

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1928.

General, Physical, and Inorganic Chemistry.

[Structure of Fraunhofer lines and quantitative spectrum analysis of the atmosphere of the sun.]

W. ANDERSON (Z. Physik, 1928, 48, 447—448).—The assumption made by Unsöld (this vol., 456) that when the partial pressure of free electrons in the chromosphere is 10^{-6} atm. the latter still shows a continuous spectrum is held to be irreconcilable with observation.

J. W. SMITH.

Ultra-violet spectrum of radium emanation. S. WOLF (Z. Physik, 1928, 48, 790—794).—About 100 new lines have been measured in the range 3600—2400 Å. A new form of spectrum tube was employed made of "uviolet" glass, one end being blown to a thin bulb through which the ultra-violet light passed readily.

J. W. SMITH.

Relative intensity of spark and arc lines in the spark spectra of various elements. G. NAKAMURA (Japan. J. Phys., 1928, 4, 165—169).—The spectrum of radiation emitted from the spark between two electrodes of different metals was analysed by a quartz spectrograph and the intensities were measured by means of a microphotometer. Two spectra of sparks between gold and the metal under test, and between this metal and one from another column of the periodic table, were obtained simultaneously and the relative intensities of the lines of the element under investigation were found. The ratio of the intensities of arc lines to spark lines in the spark spectra is intimately related to the number of the surface electrons of the atom of the material used as the opponent electrode. The ratio usually increases as the number of electrons in the atom increases.

A. J. MEE.

Absolute intensity of the mercury line 2537 Å. P. KUNZE (Ann. Physik, 1928, [iv], 85, 1013—1057).—The absolute intensity of the mercury line 2537 Å. was measured by using a photo-electric method of investigating the selective absorption without the widening due to pressure. The apparatus and method are described in detail. A resonance chamber is used the construction of which is explained. The emission from the resonance chamber is discussed and it is shown that the lines may be distorted owing to deviations from the Maxwell distribution. It is possible to reduce the widening of the line due to the Doppler effect and make the line sharper by proper arrangements. The corrections for line structure, scattering due to diffraction and refraction in the resonance chamber, secondary resonance, and vapour pressure are discussed and calculated. The intensity obtained was reduced to the value for a vapour

pressure of mercury at 20°; the graph connecting the values of the intensity so obtained and the vapour pressure was not quite horizontal, and on extrapolation to zero vapour pressure gave for the absolute intensity the value 5.78 ± 0.13 , a value considerably greater than that obtained by earlier workers. The higher value is due to the elimination of the errors mentioned above. The case of complex structure is investigated. It is shown that it is possible to obtain from observations on widened lines the intensity of the undistorted line. The intensity does not depend on the magnitude of the Doppler widening. The intensity of the line was also determined for higher temperatures of the absorption chamber (up to 305°), and it was found that on extrapolation to zero vapour pressure as before, the same value for the intensity was obtained as when the chamber was at the ordinary temperature.

A. J. MEE.

Measurement of radiation from a tungsten lamp. H. C. VON ALPHEN (Ann. Physik, 1928, [iv], 85, 1058—1088).—The spectral distribution and the intensity curve of radiation from a 6-volt lamp were determined by two methods, one photographic, the other pyrometric. The emissivity of the tungsten in the ultra-violet region was obtained as a function of the wave-length by comparison with a carbon lamp of which the emissivity is known. The agreement between the two methods is good.

A. J. MEE.

Continuous emission spectra from the electrodeless discharge. G. BALASSE (Bull. Acad. roy. Belg., 1927, [v], 13, 543—546).—Continuous spectra from electrodeless discharges have been obtained with the elements potassium, rubidium, caesium, cadmium, mercury, phosphorus, bismuth, sulphur, and iodine. These elements are distributed over five columns of the periodic table, a fact which renders it probable that the continuous spectrum should be obtainable with any element. *A priori*, the passage from one state of ionisation to another is sufficient to account for the production of the spectra.

R. A. MORTON.

New type of discharge in neon tubes. F. A. LONG (Nature, 1928, 121, 1020).—The nature of the discharge in a neon tube when used as a safety device (Proc. Leeds Phil. Soc., 1927, 1, 185) differs from that produced in normal use. The investigations will be described elsewhere.

A. A. ELDRIDGE.

Arc spectrum of chlorine. O. LAPORTE (Nature, 1928, 121, 1021).—Turner's lines (A., 1926, 550) are now identified as follows: 1396.5 , ${}^2P_1-{}^4P_2$; 1389.9 , ${}^2P_2-{}^4P_3$; 1379.6 , ${}^2P_2-{}^4P_2$; 1363.5 , ${}^2P_1-{}^2P_2$; 1351.7 , ${}^2P_2-{}^2P_1$; 1347.2 , ${}^2P_2-{}^2P_2$; 1335.8 , ${}^2P_2-$



$2P_1$. Although the terms arising from the configurations ($3p^6$) and ($3p^5, 4s$) are still approximately "normal," the higher term group arising from ($3p^5, 4p$) is of higher rank. The situation is similar to that in the arc spectrum of argon.

A. A. ELDRIDGE.

New regularities in the band spectrum of helium. W. E. CURTIS (Nature, 1928, 121, 907—908).—Experimental results in substantial agreement with those just published by Dieke, Takamine, and Suga (this vol., 677) have been obtained. The effective electronic quantum numbers of the new levels are tabulated; the parhelium values are higher than the corresponding orthohelium values. Unambiguous evidence is thus available for the existence of molecular electronic levels which are additional to the ordinary atomic system of levels.

A. A. ELDRIDGE.

Continuous and band spectra of zinc vapour. H. VOLKRINGER (Compt. rend., 1928, 186, 1717—1719).—A study of the spectra of zinc vapour resulting from an electrodeless discharge at gradually rising temperatures indicates that for low vapour densities the continuous spectrum obtained is due to the passage of free electrons from one orbit to another. For high vapour densities a band spectrum extending from 2975 to 4800 Å. results, and is due to unstable molecules formed from the zinc atoms, some of which have become excited. A number of atomic aggregations probably exist, since the bands and the continuous spectrum (maximum at 2570 Å.) on which they are superimposed have not the same origin, whilst the regions of the tube corresponding with maximum intensity are different in the two cases.

J. GRANT.

Hydrogen rays in the electric arc. (MLEE.) M. HANOT (Compt. rend., 1928, 186, 1716—1717).—The H_β and H_γ rays have been studied by means of an electric arc between two copper electrodes, of which the anode is fixed whilst the cathode is attached to an electromagnet in series with the arc so that when the arc is broken it falls back on to the anode and re-strikes the arc. The difference in the absorption effects of these two rays is attributed to the difference in their structure previously indicated by a study of the spark discharge (this vol., 209).

J. GRANT.

Spark spectra of chlorine and of bromine. L. BLOCH and E. BLOCH (Ann. Physique, 1928, [x], 9, 554—555).—A correction (cf. *ibid.*, 7, 206; this vol., 98).

C. W. GIBBY.

Band spectra of mercury. (LORD) RAYLEIGH (Proc. Roy. Soc., 1928, A, 119, 349—357; cf. A., 1927, 1122).—A mercury band spectrum excited by fluorescence, with the continuous hydrogen spectrum as a source, is described. A remarkable feature of this spectrum is that the narrow band at 2540 Å. is found, although the resonance line 2537 Å. is absent. The band 2540 Å. has never before been obtained in emission without the resonance line accompanying it in much greater intensity. It is also observed that the region of continuous emission on the short-wave side of the bands 2345, 2338, 2334, etc. is traceable as far as 2150 Å., thus extending much beyond the position of the forbidden line 2270 Å. which was in a

former investigation (*loc. cit.*) under other conditions the limit of this continuous spectrum. The series of emission bands 2345, 2338, etc. has been examined with large resolving power, using as source a high-tension alternating-current discharge in dense vapour, between mercury electrodes. No trace is observed of the underlying bands of 1 Å. spacing which are seen so clearly in absorption. A remarkable structure is found in the emission band 2482—2476 Å. described by Stark and Wendt as continuous (cf. A., 1913, ii, 647). The proper description of this structure in terms of the quantum theory is, however, problematic. This band does not occur in absorption.

L. L. BIRCUMSHAW.

Stark effect of the fine structure of hydrogen. R. SCHLAPP (Proc. Roy. Soc., 1928, A, 119, 313—334).—An investigation of the influence of an electric field on the fine structure of the levels of the hydrogen atom, by a method embodying the new theory of fine structure which has developed out of the idea of the spinning electron. The work is based on the wave equations of Darwin and Dirac. Attention is directed chiefly to the two extreme cases of weak and strong fields. In weak fields, all the fine-structure levels except the highest split up into several, with separations proportional to the first power of the field; in the highest level the separations are proportional to the square of the field. The fine structure of each of the equidistant levels of the ordinary Stark effect in stronger fields is found. The case of H_α is worked out in detail.

L. L. BIRCUMSHAW.

Spark spectrum of copper. A. C. MENZIES (Proc. Roy. Soc., 1928, A, 119, 249—256).—The method of obtaining spectrograms with one very short exposure by the fusion of wires, described previously (this vol., 99), has now been used for copper in the Schumann region, where it has several advantages over the usual arc and spark discharges in a vacuum. The lines 1358.76, 1367.92, and 1472.38 Å. are allocated to ($1^1S_0 - a^1P_1$), ($1^1S_0 - a^3D_1$), and ($1^1S_0 - a^1P_1$), respectively. This identifies 1^1S_0 , the basic term corresponding with the normal orbit of Cu II, with the term-value —21929.4. Photographs of the spectrum of copper-gold have been taken with a small quartz-prism spectrograph, the source being a Pfund arc. Taking as standards three calculated copper lines, the wave-lengths in the copper-gold spectrum have been measured, and are compared with their values as calculated by Shenstone (A., 1927, 389) and by McLennan and McLay (A., 1926, 875), respectively. The copper and gold wave-lengths are found to be consistent with one another, so that probably Shenstone's scheme of copper spark terms and McLennan and McLay's scheme for the gold arc are both correct.

L. L. BIRCUMSHAW.

Structure of the yellow sodium lines (5890, 5896). H. SCHÜLER (Naturwiss., 1928, 16, 512—513).—A special form of light source (A., 1926, 215) allows the light from metal vapours to be observed at very low temperatures. This materially reduces the Doppler effect so that finer line structure may be disclosed if electrical disturbances are eliminated. The investigation of the sodium resonance lines at the temperature of liquid air shows that the line 5890 Å.

consists of two components, $\Delta\lambda$ being 0.02 Å., and the intensity ratio being approximately 1:2.5, the weaker component being towards the violet. The line 5896 Å. also consists of two components, $\Delta\lambda$ being 0.02₃ Å. and the intensity ratio 1:2.0. The weaker component is again on the violet side. The fine structure of the *D*-lines has been analysed by means of a Perot-Fabry etalon. This has not hitherto been possible because of excessive pressure and Doppler effect. The new structure is unexpected both from quantum numbers and from the point of view of isotope effects. Nuclear effects are indicated.

R. A. MORTON.

Multiplets in the Co II spectrum. W. F. MEGGERS (J. Washington Acad. Sci., 1928, 18, 325—330).—A portion of the under-water spark spectrum of cobalt (A., 1927, 910) has been re-measured, and by comparison of their behaviour in the spark and arc, several classes of spark lines have been recognised. Many lines absorbed in the under-water spark are partly self-reversed in the spark in air. A group in the region 2249—2449 Å. has been arranged as a trio of multiplets $^5F'—^5(D', F, G')$, whilst a weaker overlapping group (2192—2339 Å.) has been arranged on the basis of line intensities as a second trio of multiplets $^3D—^3(P, D', F)$. The triplet-*D* term occurs in a strong group of lines 3353—3621 Å., constituting the intersystem combinations $^3D—^5(D', F)$. The latter appear to be the only set of strong Co II lines lying within the range of solar spectrum transmitted by the earth's atmosphere, nearly all other strong lines being on the ultra-violet side of 2900 Å. Nine lines in the region 3353—3621 Å. are shown to be coincident as regards both intensity and wave-length with absorption lines in Rowland's "Preliminary table of solar spectrum wave-lengths." The very low intensities of these Co II lines in the sun is due to the fact that the lines involve excited states of ionised cobalt atoms.

R. A. MORTON.

Pseudo-spectrum of the energy matrix. A. WINTNER (Z. Physik, 1928, 48, 731—732).

J. W. SMITH.

Explanation of some properties of spectra from the quantum mechanics of the spinning electron. II. J. VON NEUMANN and E. WIGNER (Z. Physik, 1928, 49, 73—94).—Mathematical (cf. this vol., 344).

J. W. SMITH.

Absorption by excited hydrogen. N. ROBINSON (Z. Physik, 1928, 49, 137—145).—Measurements have been made of the light absorption of hydrogen excited by unidirectional pulses of variable frequency obtained by rectifying damped wave trains of oscillations. Absorption takes place when the half-period of the frequency characteristic of the wave train is of the same order of magnitude as the life period of the excited hydrogen atom. The upper limit of the life period thus measured is 10^{-6} sec.

J. W. SMITH.

Spark spectrum of sodium. S. FRISCH (Z. Physik, 1928, 49, 52—58).—The sodium spark spectrum generated in a discharge tube containing metallic sodium has been surveyed and more than 100 lines have been measured in the range 4000—2500 Å. A number of these lines have been classified

in a manner analogous to that employed in the case of neon.

J. W. SMITH.

Series spectrum of sodium, Na II. I. S. BOWEN (Physical Rev., 1928, [ii], 31, 967—968).—Seventy-four lines in the sodium spark spectrum are classified as combinations between 23 terms of Na II. The ionisation potential is 47.0 ± 0.5 volts.

A. A. ELDRIDGE.

Theory of the excitation of spectra by atomic hydrogen. J. KAPLAN (Physical Rev., 1928, [ii], 31, 997—1002).—The theory is based on the hypothesis that in a three-body collision two hydrogen atoms can be linked to form a molecule in any one of the vibration states of its normal electronic level. It is postulated that the probability of excitation of the third body is the greater, the nearer the energy required is to the difference between the energy of recombination and that retained by the hydrogen molecule in one of its vibration states.

A. A. ELDRIDGE.

Theory of the electric discharge through gases. P. M. MORSE (Physical Rev., 1928, [ii], 31, 1003—1017).

Zeeman pattern of the hyperfine structure lines of the resonance line of mercury. W. A. MACNAIR (Physical Rev., 1928, [ii], 31, 986—996).—The results already published (A., 1927, 804) are essentially correct. In addition, four anomalous perpendicular components have been found.

A. A. ELDRIDGE.

Stark effect and series limits. H. P. ROBERTSON and (MISS) J. M. DEWEY (Physical Rev., 1928, [ii], 31, 973—982).—Following a consideration of the energy of conditionally periodic and aperiodic orbits in hydrogen-like atoms under the influence of an external electric field, it is concluded that the line spectrum of such an atom must end at a point on the long wave-length side of the normal series limit, and that the continuous spectrum may extend even further within the normal series limit.

A. A. ELDRIDGE.

Multiplet separations. S. GOUDSMIT and C. J. HUMPHREYS (Physical Rev., 1928, [ii], 31, 960—966).—Formulae for the separations of normal multiplets, arising from general configurations, are derived from the fundamental assumption that they are due to the interaction energy between spin and orbital magnetism of the electrons.

A. A. ELDRIDGE.

Multiplet separations for equivalent electrons and the Röntgen doublet law. S. GOUDSMIT (Physical Rev., 1928, [ii], 31, 946—959).—Theoretical. Expressions are derived for the separation of multiplets arising from configurations of equivalent electrons. The properties of Landé's Γ factors are studied.

A. A. ELDRIDGE.

Negative absorption of radiation. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, 122, 12—13).—When benzene is irradiated by monochromatic light, the radiation scattered by the molecules contains several spectral lines of modified frequencies. The difference between the incident and scattered frequencies is exactly equal to an infra-red frequency of the molecule, so that the process of

modified scattering involves the absorption of radiation by the molecule. Experimental results show the existence in the liquid of molecules at energy levels higher than the normal, and that the incident radiation induces a return to a lower state of energy.

A. A. ELDRIDGE.

First spark spectrum of krypton. P. K. KICHLU (*Naturwiss.*, 1928, **16**, 346).—The work of Abbink and Dorgelo (this vol., 338) furnishes material for the completion of the analysis of the first spark spectrum of krypton. The lowest states are 2P -terms originating from an electron configuration $5N_2$, and these combine with a set of terms $^4P^2P^2D^2S$ coming from $4N_2O_1$. The next set of terms are obtained from $4N_2O_2$ combination. These terms and those from $4N_2O_3$ and $4N_2P_2$ have been obtained and account for about 200 lines.

R. A. MORTON.

Structure of the negative bands of nitrogen. G. HERZBERG (*Ann. Physik*, 1928, [iv], **86**, 189—213).—The electrodeless ring discharge through nitrogen at very low pressures produces the negative bands in purity. On account of this purity of the spectrum, and because of its extent and brightness, it has been possible to observe the inversion point of the degradation of the bands. Tail bands analogous to the cyanogen tail bands appeared. It is concluded from the structure of these latter bands that N_2^+ can be dissociated in any elementary way by high-velocity electrons.

W. E. DOWNEY.

Distribution of energy and luminosity in the cross-section of the positive column in neon and helium. G. ZWIEBLER (*Ann. Physik*, 1928, [iv], **86**, 241—290).—The energy is found to decrease from the middle of the column to the edge, quickly at first but more slowly as the edge is approached. The energy decrease in a section is greater the greater is the energy of the lines emitted from the section. At fixed current density, the energy decrease is, at first, less than proportional to the pressure, but with increasing pressure tends, asymptotically, to a limiting value. The intensity of the individual spectral lines increases at a greater rate than that of direct proportionality to the current strength.

