., 1928, 10, 1213-1226).—The formation of di- and tri-glycerides by the combination of the fatty acids of olive oil and glycerol in the presence of the enzyme in the cytoplasm of the castor bean (A., 1928, 328) follows the law of mass action. The enzymic hydrolysis of these esters is shown to be a reaction similar to those due to heterogeneous catalysis.

G. A. C. GOUGH.

Influence of double linkings in the biochemical synthesis and hydrolysis of unsaturated glycerides. L. VELLUZ (Bull. Soc. Chim. biol., 1928, 10, 1227—1237).—Reactions analogous to those described in the preceding abstract in which unsaturated acids are substituted for those from olive oil show similar kinetics. The velocities of both synthesis and hydrolysis are inversely proportional to the iodine values of the acids. G. A. C. GOUGH.

Range of action of the phosphatases. C. NEU-BERG and K. P. JACOBSOHN (Biochem. Z., 1928, 199, 498-517).-Derivatives of all the three known forms of phosphoric acid undergo enzymic hydrolysis, the end-product being orthophosphoric acid. To the number of phosphates so far tested with regard to the effect of phosphatases, monomethyl phosphate, trimethyl phosphate, methylpropylcarbinyl phosphate, monocetyl phosphate, monocholesteryl phosphate, di-otolyl pyrophosphate, di-m-tolyl pyrophosphate, and di- α -naphthyl pyrophosphate are now to be added. With the exception of trimethyl phosphate all these substances are hydrolysed both by takaphosphatase and by animal phosphatases. The extent of the hydrolysis was, in almost all cases, very considerable (up to 90%). The stereochemical specificity of the phosphatases has again been confirmed in the case of the monophosphoric ester of methylpropylcarbinol. Monocholesteryl orthophosphate, m. p. 187° (uncorr.), is prepared from cholesterol and phosphorus pentoxide. It is purified by crystallisation from chloroform or by precipitation from that solvent with acetone. It is insoluble in water (cf. Euler and Bernton, A., 1927, 1066). The tolyl and α -naphthyl pyrophosphates were prepared by the action of phosphorus oxychloride on the phenols in a manner similar to that described for diphenyl pyrophosphate (cf. Neuberg and Wagner, Biochem. Z., 1926, 171, 485). The dipotassium salt of di-o-tolyl pyrophosphate crystallises in needles. It is very hygroscopic, readily soluble in water, slightly soluble in alcohol, and insoluble in ether, acetone, or chloroform. The potassium salt of di-m-tolyl pyrophosphate, prepared in the same way, has very similar properties. Di-anaphthyl pyrophosphate is precipitated in the form of rectangular plates, m. p. 78°, when strong acids are added to solutions of its dipotassium salt, which has properties resembling those of the salts of the tolyl pyrophosphates and crystallises in rhombohedra. The ester is soluble in ether and in benzene.

W. MCCARTNEY.

Phosphatases of mammalian tissues. II. Pyrophosphatase. H. D. KAY (Biochem. J., 1928, 22, 1446—1448).—Pyrophosphatase is widely distributed in mammalian tissue, the distribution being similar to that of the orthophosphoric esterase. The zone of optimal activity is between $p_{\rm H}$ 7.2 and 7.8 as against $p_{\rm H}$ 8.8—9.3 for esterase. S. S. ZILVA. Metaphosphatase. T. KITASATO (Biochem. Z., 1928, 201, 206—211).—The author's yield (20%) of orthophosphate (cf. A., 1928, 1282) obtained by the action of takaphosphatase on sodium hexametaphosphate is raised almost to 100% by increasing the enzyme concentration and decreasing the amount of substrate. The conversion is followed colorimetrically and the orthophosphate isolated as the ammonium magnesium salt. P. W. CLUTTERBUCK.

Isoelectric precipitation of pepsin. II. F. FENGER, R. H. ANDREW, and A. W. RALSTON (J. Biol. Chem., 1928, 80, 187–190; cf. A., 1927, 793).— The previous conclusion is confirmed that the most active preparations of pepsin are obtained by isoelectric precipitation at $p_{\rm H} 2.5$; in this way an ashfree product has been prepared containing C 53·15%, H 7·20%, N 14·43%, S 0·88%, P 0·13%; figures are given for the nitrogen distribution.

C. R. HARINGTON.

Stereochemical specificity of proteolytic E. WALDSCHMIDT-LEITZ enzymes. and H. SCHLATTER (Naturwiss., 1928, 16, 1026).-Trypsin-kinase, which splits off tyrosine, hydrolyses both optical antipodes of *dl*-leucylglycyl-*l*-tyrosine and of dl-bromoisohexoylglycyl-l-tyrosine; hydrolysis by erepsin, which attacks the free amino-group, takes an asymmetric course. This opens up the possibility of determining where the reaction of the peptide with the specific group of the enzyme molecule occurs by changing the arrangement of the racemic component of the molecule. J. H. BIRKINSHAW.

Effect of the hydrogen-ion concentration on the rate of hydrolysis of glycylglycine, glycylleucine, glycylalanine, glycylasparagine, glycylaspartic acid, and biuret base by erepsin. J. H. NORTHROP and H. S. SIMMS (J. Gen. Physiol., 1928, 12, 313—328).—The rates of hydrolysis by erepsin of the above dipeptides have been determined at various hydrogen-ion concentrations and it has been found that the dissociation constants of the substrate exercise a preponderating effect. In order, however, to obtain a complete formulation of these results it must be assumed that erepsin behaves like an acid or base with a dissociation constant of 10-76. This conclusion is confirmed by measurements of the rate of destruction of erepsin by heat. W. O. KERMACK.

Proteinase and polypeptidase of yeast. W. GRASSMANN and H. DYCKERHOFF (Z. physiol. Chem., 1928, 179, 41-78).-Conditions are described for preparing the polypeptidase and proteinase of yeast by autolysis in presence of chloroform. The almost pure proteinase passes into solution chiefly between the fifteenth and the twenty-fourth hour at $p_{\rm H} 4.8-5.0$. It can be purified by adsorption on alumina. The succeeding autolysate contains polypeptidase free from proteolytic action. Yeast polypeptidase is completely inactive towards all proteins, whether of animal or vegetable origin. Hydrocyanic acid and hydrogen sulphide, although inhibitors of poly- and di-peptidase, can activate yeast proteinase. The fresh proteinase preparation is inactive until hydrocyanic acid is added. After several days at neutral reaction the preparation becomes active without hydrocyanic acid. On keeping at p_{μ} 5, the natural

activator is destroyed and the preparation is again inactive without hydrocyanic acid.

The optimum $p_{\rm H}$ for gelatin hydrolysis by yeast proteinase is 5-0, for fibrin and edestin 7-0, for peptone hydrolysis by polypeptidase, 7-0. Yeast proteinase in its specific action on gelatin can be completely replaced by papain-hydrocyanic acid but not by papain alone or by pepsin. J. H. BIRKINSHAW.

Coproporphyrin synthesis by dried yeast. H. FINK and K. WEBER (Woch. Brau., 1928, 45, 478– 480).—By the addition of dried yeast to highly buffered solutions of sucrose containing carbamide and mineral salts, the optimum reaction for coproporphyrin formation is found to be $p_{\rm H}$ 4–4.5. The authors express doubt as to whether this is formed by the dried yeast or during development of the living cells contained in the preparation. F. E. DAY.

Enzymic character of coproporphyrin synthesis in yeast. Cell-free increase of coproporphyrin. R. M. MAYER (Z. physiol. Chem., 1928, 179, 99—116).—The production of coproporphyrin by autolysis of yeast is inhibited by 10% hydrocyanic acid. When the inhibitor is removed after 15 min. by a current of air, coproporphyrin is again formed; after a longer period the result is negative, as the hydrocyanic acid can no longer be completely removed. Chloroform and toluene also have an inhibitory action. Coproporphyrin is formed by cell-free yeast juice; the formation is inhibited by hydrocyanic acid but not by chloroform or toluene. Coproporphyrin is thus a true product of enzyme action. Tap-water produces a rapid disappearance of the coproporphyrin fluorescence of yeast-cells. This is due to calcium or magnesium hydrogen carbonate in solution. J. H. BIRKINSHAW.

So-called co-enzyme of alcoholic fermentation. A. J. KLUYVER and A. P. STRUYK (Biochem. Z., 1928, 201, 212-258) .- Addition of phosphate to ultrafiltered moderately washed zymase is not, but of ultra-filtrate is, able always to bring about fermentation. Addition of acetaldehyde and phosphate to washed zymase is able to bring about fermentation only when sufficient hexosephosphate is retained. By prolonged washing, a filtrate residue is obtained which cannot be reactivated by hexosephosphate, but can by boiled yeast extract. Meyerhoff's coenzyme is formed by heating a co-enzyme-free zymase solution in presence of phosphate at 100° for a short time and its role is that of inhibiting the endotryptasezymase system, *i.e.*, it is probably identical with Buchner's antiprotease. For cell-free fermentation to take place the following are necessary: zymase and phosphatase, a hydrogen acceptor, hexosephosphate, and antiprotease. P. W. CLUTTERBUCK.