W. E. DOWNEY.

Absorption of the vapour of excited mercury and reversal of the green ray and of its satellites. M. PONTE (*Compt. rend.*, 1928, **187**, 37—39).—For rays of different series no relation exists between the intensity of the rays emitted by excited mercury vapour and that of the absorption of the corresponding arc rays. The rays $^3P_{012}^3S$, $^3P_{012}^3D_{123}$, $2^1P_1-m^1D_2$, and $2^1P_1-m^3D_2$ show absorption, the latter pair to a slight extent only. The PS series is more strongly absorbed than the PD series, the absorption of the rays 2^3P_0 and 2^3P_2 being equivalent in the former case, and 2^3P_0 showing a strong absorption in the latter. Reversal of the rays is best studied by the insertion of excited mercury vapour between the plate and a cooled Cotton arc, and was observed for λ 4358, for the green ray, and for six of its satellites, but not for the yellow rays.

J. GRANT.

Photo-electric current as a function of the field in air at ordinary pressures. A. BLANC (*Compt.*

rend., 1928, **186**, 1835—1837).—Comparison of the curves obtained for the same metal subjected to different illuminations with those for different metals showed that the form of the curve depends on the nature of the metal. Saturation is attained rapidly in a vacuum, since the number of electrons emitted does not depend on the field. At sufficiently high pressures, however, the electrons ionise the gas in accordance with Thomson's theory, the mean number of ions produced by each increasing with the field in a manner depending on the metal. The initial energy and capacity for ionisation of the electrons depend on the distance they travel in the direction of the field before meeting a molecule. They may even ionise several molecules before uniting with one of them, and saturation is not attained.

J. GRANT.

Resonance line of the iodine atom and the optical dissociation of iodine molecules. L. A. TURNER (*Physical Rev.*, 1928, [ii], **31**, 983—985).—The line 1830.4 Å. is probably the resonance line of the iodine atom, corresponding with a critical potential of 6.75 volts. Strong illumination of iodine vapour apparently causes dissociation into atoms, since light of the above wave-length is more strongly absorbed by illuminated than non-illuminated vapour.

A. A. ELDRIDGE.

New photo-electric observation with thin layers of alkali metals. B. GUDDEN (*Naturwiss.*, 1928, **16**, 547).—An alternative explanation of Suhrmann's work under the above title (this vol., 680) is given.

R. A. MORTON.

Photo-electric and thermionic properties of iron. A. B. CARDWELL (*Proc. Nat. Acad. Sci.*, 1928, **14**, 439—445).—The variation of the photo-electric current of iron with time of outgassing was determined. The variation is complex. After a time the photo-electric current increased in steps as the time of heating increased, changing less rapidly as the outgassing became more complete. A thoroughly outgassed specimen showed no fatigue for 12 hrs. after treatment. When this state was reached, the strength of the photo-electric current depended on the rate of cooling of the iron filament. There was a decrease in the photo-electric sensitivity if a filament heated above 910° was suddenly cooled, this being due to the retention of part of the γ -iron. The variation of the photo-electric current with temperature of the filament was investigated for iron which had been outgassed by heat treatment for 150 hrs. The variation is complex. Between about 475° and 768° there is a decrease in photo-electric current due to a pure temperature effect. At 768° (where there is a transition of α - to β -iron) the sensitivity remains constant or increases slightly. Near 910° (transition of β - to γ -iron) there is an abrupt decrease in the sensitivity. The thermionic current was also measured and plotted against heating current. There is an abrupt change in the curve at 910°. The long wave-length limit for thoroughly outgassed iron lies between 2580 and 2652 Å. The work function, obtained by substituting these values in Einstein's photo-electric equation, is 4.72 ± 0.07 volts. The question of whether the abrupt changes in the photo-electric and

thermionic currents are due directly or only indirectly to the crystallographic changes in the iron is discussed.

A. J. MEE.

Angular distribution of slow electrons on passing through metal sheets. E. RUPP (Ann. Physik, 1928, [iv], 85, 981—1012).—The above distribution is photographically investigated. The metals used are chosen from those with cubical, tetragonal, and hexagonal space-lattices. The investigation covers two main effects: (a) the scattering of electrons in a sphere about the point of impinging as centre; (b) the "diffraction" of electrons into discrete rings. These electron diffraction rings can be fitted in with X-ray observations, using the Debye-Scherrer method. The calculated refractive indices of the metals for electrons always exceed unity. This is in apparent contradiction with the results of Davisson and Germer, who found the indices to be less than unity. If, however, the observations of these investigators for small angles only are taken, these give an index greater than one. The refractive index falls with increasing electron velocity, but for a given velocity is constant for a given metal. The inner lattice potentials are calculated from the values of the refractive indices; these lie between 10 and 20 volts for the metals considered, and within the accuracy of the experiments this potential is independent of the velocity. It appears to be a characteristic constant for any metal.

A. J. MEE.

Mobilities of gas ions in sulphur dioxide and mixtures of sulphur dioxide and hydrogen. L. DU SAULT and L. B. LOEB (Proc. Nat. Acad. Sci., 1928, 14, 384—393; cf. this vol., 453).—Two sets of values of mobilities were observed at atmospheric pressure in sulphur dioxide. The values for the supposedly less pure sample were 0.34 cm./sec. and 0.32 cm./sec., respectively, for positive and negative ions. For the other sample the values 0.48 cm./sec. and 0.44 cm./sec. on the same scale were observed. Negative electrons could not be detected down to 0.05 cm. pressure of sulphur dioxide in 3.8 cm. of pure hydrogen. The effect of sulphur dioxide at higher concentrations in sulphur dioxide-hydrogen mixtures is similar to the effect of ammonia in ammonia-hydrogen mixtures. At low concentrations the positive mobilities in hydrogen were 22 cm./sec. per volt/cm.

W. E. DOWNEY.

Statistical experiments on the motion of electrons in gases. R. D'E. ATKINSON (Proc. Roy. Soc., 1928, A, 119, 335—348; cf. Townsend, A., 1926, 3; Townsend and Focken, *ibid.*, 878).—An attempt to explain Townsend's experiments (*loc. cit.*) on the ionisation of gases by collision and the critical potential of gases on the basis of the quantum theory. The most important conclusion reached is that the ionisation potential of helium is below 25 volts. This result is discussed on the assumption that the gas always contains small quantities of impurities, and with special consideration to collisions of the second kind (*i.e.*, collisions between a normal and an excited, but not necessarily metastable, molecule, such that the potential energy of the excited molecule is wholly or partly removed from it; some

of the energy thus made available may be used to put the second molecule into an excited state, and the balance appears in the form of kinetic energy). The production of ions in the gas at a voltage well below the ionisation potential is considered to be firmly established. The fact that above about 60 volts the current rises exponentially may be explained by consideration of the normal diffusion of the metastable atoms between the time of their formation and the collision of the second kind. The distance they will diffuse depends both on the amount of impurity present and on the diameter of the metastable atom. It is shown that α/p is a single-valued function of X/p (where α is the exponential constant of the curves, p is the pressure, and X the field strength), a relation experimentally obtained by Townsend. A somewhat similar verification is found by taking the statistical figure for the average loss of energy on collision.

L. L. BIRCUMSHAW.

Direct determination of the magnetic moment of a single electron. T. SEXL (Z. Physik, 1928, 48, 729—730).—A technique is devised for determining the magnetic moment of a single electron by studying the behaviour of small droplets in a magnetic field.

J. W. SMITH.

Electrons and positive ions in pure argon. M. A. DA SILVA (Compt. rend., 1928, 187, 32—35).—Mobility measurements with alternating in place of direct fields, for effective voltages of from 40 volts/cm., have confirmed the earlier conclusions (this vol., 341) that all the negative ions in pure argon, even at atmospheric pressure, are free electrons. The mobility (K) is related to the critical voltage (V_0), the frequency of the alternating field (n), and the distance between the condenser plates (d) by the expression $K = \pi nd^2/V_0\sqrt{2}$. The critical voltage of the positive ions is also indicated on the curves.

J. GRANT.

Attempt to add an electron to the nucleus of an atom. W. D. HARKINS and W. B. KAY (Physical Rev., 1928, [ii], 31, 940—945).—Electrons with a velocity of $138-145 \times 10^3$ volts were caused to strike the surface of the liquid mercury anti-cathode of an X-ray tube; no gold was, however, detected. Hence, either too small a proportion of electrons became attached, or the nuclei produced were insufficiently stable.

A. A. ELDRIDGE.

Lead isotopes and the problem of geologic time. C. S. PIGGOT (J. Washington Acad. Sci., 1928, 18, 269—273).—The possibility of determining the ages of rocks by determination of the uranium:uranium-lead and thorium:thorium-lead ratios is discussed.

J. W. SMITH.

[Relation between atomic number and] atomic weight. A. VON FISCHER-TREUFELD (Ann. Physik, 1928, [iv], 85, 1113—1116).—The following relationship is proposed between atomic number and atomic weight: $3(2n)^{\frac{1}{2}} + 5[(n-1)/3]^{\frac{1}{2}} + 1 \approx 8w^{\frac{1}{2}}$, where n represents the atomic number and w the atomic weight of an element. The values for the atomic weights obtained by means of this expression agree fairly well with the usually accepted values. The formula is deduced from considerations of the nuclear atom.

A. J. MEE.

Preparation of highly concentrated polonium by distillation. E. RONA and E. A. W. SCHMIDT (Z. Physik, 1928, 48, 784—789).—Polonium is deposited on a large surface of platinum foil by electrolysis of a solution of radium-*D* in 0.1*N*-nitric acid, using a current density of 5×10^{-6} amp. per cm.² The electrodes are then cut into thin strips and heated in a quartz tube in a current of hydrogen, the polonium being condensed in a platinum capsule cooled by means of a large copper rod.

J. W. SMITH.

Visual observation of H-particles. H. PETERSSON (Z. Physik, 1928, 48, 795—798).—Two arrangements are described. In the first a polonium preparation is enclosed in a glass capillary of 20 μ wall thickness coated inside with a layer of paraffin wax of similar thickness. The α -particles are unable to penetrate the tube, whereas the H-particles generated in the paraffin wax pass readily through it and their paths are rendered visible by Wilson's method. In the second arrangement the polonium preparation is covered by a thin mica sheet, coated on the lower side with a thin layer of paraffin wax. Supported above this is a screen coated with zinc sulphide, scintillations being observed by means of a lens system mounted above the screen.

J. W. SMITH.

Photographic action of H-particles from paraffin and atomic fragments. M. BLAU (Z. Physik, 1928, 48, 751—764).—It is found that the sensitivity of the photographic plate is unsuitable for quantitative measurement of atomic scattering, but this method may be used conveniently for the qualitative detection of H-particles.

J. W. SMITH.

Radium content of Stone Mountain granite. C. S. PRIGOT (J. Washington Acad. Sci., 1928, 18, 313—316).—The average radium content of Stone Mountain, Georgia, granite is 4.826×10^{-12} g. per g. of granite.

C. W. GIBBY.

[Apparatus for the determination of] the number of ions produced by the α -particles of radium-*C'* in air. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1928, 186, 1722—1724).—The α -radiation of radium-*C'* has been compared with a radium standard by means of its γ -radiation and using an apparatus in which the ionisation produced by a known fraction of the total radiation of the source is measured. The low-speed β -rays are eliminated by a magnetic field, and the effect of the γ -rays is determined by measuring the ionisation produced with and without a magnetic field, and after interposing a series of aluminium screens 0.02—0.1 mm. thick. The easily absorbed γ -radiation from radium-*B* or -*C+C'* has an ionising effect which is negligible compared with that of the α -particles.

J. GRANT.

Number of ions produced by the α -particles of radium-*C'* in air. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1928, 187, 43—45).—The authors continue the description of their apparatus (see above) and its use. A final corrected value of 1944 ± 10 E.S.U. for the ionisation current produced in the angle 2π by the α -particles emitted from 1 millicurie of radium-*C'* was obtained, which gives 2.2 or 2.36×10^5 for the number of ions produced by one α -particle from radium-*C'*, according to the value

taken for the number of α -particles from 1 g. of radium (3.7 or 3.45×10^{10} , respectively). Exact proportionality of ionisation to energy is not obtained for the radiations of radium-*C'*.

J. GRANT.

Efficiency of β -recoil of thorium-*B*. K. DONAT and K. PHILIPP (Naturwiss., 1928, 16, 513).—In an earlier paper (this vol., 3) the efficiency of the β -recoil from thorium-*B* was found to be 2—6.5% of the theoretical. In order to test whether the low yield is due to evaporation of recoil atoms from the collecting surface, the latter has been maintained at low temperatures. At -90° the efficiency was 9—11%, and at -170° , 33%. Further work is necessary to determine whether the yield becomes theoretical with extremely low temperatures.

R. A. MORTON.

Visibility of β -scintillations. H. PETERSSON and G. KIRSCH (Naturwiss., 1928, 16, 463).—Polemical against Bothe and Fränz (*ibid.*, 204).

W. E. DOWNEY.

Regularity of radioactive disintegration. H. T. WOLFF (Z. Physik, 1928, 48, 745—746).—The relation advanced by Sokolow between the disintegration constant of an α -ray emitter and its number in the radioactive series also follows directly from the equation previously derived by Wolff (A., 1920, ii, 578) in connexion with the Geiger-Nuttall relation.

J. W. SMITH.

Atomic fragments, reflected α -particles, and X-rays generated by α -particles. W. BOTHE and H. FRÄNZ (Z. Physik, 1928, 49, 1—26).—The atomic disintegration, measured by the H-particle emission, when beryllium, carbon, aluminium, and iron were bombarded with α -particles from polonium has been investigated. The values obtained are in agreement with those of Rutherford and Chadwick and show that the results of Kirsch and Pettersson were too high.

J. W. SMITH.

Atomic groupings for emanations and mixtures of radioelements. (MLE.) C. CHAMÉ (Compt. rend., 1928, 186, 1838—1840).—The author's experiments (A., 1927, 1120) have been extended and have shown that radon, thoron, or actinon liberated in air or dissolved in mercury form groups of atoms, whilst in mixtures of radioelements heterogeneous groups of atoms from both sources, and groups characteristic of atoms all of the same family, are both formed.

J. GRANT.

Mechanism of the oscillation of electrons. H. E. HOLLMANN (Ann. Physik., 1928, [iv], 86, 129—188).—It is possible to obtain simultaneous electron oscillations of different kinds in the same valve. The different kinds of electron oscillation in the Barkhausen-Kurz decelerating field are described. Four frequency ranges are possible: (a) Barkhausen-Kurz oscillations; (b) Gill and Morrell oscillations; (c) by using a grid of finer mesh it is possible to obtain oscillations of higher frequency, which take place, not in the anode-cathode space, but between the anode and grid only; (d) by using a valve with electrodes of smaller dimensions it is possible to get oscillations of higher frequency.

A. J. MEE.

Refraction quotient of the De Broglie waves of electrons. A. JOFFÉ (Z. Physik, 1928, 48, 737—738).—

Although the work of Schmidt discussed by Klemperer (this vol., 344) can be explained in a simple manner on the theory of wave mechanics, it by no means proves the latter theory, since the same result can be reached from ordinary electrostatics. J. W. SMITH.

Ionisation in the upper atmosphere of the earth. E. O. HULBERT (Physical Rev., 1928, [ii], 31, 1018—1037).—A theory of the ionisation of the upper atmosphere of the earth by the ultra-violet light of the sun is based on known laws of pressures and constitution of the high atmosphere, ionic recombination, attachment of free electrons to neutral molecules, and diffusion of ions. A density of 10^4 to 10^5 electrons per cm^3 , or 10^9 to 10^{10} ions per cm^3 , or a suitable mixture of ions and electrons, seems possible down to 100 km. Ozone may be formed by ultra-violet light of wave-length 1300—1800 Å.

A. A. ELDRIDGE.

Correspondence relationship between matrices and Fourier coefficients in the theory of the hydrogen atom. C. ECKART (Z. Physik, 1928, 48, 295—301).—Mathematical. R. W. LUNT.

Theory of magnetic electrons. I. D. IWANENKO and L. LANDAU (Z. Physik, 1928, 48, 340—348).—Mathematical. R. W. LUNT.

Helium nucleus as the foundation of other atom nuclei. H. PETTERSSON (Z. Physik, 1928, 48, 799—804).—From the point of view of the new at. wt. determinations of Aston, arguments are brought forward against the theory that elements in general are built up from helium nuclei.

J. W. SMITH.

Quantum theory of rotating electrons. F. MOGLICH (Z. Physik, 1928, 48, 852—867).—Mathematical. J. W. SMITH.

Dirac's theory of spinning electrons. J. VON NEUMANN (Z. Physik, 1928, 48, 868—881).—Mathematical (cf. Dirac, this vol., 344, 456).

J. W. SMITH.

Dirac's theory of spinning electrons. A. LANDÉ (Z. Physik, 1928, 48, 601—606).—Mathematical.

J. W. SMITH.

Application of the Fermi statistics to the distribution of electrons under fields in metals and the theory of electrocapillarity. O. K. RICE (Physical Rev., 1928, [ii], 31, 1051—1059).—Theoretical. A. A. ELDRIDGE.

Statistical methods in quantum theory. R. J. CLARK and W. H. WATSON (Nature, 1928, 122, 12).