Purification of co-zymase from muscle. H. von Euler and S. GARD (Svensk Kem. Tidskr., 1928, 40, 99—100; Chem. Zentr., 1928, ii, 60).—The co-zymase in muscle juice was concentrated by lead and mercury precipitation, but appeared to lack an activator of lactic acid formation such as is present in yeast juice. A. A. ELDRIDGE.

Formation of hexosephosphates; non-fermentable sugars. M. SCHOEN and E. ELION (Compt. rend. Soc. Biol., 1928, **98**, 4-7; Chem. Zentr., 1928, i, 2951).—Zymin does not ferment galactose or arabinose; neither sugar affords hexosephosphate. The supposed connexion between fermentation and ester-formation is thus supported.

A. A. ELDRIDGE.

Inactivation of invertase and raffinase by heat. J. M. NELSON and P. PAPADAKIS (J. Biol. Chem., 1928, 80, 163—166).—Autolysed yeast, when heated at 60° for 1 hr., lost 58% of its power to hydrolyse sucrose and 75% of its power to hydrolyse raffinose; this renders the identity of invertase and raffinase doubtful (cf. Willstätter and Kuhn, A., 1923, i, 401; Josephson, A., 1924, i, 919). C. R. HARINGTON.

Aërobic and anaërobic metabolism of cultivated yeasts. F. WINDISCH (Z. physiol. Chem., 1928, 179, 88—98).—Yeast grown under anaërobic conditions presents a healthier appearance and has a much higher fermenting power than yeast grown under ordinary conditions with access of air.

J. H. BIRKINSHAW.

Decomposition of cellulose by aërobic bacteria. R. J. DUBOS (J. Bact., 1928, 15, 223-234).—By using strips of filter paper partly immersed in a solution containing sodium nitrate 0.5, dipotassium hydrogen phosphate 1.0, magnesium sulphate heptahydrate 0.5, potassium chloride 0.5, ferrous sulphate heptahydrate 0.01, water 1000 g., kept at 28°, pure cultures of cellulose-decomposing bacteria have been obtained as follows: (a) strict aërobes, unable to utilise any carbon compounds examined except cellulose, (b) strict aërobes which decompose cellulose and grow well on starch agar, but not on nutrient agar, (c) facultative anaërobes, which decompose cellulose, and grow well in ordinary media.

CHEMICAL ABSTRACTS.

Fermentation of maltose by Bacterium pullorum. P. R. EDWARDS (J. Bact., 1928, 15, 235-243).—B. pullorum does not attack dulcitol or d-maltose, but may produce acid from the products of alkaline hydrolysis of maltose.

CHEMICAL ABSTRACTS.

Carbohydrate metabolism of *P. aëruginosa* (*B. pyocyaneus*). H. J. SEARS and M. F. GOURLEY (J. Bact., 1928, 15, 357-366).—Production of acid in presence of a small quantity of dextrose was observed when the nitrogen content of the medium was low. The organism can utilise various sugars.

CHEMICAL ABSTRACTS.

Bacterial metabolism. Influence of phosphate buffer in carbohydrate-free and in dextrose-containing media. C. F. SLANETZ and L. F. RETTGER (J. Bact., 1928, 15, 297—317).—Comparative determinations of total protein-, non-protein-, ammonia-, amino-, and polypeptide-nitrogen, and of biuret were made. CHEMICAL ABSTRACTS.

Bacterial destruction of acetylmethylcarbinol. O. B. WILLIAMS and M. B. MORROW (J. Bact., 1928, 17, 43-48).—Acetylmethylcarbinol is destroyed by Aerobacter aërogenes, the green fluorescent bacterium, and by aërobic spore-formers. It probably serves as a source of carbon. CHEMICAL ABSTRACTS.

Stability of carbohydrate media. L. D. HENRY and M. S. MARSHALL (J. Lab. Clin. Med., 1927, 12,

474-477).—Unheated (20%) filtered solutions of dextrose, lactose, maltose, sucrose, mannitol, and lævulose stored at 5° retain their specific properties with regard to fermentation for at least 20 months; xylose for at least 12 months. Storage after admixture with culture medium soon renders fermentation reactions non-specific. CHEMICAL ABSTRACTS.

Bacterial oxidations by molecular oxygen. I. Aërobic oxidation of dextrose and its fermentation products in relation to the viability of the organism. R. P. COOK and M. STEPHENSON (Biochem. J., 1928, 22, 1368-1386).-B. coli is capable of oxidising dextrose and its products of fermentation such as lactate, pyruvate, acetate, and formate, by means of molecular oxygen. Ethyl alcohol and acetaldehyde are not oxidised. These compounds do not, however, act as inhibitors in concentrations of 0.01M to the oxidation of other substances. The oxidation of formate proceeds to completion, that of dextrose and lactate to two thirds, and that of acetate to three fourths of completion. When the proportion of the living cells, which varies originally from one third to one tenth of the total number of organisms, is reduced by exposure to ultra-violet light to 0.27% and 0.021% of their original number, the rate of oxidation is only slightly affected. B. alkaligenes oxidises the above substrates except dextrose. B. sporogenes, on the other hand, does not oxidise any S. S. ZILVA. of these substrates.

Production of gelatinase by B. proteus. A. T. MERRILL and W. M. CLARK (J. Bact., 1928, 15, 267— 296).—Synthetic media were employed. In the absence of both calcium and magnesium, no gelatinase was found; in presence of calcium alone the amount was small, and in that of magnesium alone only moderate. Gelatinase was produced anaërobically when dextrose or small quantities of nitrate were added to a synthetic lactate medium.

CHEMICAL ABSTRACTS.

Purification of diphtheria toxin. G. ABT (Ann. Inst. Pasteur, 1928, 42, 1336—1365).—Diphtheria toxin is adsorbed by precipitated di- or tri-calcium phosphate. The precipitate is dissolved by the addition of sodium citrate and citric acid. The calcium is removed and the liquid dialysed against distilled water. Expressed in terms of toxic units per milligram of protein the crude toxin contained only 0.55 unit, whereas the purified toxin contained 22.35 units. B. A. EAGLES.

Heart hormone. IX. Experiments with a heart extract from warm-blooded animals. L. HABERLANDT (Pflüger's Archiv, 1928, 219, 279— 285; Chem. Zentr., 1928, ii, 64).—Experiments with an extract of ox heart are described.

A. A. ELDRIDGE.

Influence of hormones on cell chemistry. J. WOHLGEMUTH [with KLOPSTOCK and HAYASHI] (Deut. med. Woch., 1928, 54, 816—817; Chem. Zentr., 1928, ii, 63).—" Thyreoglandol," "ovoglandol," "testiglandol," and adrenaline cause an increase in the respiration of the skin of the guinea-pig; insulin and hypophysin decrease it. No influence on anaërobic glycolysis was observed. Insulin, thyroxine, folliculin, adrenaline, and "thyreoglandol" stimulate the production of lactic acid from lævulose by the human placenta. A. A. ELDRIDGE.

Hyphophysin and gluconeogenesis. I. I. NTTZESCU and M. BENETATO (Compt. rend. Soc. Biol., 1928, 98, 58-60; Chem. Zentr., 1928, i, 2953).—In starving rabbits an extract of the posterior lobe of the pituitary causes gluconeogenesis in the liver, storage of glycogen up to 2% taking place. Similar results were obtained with adrenaline and insulin. Muscular glycogen is mobilised by pituitary extracts. A. A. ELDRIDGE.

Extraction of the hormone of the corpora lutea. P. GLEY (Compt. rend. Soc. Biol., 1928, 98, 656-657; Chem. Zentr., 1928, i, 2953).--"Luteocrinin" is obtained from pig's corpora lutea by soaking the minced material in dilute tartaric acid solution, toxic substances being precipitated with lead acetate; the hormone is precipitated with copper hydroxide, the precipitate redissolved in acid, the copper removed with hydrogen sulphide, and the solution neutralised. A. A. ELDRIDGE.

Testing of commercial ovarian preparations. KOCHMANN (Arch. exp. Path. Pharm., 1928, 137, 187—200).—Tests were made by noting the effect on the growth of the uterus and the production of cestrus, but mainly by observing the effect on metabolism. Several preparations for injection increased metabolism to varying degrees, although some were inactive. Some dry preparations administered by mouth were not tolerated very well and caused reduction in body-weight and in metabolism.

E. BOYLAND. Testing ovarian preparations. P. TRENDELEN-BURG and H. GREMELS (Arch. exp. Path. Pharm., 1928, 137, 201-202).—Tests of the preparations for injection, made by examination of the effect on the œstrous cycle, gave results in agreement with those of Kochmann (preceding abstract). E. BOYLAND.