Evidence for the continuous creation of the common elements out of positive and negative electrons. R. A. MILLIKAN and G. H. CAMERON (Proc. Nat. Acad. Sci., 1928, 14, 445—450).—The evidence derived from the study of cosmic rays that the more stable and abundant elements (e.g. helium, oxygen, silicon, and iron) are being formed at the present time directly out of protons and electrons is summarised. (1) Pilot balloon experiments have shown that there are no strong radiations of wave-length intermediate between those of the γ -rays and the cosmic rays entering the earth's atmosphere. (2) The cosmic-ray spectrum consists of definite

bands. Hence the rays cannot be formed in the same way as X-rays, as has been suggested, but are probably produced by definite and continually recurring atomic transformations involving energy changes of a magnitude much greater than any occurring in radioactive processes. (3) Using the Einstein equation and the Dirac formula, it is possible to show that the only transformations which can give rays of the penetrating power of the cosmic rays are those corresponding with the building up of the abundant elements from hydrogen. The complete breaking up of hydrogen might be another possibility, but there are reasons against this. (4) The results of previous work have shown that there are three cosmic-ray bands of absorption coefficients 0.35, 0.08, and 0.04 per m. of water, respectively. The theoretical absorption coefficients if the rays were produced (a) by formation of helium from hydrogen, (b) by formation of oxygen from hydrogen, (c) by formation of silicon from hydrogen, would be 0.30, 0.075, and 0.043, respectively. A. J. MEE.

Wave mechanics of the atom lattice. M. J. O. STRUTT (Ann. Physik, 1928, [iv], 86, 319—324).—Mathematical. W. E. DOWNEY.

Mechanism of the reaction between sodium vapour and copper halides. II. V. KONDRATĚV (Z. Physik, 1928, 48, 310—322).—The reaction between sodium and potassium vapour and the vapour of cupric chloride and bromide in the neighbourhood of 300° has been examined. The spectrum of the light emitted by the reacting vapour is that of the corresponding cuprous halide. Following a discussion of the energy changes taking place with the formation of excited molecules of the cuprous halide, it is concluded that the reaction takes place at the surface of the containing vessel between solid cupric halide and gaseous alkali metal forming gaseous cuprous halide and solid alkali metal halide. Analysis of the solid product of the reaction confirms this view. The distribution of alkali metal halide along the length of the tube in which the alkali metal vapour meets the cupric halide vapour shows a sharp maximum, as also does the distribution of intensity of the light emission, which, however, lies nearer to the source of alkali metal vapour; this result, which also obtains in the reaction between sodium and mercuric chloride vapours, is analogous with that between sodium and iodine vapours.

Earlier experiments indicated that the reaction between sodium and mercuric chloride vapours was homogeneous. This has been confirmed by calculating the rate of formation of sodium chloride from the vapour pressure of the reacting vapours to be 21.5×10^{20} mols. per hr., whilst the experimental value is 5.5×10^{20} . R. W. LUNT.

Afterglow of oxygen and nitrogen in air. K. STÖCK (Z. Physik, 1928, 48, 358—359).—Phenomena essentially similar to those described by Herzberg (this vol., 457) have been observed by examining the discharge in a vacuum tube in the pressure range 2—14 mm. in the direction of the flow of current.

R. W. LUNT.

H_α emission in the positive column. E. LAU (Z. Physik, 1928, 48, 824—830).—The intensity and

polarisation of the H_α line from the positive column in a discharge tube have been examined with respect to the gas pressure in the range 0.05–0.7 mm. The observed Stark effect is of the same order as that calculated by Sommerfeld's theory. R. W. LUNT.

Spectroscopic analysis of the light obtained by molecular diffusion of a monochromatic radiation by a fluid. J. CABANNES and P. DAURE (Compt. rend., 1928, 186, 1533–1534).—Spectroscopic measurements have been made of the change in wave-length, the symmetrical enlarging of the exciting ray, and of the diffusion spectra accompanying the Raman effect (this vol., 461) for benzene and ether excited by the rays 4046 and 4358 Å. Contrary to previous theories (this vol., 571, 686), secondary rays of frequency higher than that of the exciting ray were not detected in the diffusion spectra, and the emission of such rays is therefore not symmetrical with respect to the fundamental ray. J. GRANT.

First ultra-violet characteristic frequency of a simple crystal. R. HILSCH and R. W. POHL (Z. Physik, 1928, 48, 384–396).—The ultra-violet absorption spectra of thallous chloride, bromide, and iodide and of lead chloride and iodide have been observed by mounting a crystal lamina of 1 mm thickness under pressure between two silica plates. The first characteristic frequencies thus observed agree very well with those of alkali halide phosphors containing these substances in fine division. Additional data for the absorption spectra of crystalline iodine and silver halides are also given.

J. W. SMITH.

Broadening of hydrogen chloride lines by foreign gases. H. W. KUSSMANN (Z. Physik, 1928, 48, 831–844).—The influence of various indifferent foreign gases has been investigated by absorption measurements, using a quartz lens method of focal separation. Argon, in spite of its atomic symmetry, exerts a strong influence, so the broadening is supposed to be due, not to an intramolecular effect, but to Lorentzian collision damping. Hence for any single foreign gas the absorption change brought about by the broadening of the line is proportional to the increase in the number of collisions, but this proportionality factor differs with different gases.

J. W. SMITH.

Light absorption of some salts. A. HANTZSCH (Z. physikal. Chem., 1928, 134, 453–455).—The observation of Viterbi (A., 1927, 1122) that solutions of the alkaline-earth halides show marked selective absorption in the ultra-violet is confirmed for barium chloride. The relation between constitution and colour of mercuric iodide and of tin tetraiodide in the solid state and in solution is discussed. The view is maintained that red mercuric iodide is an associated "pseudo-complex salt" in the solid state, but is converted by dissolution into the unimolecular colourless pseudo-salt.

O. J. WALKER.

Spectrum of the hydrogen molecule. O. W. RICHARDSON and P. M. DAVIDSON (Nature, 1928, 121, 1018).—The following are believed to be the final vibrational differences ($1'' \rightarrow 0''$, $2'' \rightarrow 1''$, etc.) of the lowest rotational levels of the band systems previously examined (A., 1927, 916): 1312.55(4),

1276.60(2), 1242.382, 1209.062, 1176.33(3), 1144.00, 1112.08, 1081.29. Dieke and Hopfield's B states are considered to be identical with the authors' final states. The value $2B_0'' = uv_0 = 31.1$ is deduced.

A. A. ELDRIDGE.

Absorption of ultra-violet light by carbohydrates. L. KWIECINSKI, J. MEYER, and L. MARCHLEWSKI (Z. physiol. Chem. 1928, 176, 292–293).—In general, pure sugars do not show selective absorption. A concentrated solution of α -methylglucoside shows a faint band about 2800 Å, but β -methylglucoside does not. Glucosan shows strong absorption.

H. BURTON.

Absorption curves of the pulegonenols. J. SAVARD (Compt. rend., 1928, 186, 1738–1741; cf. Schoù, A., 1927, 751).—The ultra-violet absorption curves of pulegone, pulegonenol, and of their corresponding *iso*-compounds show that replacement of the CO group by the C·OH group involves the disappearance of the first band (at 3000–3200 Å.) attributed to the former group, and the appearance of the first portion of a band in the extreme ultra-violet attributed to the latter. The position of the ethylenic band is not appreciably changed, although the intensity of its absorption maximum is lowered. There is evidence of molecular combination between pulegone and *isopulegone* or its enol.

J. GRANT.

Intermetallic compounds in the vapour state. The spectra of the alkali metals, and of their alloys with each other. J. M. WALTER and S. BARRATT (Proc. Roy. Soc., 1928, A, 119, 257–275).—An apparatus is described for the determination of the vapour density of potassium by the Victor Meyer method at 950°. A special device was employed for the accurate weighing of the potassium (free from oxide) into the steel bottle. The results show that at 935° the ratio $[K_2]/[K]$ does not exceed 5×10^{-2} , and the conclusion is reached that the alkali metals at their b. p. contain not more than 5%, and probably only about 2%, of molecules of the type M_2 . The band spectra of the alkali metals lithium, sodium, potassium, rubidium, and caesium have been re-investigated and a number of new bands are described. Metals which are known to possess a measurable proportion of polyatomic molecules show bands in their absorption spectra, and the observation of such bands is considered a delicate test for the existence of association in the vapours. From an examination of the absorption spectra of the mixed vapours of the alkali metals it is shown that these metals form a complete series of binary molecules with each other in the vapour state. The band systems lie, in general, near the lines of the principal series of the constituent atoms, but the molecules containing lithium are exceptions to this rule. Most of the alkali metal molecules possess a distinct type of absorption spectrum, in addition to these band systems. The second type consists of an isolated diffuse band, which is probably a true continuous spectrum. It is suggested that these regions correspond with the continuous absorption of the halogen molecules, and the heats of formation of the alkali metal molecules have been worked out on this basis.

L. L. BIRCUMSHAW.

Ultra-violet absorption spectrum of chlorophyll in alcoholic solution. E. LEWKOWITSCH (Biochem. J., 1928, 22, 777—778).—Absorption maxima are shown at 4200 and 3250 Å. No trace could be found of any further minimum or descent of the curve, which rose steeply below a wave-length of 2400 Å. S. S. ZILVA.

Absorption of plane polarised infra-red radiation by calcspar. F. MATOSI (Z. Physik, 1928, 48, 616—623).—The absorption of plane polarised infra-red radiation by calcspar, with the optical axis parallel with the electrical vector, has been investigated over the range 2—16 μ . Between 5.3 and 8 μ and round 11.5 μ measurements were also made with the optical axis in different positions. The loss by reflexion was measured and correction applied. Combination relations between the different absorption bands are deduced. J. W. SMITH.

Spectrum of gold chloride. W. F. C. FERGUSON (Physical Rev., 1928, [ii], 31, 969—972).—Auric chloride vapour was introduced into a stream of active nitrogen, and the spectrum thus excited was examined in the region 7000—2000 Å. Except for certain atomic lines, it consisted of 43 bands comprising, for each isotope of aurous chloride, two intermingled systems in the green; all the bands were shaded towards the red. The vibrational intensity distribution agreed with that anticipated. Attempts to excite the spectra of gold bromide and iodide similarly were unsuccessful. A. A. ELDRIDGE.

Absorption spectrum of vitamin-A. R. A. MORTON and I. M. HEILBRON (Nature, 1928, 122, 10).—Vitamin-A concentrates show a prominent absorption band at 328.5 μ , the intensity of which accords with the potency as determined by the antimony trichloride test. Irradiation results in the disappearance of the chromogenic substance, and the destruction of the vitamin by aëration or oxidation is also confirmed by spectrographic observations. It appears probable that the first decomposition products of vitamin-A include a substance possessing an absorption band in the region 275—285 μ . A. A. ELDRIDGE.

Secondary radiation observed in the molecular diffusion of light by fluids (Raman effect). P. DAURE (Compt. rend., 1928, 186, 1833—1835; cf. this vol., 461).—The frequencies of the secondary radiations are given by the formula $N - n_p$, where N is the frequency of the exciting radiation and n_p represents the characteristic constants of the fluid and is probably related to its infra-red absorption spectrum. Values of the latter are given. It has been shown for ether, ethyl alcohol, benzene, toluene, and aqueous salt solutions that spectra of fluids having a common radical contain some rays in common, some different, and some slightly displaced. Rays corresponding with the same molecular frequency have the same degree of polarisation, and the spectrum of a benzene-toluene mixture is the superposition of the constituent spectra (cf. Wood's fluorescence spectra). The intensities probably depend on that of the exciting ray and on the molecular density. J. GRANT.

Chemistry and band spectra. R. MECKE (Naturwiss., 1928, 16, 521—529).—A lecture.

R. A. MORTON.

Absorption spectra of quinolphthalein and quinolsulphonephthalein. C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, 50, 1772—1778).—The absorption spectrum of quinolsulphonephthalein in water or alcohol is closely similar to those which it and quinolphthalein exhibit in sulphuric acid and alcoholic hydrogen chloride, but differs entirely in type from the lactonoid spectrum of quinolphthalein or phenolphthalein in alcohol. This confirms the view (cf. *ibid.*, 1730) that free quinolsulphonephthalein is an internal salt, and suggests that all solutions of the first type contain salts of *m*-quinonoid derivatives. Quinolsulphonephthalein dibenzoate is probably also quinonoid, since its absorption spectrum differs in type from that of quinolphthalein dibenzoate. In alcoholic solution 100 mols. of potassium hydroxide convert quinolphthalein into a mixture of the blue di- and colourless tri-potassium salts and quinolsulphonephthalein into the dipotassium salt, whilst smaller proportions of alkali give mixtures of dipotassium salt and unchanged phthalein. In 33% aqueous potassium hydroxide both yield nearly colourless solutions of tri-potassium salts. H. E. F. NOTTON.

Fluorescence of mercury vapour. H. NIEWODNICZAŃSKI (Z. Physik, 1928, 49, 59—72).—The spectrum of the fluorescence radiation emitted by superheated mercury vapour excited by an aluminium spark has been investigated over the temperature range 245—910°. The bands generally became weaker with rising temperature, except the continuous band with an intensity maximum at about 3300 Å. which attains a maximum intensity at about 500°. In the presence of hydrogen all the lines and bands were much weaker, except the band with a long-wave convergence frequency of 2349 Å., of which the intensity remained unchanged. From the data obtained the carriers of the bands are deduced. The decrease in the intensity of the band with a convergence frequency of 2349 Å. with increasing vapour density in the saturated vapour is attributed to increased band absorption. J. W. SMITH.

Resonance fluorescence of cyanogen. G. HERZBERG (Naturwiss., 1928, 16, 464—465).—The cyanogen bands occurring in the spectrum of active nitrogen are found to be due to resonance fluorescence excited by the ultra-violet bands.

W. E. DOWNEY.

Fluorescence of electrically [and optically] excited mercury vapour. S. PIENKOWSKI (Compt. rend., 1928, 186, 1530—1532).—A study of the electrically excited fluorescence of moving mercury vapour of different densities by the use of colour filters has shown that the ray 4358 ($2^3S-2^3P_1$) is principally responsible for its excitation and the rays 4047 ($2^3S-2^3P_0$) and 5461 ($2^3S-2^3P_2$) to smaller extents. Optical excitation is produced principally by the ray 2537, and affects mercury atoms in the state 2^3P_1 . The atoms then change into the state 2^3S under the influence of the ray 4358, the emission of fluorescence being connected with the subsequent

return of the atom to its normal state. The fluorescence of atomic mercury shows no appreciable retardation. J. GRANT.

Photo-luminescence of uranium salts. S. J. VAVILOV and V. L. LEVSHIN (Z. Physik, 1928, 48, 397—425).—The phosphorescence of uranium salt crystals, uranium glasses, and solutions follows the equation $I = I_0 e^{t/\tau}$. Only on excitation by short-wave ultra-violet radiation does a second type of resonance appear, and this is of short duration. The resonance of solutions is dependent on the concentration and to a smaller extent on the temperature. The light emitted is not polarised. It is concluded that the photo-luminescence arises from radiating transformation in the excited molecule. J. W. SMITH.

Tesla luminescence spectra of the halogens. I. Iodine. S. S. BHATNAGAR, D. L. SHRIVASTAVA, K. N. MATHUR, and R. K. SHARMA (Phil. Mag., 1928, [vii], 5, 1226—1239).—The Tesla luminescence spectrum of iodine has been shown to have a continuous luminous background with sharp edges extending over the range λ 4800—2130 Å. A number of electronic emission bands are superimposed on this background. These comprise four systems, of which one has been analysed and shown to agree with the equation $\nu = 29078 + (710n' - 8n'^2) - (213.7n'' - 0.6n''^2)$, where 29078 is the wave-number of the band at the head of the system. The fluorescence term $(213.7n'' - 0.6n''^2)$ is shown to arise from emission as the molecule returns from a higher excited state to the metastable $2p_1$ state. The strong bands at λ 4800 and 3440 are discussed and an attempt is made to explain the continuous background. A. E. MITCHELL.

Chemiluminescence by oxidation of dyes with ozone. N. N. BISWAS and N. R. DEAR (Z. anorg. Chem., 1928, 173, 125—136).—A large number of dyes (e.g., eosin, safranin, thioflavine, etc.) dissolved in various solvents were treated with ozonised oxygen. Many of them emitted radiation in the form of light of definite wave-lengths. No light is seen if oxygen alone is used. It was found impossible to photograph the spectrum of the emitted light owing to its feebleness, but the wave-lengths were measured by means of a quartz spectrograph, and the intensities by a spectrophotometer. The relative intensity of the light for any particular dye depends on the solvent. The intensity is usually less in water than in alcohol. The effect of the addition of various substances (e.g., nicotine, strychnine, benzaldehyde, etc.) to the dyes was investigated. In no case was the light increased by the addition of a foreign substance. Reducing substances suppressed it. The light is equally bright if the substance is fluorescent. The chemiluminescence spectrum does not correspond with the fluorescence spectrum. The relationship between chemiluminescence and fluorescence is discussed from the point of view of the activation of molecules, and the theory is applied to previous work on oxidation. A. J. MEE.

Supposed luminescence of liquids on adiabatic compression. G. TAMMANN and C. KRÖGER (Z. anorg. Chem., 1928, 171, 364—366).—The momentary luminescence of liquids when subjected to sudden compression appears in some instances to be due to

the compression of air bubbles present in the liquid, but it is not certain that this is always so.

R. CUTHILL.

Light emitted by the reunion of iodine [atoms]. V. KONDRATÉV and A. LEIPUNSKI (Naturwiss., 1928, 16, 463—464).—The light emitted by heating iodine in air or in a vacuum has been examined by means of a visual spectroscope. Bands are found in the red, yellow, and green regions. It is concluded that the light has its origin in the reunion of an excited iodine atom with a normal atom to form a molecule. W. E. DOWNEY.

Chemiluminescence; energetics, spectra, intensity, and efficiency. E. Q. ADAMS (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 30—40).—For the emission of visible light, some atomic or molecular system must be in a state richer in energy by 37—71 kg.-cal. per mol. than some lower state to which spontaneous transition is possible. Quantitative data for luminescence spectra are surveyed. The efficiency of chemiluminescence reactions is usually far below 1%. CHEMICAL ABSTRACTS.

Chemiluminescence; photochemistry and chemiluminescence; kinetics of chemiluminescence. H. S. TAYLOR (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 41—49).—Chemiluminescence processes, which are the reversal of photochemical and photosensitised processes respectively, are considered generally. CHEMICAL ABSTRACTS.

Chemiluminescence; experimental methods. A. H. PFUND (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 23—29).—A survey. CHEMICAL ABSTRACTS.

Chemiluminescence; types. A. D. GARRISON (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 7—22).—Chemiluminescence reactions are direct or indirect; in the latter the chemical reaction occurs as an intermediate transformation of some other form of energy into light. CHEMICAL ABSTRACTS.

Bioluminescence. E. N. HARVEY (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 50—62).—A survey of the bioluminescence of *Cypridina*, and its mechanism. CHEMICAL ABSTRACTS.

Phosphorescence in relation to electrical phenomena. R. W. POHL (Naturwiss., 1928, 16, 477—484).—A crystalline phosphor at a low temperature can store up radiant energy and retain it. Excitation at higher temperatures is accompanied by emission of a part of the absorbed energy during the activation process. The liberation of energy is increased by exposure to infra-red or long-wave radiation. By long-wave radiation is meant those rays which are absorbed by the excited phosphor and not by the unexcited material. Excitation consists in the liberation of electrons by photo-electric effects; luminosity arises from the return of such electrons to the normal state. When it is stated that phosphorescence is a result of photo-electric phenomena, it is not implied that photo-electric conduction is restricted to phosphors. With crystals exhibiting a high refractive index (e.g., >2), a photo-electric primary current is quite general, and with crystals showing a lower refractive index the effect can be obtained by pre-

paring special crystals; *e.g.*, sodium chloride which has been treated with sodium vapour becomes yellow and exhibits photo-electric conduction. The return to its normal position of a photo-electrically displaced electron is not the sole condition determining phosphorescence. The best definition of a phosphor appears to be: an insulating crystalline material with which a minute trace of a highly refracting substance has been incorporated in the molten state. Luminescence is only an accessory phenomenon, and it may be absent in cases where the essentials (light absorption, electrical phenomena, etc.) are present. This view makes the absorption spectra of phosphors very important; in most cases, however, the sintered micro-crystalline powders are difficult to investigate, not only because of their physical nature, but also because the absorption of the phosphorogen may be masked by that of the diluent.

A series of alkali halide phosphors with traces of thallium chloride and lead chloride as phosphorogens has been prepared and has proved amenable to spectroscopic investigation because large crystals can be grown and polished and cut into sections. The thallium phosphors exhibit sharp absorption bands at about 250 and 193 μ , whilst a lead-potassium chloride phosphor shows bands at 273 and 196 μ . Pure thallium chloride shows bands at about 250 and 220 μ , whilst lead chloride has bands at 270 and 220 μ . These results show that a phosphor can be regarded as a mixed crystal with a very low concentration of one component. Apart from secondary "solvent" shifts, the absorption spectra show that the characteristic frequencies of the ultra-violet dispersion electrons of the substance present in small concentration (phosphorogen) represent the activating rays of the phosphor. R. A. MORTON.

Quantum yield in the photolysis of silver chloride. P. FELDMANN (Naturwiss., 1928, 16, 530—531).—Gelatin-free silver chloride has been exposed to monochromatic light (365 μ) under conditions such that the whole of the incident light was absorbed. The halide was immersed in water so that the liberated chlorine would appear as hydrochloric and hypochlorous acids. Analysis of the solution by the method of Lange and Schwartz (A., 1926, 701) indicated that the ratio chlorine atoms/quantum is $0.86 \pm 2\%$. The ratio is much lower with silver chloride exposed to light before the experiment. The slight departure from Einstein's law of photochemical equivalence is ascribed to absorption by silver formed in the photochemical reaction.

R. A. MORTON.

Dielectric constant of benzene-toluene mixtures. R. D. SCHULWAS-SOROKINA (Z. Physik, 1928, 48, 426—437).—Colley (*ibid.*, 1909, 10, 663) reported that in benzene-toluene mixtures the dielectric constant measured for damped wave trains, in which the train frequency was 10^8 sec^{-1} , when expressed as a function of the toluene concentration exhibited a number of maxima which were attributed to the liberation of photo-electrons by the electric field. In order to investigate this phenomena, determinations of the dielectric constant of such mixtures have been made in undamped alternating electric fields of

frequency corresponding with a wave-length of 190 m. No evidence of the phenomena reported by Colley has been observed. R. W. LUNT.

Effect of radioactive radiation on the dielectric constant. G. GUÉBEN (Bull. Acad. roy. Belg., 1927, [v], 13, 509—525).—A more detailed account of work already published (this vol., 460).

Dielectric constants of ammonia, phosphine, and arsine. H. E. WATSON (J. Indian Inst. Sci., 1928, 11A, 41—61).—An amplified account of work already published (see this vol., 107).

Variation of dielectric constant of liquids with pressure. L. CAGNIARD (Ann. Physique, 1928, [x], 9, 460—553).—A sensitive method for measuring dielectric constants by means of a Wheatstone's bridge is described, having a sensitivity of 1 in 6×10^4 . The variation of the pressure coefficient with temperature has been measured for carbon tetrachloride, hexane, cyclohexane, and amyl alcohol, from 1° to 24°. For dipolar dielectrics $\partial\epsilon/\partial p$ and $[1/(\partial\epsilon/\partial p)](\partial^2\epsilon/\partial p \partial T)$ are less, and for other dielectrics greater, than the values calculated from Debye's formula. C. W. GIBBY.

Variation of dielectric constant of some gases with temperature at different pressures. H. A. STUART (Z. Physik, 1928, 48, 747).—A discussion of Forró's results (this vol., 347).

Dielectric polarisation of liquids. I. Dielectric constants and densities of solutions of the chlorobenzenes in benzene and in hexane. C. P. SMYTH, S. O. MORGAN, and J. C. BOYCE (J. Amer. Chem. Soc., 1928, 50, 1536—1547).—A capacity bridge suitable for determining the dielectric constants of liquids is described. The constants and densities at 0°, 25°, and 50°, of solutions of chlorobenzene, and *o*-, *m*-, and *p*-dichlorobenzenes in benzene and in hexane are recorded. The curves representing the variation of density, dielectric constant, and polarisation as functions of the mol. fraction of solute indicate that the molecules influence one another more strongly the greater are their moments and their concentrations, and the lower is the temperature.

S. K. TWEEDY.

Dielectric polarisation of liquids. II. Temperature dependence of the polarisation in certain liquid mixtures. C. P. SMYTH and S. O. MORGAN (J. Amer. Chem. Soc., 1928, 50, 1547—1560).—The dielectric constants and densities of liquid solutions of ethyl bromide, chloroform, and chlorobenzene in hexane are recorded over the maximum temperature range. A special form of pycnometer is described. Approximate values for the polarisation due to the shifts of atoms and groups of atoms are obtained, and Debye's equation is shown to hold for infinitely dilute liquids. As before, the molecules affect one another more strongly the greater are their moments and concentrations and the lower is the temperature (cf. preceding abstract).

S. K. TWEEDY.

Molecular and atomic volumes. XIX. Density of the chlorides of uranium, tungsten, and molybdenum. W. BILTZ and C. FENDIUS (Z. anorg. Chem., 1928, 172, 385—394).—Details are

given of the preparation and the results of density determinations of the following chlorides: UCl_4 , d 4.854; UCl_3 , d 5.440; WCl_6 , d 3.520; WCl_5 , d 3.875; WCl_4 , d 4.624; WCl_2 , d 5.436; MoCl_5 , d 2.928; MoCl_3 , d 3.578; MoCl_2 , d 3.714. The molecular volume of chlorine in the different compounds at 0° has been calculated and compared with the molecular volume of free chlorine. In the higher chlorides the two agree very closely, but in the lower chlorides the molecular volume of combined chlorine is either above or below that of free chlorine, the largest value being in the lowest, *i.e.*, the most unsaturated chloride. If the molecular volumes of the halides are compared in the uranium, aluminium, and indium chlorides, bromides, and iodides, it is found that, for UCl_4 , AlCl_3 , InCl_3 , and InBr_3 the molecular volumes of the halogens are practically the same in the free and combined states. These substances all form an ionic crystal lattice. For UBr_4 , AlBr_3 , UI_3 , AlI_3 , and InI_3 the molecular volume of the combined halogen is considerably greater in all cases than that of the free halogen, and the deviation is about the same for each. These substances all form a molecular lattice. The results thus point to a morphological origin for the deviation of molecular volumes from additivity. M. S. BURR.

Molecular and atomic volumes. XX. Density measurements of iodine chlorides. E. BIRK (Z. anorg. Chem., 1928, 172, 395—402).—Density determinations have been made on solid α - and β -iodine monochlorides with air in the pycnometer instead of liquid, the volume of the air being determined by driving it out with a current of carbon dioxide and measuring in a eudiometer. The stable α -form has a molecular volume of 42.1 at 0° , and the labile β -form 44.8, whilst liquid iodine monochloride has a molecular volume of 52.3 at 29° . The results are in agreement with the rule that the labile form of a monotropic substance passes into the stable form with contraction of volume, and also that the molecular volume of the α -form is equal to the product of the factor 0.81 and the molecular volume of the liquid phase in the neighbourhood of the m. p. At 0° Abs. the molecular volume of α -iodine monochloride is corrected to 40.9, and the sum of the molecular volumes of iodine and chlorine is 40.8. The agreement is within the limits of experimental error. The density of solid iodine trichloride has been determined, using liquid chlorine as the pycnometer liquid. The molecular volume at -40° is 72.84. When reduced to 0° Abs. this becomes 70.7, whereas by calculation it is 73.8, indicating that the formation of the trichloride is accompanied by a small contraction. M. S. BURR.

Non-polar linking and atomic refraction. I. R. SAMUEL (Z. Physik, 1928, 49, 95—136).—A modification of Lewis' octet theory is suggested by the assumption that even in non-polar combination one electron only is essentially concerned in the union, so that one atom is more positive and the other more negative than its partner. For non-polar inorganic molecules, molecular refraction can be divided into atomic refractions so long as the kind of linking and valency are borne in mind. Thus from atomic

refractions the type and strength of the bindings in a non-polar compound can be deduced.

J. W. SMITH.

Dispersion of magnesium sulphide. M. HAASE (Z. Krist., 1927, 66, 236—238; Chem. Zentr., 1928, i, 1012).—Magnesium sulphide has n_{540} 2.284 ± 0.002 , n_{570} 2.277 ± 0.002 , n_{615} 2.266 ± 0.001 , n_{640} 2.259 ± 0.001 , V 41 ± 3 . A. A. ELDRIDGE.

Potassium, rubidium, caesium, ammonium, and thallium tetroxalates. M. W. PORTER (Z. Krist., 1927, 66, 217—235; Chem. Zentr., 1928, i, 1015).—Potassium trihydrogen oxalate, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, has d 1.860, and is triclinic, $a:b:c=0.6001:1:0.6643$, α $86^\circ 2'$, β $100^\circ 4'$, γ $78^\circ 42'$; strong negative double refraction; n_α 1.4152, n_β 1.5364, n_γ 1.5604. The rubidium salt has d 2.124, $a:b:c=0.5909:1:0.6774$, α $85^\circ 20'$, β $97^\circ 43.5'$, γ $97^\circ 36'$ (?); strong negative double refraction; n_α 1.4210, n_β 1.5428, n_γ 1.5595. The ammonium salt has d 1.655, $a:b:c=0.6019:1:0.6865$, α $85^\circ 49'$, β $97^\circ 50'$, γ $79^\circ 43'$; n_α 1.4237, n_β 1.5500, n_γ 1.5687. The caesium salt has d 2.352, $a:b:c=0.5826:1:0.6917$, α $85^\circ 23'$, β $95^\circ 13'$, γ $80^\circ 34'$; n_α 1.4365, n_β 1.5523, n_γ 1.5621. The thallous salt has d 2.992, $a:b:c=0.5854:1:0.6859$, α $84^\circ 58'$, β $96^\circ 59'$, γ $80^\circ 4'$; n_α 1.5097, n_β 1.6319, n_γ 1.6538. A. A. ELDRIDGE.

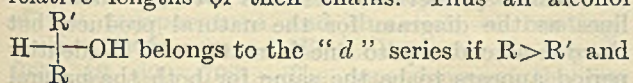
Rotatory dispersion of solutions. R. LUCAS (Ann. Physique, 1928, [x], 9, 381—459).—The rotatory dispersion of tartaric acid and of ethyl and methyl tartrates has been measured in various solvents, for seven wave-lengths between 6780 and 4358 Å. The results can be explained on the assumption that mixtures of three forms, in discontinuous equilibrium, are being dealt with. Stereochemical configurations are proposed in the light of this suggestion, and their consequences applied to anomalous electric and magnetic birefringence and to polymorphism. Similar measurements on camphor and *l*-isoborneol indicate the existence of two forms. C. W. GIBBY.

Anomalous rotatory dispersion from the point of view of the Drude equation. C. E. WOOD and S. D. NICHOLAS (J.C.S., 1928, 1671—1696).—The rotatory dispersions of monoacetyl, diacetyl, monobenzoyl, and dibenzoyl derivatives of dimethyl and diethyl *d*-tartrates have been measured together with those of ethyl thionyl-*d*-tartrate and ethyl dichlorosuccinate. For all compounds exhibiting anomaly, inflexion and maxima were confined to the positive region of rotation, and at the crossing of the axis $d\alpha/d\lambda$ was always positive. The interpretations of anomaly in terms of the theories of Wood or Lowry are rejected as being incomplete and it is suggested that anomaly is due to one or more rotations of electronic origin in the ultra-violet, together with a rotation of molecular origin, due to atomic oscillations in the infra-red. The sign of the infra-red term is dependent on the configuration of the molecule and is negative for the *d*-configuration and positive for the *l*-configuration. Lowry's criteria for anomaly (A., 1915, ii, 660) are, therefore, also criteria for relative configuration. F. J. WILKINS.

Rotatory dispersion. Intersections of dispersion curves and of temperature-rotation

curves. C. E. WOOD and S. D. NICHOLAS (J.C.S., 1928, 1696—1712; cf. preceding abstract).—The curves are discussed from the point of view of the evidence which they provide for the decision of problems of relative configuration. If the maxima of positive or negative rotation are to the right of the region of anomaly, then at the crossing of the axis da/dT is positive for a compound of *d*-configuration and negative for a compound of *l*-configuration, and maxima move to a higher temperature with decrease of wave-length. If the maxima are to the left, the contrary relationships hold. In the absence of anomaly the configuration may be decided by a consideration of the direction of crossing of the axis, and the possibility of the intersection of temperature-rotation curves in the positive region. It is further assumed that the presence and movement of negative minima are temperature relationships for enantiomorphs. These in conjunction with an analogous set of defining conditions to those used with maxima of positive and negative rotation may be employed to solve problems of configuration. F. J. WILKINS.

Anomalous rotatory dispersion of configurationally related compounds. C. E. WOOD and S. D. NICHOLAS (J.C.S., 1928, 1712—1727; cf. preceding abstracts).—The application of anomalous rotatory dispersion to the determination of relative configuration is made according to the criteria established in the previous papers. In this way the configurations assigned to *l*-lactic, *l*-malic, *d*-hexahydro-mandelic, and *d*-tartaric acids are respectively "*d*," "*l*," "*l*," and "*d*," which is in agreement with the conclusions of other investigators. Further, from a detailed consideration of a series of optically active alcohols it is shown that the distinction between "*d*" and "*l*" normal alcohols depends only on the relative lengths of their chains. Thus an alcohol



to the "*l*" series if $\text{R} < \text{R}'$. The relationship of the α -hydroxy-acids to these alcohols is also discussed. The influence of variation of radicals and temperature on the rotatory dispersion of series of alcohols is considered particularly in relation to their bearing on the question of relative configuration.

F. J. WILKINS.

Rotatory dispersion of optically active co-ordination compounds. C. E. WOOD and S. D. NICHOLAS (J.C.S., 1928, 1727—1738; cf. preceding abstracts).—The methods have been applied to a discussion of the configuration of co-ordination compounds in the light of measurements of their rotatory dispersions. The results support Werner's view, as against Jaeger's, that the dextrorotatory rhodium and iridium compounds have the "*l*"-configuration. Whilst the algebraic sign of the hemihedral form of the co-ordination compounds considered indicates the relative configuration, no generalisation can, at present, be made.

F. J. WILKINS.

Uniaxial optically active crystals. G. FRIEDEL (Compt. rend., 1928, 186, 1788—1790).—The author contests the deductions of Burger (A., 1927, 1126), particularly his fundamental supposition that the

lattice of uniaxial optically active crystals results from the pseudo-symmetry of the crystal edifice regarded as a whole. He considers that the stability of the edifice does not necessarily depend on periodicity or quasi-periodicity, since a lattice may be formed when the periodicity is interrupted and the edifice composed of a number of homogeneous elements variously oriented. Calcite, in which there is not the least pseudo-symmetry with respect to the plane (110), is cited as an example. J. GRANT.

[Rotatory dispersion of alkyl aspartates.] M. L. PAGLIARULO (Atti R. Accad. Lincei, 1928, [vi], 7, 577—579).—A reply is made to Mazza's criticism (A., 1927, 500; this vol., 460) of the author's results (A., 1927, 610), which represent the mean values of large numbers of measurements and may be regarded as accurate. T. H. POPE.