Estrus-producing hormone : its preparation and standardisation in a water-soluble form. H. ALLAN, F. DICKENS, E. C. DODDS, and F. O. HowITT (Biochem. J., 1928, 22, 1526-1543).-The method consists of the saponification of the minced placenta with barium hydroxide and a series of purifications by repeated extraction with butyl alcohol and with ether and by saponification. The active material passes through a porcelain filter and dialyses through parchment. It is stable to prolonged incubation and to short exposures to high temperatures. The preparation is inactive in a single dose, but produces œstrus when given in a series of small injections. A method for the standardisation of the product based on a combination of the multiple dose technique with the statistical method (cf. Coward and Burn, J. Physiol., 1927, 63, 270) is described. By this method the weight of one unit is calculated to be 0.01 mg. The preparation is without effect on blood-pressure or respiration and no ill effects follow when it is injected daily for some months into patients. S. S. ZILVA.

Heart-lung-adrenal preparation. S. V. ANIT-SCHKOW and A. I. KUSNETZOW (Arch. exp. Path. Pharm., 1928, 137, 168-179).—The adrenals are included in the circuit of the Starling heart-lung preparation. Electrical stimulation of the gland causes a marked temporary increase in the secretion of adrenaline; treatment with nicotine produces a permanent increase in the secretion of adrenaline.

E. BOYLAND.

Rôle of lipins in the vegetative system. I. Antagonistic influence of the physico-chemical state of lipin sols. K. DRESEL and R. STERN-HEIMER. IV. Effect of lipins on the blood picture [with R. HIRSCH]. V. Effect of adrenaline on the serum-lecithin and -cholesterol [with F. HIMMELWEIT] (Z. klin. Med., 1928, 107, 739-758, 796-802, 803-809; Chem. Zentr., 1928, ii, 67-68).--V. Injection of adrenaline normally causes an increase of cholesterol and a decrease of lecithin in human blood-serum. In certain pathological conditions the reverse is the case. A. A. ELDRIDGE.

Absorption of calcium by the musculature of the small intestine during the action of adrenaline. L. JENDRASSIK and S. DONHOFFER (Biochem. Z., 1928, 201, 199-205).—The experiments of Dresel and Wollheim (A., 1925, i, 616) on calcium absorption by the intestine during the action of adrenaline are repeated with a large number of rabbits, but no regularity of results could be obtained.

P. W. CLUTTERBUCK.

Behaviour of the hexosephosphoric acid of the blood towards adrenaline. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 159, 257-266; Chem. Zentr., 1928, ii, 67).—Injection of 1% adrenaline solution (1 c.c.) causes a fall, maximal in 10-15 min., in the blood hexosephosphoric acid; normal values are regained, and a small rise is observed, in 60 min. The blood-sugar value is maximal when the hexosephosphoric acid value has become normal. When defibrinated blood is kept *in vitro*, the hexosephosphoric acid in appreciably increased in 60 min.; the rise is not affected by addition of adrenaline.

A. A. ELDRIDGE.

Behaviour of the hexosephosphoric acid of the blood towards insulin. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 159, 267—274; Chem. Zentr., 1928, ii, 67).—Injection of insulin (30—40 units) causes a rise of blood hexosephosphoric acid (15 min.) followed by a fall (1—1.5 hrs.) to subnormal values. Thus the effect on the acid is most marked when that on the blood-sugar has just begun. Insulin in vitro had no effect. A. A. ELDRIDGE.

Regulation of the production of insulin. III. Action of anhydro-sugars and sugar derivatives. E. GRAFE and F. MEYTHALER (Arch. exp. Path. Pharm., 1928, 136, 360—369; cf. A., 1927, 1115; 1928, 925).—By use of the technique previously described (*loc. cit.*) it is shown that the production of insulin is stimulated by sugar derivatives which contain or can give rise by hydrolysis to a reducing group, such as hexosans, glucosamine, glycuronic acid, dihydroxyacetone, and glyceraldehyde. Nonreducing sugar derivatives such as sorbitol and saccharic acid do not affect the production of insulin. H. R. ING.

Effect of insulin injected directly into the renal artery on the nitrogen and sugar elimination of the phloridzinised dog. J. GOLDSTEIN and W. J. STEPHENS (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1927, 81, 480).—An immediate decrease in the elimination of sugar and increase in that of nitrogen was observed.

CHEMICAL ABSTRACTS.

Optical activity of insulin-muscle-dextrosesodium chloride mixtures and hydrogen-ion concentration. C. N. J. GRAM and O. J. NIELSEN (Biochem. Z., 1928, 201, 369-390).-When fresh muscle was introduced into a mixture of dextrose, salt, and water the dialysate showed in many cases a lower rotatory power than corresponded with the reducing power. In some of these cases insulin was also added to the mixture. Sometimes in presence of insulin the difference disappeared on keeping, the two dextrose figures becoming identical. This subsequent adjustment was observed only in presence of insulin. The p_{μ} of the mixture, originally 7.4, rapidly adjusts itself to 6.0-6.2 when muscle is added. A borate buffer has a disturbing effect on the rotation of dextrose owing to complex formation. The cause of these rotation phenomena is obscure.

J. H. BIRKINSHAW.

Anti-insulin and external secretion of the pancreas. R. MEYER-BISCH, D. BOCK, and W. WOHLENBERG (Arch. exp. Path. Pharm., 1928, 136, 185—202).—Ultra-filtered human pancreatic juice, intravenously administered to rabbits, usually produces a rise in the amount of blood-sugar. The juice contains some substance toxic to these animals. Juice from dogs is less toxic to rabbits and produces smaller increases of blood-sugar. As a rule the amount of blood-sugar increases only when the animals under treatment have previously been receiving acid food. In an alkaline medium the action of anti-insulin is not only suppressed, but may even be reversed as a result of an increased production of insulin. In dogs from which the pancreas has been removed pancreatic juice has a stronger effect than in normal dogs. The external secretion of the pancreas produces in dogs an increase in the protein content of the lymph, a decrease in its alkali reserve, and simultaneous decrease in its sugar content. Anti-insulin is produced in the pancreas and is present in the pancreatic juice.

W. MCCARTNEY.

Iodine content and action of the thyroid gland. Biological method for evaluation of thyroid preparations. H. KREITMAIR (Z. ges. exp. Med., 1928, 61, 202—209; Chem. Zentr., 1928, ii, 366).— The action of the thyroid hormone can best be followed by observing the loss of weight of guinea-pigs. According to this method the biological action of thyroid preparations is unrelated to the iodine content. A. A. ELDRIDGE.

Separation of vitamin fraction from cod-liver oil. J. K. MARCUS (J. Biol. Chem., 1928, 80, 9— 14).—The oil is hydrolysed with concentrated aqueous potassium hydroxide together with a trace of alcohol; the resulting soaps are treated with a small amount of water, and the unsaponifiable matter, containing all the vitamins-A and -D of the original oil, is separated by extraction with ethylene dichloride.

J. H. BIRKINSHA

C. R. HARINGTON.

Cod-liver oil. E. M. BAILEY, H. C. CANNON, and H. J. FISHER (Conn. Agric. Exp. Sta. Bull., 1928, No. 295, 334-337).—Drummond's colour test for vitamin-A agrees fairly well with standard U.S. Pharmacopœia animal feeding tests. Samples gave the following colour values: six, 5 or less; nine, 5-10; two, 10-20; three, more than 20.

CHEMICAL ABSTRACTS. Determination of vitamin-A. E. M. NELSON and D. B. JONES (J. Biol. Chem., 1928, 80, 215— 226).—The method laid down in the U.S.P., X, for the determination of vitamin-A is criticised on the ground that account is not taken of the growthpromoting effect of vitamin-D. An improved method is suggested by which the rats are kept on a diet deficient in vitamin-A until the onset of xerophthalmia; the oil to be tested is then added to the diet, and its efficacy determined by the effect on the ophthalmia and on the growth curve.

C. R. HARINGTON.

Distribution of vitamin-A in maize. S. M. HAUGE and J. F. TROST (J. Biol. Chem., 1928, 80, 107-114).—Inheritance of vitamin-A in a cross of a yellow and white maize followed exclusively that of the yellow colour of the endosperm, and, like the latter, therefore shows Mendelian characteristics.

C. R. HARINGTON.

Relation between antimony trichloride reactions of vitamin-A and of certain carotinoids. B. VON EULER, H. VON EULER, and H. HELLSTRÖM (Svensk Kem. Tidskr., 1928, 40, 256—262).—Carotin gives a colour with antimony trichloride similar to that given by materials containing vitamin-A. The colour given by materials containing vitamin-A. The colour given by carotin has been examined by means of the photospectrometer and the Lovibond tintometer. The results are similar to but not identical with those given by vitamin-A. The reaction between antimony trichloride and arachis oil has also been examined. W. O. KERMACK.