New quantum statistics of distribution phenomena. R. FURTH (Z. Physik, 1928, 48, 323—339).—Mathematical. R. W. LUNT.

Nature of the *cis*- and *trans*-isomerism of platinum salts. A. A. GRINBERG (Ann. inst. platine, 1927, 5, 365—366).—By Kurnakov's reaction with thiocarbamide, the nature of the isomerism of diamminoplatinous thiocyanate is shown to be identical with that of the isomerism of Peyronet's chlorides and other salts, and Reise's second base. Both isomerides are unimolecular.

CHEMICAL ABSTRACTS.

Valency and the rule of eight. W. H. RODEBUSH (Nature, 1928, 122, 56—57).—A critical note concerning London's theory of valency (this vol., 344).

A. A. ELDRIDGE.

Constitution rules. F. WRATSCHKO (Pharm. Presse, 1928, 33, 11—14; Chem. Zentr., 1928, i, 1015).—Two rules, the linking rule and the nucleus rule, are put forward, whereby the structure of organic compounds can be derived from a knowledge of the empirical formula and the density of the liquid substance. A. A. ELDRIDGE.

Electronic theory of valency. VI. Molecular structure of strong and weak electrolytes. (b) Reversible ionisation. T. M. LOWRY (Phil. Mag., 1928, [vii], 6, 50—63).—See A., 1927, 1026.

Exact measurements in the *K*-series of tin. J. STENMAN (Z. Physik, 1928, 48, 349—357).—The following values have been assigned to the *K* α_1 , α_2 , β_1 , β_2 , and β_3 lines of tin from measurement with a calcite grating: 489.572, 494.016, 434.297, 424.992, and 434.947 X., respectively. The wave-length of the *K* absorption limit of bromine is 918.091 X.

R. W. LUNT.

Precision measurements of the *K*-series of iron, cobalt, nickel, manganese, and chromium. S. ERIKSSON (Z. Physik, 1928, 48, 360—369).—By using a calcite grating and a new form of precision telescope spectrometer, measurements have been made of a number of lines in the *K*-series of iron, nickel, cobalt, chromium, and manganese. The following values are given: Fe α_1 , α_2 , β_1 , β' , β_2 , 1932.076, 1936.012, 1753.013, 1756.46, 1740.80; Ni α_1 , α_2 , β_1 , β' , β_2 , 1654.503, 1658.353, 1497.045, 1499.10, 1485.61; Co α_1 , α_2 , β_1 , β' , β_2 , 1785.287, 1789.187,

1617-436, 1620-11, 1605-62; Cr α_1 , α_2 , β_1 , β_2 , 2285-033, 2288-907, 2080-586, 2066-71; Mn α_1 , α_2 , β_1 , β' , β_2 , 2097-506, 2101-489, 1906-195, 1910-50, 1893-27 X., respectively. R. W. LUNT.

X-Ray examination of celluloid. K. H. UEDA (Z. physikal. Chem., 1928, 133, 350—356).—If nitrated ramie fibres are caused to take up camphor, two "amorphous" rings, due to the superposition of the interferences of camphor and cellulose nitrate, appear in the X-ray diagram, and with increase in the amount of camphor these become more and more intense, and the original fibre diagram becomes less and less distinct, until ultimately the diagram becomes identical with that of celluloid. With variations in the relative amounts of the components of celluloid, the positions and intensities of the two rings constituting the diagram vary, but the effects observed are merely those which would be expected from a solid solution; there is no indication of compound formation. With celluloid containing 70% of camphor, camphor crystals can be detected, and crystallisation can also be induced by stretching in celluloid containing less camphor. A cellulose nitrate film gives the cellulose nitrate fibre diagram if stretched. R. CUTHILL.

Quantitative X-ray analysis by cold excitation of spectra. R. GLOCKER and H. SCHREIBER (Ann. Physik, 1928, [iv], 85, 1089—1102).—The various errors attending the use of X-ray analysis for quantitative analysis by finding the intensities of lines in the spectrum can be diminished by using the cold excitation of the characteristic radiation of the substance by means of X-rays. The proportions of two elements in a mixture can then be determined by comparing the intensities of the lines due to each substance. The theory of the method is given, and the relationship between the potential of the tube and the intensities of the lines is investigated theoretically and experimentally using the $K\alpha$ lines of vanadium and titanium. The effect of the mixture of different elements is also worked out. A. J. MEE.

Fluorescence secondary X-radiation and the J-phenomenon. W. H. WATSON (Phil. Mag., 1928, [vii], 5, 1145—1163).—Previous work (A., 1927, 3) in which evidences of the "J" absorption effect in the transmission of the secondary X-radiation from paraffin wax through aluminium were obtained has been confirmed and extended to absorption by silver and copper. The ratio of the ionisations produced by two secondary beams from a radiator the K -characteristic radiation of which was excited did not change continuously when the amount of absorbing material was increased, but exhibited discontinuities in relation to this thickness which are apparently identical with the J-absorption discontinuities previously observed. Except for the effects of crystal reflexion in the radiator, practically pure monochromatic K -radiation was obtained. The changing of the orientation of the radiator with respect to the primary beam led to the displacement of a discontinuity, necessitating a different thickness of absorbing material for its reproduction. The results show that the J-phenomenon may be of periodical recurrence in absorption without appreci-

able change in the absorption coefficient of the beam in its passage through the absorber. A. E. MITCHELL.

Modified scattered X-radiation and superposition. The J-phenomenon. VIII. C. G. BARKLA (Phil. Mag., 1928, [vii], 5, 1164—1171).—The change from unmodified to modified scattered radiations has been shown to occur not by passing through a certain critical average frequency as measured by the average absorption coefficient as shown previously by Barkla and Sale (Phil. Mag., 1923, [vi], 45, 737) and others, but in this case it has been obtained by the superposition of radiations of the same frequencies in almost exactly the same proportions. The degree of modification, as measured by absorption methods, increased rapidly with the thickness of the scattering medium and approached a limiting value. A. E. MITCHELL.

X-Ray investigation of stannic sulphide, and titanium disulphide, diselenide, and ditelluride. I. OTTEDAL (Z. physikal. Chem., 1928, 134, 301—310).—The position of the lines and their intensity in the X-ray diagram of titanium disulphide, diselenide, and ditelluride were determined, and it was shown that they could be explained by assuming a structure similar to cadmium iodide. This had already been shown for stannic sulphide. The powder method was used. The intensities calculated agree well with those observed. A table of dimensions of the lattices is given. A. J. MEE.

Structure of stretched synthetic rubber. L. HOCK and W. BARTH (Z. physikal. Chem., 1928, 134, 271—278).—The Röntgen diagram of stretched synthetic rubber at the ordinary temperature and at -60° was investigated, and compared with that of the natural product. The diagram for stretched and cooled synthetic rubber does not show such clear lines as the diagram for the natural product, but there is a tendency to line formation. The identity period appears to be the same for both the natural and synthetic rubber, but owing to experimental difficulties it was impossible to make any very accurate numerical deductions. A. J. MEE.

Röntgen diagrams of cellulose nitrate and cellulose acetate. S. VON NÁRAY-SZABÓ and G. VON SUSICH (Z. physikal. Chem., 1928, 134, 264—270).—The Röntgen diagram of cellulose nitrate was investigated, the distances being measured with a probable error of ± 0.1 mm. The value of the "identity period" is 26.6 ± 0.5 Å. The experiments were carried out with cellulose nitrates of varying nitrogen content. Those with nitrogen contents between zero and that required by cellulose trinitrate give diagrams in which the interference due to pure cellulose and that due to cellulose trinitrate are superimposed. It thus appears that the mono- and di-nitrate do not have definite lattices like the trinitrate, and that their existence as well-defined, stable, stoichiometric compounds is improbable. Cellulose acetate was also investigated, compounds with an acetyl content of from 20% to 42% being used. The "identity period" in this case is 10.3 ± 0.3 Å. Here, too, the positions of the points in the diagram did not vary with the acetyl content. It is

therefore concluded that only the triacetate exists as a well-defined compound with a definite lattice.

A. J. MEE.

Spectrography of γ -rays by crystalline diffraction. M. FRILLEY (Compt. rend., 1928, 186, 1614—1615).—The author's apparatus (this vol., 215) has been used to study the lines 16, 24, and 29.5 (from radium-C) and 26 (from radium-B). With these high-frequency rays, a lead filter 0.5 mm. thick may be used to eliminate diffusion of soft X-rays without producing a diminution in the sharpness of the spectrum.

J. GRANT.

Crystal structure of thiocarbamide. L. DEMÉNY and I. NITTA (Bull. Chem. Soc. Japan, 1928, 3, 128—136).—The crystal structure of thiocarbamide has been determined from Laue photographs and X-ray measurements. The unit group is Γ_0 , having a 5.47, b 7.64, c 8.54 Å., and contains 4 molecules of $\text{CS}(\text{NH}_2)_2$; $d_{\text{calc.}}$ 1.408. The probable space-group is V_h^{10} , and a possible atomic arrangement, neglecting hydrogen atoms, is indicated. The molecule has one plane of symmetry; the distance carbon—sulphur is 1.81 Å., and carbon—nitrogen is 1.39 Å.

C. J. SMITHELLS.

Dispersion of long wave-length X-rays in platinum and calcite. E. DERSHEM (Proc. Nat. Acad. Sci., 1928, 14, 380—384).—For platinum the dispersion increases with wave-length as far as 7 Å. and probably continues to do so as far as the beginning of the N -series of absorption limits. The examination of calcite near the K -limit of calcium showed that anomalous dispersion of the type predicted by the theories of Kronig and of Kallmann and Mark takes place near a K -absorption limit. The agreement is not quantitative.

W. E. DOWNEY.

Broadening of the Debye-Scherrer lines of cold-worked tungsten wires and strips as a function of the temperature and duration of heating. A. E. VAN ARKEL and W. G. BURGERS (Z. Physik, 1928, 48, 690—702).—The dependence of the line broadening in the X-ray absorption of cold-drawn tungsten wires and cold-rolled tungsten strips on the temperature and duration of heating was investigated by determination of the ratio between the intensity of the strongest line in the copper $K\alpha$ doublets and the intensity in the minimum between the two lines. The sharpness of the doublets increases rapidly with the temperature of heating. It also increases at first with time, but at temperatures where recrystallisation does not markedly occur the ratio soon assumes a constant value for each temperature.

J. W. SMITH.

X-Ray investigations on cellulose. IV. R. O. HERZOG and W. JANCKE (Z. Physik, 1928, 49, 27—30).—The employment of a monochromatic beam of X-rays shows that cellulose has only a single crystal structure (cf. Gonell, A., 1924, ii, 588).

J. W. SMITH.

Fine structure in the K -series of copper and nickel and the width of spectral lines. H. PURKS (Physical Rev., 1928, [ii], 31, 931—939).—At 40 kilovolts and in the first order the widths (X.) at half-maximum were: nickel $K\alpha_{1,2}$ 0.66, copper $K\alpha_{1,2}$ 0.63, molybdenum $K\alpha_{1,2}$ 0.47, $K\beta_{1,2}$ 0.43,

silver $K\alpha_{1,2}$ 0.43, $K\beta_{1,2}$ 0.40; in the second order the estimated width of the components of nickel and copper $K\alpha_{1,2}$ and $K\beta_{1,2}$ was 0.4 X. Weak lines were present at displacements 0.42 and 0.35 X. from Cu $K\alpha_2$ and Cu $K\alpha_1$, respectively, and 0.45 and 0.38 X. from Ni $K\alpha_1$ and Ni $K\alpha_2$, respectively. The following separations are recorded: Ag $K\beta_2$ — $K\beta_1$ 0.63, Mo $K\beta_2$ — $K\beta_1$ 0.58, Cu $K\beta_2$ — $K\beta_1$ 0.32, Ni $K\beta_2$ — $K\beta_1$ 0.29 X. The variation of the width with potential was studied; a limiting value is approached at 40 kilovolts.

A. A. ELDRIDGE.

X-Radiation from gases. A. BJÖRKESON (Nature, 1928, 122, 13—14).—A method is briefly described whereby an X-ray spectrum can be obtained with a gas (sodium or sulphur vapour) as radiator.

A. A. ELDRIDGE.

General X-radiation from mercury vapour. W. DUANE (Proc. Nat. Acad. Sci., 1928, 14, 450—458).—An apparatus is described by which the radiation projected from impacts of electrons with mercury vapour atoms can be investigated both in the direction of the electron stream and at right angles to it. The intensity and penetrating power of the radiation were measured by means of the ionising effect. The penetration of the rays was tested with a sheet of aluminium, and it was found that the mercury radiation both in the direction of the electron stream and at right angles to it became more and more penetrating as it passed through successive layers of aluminium, showing that neither beam of rays is homogeneous. The wave-lengths of these inhomogeneous beams are a little longer than that of the short wave-length limit of the X-ray spectrum. The intensities of the rays per mercury atom in the direction of motion of the electron stream and perpendicular to it are of the same order of magnitude. Experiments were made from which the amount of radiation that should pass through the test sheet of aluminium could be obtained. The values for the fraction of radiation passing through, determined experimentally, agreed with that calculated from the "inverse square of the wave-length" law.

A. J. MEE.

Secondary electrons from cobalt. M. N. DAVIS (Proc. Nat. Acad. Sci., 1928, 14, 460—465).—The secondary emission from cobalt was found to be greater than that observed for any other metal. The target of cobalt was given special heat treatment to ensure complete outgassing. The ratio of secondary current to primary current is plotted against the accelerating potential. It is shown that before outgassing the emission was low, but the current began to show maximum and minimum values at certain accelerating voltages as outgassing proceeded. Curves for iron and nickel previously obtained show something of the same form as the curve for cobalt, but the breaks are not so pronounced.

A. J. MEE.

Diffusion of cathode rays, of 100 volts velocity, in gaseous media. O. HOLTZMANN (Ann. Physik, 1928, [iv], 86, 214—240).—True reflexion of electrons (i.e., large angle deflexion from the original line of travel) is found to occur in hydrogen, nitrogen, helium, neon, and argon. An electron suffering

such reflexion undergoes no loss in velocity. The true reflexion masks the diffusion so that it was possible only in the case of nitrogen to determine the value of the "turbidity factor" in the absorption equation.

W. E. DOWNEY.

X-Ray analysis and crystal structure of cadmium-silver alloys. III. G. NATTA and M. FRERI (Atti R. Accad. Lincei, 1928, [vi], 7, 406—410; cf. this vol., 223, 464).—Mainly a discussion of the work of Petrenko and Fedorov on the thermal investigation of cadmium-silver alloys. The authors' X-ray investigations of these alloys described in the first two papers appear to render necessary an accurate revision of the thermal analysis. There is a great similarity in crystal structure between copper-zinc and silver-cadmium alloys. All the phases which are present in tempered silver-cadmium alloys are also found with similar lattices in brasses. This is in accord with the homologous positions which silver and cadmium occupy in the periodic system with respect to copper and zinc. O. J. WALKER.

Atomic arrangement in crystals of the alkali thiocyanoplatinates. S. B. HENDRICKS and H. E. MERWIN (Amer. J. Sci., 1928, [v], 15, 487—494).—The atomic arrangement has been determined in crystals of ammonium, potassium, and rubidium thiocyanoplatinates. Oscillation spectrum (30°) photographs were made with the a axis either coincident with or at an angle of 30° to the axis of oscillation. In addition, Laue photographs were made with the incident X-ray beam parallel to and making small angles with the normal to (001). The agreement between the observed density and the density calculated assuming that the unit of structure contains $1R_2Pt(SCN)_6$ was satisfactory. The units of structure had the dimensions: (NH_4) , a 6.77 Å.; c 10.45 Å.; (K), a 6.73 Å.; c 10.26 Å.; (Rb), a 6.75 Å.; c 10.47 Å. Laue photographs made with the incident X-ray beam normal to (001) showed a three-fold axis and three planes of symmetry, and this observation, coupled with crystallographic evidence, leads to two possible atomic arrangements, in either of which the sulphur atom is adjacent to the platinum atom. These crystal structures are compared with that of the cadmium iodide type.

R. A. PRATT.

Distances apart of atoms in metals. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1928, 133, 397—419).—In comparing values of the atomic radii of the elements with the view of discovering relations between the atomic volumes, the figures must relate to lattices which are all of the same type, and for all of which the co-ordination number, i.e., the number of atoms by which each individual atom is immediately surrounded, is the same. As the basis of comparison, either the regular face-centred or the hexagonal most densely packed lattice may be used, or, in fact, both of these, since in respect of inter-atomic distances they are accurately equivalent, and both have the co-ordination number 12. Calculations of atomic radii have been made on these lines, using available X-ray data, supplemented by some new determinations, the figures for certain metals not crystallising in the pure state with either of the

requisite lattices being derived from measurements on mixed crystals having lattices of the closely-packed hexagonal type. Reduction of the co-ordination number of a particular atom from 12 to 8, 6, or 4 causes the inter-atomic distance to fall by 3, 4, or 12%, respectively.

R. CUTHILL.

Crystal structure of the alums. L. VEGARD and E. ESP (Ann. Physik, 1928, [iv], 85, 1152—1164).—The crystal structure of the alums was investigated by means of the Debye-Scherrer method. The four alums used were ammonium alum, potassium alum, ferric ammonium alum, and chrome alum, and the radiation used was the $K\alpha$ radiation of chromium. The intensity of the lines was estimated. The results of the identification of the lines leading to the determination of the unit cell are in agreement with those obtained by Vegard and Schjelderup. The structure of the alums is discussed, the general result arrived at being that there are six atoms of oxygen from the water next to the univalent metal, then the sulphate group with the base of the tetrahedron towards the water group, and the point directed towards the trivalent metal. The whole forms a compact unit along the trigonal axis, which is terminated at each end by a metallic atom. Diagrams are given. The structure given cannot be regarded as final.

A. J. MEE.

Crystal structure of α -manganese. G. D. PRESTON (Phil. Mag., 1928, [vii], 5, 1198—1206).— α -Manganese (d^{25} 7.44) crystallises as a body-centred cube of side 8.894 ± 0.002 Å. Thus 58 atoms must be associated with the crystal unit, a result in agreement with that of Bradley and Thewlis (A., 1927, 814). The crystal is assigned to the space-group T_d .

A. E. MITCHELL.

Crystal structure of β -manganese. G. D. PRESTON (Phil. Mag., 1928, [vii], 5, 1207—1225).— β -Manganese, stable above 742° , crystallises in the cubic system, the unit having a side of 6.29 Å., and containing 20 atoms, a result in agreement with that of Westgren and Phragmén (A., 1925, ii, 1035). The space-group may be either of the enantiomorphs O^7 or O^6 , it being impossible to distinguish between these by X-ray methods.

A. E. MITCHELL.

Crystallography and optical properties of β -lactose. E. T. WHERRY (J. Washington Acad. Sci., 1928, 18, 302—304).— β -Lactose crystals are monoclinic, holoaxial-polar; $a : b : c = 0.817 : 1 : 0.377$. The optical constants of α -lactose, β -lactose, and sucrose are tabulated, and directions are given for distinguishing between the three.

C. W. GIBBY.

Crystal form of atoxyl [sodium p -amino-phenylarsinate]. G. CESÀRO (Mem. Soc. Roy. Sci. Liège, 1924, 12, 1—11).—The results obtained by Mélon (A., 1923, i, 407) and by Giltia (A., 1922, i, 961) are discussed in regard to the relationship between the two different orientations of the crystal adopted.

W. E. DOWNEY.

Tetrahedral carbon atom and crystal structure of pentaerythritol. K. WEISSENBERG (Naturwiss., 1927, 15, 995—996; Chem. Zentr., 1928, i, 787).—Polemical against Schleece and Schneider (this vol., 224).

A. A. ELDRIDGE.

Tetrahedral carbon atom and the crystal structure of pentaerythritol. A. HETTICH, A. SCHLEEDE, and E. SCHNEIDER (Naturwiss., 1928, 16, 547).—The authors' experimental results can be interpreted only in terms of a tetrahedral molecular structure, as against the pyramidal structure (cf. Weissenberg, this vol., 462). R. A. MORTON.

Molecular symmetry of pentaerythritol. S. B. HENDRICKS (Z. Krist., 1927, 66, 131—135; Chem. Zentr., 1928, i, 638).—A repetition gives space-group S_6^2 or C_4^2 . A sphenoid arrangement of the $\text{CH}_2\text{-OH}$ groups around the central carbon atom is possible.

A. A. ELDRIDGE.

Molecular theory of crystal growth. E. BRANDENBERGER (Z. Krist., 1927, 66, 120—130; Chem. Zentr., 1928, i, 878).—A molecular theory of crystal growth, in accord with the lattice theory of crystal structure, is proposed. A. A. ELDRIDGE.

Carrollite (synchodymite). W. F. DE JONG and A. HOOG (Z. Krist., 1927, 66, 168—171; Chem. Zentr., 1928, i, 896).—Carrollite (synchodymite), CuCo_2S_4 , exhibits hexakisoctahedral symmetry (O_h , $u \sim N_2^2$); length of edge of unit cell 9.458 ± 0.003 Å., distance Cu—S 2.05 Å., Co—S 2.36 Å.

A. A. ELDRIDGE.

Structure analysis. H. OTT (Z. Krist., 1927, 66, 136—153; Chem. Zentr., 1928, i, 550—551).—A general method for the determination of the positions of atoms in a lattice without the assistance of the structure theory is based on the extinction of X-ray interference.

A. A. ELDRIDGE.

Structure of monticellite, MgCaSiO_4 . G. B. BROWN and J. WEST (Z. Krist., 1927, 66, 154; Chem. Zentr., 1928, i, 636).—Monticellite contains SiO_2 36.8, FeO 4.75, MnO 1.62, MgO 21.6, CaO 34.31, H_2O 0.95; the edges of the unit cell of four molecules are a 4.815, b 11.08, c 6.37 Å.; space-group V_h^h . The relation between monticellite and olivine is discussed.

A. A. ELDRIDGE.

Space-group of staurolite. C. GOTTFRIED (Z. Krist., 1927, 66, 103—107; Chem. Zentr., 1928, i, 636).—The unit cell, containing two molecules, has a 7.84, b 16.52, c 5.61; space-group V_h^h .

A. A. ELDRIDGE.

Crystal structure of zircon and criteria for special positions in tetragonal space-groups. R. W. G. WYCKOFF and S. B. HENDRICKS (Z. Krist., 1927, 66, 73—102; Chem. Zentr., 1928, i, 637).—The unit cell of zircon, containing four molecules, has a 6.60, c 5.88 Å.; space-group D_{2h}^2 .

A. A. ELDRIDGE.

Morphological and structural relationships of meteoric iron in relation to its evolution. J. LEONHARDT (Fortschr. Min. Kryst. Petr., 1927, 12, 52—55; Chem. Zentr., 1928, i, 897).—Two kinds of meteoric iron are differentiated by means of Laue photographs. Kamazite has in both groups a cubic body-centred lattice with edge of unit cube 2.84 Å.

A. A. ELDRIDGE.

Crystal form of artificial vivianite. G. CESARO (Bull. Acad. roy. Belg., 1928, [v], 14, 260—264).—The crystallographic constants of artificial vivianite, prepared by the action of air on a slightly acid

solution of ferrous phosphate, $\text{Fe}(\text{H}_2\text{PO}_4)_2$, are practically identical with those of the natural product.

C. W. GIBBY.

Fine structure of the feldspars. E. SCHIEBOLD (Fortschr. Min. Kryst. Petr., 1927, 12, 78—82; Chem. Zentr., 1928, i, 895).—The monoclinic feldspars are basal-face-centred, the edges of the unit cell being parallel with the crystallographic axes a , b , and c . Values of a_0 , b_0 , and c_0 , respectively, are as follows: adularia 8.61, 13.07, 7.26; sanidine 8.42, 12.92, 7.14; microcline 8.44, 13.00, 7.21; hyalophane 8.50, 12.92, 7.12; albite 8.23, 13.00, 7.25; oligoclase 8.16, 12.90, 7.13; labradorite 8.23, 12.91, 7.16; anorthite 8.185, 12.895, 7.09 Å. The space-group for the monoclinic feldspars is C_{2h}^2 , and for the triclinic, C_1^1 . The effect of changes of composition on the dimensions of the unit cell is considered.

A. A. ELDRIDGE.

Study of copper alloys by X-ray diffraction. J. LOISEAU (Compt. rend., 1928, 186, 1732—1733).—The Laue radiograms of laminated copper, and brasses containing 33 and 40% of zinc with and without traces of lead, have been studied during and after annealing at 1050°, 900°, and 700°, respectively, and are fully described. The reflecting planes were simple (100) cubic lattices with the dimensions 3.60, 39.98, 93.60 $\times 10^{-8}$ cm., respectively. The deformations due to lamination are modified by annealing, which induces the orientation of the (100) planes around an axis perpendicular to the laminations. Comparison of the spectrograms, micrographs, and tensile curves showed the existence of the four classic zones.

J. GRANT.

Constitution of silicates. W. EITEL (Naturwiss., 1928, 16, 421—423).—A review of the problem from the point of view of chemical constitution, crystalline structure, the vitreous state, and colloidal properties.

R. A. MORTON.

Crystal structure of antimony oxides. U. DEHLINGER (Z. Krist., 1927, 66, 108—119; Chem. Zentr., 1928, i, 636—637).—The oxides Sb_2O_3 , Sb_2O_4 , Sb_6O_{13} , and Sb_2O_5 were examined by the powder method. The trioxide exhibits the senarmontite form; space-group O_h^h , a 11.14 Å., the unit cell containing 8 mols. Sb_4O_6 . The tetroxide also has a cubic structure, a 10.22 Å., the senarmontite lattice being contracted by 10%. The oxide Sb_6O_{13} has approximately the same cubic lattice constant as the tetroxide, but double refraction indicates a pseudocubic structure (tetragonal, $c/a=3.0$). The unit cell consists of three superposed senarmontite cells. The pentoxide is cubic, with the same lattice constant as the tetroxide.

A. A. ELDRIDGE.

[Crystal] structure of beryllium oxalate trihydrate. L. HAVESTADT (Z. anorg. Chem., 1928, 171, 351—354).—By the X-ray method it is found that the unit cell of crystals of the above salt contains 4 molecules, and has the values of 6.37, 7.53, and 12.45 Å. for a , b , and c , respectively. The translation group is Γ_0 , and the space-group V_h^h .

R. CUTHILL.

Crystal structure of mercuric cyanide. R. FRICKE and L. HAVESTADT (Z. anorg. Chem., 1928, 171, 344—350).—X-Ray investigation shows the

unit cell of crystals of mercuric cyanide to contain 8 molecules, and to have the dimensions $a=b$, 9.74 Å., and c 8.94 Å. The translation group is Γ'_c , and the space-group is probably V_1^{12} . R. CUTHILL.

Complex structure of the copper-tin inter-metallic compounds. J. D. BERNAL (*Nature*, 1928, 122, 54).—The three phases δ -, η -, and ε -bronze have been examined by X-ray analysis, and found to be more complex than has been assumed. δ -Bronze contains 416 atoms in the unit cell, so that the simplest formula is $\text{Cu}_{41}\text{Sn}_{11}$; the space-group is T_d^2 . η -Bronze has the molecular formula $\text{Cu}_{50}\text{Sn}_{16}$; the space-group is probably Q_h^{17} . ε -Bronze contains 250 atoms of tin and 280–300 of copper in the unit cell; the molecular formula Cu_6Sn_5 is given with reserve. A. A. ELDRIDGE.

Diameter of the CH_2 chain in aliphatic acids. C. S. PIGGOT (*J. Washington Acad. Sci.*, 1928, 18, 330–333).—Within the limits of error, the short dimension in the X-ray crystal structure of pentadecanoic, palmitic, stearic, and behenic acids is the same, viz., 4.235×10^{-8} cm. This is apparently the diameter of all organic CH_2 chains. R. A. MORTON.

X-Ray spectroscopic examination of a cellobiose anhydride. M. BERGMAN, R. O. HERZOG, and W. JANCKE (*Naturwiss.*, 1928, 16, 464).—The hexa-acetyl derivative of the cellobiose anhydride described by Bergmann and Knehe (*A.*, 1925, i, 1384) has been examined by means of X-rays. The photographs are identical with those given by cellulose triacetate. W. E. DOWNEY.

Distinction between d - and l -crystals by means of X-rays. A. HETICH (*Z. Physik*, 1928, 48, 614–615).—The differentiation between d - and l -crystals is discussed with particular reference to quartz. J. W. SMITH.

Study of chlorites by means of X-rays. C. MAUGUIN (*Compt. rend.*, 1928, 186, 1852–1855).—The crystal characteristics of the three chlorites studied (pennine, leuchtenbergine, and grochauite) are analogous to those of the micas (this vol., 463, 611) and are due to piled elementary leaflets about 14×10^{-8} cm. thick, separable by cleavage. The Laue diagrams show a well-defined ternary symmetry. The crystalline pattern is always composed of 6 electro-negative oxygen atoms and 6 electro-positive atoms, but it is not possible to assign formulæ to the chlorites in which the atoms are represented by whole numbers. Since the number of hydrogen atoms is always found equal to 8/3, it is thought that X-ray examination gives a crystal lattice one third of that actually present, the true lattice containing 18 atoms of oxygen and 8 of hydrogen. J. GRANT.

Reticular-plane contraction at crystal surfaces. W. BRAUNBEK (*Naturwiss.*, 1928, 16, 546).—The results of Davisson and Germer on the scattering of electrons by nickel single crystals (*A.*, 1927, 492) are in formal agreement with a contraction of the lattice in a direction vertical to the surface. According to Patterson (*ibid.*, 817) the experimental data demand on this basis a contraction of 35% in the first spacing between the like planes as compared

with the normal spacing inside the crystal. Bethc (*Naturwiss.*, 1927, 15, 786; 1928, 16, 333) has accounted for the electron diffraction by introducing a refractive index for electron waves. The author has calculated the magnitude of the change in spacing for successive like planes in a crystal of the sodium chloride type with a (100) surface plane. The magnitude of the change is of the order 0.3% for the first spacing and very much smaller for the second and subsequent spacings. Even with less rigid lattices in which the contraction (or expansion) may be greater, it would seem that the effect could not exceed the experimental error of measurements.

R. A. MORTON.

Atomic arrangement in orthorhombic iodine. P. M. HARRIS, E. MACK (jun.), and F. C. BLAKE (*J. Amer. Chem. Soc.*, 1928, 50, 1583–1600).—The unit cell has orthorhombic bipyramidal symmetry corresponding with the space-group V_1^{18} (Wyckoff's notation), the atoms being arranged according to scheme (f) with parameter values $u=0.150$, $v=0.117$. The cell contains 8 atoms and has a_0 4.795 Å., b_0 7.255 Å., c_0 9.780 Å., corresponding with a (Groth) axial ratio of 0.661:1:1.348 and d 4.913. The parameter values were determined by both the structure factor and Fourier series methods; in the latter method the question of crystal perfection is not serious. The atoms are grouped in molecules of I_2 , the distance between the atomic centres being 2.70 Å. The conditions of the formation of monoclinic iodine are questioned. S. K. TWEEDY.

Lattice structure transformation in metallic mixed crystals. G. BORELIUS, C. H. JOHANSSON, and J. O. LINDE (*Ann. Physik*, 1928, [iv], 86, 291–318; cf. *A.*, 1927, 400).—Temperature-resistance measurements have been made of the metallic additive compounds, Cu_3Au , CuAu , Cu_3Pd , and CuPd . The measurements confirm the view that at low temperatures the atoms in these compounds are in an ordered, stable distribution, but that at higher temperatures there is a disordered distribution of the atoms. The conversion between the ordered and disordered states in the region of Cu_3Au , CuAu , and Cu_3Pd appears continuous. In the case of CuPd , the disordered arrangement of atoms has a face-centred cube lattice, and the ordered state, a body-centred cube lattice, so that the conversion must be discontinuous. W. E. DOWNEY.

Study of the structure of electrolytic copper by means of X-rays. J. J. TRILLAT (*Rev. Mét.*, 1928, 25, 286–288).—The unit cell of electrolytic copper is a face-centred cube, of length 3.68 Å. The presence of gelatin during electrolysis has no appreciable effect on the dimensions of the unit cell. By the Debye-Scherrer method it is shown that copper deposited in the presence of gelatin has a very fine-grained structure, and that much larger crystals are obtained in its absence. C. W. GIBBY.

Constitution of hydroxides and hydrates. I. G. NATTA (*Gazzetta*, 1928, 58, 344–358).—The hydroxides of metals which, as bivalent ions, have a radius between 0.77 and 1.10 Å. belong to the isomorphic class of rhombohedral hydroxides; this class includes the hydroxides of calcium, cadmium,

nickel, magnesium, manganese, iron (ferrous), and cobalt (ous), but not zinc hydroxide, since the radius of the zinc ion is less than 0.77 Å. All these hydroxides belong to the holohedral class of the rhombohedral system and have an orthorhombic unit cell defined by the co-ordinates of the atoms: $M^{++} = (0, 0, 0)$, $O^{--} = (\frac{1}{2}, \frac{2}{3}, u)$ ($\frac{2}{3}, \frac{1}{3}, u$), the value of the parameter u depending on the magnitude of the metallic ion and increasing from 0.25 to 0.28 as this varies from 0.77 to 1.06 Å. The side of the base of the elementary cell of the rhombohedral hydroxides increases regularly with increase in the radius of the metallic ion, but only a very imperfect relation exists between the value of $c : a$ for crystals of the composition MX_2 and the ratio $R_x : R_m$ for the component ions.

From the distance O—M it is calculated that oxygen has a radius between 1.33 and 1.38 Å., which agrees well with the value determined for the bivalent oxygen ion in other ways; the semi-distance O—O is about 10% greater than this value. The oxygen ion being only slightly deformable, it may be assumed that the hydrogen ion which would occupy the positions ($\frac{1}{2}, \frac{2}{3}, v$) and ($\frac{2}{3}, \frac{1}{3}, -v$) hinders contact between the oxygen atoms. On the assumption that the oxygen and hydrogen ions are spherical, the radius of action of the hydrogen ion is calculated to be 0.3—0.4 Å. If the hydroxyl ion in the lattice is considered as an entity, it would be limited by a non-spherical surface with radii varying from 1.35 to 1.50 Å., and would thus have the form of a strongly deformable ion analogous to that of polarisable ions like iodine, and would form the stratified lattices typical of compounds of polarisable ions.

T. H. POPE.

Electrolytic conduction of solids. E. FRIEDERICH (Z. Physik, 1928, 48, 446).—A claim for priority over Reis (*ibid.*, 46, 444). J. W. SMITH.

Electrolytic conduction of solids. A. REIS (Z. Physik, 1928, 48, 446).—A reply to Friederich (cf. preceding abstract). J. W. SMITH.