Fluorescence of some fats containing vitamin-A. R. S. MORGAN and K. MACLENNAN (Biochem. J., 1928, 22, 1514-1522).-The unsaponifiable matter from cod-liver oil shows a bright fluorescence when illuminated by ultra-violet light filtered practically free from visible light. The effect of the addition of this fraction on the fluorescence of "jus" (pure rendered beef fat) which is already slightly fluorescent and of hardened coconut oil which is brightly fluorescent has been studied. The fluorescence of butter or butter-fat is yellow, that of margarine blue. The blue fluorescence of margarine can be modified by varying the fat mixture, by addition of unsaponifiable matter from cod-liver oil (small additions of which increase the brightness and diminish the blueness of the fluorescence), and by varying the nature of the pigment present. A sample of "oleo" coloured with sufficient red palm oil to match it with butter-fat and with sufficient unsaponifiable matter from codliver oil to bring it up to butter-fat in vitamin-A potency matches butter-fat exactly in fluorescence. A method is described for the determination of the brightness of the fluorescence of a solid fat, the colour being expressed in terms of three additive primaries, red, green, and blue. S. S. ZILVA.

Synthesis of vitamin-B in the rumen of the cow. S. I. BECHDEL, H. E. HONEYWELL, R. A. DUTCHER, and M. H. KNUTSEN (J. Biol. Chem., 1928, 80, 231-238).-The contents of the rumen of a cow on a diet deficient in vitamin-B were obtained by fistula, allowed to ferment for 5 days at 37°, and extracted with alcohol; the extract was found to be rich in vitamin-B. The predominant organism of the flora of the rumen, Flavobacterium vitarumen, was grown on media free from vitamin-B, and the dried bacteria were found to contain the vitamin; the synthesis of vitamin-B by this organism explains why the cow needs minimal amounts only of this vitamin C. R. HARINGTON. in the diet.

Dietary requirements for fertility and lactation. XIX. Does copper supplement vitamin-B for lactation? XX. Differentiation of vitamin-B complex in rice-polishings. B. SURE [with D. J. WALKER and E. H. STUART] (J. Biol. Chem., 1928, 80, 289-295, 297-307).-XIX. Addition of copper to a vitamin-B concentrate did not reduce the amount of the latter which was required by lactating rats.

XX. The previously observed (A., 1928, 555) inefficiency of the lactating rat in secreting vitamin-Bin the milk extends to both vitamin- B_1 and vitamin- B_2 ; as determined by requirements for lactation, ricepolishings are relatively rich in $-B_1$ and poor in $-B_2$. C. R. HARINGTON.

Antineuritic vitamin. II. Properties of the "curative" substance. J. L. ROSEDALE and C. J. OLIVEIRO (Biochem. J., 1928, 22, 1362-1367).-The antineuritic vitamin of an extract of rice-polishings is destroyed by fermentation and by sterilisation. It contains sucroclastic and lipoclastic but not proteo-clastic enzymes. In "dry" beri-beri the pancreas is incapable of lipoclastic and tryptic digestion.

S. S. ZILVA.

Effect of p_{μ} on adsorption of active factors of vitamin-B by fuller's earth. W. D. SALMON, N. B. GUERRANT, and I. M. HAYS (J. Biol. Chem., 1928, 80, 91–101).—Optimal adsorption of vitamin- B_1 by fuller's earth was obtained at $p_{\rm H}$ 4.0, the efficacy of adsorption decreasing rapidly with increasing alkalinity (which led to simultaneous inactivation) and more slowly with increasing acidity. Adsorption of vitamin- B_2 increases in efficiency up to $p_{\rm H}$ 0.08, which was the most acid reaction tested. Over the range studied adsorption of vitamin- B_1 was more complete, under the best conditions, than that of C. R. HARINGTON. vitamin- B_2 .

Conversion of vitamin-B into automatin by activation through irradiation. H. ZWAARDE-MAKER (Compt. rend. Soc. Biol., 1928, 98, 183-184; Chem. Zentr., 1928, ii, 166) .- By irradiation of automatinogen, active automatin could be obtained in heart muscle. Automatin is apparently identical with Demoor's active substance and Haberlandt's heart hormone; it also has properties similar to those of d'Eykmann's irradiated vitamin-B.

A. A. ELDRIDGE. Antiscorbutic vitamin in cabbage soup, cabbage puree, and turnip juice. E. Tso (Chinese

J. Physiol., 1928, 2, 403-408).-All three preparations protected guinea-pigs from scurvy and also promoted normal growth. F. C. HAPPOLD.

Fluorescence of oils and fats. J. F. CARRIÈRE. -See B., 1929, 26.

Vitamin contents of Japanese foodstuffs. SHIMODA, FUJIMAKI, and SAIKI.—See B., 1928, 942.

Characterisation of the immediate physiological action of water-soluble vitamins. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1928, 10, 1179-1198).-Guinea-pigs fed on a diet deficient in vitamin-C show, on administration of vitamin-C, an increase in the bromine titre of the urine in the case of adult animals, a decrease in the case of young growing animals, and the appearance of a blue reaction of the urine with monomolybdophosphotungstic acid (which is absent during avitaminosis, Bezssonoff, A., 1926, 722). Increase in weight becomes perceptible after 48 hrs. The bromine titre of the urine is proportional to the content of phenol and p-cresol and approximately to the density; it has no relation to the degree of pigmentation. The has no relation to the degree of pigmentation. bromine absorbed corresponds approximately with twice the amount of carbon in the urine.

G. A. C. GOUGH.

Immediate physiological effects of avitaminosis-C. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1928, 10, 1199-1212).—Avitaminosis-C causes accumulation of toxic phenolic substances in the blood and consequent inanition. G. A. C. GOUGH.

Antirachitic substances. VIII. Purified ergosterol and its esters. C. E. BILLS and E. M. HONEYWELL (J. Biol. Chem., 1928, 80, 15-23) .---The crude sterol from yeast is dissolved in a mixture of 95% alcohol (2 parts) and benzene (1 part), the solution is cooled slowly to commencing turbidity of the mother-liquor, and the crystals of ergosterol are collected; one more recrystallisation from alcoholbenzene gave a product, m. p. 166-183° according to the degree of hydration, $\lceil \alpha \rceil_{10}^{20} - 132^{\circ}$, $\lceil \alpha \rceil_{1561}^{20} - 171^{\circ}$, the rotation of which could not be altered by conversion into an ester and recovery by hydrolysis. Ergosterol purified by the above method yields an acetate, m. p. 181°, $[\alpha]_{D}^{25} - 90^{\circ}$; isobutyrate, m. p. 162° after sintering, $[\alpha]_{D}^{25} - 84^{\circ}$; isovalerate, m. p. 160° after sintering, $[\alpha]_{D}^{25} - 82^{\circ}$; benzoate, m. p. 168°, $[\alpha]_{D}^{25} - 177^{\circ}$; cinnamate, m. p. 179°, $[\alpha]_{D}^{25} - 22^{\circ}$, all rotations in chloroform. Careful purification of ergosterol fails to affect its spectrographic properties.

C. R. HARINGTON.

Vitasterol-D. II. Activation of ergosterol. A. JENDRASSIK and A. G. KEMÉNYFFI (Biochem. Z., 1928, 201, 269–280).—Ergosterol attained its maximum antirachitic activity after 30 min. irradiation; after 10 hrs. the activity was destroyed. No unchanged ergosterol then remained. A material having five times the activity of the irradiated product was obtained by fractionation with ethyl alcohol. The unchanged ergosterol after removal of the active product can be again activated by irradiation. The intensity of the orange colour produced with iodine seems to give an indication of the content of vitasterol-D. J. H. BIRKINSHAW.

Biological inertness of irradiated mycosterols other than ergosterol. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1928, 22, 1426-1428).—A mycosterol "fungisterol" was isolated as the acetate m. p. 117—118°, $[\alpha]_{5461}^{29}$ -43°, from the mother-liquor after removal of crystallisable ergosterol from ergot. This sterol, and also two other sterols from the same source were found to be biologically inactive after irradiation. S. S. ZILVA.

Chronic effects of irradiated saponin and irradiated ergosterol. H. HANDOVSKY (Arch. exp. Path. Pharm., 1928, 137, 264-268).-Administration to rabbits of saponin irradiated by a mercury vapour lamp results in an increase of the carbohydrate of their muscles, whereas administration of nonirradiated saponin causes a decrease. Administration of irradiated ergosterol causes a decrease in the carbohydrate content of the muscles.

W. O. KERMACK.

Duration of effect of ultra-violet irradiation of chickens. W. C. RUSSELL, O. N. MASSENGALE, and C. H. HOWARD (J. Biol. Chem., 1928, 80, 155-162).—The calcium and phosphorus concentrations in the blood of chickens on a diet deficient in vitamin-D was proportional to the time of exposure of the birds to ultra-violet irradiation; a parallelism was observed between the calcium and phosphorus of the blood and the percentage of bone-ash. One exposure of the bird to ultra-violet light of 45 min. duration produced an effect lasting 1 week, whilst longer single exposures up to 270 min. were active for 2 weeks. C. R. HARINGTON.

Yeast ergosterol. III. F. REINDEL.-See this vol., 61.