Magnetisation of single crystals of iron at high temperatures. K. HONDA, H. MASUMOTO, and S. KAYA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 111—130).—The magnetisation of a single iron crystal between -190° and 790° was measured in the direction of the principal axes. The variation in saturation value with temperature was almost the same as for a polycrystalline iron rod. At the ordinary temperature the curve is almost straight up to a magnetisation of 1000 c.g.s. units, the slope then changing up to the saturation value of 1707 c.g.s. units. As the temperature is raised the break in the curve occurs at progressively lower fields, and the saturation value decreases until it vanishes at 790° . By extrapolation the saturation value at 0° Abs. is 1752 c.g.s. units. The results are explained on the theory previously advanced by Honda and Okubo (*ibid.*, 1916, 5, 153). C. J. SMITHELLS.

Division of the Faraday effect into two phenomena of different origins. Diamagnetic and paramagnetic rotatory polarisation. J. BECQUEREL and W. J. DE HAAS (Compt. rend., 1928, 186, 1720—1722).—Experiments with tysonite, which

has a considerable negative rotatory power, at 1.39—4.21 Å. for the wave-lengths 4258.9—6249.5 Å., have proved the existence of a paramagnetic rotatory polarisation proportional to the thickness of the crystal but not to the field strength. The rotation is exactly represented by a hyperbolic tangent, and at saturation, is a function of wave-length and decreases with the temperature for a given wave-length. This explains the deviations from Curie's law. J. GRANT.

Paramagnetism. Magnetic moment of ions of elements of the transition groups. D. M. BOSE and H. G. BHAR (Z. Physik, 1928, 48, 716—721).—Preliminary measurements have been carried out on the magnetic susceptibility of salts of metals in the transition groups of the periodic system. Their Weiss magneton numbers calculated according to the method developed by Hund (A., 1925, ii, 912) and Bose (A., 1927, 805) are compared. J. W. SMITH.

Electronic theory of metals from the point of view of Fermi's statistics. E. KRETSCHMANN (Z. Physik, 1928, 48, 739—744).—It is pointed out that the formulæ deduced by Sommerfeld (this vol., 467) for electrical and thermal conductivity are not dependent on the assumption made by him that the mean free path of the electrons is, as a first approximation, independent of temperature. J. W. SMITH.

Theory of the magnetic and electrical properties of metals at 0° Abs. J. FRENKEL (Z. Physik, 1928, 49, 31—45).—From statistical considerations the paramagnetic susceptibility of metals at 0° Abs. is deduced. Ferromagnetism is qualitatively discussed and calculations are made of the energy of evaporation of electrons from metals, the contact potentials between different metals, and of the density and compressibility of metals. J. W. SMITH.

Paramagnetism of iron in potassium ferri-cyanide. (Mlle.) P. COLLET and F. BIRCH (Compt. rend., 1928, 187, 35—36).—Iron in potassium ferri-cyanide has a moment of 12 magnetons at $0-200^\circ$, and probably a moment of 13 magnetons below 0° .

J. GRANT.

Magnetic changes of iron sesquioxide, its solid solutions, and ferromagnetic compounds. H. FORESTIER (Ann. Chim., 1928, [x], 9, 317—401).—A thermal dilatometric examination of iron (Fe_2O_3 , Fe_3O_4 , and FeO), aluminium, chromium, and magnesium oxides, compressed into short rods, has been made. When the heating is not continued beyond a certain temperature, which varies from substance to substance (940° for aluminium, 1000° for magnesium oxides), a reversible contraction occurs, but above this temperature the slope of the curve changes abruptly and it is no longer possible to get reversibility no matter at what temperature the material has previously been heated. The curves for magnesium oxide which has been preheated either to 1000° or 2000° both show an abrupt change of direction at 500° . From these results it is deduced that two distinct processes take place: (1) a continuous and irreversible contraction due to the disappearance of the spaces between the grains which runs parallel with changes in the apparent density of the material, (2) the occurrence of plasticity in the

grains after a certain temperature. No allotropic changes occur. The paper gives a detailed account of investigations the results of which have already been summarised (Forestier and Chaudron, A., 1924, ii, 617; 1925, ii, 534, 1159; 1926, 566; 1927, 11).

J. W. BAKER.

Mechanical twinning in zinc crystals. E. SCHMID and G. WASSERMANN (Z. Physik, 1928, 48, 370—383).—The changes in the mechanical properties of single crystals of zinc are shown to be related to the formation of twinned crystals. J. W. SMITH.

Influence of the mother-liquor on crystal form. M. YAMADA (Japan. J. Phys., 1928, 4, 159—163).—The effect of mother-liquor on crystal form is investigated, a simple law of atomic action being postulated. The regular arrangement of atoms in the crystal is assumed to have some effect on the atoms of the liquid in the neighbourhood of the surface of the crystal. The atoms of the liquid will themselves be arranged regularly on the surface of the crystal. If the diameter of the atoms (assumed spherical, although ellipsoids or more complicated forms would do as well) of the liquid is greater than that of the atoms of the solid they cannot lie on the surface of the crystal without some heaping up. This means that the mutual potential energy between crystal and liquid is less than when the two diameters are equal. If a step is now made on the surface of the crystal the liquid atoms can come into contact with the surface without any heaping. If steps are made at every place where otherwise there would be heaping the surface energy will be minimal. Protruded atoms will then be regularly arranged, giving rise to surfaces with rational indices. Surfaces of high indices (vicinal planes) may be explained if the atoms of the liquid are only slightly larger than those of the solid. The theory will explain the observation that when a crystal of nickel chloride in a solution of the same substance is placed in a strong magnetic field slightly inclined faces appear on the crystal. A. J. MEE.

Hylotropic-isomeric forms. IV. K. SCHAUM (Annalen, 1928, 462, 194—209).—A continuation of previous work (A., 1916, i, 405; 1924, i, 520, etc.). The author classifies cases of polymorphism as follows: (1) Physical polymorphism. Here identical units form different space-lattices; small differences in the molecular anisotropy disappear on destroying the space-lattice, i.e., the liquid obtained by just melting either form is the same. (2) Cryptochemical polymorphism, subdivided into (2a) cryptochemical metameric polymorphism and (2b) cryptochemical polymeric polymorphism. The fused mass obtained from the two forms shows slight differences in (2a) and (2b); (2a) arises with complex molecules of fairly stable forms caused by intramolecular change, whilst (2b) is found with substances which tend to associate. High rates of interconversion are found in cases of (2b). (3) Chemical polymorphism. This may be of two kinds, I and II. (3) I is further divided into metameric and polymorphic cases (a and b). Under (3) Ia are cases where the two forms in the fused condition are quite different, there being in these cases two distinct chemical isomerides, convertible one into the other. If (3) Ia is represented by

$B \rightleftharpoons B'$, (3) Ib is represented by $nB \rightleftharpoons B_n$, where B =unit. In the b cases the fusions and interconversion are as in a. Chemical polymorphism II, giving very low interconversion velocities, is a limiting case of (3) I, each form containing a mere trace of the unit corresponding with the second form.

A number of substances have been investigated with a view to their classification on the above lines, the main results being as follows: Benzophenone: f. p. depends on the previous history; very high rate of interconversion (R). Phenyl *p*-tolyl ketone, low R . In these two cases the formation of the metastable form is aided by prolonged heating of the fused substances at relatively high temperatures. Fresh fusions of the different forms show great diversity of behaviour as regards supercooling and crystallisation, and further show small differences in physical constants. Both cases are probably examples of (2b), possibly (3) Ib in addition. *p*-Chloro-, *p*-bromo-, *p*-iodo-, and *p*-hydroxy-benzophenone and *p*-ditolyl ketone are apparently cases of (3) Ib (R , low, measured for the hydroxy-compound). Benzoin: R , low, measured. Dibenzoylacetone: case of (3) Ia; R , moderate, measured. Ethyl mesityloxideoxalate (ethyl $\alpha\gamma$ -diketo- ϵ -methyl- Δ^8 -heptenoate): case of (3) IIa (R , moderate, measured). Benzil-*o*-carboxylic acid: case of (3) Ia or (3) IIa with transition temperature about 66° (cf. Vixseboxe in Smits: "Allotropie," 1921); R , low, measured. β -Naphthyl salicylate: R , measured. 3-Nitro-*p*-acetotoluidide: R , low, measured: case of (3) Ia. 2-Nitro-*p*-toluidine: R , measured; the stability of the β -form (m. p. 69.5°) is increased by long heating of 2:6-dinitrotoluene: heat treatment of the fused mass has no effect on the transition, occurring at 40.5°. *m*-Nitrobenzoic acid: R , moderate, measured. 2:6-Dinitro-*p*-chlorophenol: metastable form appears below -3°, passing fairly rapidly into the stable form. α -Nitronaphthalene: a metastable form appears, together with the stable form, at the ordinary temperature, rapidly passing into the latter; at higher temperatures only the stable form is produced. 4-Nitrotriphenylcarbamide has a very low R . Triphenylmethane: R , high, measured. The transition temperatures and m. p. of the β -forms of other compounds are given as: Tetra bromomethane, 46.7° and 94.3°; succinic anhydride, 110.1° and 120.2°; orcinol, 53.3° and 197.5°; *as*-tetrachloroaniline, 117.8° and 118.1°; ethyl azoxybenzoate, 112.6° and 119.2°. Other less definite cases are also discussed. E. E. TURNER.

Conductivity and Hall effect in sputtered platinum films. A. RIEDE (Z. Physik, 1928, 48, 302—309).—The conductivity of platinum films sputtered on glass in the presence of hydrogen is proportional to the thickness of the film in the range 4.7—136 m μ . The Hall effect in such films is constant until the thickness is reduced below 30 m μ , when the magnitude of the effect diminishes rapidly.

R. W. LUNT.

Resistivity of thin metallic layers obtained by cathodic disintegration. F. JOLIOR (Compt. rend., 1928, 186, 1526—1528).—The resistance of thin films of platinum deposited on glass at the rate of 0.2×10^{-5} g./cm.²/min. from a cathode placed 3 cm.

away from the anode, at 900 volts, and an air pressure of 0.01 mm. of mercury, varies with the thickness of the film according to a curve of an exponential type, and for a constant film thickness, decreases with an increase in voltage. The effect of heat, which changes the resistance and its temperature coefficient in the direction of that of ordinary platinum, is attributed principally to the removal of gas occluded by the film.

J. GRANT.

Wiedemann-Franz law. III. A. EUCKEN (Z. physikal. Chem., 1928, 134, 220—229).—It is shown that the equation connecting the total specific thermal resistance of a metal with its specific electrical resistance proposed by Grüneisen and Goens cannot hold. The observations of Grüneisen and Goens can be utilised more satisfactorily if the fact that the "non-metallic" conductivity will be considerably lowered by deformation of the lattice is taken into account. A new evaluation of the results gives a somewhat better agreement. The Wiedemann-Franz constant for metals at low temperatures is in all cases much below its normal value for high temperatures. This constant seems to show very little dependence on lattice deformation.

A. J. MEE.

Electron "free path" and super-conductivity in metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, 14, 377—380).—Theoretical. The termination of a "free path" is taken to occur when the free electron is captured by a positive ion. The effect of this definition on specific heat, dependence of conductivity on temperature, super-conductivity, and on thermal conductivity at low temperatures is discussed.

W. E. DOWNEY.

Sommerfeld's electron theory of metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, 14, 370—377).—A critical examination of the conclusions reached by Sommerfeld and others (this vol., 467).

W. E. DOWNEY.

Specific resistance of bismuth crystals and its change in strong magnetic fields and some allied problems. I. Growth of crystal rods with a definite orientation of the crystal planes and the specific resistance of bismuth crystals. II. Method and apparatus for observing the change of resistance of bismuth in strong magnetic fields. III. Change of resistance of bismuth and the time lag in magnetic fields. P. KAPITZA (Proc. Roy. Soc., 1928, A, 119, 358—386, 387—401, 401—443).—I. A method is developed for growing bismuth crystals in the form of small rods, 3—5 mm. long and about 1 sq. mm. cross-section, in which the cleavage planes are oriented at any desired angle relative to the axis of the rod. An essential condition for the growth of such rods is that no strain must be set up in the bismuth during crystallisation. A small strain set up in the material has the effect of changing the perfect cleavage plane from one of the pseudo-octahedral planes to one of the three remaining planes of the same pseudo-octahedron, according to the nature of the strain. Measurements of the resistance of bismuth rods in a compressed state suggest that during the process of the growth of the crystals, cracks and imperfections are developed in the lattice which account for the variation of the

specific resistance in bismuth previously observed. By means of compression the cracks close, and the limiting value of the specific resistance perpendicular to the cleavage plane, reached when all the cracks have closed, is 1.39×10^{-4} at 16° . The limiting value parallel to the perfect cleavage plane is $1.07 \times 10^{-4} \pm 1\%$ at 16° . The origin of the cracks is studied, and it is found that their development probably occurs almost at the moment when the bismuth passes from the liquid to the solid state. A close relation is observed between the flexibility of the rods and their specific resistance. An ideal bismuth crystal at the ordinary temperature will probably have no well-defined cleavage plane and will be perfectly flexible. To explain the origin of the cracks, the hypothesis is advanced that there are two crystalline bismuth modifications; one of them, at present unknown, but probably cubic, is transformed into the ordinary rhombohedral form at a temperature slightly below the m. p. Since this transformation takes place when the bismuth is in a solid state and must be accompanied by changes in shape, stresses are set up in the crystal lattice which account for the spoiling of the lattice and the formation of "cracks." On the basis of this hypothesis several physical properties of bismuth may be explained.

II. A detailed description is given of a method for measuring the change of resistance of a bismuth crystal when it is placed in a magnetic field which exists for 0.01 sec. only and varies during the whole of this time. The study of the change of resistance is made possible by the fact that large current densities are permitted in the conductor, for such a short time, without heating the conductor, and no specially sensitive apparatus is required. The method adopted was to send a known current through the bismuth crystal and by means of potential leads to observe the difference of potential across the crystal, both the current and the *P.D.* being measured by oscillographs. A special switch is described which permits the current to be sent through the conductor for a very short time during the existence of the magnetic field. The make and break of this switch can be adjusted relative to the current wave through the coil with an accuracy of $1/5000$ sec. The elimination of errors and stray effects, due to the *E.M.F.* in the potential leads induced by the variation of the magnetic field and to the heating of the crystal produced by the current, is discussed.

III. A method is described for eliminating the *E.M.F.* in the bismuth crystal which accounts for the time lag phenomenon in the measurement of the change of resistance of bismuth in a magnetic field. Results are given for the change of resistance of bismuth crystals when the current is flowing perpendicular to the magnetic field, for different orientations of the crystal axis relative to the field, at 15° , -80° , and -182° . The presence of impurities and imperfections of the crystal lattice have a marked effect in diminishing the change of resistance of bismuth, particularly in strong fields and at low temperatures. The change of resistance of an ideal crystal in a magnetic field is discussed, and it is shown that in weak fields it follows a square law and in strong fields a linear law. The linear law is

practically independent of the orientation of the crystal relative to the magnetic field. A study has also been made of the case when the current is parallel to the magnetic field, for different orientations of the crystal axis relative to the field. Here the change of resistance is very small and a definite limiting value is reached. The magnitude of the change is little affected by the temperature, but is strongly influenced by imperfections of the crystal, being much larger for imperfect than for perfect crystals. It is suggested that this small change of resistance is due to the imperfection of the crystals and to the defective alinement of the current in the crystal with the lines of force of the magnetic field. An attempt was made to produce perfect bismuth crystals, growing them by means of direct deposition of bismuth vapour on cooled quartz plates in a vacuum. The experiments for obtaining single crystals were unsuccessful, but by studying the change in resistance of the deposits formed in a strong magnetic field, explanations were found for certain phenomena previously observed in thin bismuth layers (cf. Patterson, *Phil. Mag.*, 1902, **64**, 562). From a general study of the residual *E.M.F.* developed in bismuth in a magnetic field, it was found that the ratio, residual *E.M.F.*/resistance, is independent of the strength of the magnetic field in the region of investigation but is strongly influenced by the orientation and by the degree of perfection of the crystal. The origin of the residual *E.M.F.* is discussed. The failure of the present theory of metallic conductivity to account for the large change of resistance of bismuth in a magnetic field is considered, and reasons for the discrepancies between theory and experiment are suggested. A mechanism is suggested by means of which several phenomena observed in conductors may be explained. L. L. BIRCHUMSHAW.

Interferential method for measuring magnetic susceptibility of liquids. O. SPECCHIA (*Atti R. Accad. Lincei*, 1928, [vi], 7, 574—576).

Thermoelectric power in cold-worked metals. W. F. BRANDSMA (*Z. Physik*, 1928, **48**, 703—705).—The thermoelectric power appearing between cold-worked and recrystallised copper rods was found to be reproducible, providing the preliminary treatment was identical. The effect increases with the degree of working. On heating the cold-worked wire to a definite temperature the effect was found to decrease slowly to a value characteristic of the temperature.

J. W. SMITH.

Temperature of the acetylene-oxygen flame. F. HENNING and C. TINGWALDT (*Z. Physik*, 1928, **48**, 805—823).—The temperature in different parts of the acetylene-oxygen flame was determined by Kurlbaum's method of spectral line inversion. Observations were made in the visible region by colouring the flame by means of lithium carbonate and in the infra-red region by measurements on the carbon dioxide band $4.39\ \mu$ in the colourless flame, the former giving the temperature in the interior of the flame and the latter that of the outer cone. The hottest point in the normal flame is about 3 mm. above the tip of the luminous cone, where the temperature is about 3100° .

J. W. SMITH.

Specific heats of liquids and saturated vapours. J. J. VAN LAAR (*Z. physikal. Chem.*, 1928, **134**, 311—328).—Mathematical. A. J. MEE.

Specific heats of solid substances at low temperatures. K. CLUSIUS and P. HARTECK (*Z. physikal. Chem.*, 1928, **134**, 243—263).—The specific heats of gold, zinc, gallium, zinc oxide, copper oxide, zinc sulphide, ammonium carbamate, and silver chloride were determined at temperatures down to about 10° Abs. The apparatus and method of working are described. The results are given and curves drawn showing the variation of atomic heat with temperature. The results are discussed generally.