"Hypervitaminosis " and " vitamin balance." L. J. HARRIS and T. MOORE (Biochem. J., 1928, 22, 1461-1477).-Young rats lose weight rapidly and die on a synthetic diet containing 0.1% of irradiated ergosterol. An increase of vitamin-B in the form of marmite to four times the normally adequate level does not appreciably influence this decline. On the other hand further addition of vitamin-B (and -C), through the medium of wheat-germ and orange juice, prevented the loss in weight in two animals. Rats on a diet containing 15% of cod-liver oil and a restricted allowance of the vitamins-B do not thrive as well as animals on a diet containing a similar content of arachis oil. In the former case normal gestation fails (cf. Hartwell, A., 1927, 1107; Sure, ibid., 905). 0.001% of irradiated, non-irradiated, or heated ergosterol in the diet makes no appreciable difference in the condition of rats subsisting on vitamin-B-restricted or vitamin-B-free diet. Massive doses of vitamin-A and -D concentrate from cod-liver oil produce, in conjunction with vitamin-B deficiency, changes such as loss of hair and severe skin lesions. The lethal dose of irradiated ergosterol becomes nontoxic concurrently with the destruction of vitamin-D by over-irradiation. S. S. ZILVA.

Daily growth and oil content of flax seeds. A. C. DILLMAN (J. Agric. Res., 1928, 37, 357-377).—The most rapid formation of the oil in flax seeds begins about the seventh day after flowering and continues for a period of 15-18 days. It reaches a maximum 33 days after flowering, coincident with the maximum dry weight of the seed. The bearing of this on the harvesting of flax is discussed.

E. A. LUNT.

Chemical composition of the oil in relation to the morphological and physiological characters of the plant. S. FACHINI and G. DORTA (Giorn. Chim. Ind. Appl., 1928, 10, 460-462).-Olive oils from the northern parts of Italy (Lake Garda, Liguria) contain only small proportions (2-6%) of linoleic acid, whereas certain oils from Southern Italy, Greece, and Northern Africa contain considerable quantities, even as much as 17%, of this acid, together with a high percentage of saturated fatty acids. This result appears to be opposite to that found by Ivanov (A., 1927, 906) for seed oils. The composition of olive oil seems to be influenced by the age and degree of acclimatisation of the plant. The characteristics of an oil depend largely on the biological and morphological factors of the plant furnishing it.

T. H. POPE.

Carbon dioxide assimilation of the sugar beet. H. LUNDEGARDH (Flora, 1928, [ii], 21, 273-300; Chem. Zentr., 1928, ii, 257).-The dependence of the assimilation on temperature follows the same regularities for different plants, but differences exist in the position of the optimum. The results are considered in relation to plant geography. A. A. ELDRIDGE.

Evolution of carbon dioxide and absorption of oxygen in germinating seeds. G. FRIETINGER (Flora, 1927, [ii], 22, 167-201: Chem. Zentr., 1928, ii, 160).-No parallelism between carbon dioxide evolution and oxygen assimilation was observed, although both are greatly influenced by the medium. A. A. ELDRIDGE.

Decomposition of hexoses in plants. III. Co-zymase of plants. W. ZALESKI and E. SCHATALOWA-ZALESKAJA (Biochem. Z., 1928, 201, 190-198).-The power of pea-meal to utilise acetaldehyde is lost on dialysis but regained on adding boiled extract of dried yeast, a co-enzyme probably identical with co-zymase. The difference between the aldehydase activity of non-germinating and germinating peas can be compensated for by addition of excess of co-enzyme (cf. A., 1927, 1226). P. W. Clutterbuck.

Catalase in relation to growth and other changes in plant tissue. J. E. KNOTT (N.Y. Agric. Exp. Sta. Mem., 1927, No. 106, 63 pp.).—The catalase activity of spinach and celery leaves is generally greatest at intermediate ages. Rise (10°) of temperature increased the catalase activity of celery plants; the $p_{\rm H}$ of the plant juice could not be correlated with catalase activity, which was increased by fertilising with phosphorus and nitrogen.

CHEMICAL ABSTRACTS.

Catalase reaction in pollen. G. LOPRIORE (Ber. deut. bot. Ges., 1928, 46, 413-423).-In general the catalase content of the pollen from various plants increases with the increasing ripeness of the pollen,

E. A. LUNT.

Sodium and potassium content of lentils and peas. W. KÜSTER and J. UMBRECHT (Z. physiol.

Chem., 1928, 179, 139-148).-The sodium and potassium content of the ash of lentils and peas was determined. The average value for small lentils was Na₂O, 0.782%; K₂O, 31.95%, for cultivated lentils, Na₂O, 3.06%; K₂O, 37.4%. Peas had 1.81% Na₂O, 40.35% K₂O in the ash. J. H. BIRKINSHAW.

Physiological function of magnesium in plants. E. CANALS (Bull. Soc. Chim. biol., 1928, 10, 1260-1270).—The magnesium and calcium contents of the ash from various parts of a large number of plants show wide variations (Ca $2\cdot 2$ -35.5, Mg $0\cdot 8$ -5.7%; Ca : Mg $0\cdot 81$ -32.2). Except in herbaceous plants, the leaves contain more magnesium than the stems and the amount of calcium generally increases with the age of the tissue. Dialysis of the juices of fungi and potato shows that a large proportion of the magnesium and calcium exists in an inorganic form, G. A. C. GOUGH. probably as phosphate.

Effect of plasmolysis on carbon dioxide assimilation in plants. H. WALTER (Ber. deut. bot. Ges., 1928, 46, 530-539).—The effect of plasmolysis induced by immersion in sucrose solutions of varying concentrations on the capacity for carbon dioxide assimilation has been investigated in the case of Elodea canadensis. E. A. LUNT.

Determination of sulphur and phosphorus in vegetable tissues. R. ECHEVIN and A. CRÉPIN (Bull. Soc. Chim. biol., 1928, 10, 1248-1259).-After oxidation by means of nitric acid, the sulphur is determined as barium sulphate and the phosphorus titrated with uranium acetate solution.

G. A. C. GOUGH. Valerian root and the formation of sucrose. H. KUNZ-KRAUSE (Apoth.-Ztg., 1928, 43, 484-485; Chem. Zentr., 1928, i, 2733).-Sucrose was deposited from ethereal tincture of valerian. The occurrence of sucrose with certain monocarboxy-acids suggests a relationship between the genesis of sucrose and the appearance of fatty acids, particularly butyric and valeric. A. A. ELDRIDGE.

Glucosides of digitalis leaves. A. WINDAUS (Arch. exp. Path. Pharm., 1928, 135, 253-258).-A comparative review of the work of Cloetta (A., 1926, 755) and of the author (A., 1923, i, 1107; 1924, i, 1215; 1925, i, 1295; 1926, 153; Nachr. Ges. Wiss. Göttingen, 1926, 170; 1927, 422) on the chemistry of digitoxin, gitoxin (bigitalin), and gitalin.

Glucosides of Adonis vernalis. K. FROMHERZ (Münch. Med. Woch., 1928, 75, 818-820; Chem. Zentr., 1928, ii, 75).-Two highly active digitalis-like glucosides differing in degree of activity can be isolated from Adonis vernalis. A. A. ELDRIDGE.

Ocnanthe sarmentosa. F.J. GOODRICH and E.V. LYNN (J. Amer. Pharm. Assoc., 1928, 17, 1096-1104).-The dried leaves and stems of O. sarmentosa grown on the American Pacific coast contain 0.038% of oil having $d^{15\cdot5}$ 0.9188, $[\alpha]_D^{20}$ +7.78°, n_D^{20} 1.4918, and congealing at -12°. It is principally composed of terpenes and contains sulphur (1.28%) and furfur-aldehyde. The dried fruit gives 0.35% of oil $(d^{15\cdot5}$ $0.9032, [\alpha]_D^m + 7.52^\circ, n_D^\infty 1.4942$, congealing pt. -10.5°) also containing sulphur (0.91%) but no furfuraldehyde.

It consists mainly of terpenes and contains phellandrene, probably a-phellandrene: The rhizomes and roots yield 0.1% of oil (on dried material) having $d^{15.5} 0.9304$, $\lceil \alpha \rceil_{D}^{\circ} + 7.52^{\circ}, n_{D}^{\circ}$ 1.4898, and containing furfuraldehyde and a small amount of sulphur. Pectin is present in the rhizome in an amount equivalent to 2.36% of pectic acid (on dry material). The dry material also contains 3.14% of reducing sugars, starch, sucrose, gums, and resins. Alkaloids were not present in any part of the plant, but small amounts of glucosides may be present. The plant is not toxic to guinea-pigs E. H. SHARPLES. or rats.

Principle extracted from Sphacele parviflora, Linn. V. HASENFRATZ (Compt. rend., 1928, 187, 903-904).-The white solid, m. p. 105°, isolated from the dried leaves of S. parviflora, Bentham (yield 3 g./kg.), by steam-distillation and crystallisation of the product from alcohol, is proved to be identical with the sesquiterpene alcohol ledol, C₁₅H₂₆O (Hjelt, A., 1896, i, 248), isolated from Ledium palustre, Linn. J. W. BAKER.

Isolation of mesaconic acid from cabbage leaves. H. W. BUSTON (Biochem. J., 1928, 22, 1523-1525).-Mesaconic acid is present in the fraction of the ether-water extract of leaves which is precipitated by alcohol and in the "dicarboxylate" fraction left after precipitation of bases with phosphotungstic acid. In the former it is liberated from its calcium salt by dilute sulphuric acid and extracted with alcohol. From the latter fraction after decomposing the barium dicarboxylates it is extracted with alcohol and purified partly by extraction with ether and partly by precipitation as the calcium salt from this alcoholic extract. S. S. ZILVA.

Amaryllis. NARITA (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481-504, 524-551).-The air-dried plants contained : water 80.53, crude protein 1.19, crude fat 0.23, crude fibre 0.72, carbohydrates (as dextrose) 17.32, ash, 0.01%. "Sekisanine," $C_{24}H_{36}N_2O_6$, m. p. 200° (0.05%), and "lycorine," $C_{32}H_{32}N_2O_2$, m. p. 248° (0.13%), were CHEMICAL ABSTRACTS. present.

Nutritional chemistry of raw food sub-ances. I. The banana. K. KONDO, M. NAKAstances. I. The banana. K. KONDO, M. NAKA-JIMA, and T. SUZUKI. II. The water-melon. K. KONDO and T. HAYASHI (Mem. Coll. Agric. Kyoto, 1928, 6, 23-53, 55-72).-I. The following percentage composition is given for the edible portion of the banana fruit : water 70%, total nitrogen 0.29%. protein 1.83%, starch 4.69%, reducing sugars 12.23%, non-reducing sugar 1.94%, pectits 0.38%, fibre 0.34%, ash 1.04%. II. Analyses of the juice of different varieties of

ripe water-melons give the following average results: water 92%, sugars 6-8%, chiefly lævulose, ash 0.3%, nitrogen 0.08%. E. A. LUNT.

Comparative plant chemistry. XXI. Chemistry of latex-bearing plants. IV. J. ZELLNER (Monatsh., 1928, 50, 211-215).—The dried latex of Campanula trachelium, L., yielded a small ether-soluble fraction containing resin acids, but no sensible quantity of fatty acids. A wax alcohol, m. p. 87°, was isolated. Euphorbone or sterols were absent. The alcoholic extract, evaporated to dryness and

W. O. KERMACK.

crystallised from water, yielded a glucoside, campanulin, (?) $C_{12}H_{18}O_{0}$, m. p. 210° (decomp.), from which dextrose and a phenolic substance were obtained. Acetylation of the glucoside yielded an acetyl compound, $C_{24}H_{28}O_{14}$, m. p. 202°, with simultaneous loss of water. The mother-liquors of the campanulin contained "tannoid" substances, but no sugars or alkaloids. The aqueous extract of the dried latex contained chiefly inorganic salts. The extract with dilute alkali contained proteins.

The dried latex of *Lactarius rufus*, Scop., yielded, on extraction with light petroleum, a considerable amount of lactaric acid. Only resinous substances could be isolated from the mother-liquors. The small alcoholsoluble fraction contained mannitol and dextrose. The aqueous extract appeared to contain a weakly acidic carbohydrate as a potassium compound. The extract of the residue with alkali yielded proteins on acidification. The composition is similar to that of the latex of *L. vellereus* (A., 1921, i, 212).

R. K. CALLOW.

Plugging substance in the vessels of hops. T. C. THRUPP (Ann. Bot., 1928, 42, 1027-1028).— A plugging substance, insoluble in concentrated acids and incapable of ordinary staining, has been found in the vessels of hops. E. A. LUNT.

Water-soluble protein in wheat seed. R. HERZNER (Biochem. Z., 1928, 202, 320-328).—The properties of the carefully purified water-soluble protein of wheat seeds (leucosin) show that it belongs to a group of substances analogous to the animal pseudoglobulins. W. MCCARTNEY.

Proteins of buckwheat flour. M. HARA (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481-504, 524-551).—The following values are recorded (percentages of total nitrogen within parentheses): amino-nitrogen 0.0525 (8.19), humin-0.0487 (7.60), cystine- 0.0117 (1.82), arginine- 0.1527 (23.82), histidine- 0.0158 (2.43), lysine- 0.0204 (3.19), monoamino- 0.2599 (40.53), non-amino- 0.0874 (13.63), total 0.6590 g. CHEMICAL ABSTRACTS.

Protein content of Italian millet. KONDO (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The following values are recorded: water 13.57, crude protein 11.12, albuminoids 10.36, fat 5.32, nitrogen-free extract 63.68, fibre 1.71, ash 0.87%. The protein (30 g.) contained: total nitrogen 0.6009, humin- 0.0155 (2.54% of total), amide- 0.0734 (12.03), arginine-0.0592 (9.71), cystine- 0.0135 (2.21), histidine- 0.0720 (11.81), lysine- 0.0369 (6.05), monoamino- 0.3015 (49.43), non-amino- 0.0290 g. (4.76).

CHEMICAL ABSTRACTS.

Prearginine in edestin and its resistance to hydrolysis. H. S. SIMMS (J. Gen. Physiol., 1928, 12, 231-239).—Titration data indicate that edestin contains no free arginine but that this amino-acid is present in the form of prearginine (cf. A., 1928, 837). Partial hydrolysis of edestin (up to 18% of the total hydrolysis) by pepsin does not convert prearginine into arginine. The second carboxyl groups of glutamic and aspartic acids are in part present as amides and 50% are otherwise combined, possibly as anhydrides, whilst 6% are free to ionise. Samples of edestin hydrolysed to the extent of 5, 14, or 18% were equally effective in promoting growth of sarcomatous fibroblasts. W. O. KERMACK.

Basic nitrogen of plant extracts. H. B. VICKERY (Plant Physiol., 1927, 2, 303—311).— Phosphotungstic acid is an uncertain precipitating agent for the true basic nitrogen of plants, since it may precipitate non-basic nitrogenous substances as well as compounds of polypeptide nature which yield simple monoamino-acids on hydrolysis. The method is satisfactory with simple mixtures.

CHEMICAL ABSTRACTS.

Purine bases of the seed and meal of the soya bean. V. DUCCESCHI (Arch. Sci. Biol., 1928, 12, 181–184; Chem. Zentr., 1928, i, 3082-3083).— The dry seed contains 0.191% and the dry meal 0.233% of purine bases. A. A. ELDRIDGE.

Location and disappearance of alkaloids in the epidermis of the tobacco leaf. J. CHAZE (Compt. rend., 1928, 187, 837-839).—The epidermal cells of the tobacco leaf present several types in regard to their nicotine content; in one type, a brown liquid containing alkaloids is observed to exude. When the hairs of the leaf exude this liquid the nicotine content of the cell at the base of the hair diminishes. G. A. C. GOUGH.

Origin of ethereal oils in plants. L. FRANCES-CONI (Riv. Ital. Ess. Profumi, 1928, 10, 2-6, 33-36; Chem. Zentr., 1928, i, 2414).-It is supposed that isoamyl alcohol, from the decomposition of protein, vields isovaleraldehyde, whence isocitronellal, rhodinal, and citronellal are produced. Citronellal gives rise to geraniol and hence linalool; ring-closure affords limonene or terpineol. Ring-closure of rhodinal gives rise to menthone, and of citronellal to isopulegol. Geraniol by ring-closure and hydration gives a-pinene; linalool by ring-closure and wandering of a hydroxyl A. A. ELDRIDGE. group gives terpineol.

Potentiometric determinations in the protoplasm and cell sap of Nitella. C. V. TAYLOR and D. M. WHITAKER (Protoplasma, 1927, 3, 1--6).--A non-polarisable micro-electrode is described and figured. The protoplasm produced a potential of +0.093 to +0.030 volt; the values are considered to indicate the oxidation-reduction potential. The $p_{\rm ff}$ of the cell sap was 5.47--6.16.

CHEMICAL ABSTRACTS.

Composition of the cellular fluid of Valonia macrophysa. R. HÖBER and J. HÖBER (Pflüger's Archiv, 1928, 219, 260—272; Chem. Zentr., 1928, i, 2945—2946).—The cellular fluid of Valonia macrophysa contains more potassium, but less sodium, calcium, magnesium, and sulphate than the sea-water; the concentrations of chloride are equal. A. A. ELDRIDGE.

Influence of oxygen and carbon dioxide on the growth of Ophiobolus graminis. H. FELLOWS (J. Agric. Res., 1928, 37, 349—355).—The variation in the amount of growth obtained both on solid and on liquid media of the wheat fungus, O. graminis, with variation in oxygen and earbon dioxide concentrations has been observed. It is unlikely that the variations in these two gases as found in arable soils are great enough to affect materially the growth of this organism. E. A. LUNT. Importance of oxygen in the formation of carbamide by fungi. N. N. IVANOV and M. I. SMIRNOVA (Biochem. Z., 1928, 201, 1–12).—Mushrooms accumulate carbamide only when in an atmosphere containing oxygen. The rôle of oxygen in the synthesis of carbamide is discussed and is regarded as analogous to its rôle in the synthesis of asparagine (cf. A., 1927, 383). P. W. CLUTTERBUCK.

Colour variation in the moulds. A. BLOCH-WITZ (Ber. deut. bot. Ges., 1928, 46, 516–524).— A review is given of the literature dealing with the colour variations in the vegetative filaments and conidia of the moulds, and of individual experiments on Aspergillus flavus relating the colour variation with the $p_{\rm H}$ of the medium. E. A. LUNT.

Chemistry of the higher fungi. XIX. Polyporus pinicola, Fr. E. HARTMANN and J. ZELL-NER. XX. Omphalia Campanella, Batsch, Marasmius Scorodonius, Fr., Boletus cavipes, Opat., and Calocera viscosa, Pers. N. FRÖSCHL and J. ZELLNER (Monatsh., 1928, 50, 193-200, 201-210).-XIX. Fractionation of the alcoholic extract o Polyporus pinicola yielded a substance, m. p. 140of (acetyl compound, m. p. 67-68°), identical with 141° the cerebrin from Amanita muscaria (Zellner, A., 1911, ii, 425), trehalose, and a final fraction. Extraction of the final fraction with light petroleum yielded, after saponification, sterols (0.3-0.4%) of the dry fungus), separated into ergosterol and fungisterol, resin, acetic and butyric acids, glycerol, choline, and an acid fraction insoluble in water, from which was separated a neutral, crystalline substance, m. p. 195-196° (possibly identical with a product obtained from Scleroderma aurantium, Vaill., by Bamberger and Landsiedl; A., 1907, ii, 45), an amorphous neutral substance, m. p. 87–88°, a substance giving a cholesterol reaction, $(C_{10}H_{18}O)_n$, m. p. 142–144°, and amorphous resin acids. Extraction of the final alcohol fraction with ether yielded similar fractions, substances, m. p. 221-222° and 215°, and a substance of sterol character, (C4H8O), m. p. 188°. Tannins were obtained by extraction of the final alcoholic fraction with water, leaving a residue containing phlobaphens. The results are contrasted with those of the investigation of Polyporus officinalis by Schmieder (Diss., Erlangen, 1886).

XX. Omphalia Campanella, examined by similar methods, yielded sterols, liquid and solid fatty acids, resin, mannitol, dextrose, choline, phlobaphen, and amorphous carbohydrates.

Marasmius Scorodonius was subjected to steamdistillation. The ethereal extract of the distillate vielded a paraffin, m. p. 55°, and an oil with a garliclike odour, (?) $(C_2H_5S)_n, 0.2\%$ of the dry fungus. The aqueous extract of the fungus yielded marasmin, $C_7H_{15}O_3N$, m. p. 242° after darkening at 195°, a neutral substance with reducing properties, and from the mother-liquors were obtained choline and dextrose, but neither mannitol nor trehalose. The portion of the aqueous extract insoluble in alcohol yielded a glucosan. From the portion insoluble in water was obtained a substance of cerebrin character, m. p. 133°, a mixture of sterols, and liquid and solid fatty acids, the last containing palmitic and stearic acids and a higher fatty acid.

From *Boletus cavipes*, well-defined products were isolated with difficulty. The ethereal extract yielded sterols, resin, and liquid fatty acids, identified with oleic acid and linoleic acid by oxidation to dihydroxyand tetrahydroxy-stearic acids, respectively. The alcoholic extract yielded mannitol and a syrupy glucosan. The aqueous extract contained polysaccharides of the type of viscosin.

The alcoholic extract of Calocera viscosa yielded trehalose. The light petroleum extract of the final fraction from alcohol yielded, after saponification, a mixture of sterols of the usual type, in the motherliquors of which the amorphous, reddish-yellow colouring-matter collected, and a mixture of fatty acids in which isovaleric, oleic, palmitic, and stearic acids were recognised. The ethereal extract of the final alcohol fraction yielded, after separation of resin acids and resin, calocerol, m. p. 255° (decomp.), a neutral, stable substance for which the formula $C_{22}H_{38}O_8$ is proposed. With acetyl or benzoyl chlorides, two substances of similar character, m. p. 128°, were formed. Dextrose and choline were separated from the residue of the alcoholic extract. The aqueous extract of the fungus yielded slimy polysaccharides, probably present in the fungus as potassium or magnesium compounds, yielding mannose on hydrolysis. R. K. CALLOW.

Alcoholic fermentation by Aspergillus flavus, Brefeld. J. L. YUILL (Biochem. J., 1928, 22, 1504—1507).—A. flavus does not produce kojic acid under conditions in which A. oryzæ produces it. In presence of chalk the former organism, unlike the latter, produces considerable quantities of ethyl alcohol (equivalent to 15-25% of the sugar consumed) in the presence of air. During the fermentation with A. flavus some calcium citrate is formed and some soluble calcium salts precipitable by alcohol. When the mould forms spores the yield of alcohol is much reduced and the quantity of citrate increased.

S. S. ZILVA.

Conditions of the action of asparaginase from Aspergillus niger. D. BACH (Compt. rend., 1928, 187, 955—956).—The action of asparaginase from A. niger in the conversion of asparagine into ammonium aspartate occurs only on the alkaline side of the isoelectric point of the acid $(p_{\rm H} 4.5-10)$ and is greatest at 42° and $p_{\rm H} 8.6$. At $p_{\rm H} 7.6$ the optimum temperature is 31° and in both cases the action extends from 7° to 70°. The reaction is never more complete than 80%, and the destruction of the enzyme, which occurs in the extract of the mould, is inhibited by asparagine. G. A. C. GOUGH.

Formation of calcium oxalate crystals in vegetable cells in ultra-violet light. G. NADSON and E. ROCHLINE-GLEICHGERWICHT (Compt. rend. Soc. Biol., 1928, 98, 363—365; Chem. Zentr., 1928, i, 2949).—Exposure to ultra-violet light causes the appearance of calcium oxalate in *Elodea densa*, *E. canadensis*, and *Pterygophyllum hepaticæfolium*.

A. A. ELDRIDGE.

Diurnal variation of the gaseous constituents of river waters. IV. R. W. BUTCHER, F. T. K. PENTELOW, and J. W. A. WOODLEY (Biochem. J., 1928, 22, 1478-1489; cf. A., 1927, 899; 1928, 1163).
-The effect of the pollution by effluents on the dissolved oxygen of the river Lark was less marked on Jan. 25-27th, 1928, than in November, 1927. The diurnal variation was still evident. During February 16-17th, when the effects of the winter pollution were disappearing, the range of variation of oxygen content was smaller than at any other time of the year, *i.e.*, 66-77% saturation. The figures obtained in March 1928 indicate the commencement of that rapid increase of diatoms which occurs every spring. In the case of the river Itchen the oxygen curves of January, February, March, and May show an increasing range of variation with the increase in the hours of daylight and with increase in the number of diatoms. The river Lark results are summarised for the period March 1927-March 1928. The factors affecting the dissolved oxygen content of river water are discussed.

S. S. ZILVA.

Sunlight and chemical nitrification. J. ZÓŁCIŃ-SKI (Pedologie, 1928, 19, No. 1-2; Chem. Zentr., 1928, i, 2443).-Nitrification takes place in sunlight in aqueous ammonium salt solutions of humus substances; the nitrate disappears again in the dark. The effect is more pronounced in silica vessels than in glass. Nitrification does not take place in colloidal solutions. Natural humus undergoes nitrification more slowly than artificial; the presence of ignited alumina promotes the change. A. A. ELDRIDGE.

Laboratory apparatus. II. H. J. FUCHS (Biochem. Z., 1928, 201, 332-337).-1. An apparatus is described for low-temperature evaporation in a vacuum. Only ground-glass joints are used. The liquid is allowed to drop into the distillation flask, where it is sprayed over the walls. The receiver contains concentrated sulphuric acid and is cooled in a water-bath.

2. A fractional distillation apparatus for the purification of liquids of low b. p. consists of a double rectifier so arranged that the heat for the second stage of evaporation is supplied by the vapour of the first stage. J. H. BIRKINSHAW.

New micro-burette. E. M. P. WIDMARK and S. L. ORSKOV (Biochem. Z., 1928, 201, 15-21).-The principle of the instrument is based on the displacement of a volume of the titration fluid by mercury which in turn is displaced as the result of the movement of a steel cylinder operated by means of a micrometer screw, the reading on the screw (calibrated against the amount delivered) thus giving the volume of fluid used. The instrument has a capacity up to 200 mm.³, it can be connected directly with the titration flask, air thus being excluded, and provision is made for easy washing (cf. A., 1926, 211). P. W. CLUTTERBUCK.

Haldane apparatus for small volumes of gas. H. C. BAZETT (Amer. J. Physiol., 1928, 86, 556-564). -A modified gas analyser is described capable of analysing mixtures of carbon dioxide and oxygen with a neutral gas in any proportion in volumes up to 2.0 c.c. The error varies from ± 0.04 to $\pm 0.2\%$, according to the volume available. B. A. EAGLES.

Improvements in Carpenter's apparatus for gas analysis. F. STRIECK (Biochem. Z., 1928, 202, 1-4).-Two changes are made which enable a double

analysis to be carried out in 12-14 min. (see Z. ges. exp. Med., 1920, 54, 613). R. W. CLUTTERBUCK.

Manometric measurement of small partial pressures of oxygen. O. WARBURG and F. KUBO-WITZ (Biochem. Z., 1928, 202, 387–389).—A description of an apparatus for determining the partial pressure of oxygen is given. The oxygen is absorbed by a solution of ferrous pyrophosphate. Partial pressures of a few ten thousandths of an atmosphere may be measured. W. MCCARTNEY.

Micro-determination of hydrogen peroxide, nitrogenous compounds, and fermentation carbon dioxide. Paechtner's ponderovolumeter. P. LUY (Biochem. Z., 1928, 201, 165-184).-Paechtner's ponderovolumeter for the determination of small amounts of gas in terms of pressure changes in a closed space within which the gas is formed is successfully used to follow the decomposition of hydrogen peroxide by permanganate, the formation of nitrogen by treatment of carbamide or ammonium sulphate with hypobromite, and the production of carbon dioxide during the fermentation of dextrose by yeast.

P. W. CLUTTERBUCK.

Determination of p_{ii} in cells and tissues. T. PETERFI (Z. wiss. Micros., 1928, 45, 56-59; Chem. Zentr., 1928, i, 2737).---A technique employing gelatin coloured with Clark's indicators is described. A. A. ELDRIDGE.

Use of the quinhydrone electrode. R. R. MCKIBBIN and L. I. PUGSLEY (Canadian Chem. Met., 1928, 12, 283-286).-Comparative pn determinations were made on a number of biological solutions with the hydrogen gas electrode, the quinhydrone electrode, and where possible colorimetrically. With fruit juices the quinhydrone electrode consistently gave rather higher results than the other and equilibrium was reached at once. With milk, urine, and soil extracts agreement was close. With human saliva the results appear uncertain. The use of the quinhydrone electrode with gold wire, which is described in detail, is very convenient with such solutions and quite accurate below $p_{\rm H}$ 8.0. C. IRWIN.

Wash-bottle for the gas cell. H. SCHREUS (Biochem. Z., 1928, 200, 339).-A wash-bottle is described which permits rapid change of the washing fluid without loss and without entrance of air into the flask.

P. W. CLUTTERBUCK.

Apparatus for the micro-determination of carbon by the method of Nicloux. N. BEZSSO-NOFF (Bull. Soc. Chim. biol., 1928, 10, 1273-1276) .---Another method of avoiding the use of a stopcock in the apparatus of Nicloux is described. This consists of a bulb pipette filled with sulphuric acid and bent in such a way that the hydrostatic pressure at the capillary tip is small. The flow of acid is regulated by means of a rubber tube and clip. G. A. C. GOUGH.

Micro-determination of potassium in biological media. A. LEULIER, L. VELLUZ, and H. GRIFFON (Bull. Soc. Chim. biol., 1928, 10, 1238-1247).-Directions are given for the adaptation of the method already described (A., 1928, 1205) to biological substances. Deproteinisation is effected by means of trichloroacetic acid in the cases of milk and blood and the resultant filtrates are neutralised with lithium

carbonate. Tissue is oxidised either by treatment with nitric acid and hydrogen peroxide or by sulphuric and perchloric acids. Ammonia is eliminated in all instances with sodium nitrite and acetic acid.

G. A. C. GOUGH.

Determination of small amounts of iodine in organic products. II. G. PFEIFFER (Biochem. Z., 1928, 201, 298—304; cf. A., 1928, 928).—Fatty acids which would otherwise distil into the receiver are intercepted by a special condenser from which the condensate can be run off. They are received in dilute potassium hydroxide solution and removed as calcium salts. J. H. BIRKINSHAW.

Determination of small amounts of iodide in presence of much chloride. F. KIEFERLE and E. ERBACHER (Biochem. Z., 1928, 201, 305—317).— Potentiometric titration with mercuric perchlorate gave exact results and was superior to titrations with silver nitrate and with palladium chloride. The method could not be applied to milk, for which it was originally intended. J. H. BIRKINSHAW.

Micro-titration of iodine. A. STURM (Biochem. Z., 1928, 200, 273-279).—Comparative determinations of iodine by the colorimetric micro-method of Fellenburg (A., 1925, i, 329) and by the titrimetric method of Winkler (A., 1916, ii, 109) showed that the former gives low results in presence of moderate concentrations of salts. On the other hand, when the iodine content of the investigated solution is less than 3 γ , the change of colour of the starch iodide in the titration is delayed. A curve is given showing the variation of this delay with the iodine content of the solution (from 1 to 3 γ) and from this the error due to the delay may be corrected. Very small amounts of iodine cannot be determined by either method in presence of high concentrations of salts.

P. W. CLUTTERBUCK.

Methods for the determination of fat. G. ROSENFELD (Biochem. Z., 1928, 200, 280-288).-A large number of determinations of fat in a variety of dried tissues are carried out by the author's method, boiling with alcohol and extracting for 6 hrs. with chloroform (Centr. inn. Med., 1905, No. 14), and by other methods, special attention being directed to the effect on the result of choice of extraction solvent, the manner of its use, and the method of decomposition of the tissue. The author's method gives results 30% higher than that of Kumagawa and Suto and higher results also than those of Dormever, Liebermann, and Nerking. Soxhlet extraction of the dried ground tissue with chloroform removes more fat than extraction with either ether or light petroleum. Carbon tetrachloride extracts much less fat than chloroform and the extract is also very nitrogenous. Acetone gives good extraction. P. W. CLUTTERBUCK.

Quantitative extraction of cholesterol and its esters from tissues and body fluids. E. MÜLLER (Z. Biol., 1928, 88, 132–138).—Of many methods only a modification of that of Fex (cf. A., 1920, i, 697) is found to be quantitative. Tissue in the moist state gives better extraction than that dried either in air or by treatment with plaster of Paris or anhydrous sodium sulphate. Serum or liver is treated with 2% sodium hydroxide solution and the solution is extracted with ether in a continuous extractor. The extracted cholesterol is precipitated from alcoholic solution with digitonin. E. BOYLAND.

Micro-determination of cholesterol. Y. HORIXE (Biochem. Z., 1928, 202, 403-408).—The titrimetric method of Szent-Györgyi (A., 1923, ii, 344) gives unsatisfactory results. His gravimetric method is much better, especially when the washliquor of Caminade (A., 1923, ii, 264) is used.

W. MCCARTNEY. Colorimetric determination of lactic acid. B. MENDEL (Biochem. Z., 1928, 202, 390; cf. A., 1926, 212).—The concentration of the sulphuric acid should be kept constant and the colour allowed to develop at 25°. As little as 1 g. of lactic acid can then be determined. W. MCCARTNEY.

Chlorophyll from tropical plants and its determination by means of the spectrograph. R. H. DASTUR and N. A. BUHARIWALLA (Ann. Bot., 1928, 42, 949—964).—A spectrographic method is described by means of which the chlorophyll content of single leaves can be compared. This method has been applied to a study of the correlation between the chlorophyll content and the water content of the leaves of a number of plants. E. A. LUNT.

Membranes for ultra-filtration, of graduated fineness down to molecular sieves. J. W. McBAIN and S. S. KISTLER (J. Gen. Physiol., 1928, 12, 187-200).-Cellophane has many advantages as a membrane for use in ultra-filtration. Its permeability may be increased by allowing it to swell in water, when it becomes permeable to most substances soluble in water but impermeable to all but the finest collodial particles. Cellophane may be made permeable to solvents not completely miscible with water by allowing it to swell in water, and then replacing water by other solvents, if necessary through one or more intermediate solvents, e.g., by replacing the water first with ethyl alcohol and then with amyl alcohol. Cellophane membranes may be made impermeable to simple solute molecules by filtering through them a suitable colloidal material, e.g., cellulose dissolved in Schweitzer's reagent. A method is also given for the preparation of collodion membranes of graded permeability, and the properties of certain membranes of animal origin are discussed. W. O. KERMACK.

Technique of electrodialysis. G. ETTISCH and W. EWIG (Biochem. Z., 1928, 200, 250—257).—A cell is described for electrodialysis, usable with any membrane, the middle chamber of which can be varied in size from 50 to 1 c.c., the $p_{\rm H}$ being controlled by an indicator paper method.

P. W. CLUTTERBUCK.

Electrolysis in biochemistry. A. W. KEL and H. G. SCHIECK (Z. Biol., 1928, 88, 153-156).-Electrolysis was efficacious in preparing hexone bases from protein hydrolysates, as found by Foster and Schmidt (cf. A., 1923, i, 963), in separating glycocholic acid from bile, and creatinine from meat extract. Up to 80 volts and 120 amp. are used, sometimes with water-cooling. Lead electrodes in place of carbon, and porcelain diaphragms, with or without celluloid, in place of gelatin treated with formaldehyde, give better results. E. BOYLAND.