A. J. MEE.

Specific heats at constant pressure and at constant volume of some substances in the solid, liquid, and hypercritical states between 80° and 320° Abs. A. EUCKEN and F. HAUCK (*Z. physikal. Chem.*, 1928, **134**, 161—177).—The specific heats of various gases in the condensed state were determined by means of an apparatus previously described by Eucken, but slightly modified for this purpose. The specific heats of carbon dioxide (solid and liquid), nitrous oxide (solid), ethylene (solid and liquid), methyl chloride (solid and liquid), ethane (liquid), air (liquid), and argon (liquid) were determined at constant pressure and at different temperatures. The specific heats of ethane, argon, air, and carbon dioxide were also determined at constant volume, and in the case of the last three above the critical point. The behaviour of the specific heats with temperature was investigated. The specific heat increased only slightly with rise of temperature for ethane, a little more rapidly for carbon dioxide, whilst for air and argon there was a considerable decrease of specific heat with rise of temperature, although the substances were still some distance below the critical point, and therefore still in the liquid state. The results obtained for the specific heat of air at constant volume in the hypercritical state are compared with those of Hausen.

A. J. MEE.

Heat conductivity of solid crystalline substances between 0° and -190° . A. EUCKEN and G. KUHN (*Z. physikal. Chem.*, 1928, **134**, 193—219).—The heat conductivities of a large number of crystalline substances and crystalline aggregates were measured at temperatures from 0° to -190° . The fact previously found by Eucken and Neumann that the conductivity decreased if a substance in the form of large crystals was converted into small crystals holds for calcite, but not for crystalline aggregates of regularly crystallised substances if these are made up of a single component. The formation of mixed crystals was investigated; there was a very considerable decrease in the absolute value of the conductivity as well as in the temperature coefficient. The effect of an impurity on the heat conductivity of a crystal can be expressed by Matthiessen's law. The results for the series of alkali halides are collected; in general the conductivity, as well as the temperature coefficient between 0° and -190° , reaches a maximum when the two atoms composing the molecule are of nearly equal weight. There is a parallelism between heat conductivity and hardness if the

crystals are arranged in groups according to their constitution. The results are discussed in connexion with Debye's theory of heat conductivity of solids.

A. J. MEE.

Theory of specific heat c_v of monatomic liquids at high temperatures. A. EUCKEN and H. SEEKAMP (Z. physikal. Chem., 1928, 134, 178—189).—Mathematical. It is assumed that the molecules in a liquid have a periodic motion not necessarily harmonic, as has usually been supposed in order to explain the fact that the specific heat at constant volume of a liquid is more nearly equal to $6R/2$ than to $3R/2$, as the kinetic theory indicates. The atom is supposed to be surrounded by an elastic envelope, the repulsive force being expressed by a given law. The molecular heat of liquid argon was calculated at various temperatures and the results were compared with the measured values. There is only a qualitative agreement between the two results.

A. J. MEE.

Allotropic modifications and solid solutions of phosphorus. J. W. NICOLAÏEV (Compt. rend., 1928, 186, 1621—1624).—The mixture of crystals of phosphorus obtained in the Ipatiev bomb was separated by hand under the microscope and shown to consist of purple (1.90, 4.4 mm., 200°), ruby (2.11, 1.4 mm., 346°), and black (2.7, <0.5 mm., 490°) modifications, the figures in parentheses being the corresponding d , vapour pressures at 21°, and inflammation points, respectively. These and white phosphorus form a continuous series of solid solutions, red phosphorus being a mixture of ruby and purple phosphorus, and violet phosphorus a mixture of the ruby and black varieties. Black and purple phosphorus form a eutectic.

J. GRANT.

Critique of the electrical differential method of measuring the specific heats of gases at constant volume. M. TRAUTZ and O. TRAUTZ (Ann. Physik, 1928, [iv], 86, 1—65).—A comprehensive paper giving a systematic account of the errors in the above method of determining the specific heats of gases at constant volume. The errors are investigated both theoretically and practically. An outline of a complete c_v measurement is given. There is a table of corrections giving their estimated values. It now appears possible to make measurements of c_v correct to 1 part in 2000 parts.

A. J. MEE.

Effect of cold working on specific heat. W. GEISS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1928, 171, 317—322).—The specific heat of tungsten or nickel in the form of cold-drawn wire is not appreciably different from that of the recrystallised metal, a fact which is in agreement with the relationship previously developed (A., 1925, ii, 372) between cold working and the energy content of metals.

R. CUTHILL.

M. p. and b. p. of homopolar compounds as a function of the distribution of electrons in the molecule. A. DIBROVA (Ukraine Chem. J., 1928, 3, [Sci.], 1—38).—A consideration of Bohr's theory of the structure of the atom (Ber., 1925, 58, 1565) and of Remy's conception of molecular structure leads to the conclusion that any physical property g of a homopolar substance may be expressed as a function

of N_m , the number of valency electrons, N_a , the number of nuclear electrons not taking part in chemical reactions, N , the number of nuclear charges, and K , a constant depending on given external conditions. A comparison of the m. p. and b. p., of members of homologous series of aliphatic hydrocarbons, alcohols, mercaptans, disulphides, tellurides, and mono- and di-basic acids leads to an expression $T=f(N,P).N_a/\sqrt{N_m}$, where P represents pressure. Where $P>0$, $f(N,P)$ is a linear function, which, although not constant for different compounds, yet differs little. At pressures below 1 atm. the value of $f(N,P)$ is below 30 for m. p. and below 40 for b. p. Where $P=0$, $f(N,P)$ is constant (its value is about 20 for the m. p.), and the m. p. and b. p. equal the quotient, $N_a/\sqrt{N_m}$. Where P is variable, the value of $f(N,P)$ is best expressed as $a[(b-N)P^{1/5}+d]$, where a , b , and d are constants for the given homologous series; and $ad=\text{const.}=20$.

R. TRUSZKOWSKI.

Fusion of cyclohexanol. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 593—599).—*cyclohexanol* exhibits dimorphism, transition from transparent to translucent crystals occurring at 21.4°. The latter form has a marked solvent action on atmospheric gases, which are evolved again when the temperature falls below 21.4°. The fusion pressure P of *cyclohexanol* is determined at temperatures of from 25.10° to 29.22°, and over this range P increases from 27.39 to 127.10 megabars and dP/dt from 18.48 to 29.97. The latent heat of fusion is a linear function of temperature, and amounts at 23.7° to 2.71 g.-cal.

R. TRUSZKOWSKI.

Specific heat of nickel above the Curie point. P. WEISS (Compt. rend., 1928, 187, 12—14).—The atomic heat of nickel corrected for the heat of demagnetisation in accordance with the theory of the molecular field (cf. Lapp, this vol., 577), increases with temperature from 0 to 550° and remains constant at the Curie point, the rise being equal to that portion of the atomic heat corresponding with the kinetic energy of a degree of freedom. The experimental error is 2.5%. It is probable that the rise is connected with the change of atomic moment from 3 to 8 magnetons shown by nickel at high temperatures, the fourth degree of freedom being represented by the penetration of thermal agitation into the atom.

J. GRANT.

Gaseous state of normal substances. K. WOHL (Z. physikal. Chem., 1928, 133, 305—349).—The applicability of Wohl's equation of state is considered in the case of normal substances, i.e., those for which $RT_c/p_c v_c$ (where T_c , p_c , and v_c are the critical temperature, pressure, and volume, respectively) has the value 3.5—3.95, and T_c lies between 0° and 300°. Below T_c , the equation is valid for the entire stable gaseous state, and at T_c its validity extends to v_c , the deviations of the pressure from the theoretical value never exceeding 1%. For *isopentane*, *ethyl ether*, and *carbon dioxide* above T_c , the limit of applicability rises to $1.7v_c$ and $4p_c$ as the temperature rises to $1.75T_c$, the maximum error in the pressure being 2%. Since in these applications of the equation it is necessary to introduce only two

constants which are characteristic of the particular gas considered, viz., T_c and p_c , it follows that the theorem of corresponding states is true over the same range as the equation. Applying the equation to sulphur dioxide, it seems that the experimental data for the volumes of the saturated vapour at low temperatures are incorrect, and that the gas is a normal substance, and not, as previously supposed, associated. Between temperatures of $0.8T_c$ and $2.5T_c$, the equation gives accurate values for the second virial coefficients of all the normal gases, whilst below $0.8T_c$ there are deviations which show that the attraction potential of the molecules is no longer proportional to the inverse power of the temperature, but varies somewhat more rapidly. The possession of a high dipole moment is not in itself sufficient to ensure that a substance shall be associated; it is essential that the orientation polarisation due to the rigid dipole moment shall greatly preponderate over the polarisation depending on the displacement of electrons and atoms in the electric field. The magnitude of the dipole moment or even a very wide variation in the ratio of the two polarisation effects has no effect on the behaviour of the substance in the gaseous state.

R. CUTHILL.

Velocity of sound in liquids at high frequencies by the sonic interferometer. J. C. HUBBARD and A. L. LOOMS (Phil. Mag., 1928, [vii], 5, 1177—1190).—High-frequency vibrations are set up in a column of liquid by means of a quartz piezo-electric vibrator. The resonance lengths of the column are then determined by means of a piston moving at the other extremity of the column. From the frequency of the oscillator the velocity of sound in the liquid is determined. Measurements have been made with mercury, water, and several salt solutions and the thermodynamic coefficients deducible therefrom are in good agreement with those obtained by Bridgman (Proc. Amer. Acad. Sci., 1912, 47, 549).

A. E. MITCHELL.

Molecular force. I. The change of vapour pressure of a liquid in the presence of compressed gas and its relationship to the van der Waals constant a_{12} . A. EUCKEN and F. BRESLER (Z. physikal. Chem., 1928, 134, 230—242).—It is shown that the increase of vapour pressure of a liquid through the presence of another substance in the form of a highly compressed gas provides a method of obtaining the van der Waals constant a_{12} , which is proportional to the reciprocal molecular attraction. The substance used was carbon disulphide. The gas (carbon dioxide, nitrogen, or hydrogen) was saturated with the vapour and compressed. The amount of carbon disulphide vapour contained was then determined at atmospheric pressure by means of an interferometer. The a_{12} values were calculated from the results and from those of other observers. The Bertholet relationship $a_{12} = \sqrt{a_1 a_2}$, where a_1 and a_2 are the values for the single components, was verified.

A. J. MEE.

Volume chemistry. III. Oxygen compounds. (2) Carbonyl group. F. WRATSKO (Pharm. Presse, 1927, 32, 456—460; Chem. Zentr., 1928, i, 1001).

Determination of the vapour pressure of scented substances. G. TAMMANN and W. OELSEN (Z. anorg. Chem., 1928, 172, 407—413).—With a knowledge of the threshold value, or weight of material which can be detected by smell, the vapour pressure of a scented substance at different temperatures may be determined. The sensitiveness to smell of the investigator must first be measured. At a temperature at which the vapour pressure of the scent is known a fixed volume of air v_1 is saturated with it and then diluted by a volume of air v_2 until the scent can only just be perceived. From the dependence of the quotient $(v_1 + v_2)/v_1$ on temperature the vapour-pressure curve may be obtained. This was tested and found to be satisfactory for substances with small threshold values by determining the vapour pressures of camphor and butyric acid and comparing with values found by other methods. The method should be employed only at very low pressures, where other methods become difficult. Substances of which the vapour pressure at the temperature of the nose is below the threshold value cannot be perceived by smell.

M. S. BURR.

Has aluminium a transition point? A. SCHULZE (Z. Physik, 1928, 49, 146—154).—Measurements of the electrical resistance of very pure aluminium (99.94%) indicate that no allotropic change occurs in that metal in the neighbourhood of 610° .

J. W. SMITH.

Absorption of ultrasonic waves by various gases. T. P. ABELLO (Physical Rev., 1928, [ii], 31, 1083—1091).—The increase in the absorption coefficient (cm^{-1}) for ultrasonic waves of frequency 612 kilocycles in air containing 1 vol.-% of various gases, compared with air, was: carbon dioxide 0.029, nitrous oxide 0.034, hydrogen 0.014, helium 0.0025; for argon mixtures no absorption was observed.

A. A. ELDRIDGE.

Connexion between the properties of liquids and orthobaric densities. W. HERZ (Z. anorg. Chem., 1928, 172, 414—416).—From McLeod's relationship $\gamma/(d_l - d_g)^4$, where γ is the surface tension and d_l and d_g are the densities of the liquid and saturated vapour, respectively, is a constant for any one substance independently of temperature, and from certain relationships found by the author between the number of molecules per c.c. and the viscosity, heat of vaporisation, and surface tension, respectively (this vol., 229, 368, 697), the following formulæ have been deduced: $L^{1/2}(d_l - d_g) = \text{const.}$ and $\eta^{1/5}/(d_l - d_g) = \text{const.}$, L being the heat of vaporisation and η the viscosity. The first formula has been tested by reference to the available data for pentane, ethyl ether, and tin tetrachloride over a large range of temperature, and the second by reference to the data for fluorobenzene and methyl acetate. The agreement is satisfactory.

M. S. BURR.

Method for measurement of vapour pressure of small quantities of substance. The vapour pressure of chloropicrin. H. BEASZKOWSKA-ZAKRZEWSKA (Rocz. Chem., 1928, 8, 219—228).—Using a method based on Smith and Menzies' submerged bulblet method (cf. A., 1910, ii, 1036), together with Swientoslawski's ebullioscopic thermostat, the vapour pressure of chloropicrin has been

determined between 78° and 112°. The constants α , β , and γ are calculated for the formula $\log p = \alpha - \beta/(273+t) - \gamma \log (273+t)$, connecting vapour pressure with temperature. These constants apply to chloropicrin between 0° and its b. p.

R. TRUSZKOWSKI.

Determination of vapour pressure of chloropicrin at about 100°. H. BŁASZKOWSKA-ZAKRZEWSKA (Rocz. Chem., 1928, 8, 210—218).—The vapour pressure of chloropicrin is determined between 98° and 105°, using the air-current method, which consists of determining the loss in weight of chloropicrin after a known volume of air at a given temperature has been passed through the liquid. Swientosławski's ebullioscopic thermostat, which maintains temperatures constant to within 0.01—0.02°, was used for the above purpose.

R. TRUSZKOWSKI.

Influence of glass on vapour pressure. J. RINSE (J.C.S., 1928, 1442—1449; cf. McHaffie and Lenher, A., 1925, ii, 854; 1926, 898; 1927, 198; Frazer, Patrick, and Smith, A., 1927, 722).—The vapour pressure-temperature curves of mercuric iodide, bromide, and chloride and iodine, when measured with a glass-spring indicator which had been heated previously at above 500°, instead of changing abruptly to the linear form on passing the saturation point, were continuous. Mercury and mercurous chloride did not behave in this way. Experiments with carefully dried materials indicated that water was not the cause of this effect. The addition of glass powder considerably augmented it. Further, the effect is not to be explained either in terms of adsorption, for the adsorbed layers would have to be at least 500 molecules thick, or in terms of a reaction between glass and the substance; experiment failed to reveal such a reaction.

F. J. WILKINS.

Dissociation of ammonium chloride vapour. H. BRAUNE and S. KNOKE (Z. physikal. Chem., 1928, 135, 49—62).—Accurate measurements of the vapour density of ammonium chloride at temperatures between about 200° and 400° indicate that complete dissociation takes place, in contradiction to the work of Smith and others.

H. F. GILLBE.

Cohesion and intermolecular repulsion. R. K. SCHOFIELD (Phil. Mag., 1928, [vii], 5, 1171—1176).—Cohesion is defined as the quantity $(dU/dv)_T$ in the relation $(dU/dv)_T = T(dp/dT)_v - p$, where U is the internal energy of the substance under consideration. No effect of chemical union is considered and effects due to translational kinetic energy are ignored. The magnitude of this quantity has been calculated for a number of liquids up to pressures of 3000 atm. As the volume is reduced the cohesion first increases to a maximum and then decreases. The results are not in accordance with the view that molecules resemble rigid spheres. They are readily explainable if the molecular fields are of the complex type considered by Lennard-Jones (A., 1926, 888), the force between two molecules being repulsive when they are very close together and attractive when they are farther apart.

A. E. MITCHELL.

Diffusion problem for a solid in contact with a stirred liquid. H. W. MARCH and W. WEAVER

(Physical Rev., 1928, [ii], 31, 1072—1082).—Mathematical. The problem considered is that of the one-dimensional flow of heat which occurs when a solid is in contact with a stirred liquid. Its connexion with material diffusion is shown. A. A. ELDRIDGE.

Density of fused mixtures of cadmium and potassium chlorides. R. LORENZ and H. ADLER (Z. anorg. Chem., 1928, 172, 372—374).—The density of fused mixtures of cadmium and potassium chlorides has been determined at different temperatures by a modification of Tammann and Brunner's method (cf. A., 1904, ii, 244). The results are tabulated. At constant temperature the variation of density with composition is approximately linear. M. S. BURR.

Binary azeotropic mixtures containing a lower alcohol as one component. Y. TANAKA and T. KUWATA (Chem. News, 1928, 137, 13—14).—From observations on azeotropic mixtures containing a lower alcohol as one component it is deduced that a rise of temperature or an increase of pressure causes an increase in the proportion of that component of the mixture which has the greater heat of vaporisation, and that two substances which have the same heat of vaporisation at the same temperature cannot form an azeotropic mixture.

A. R. POWELL.

Peculiar results in hardness tests of lead-antimony alloys. L. O. HOWARD (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 90, 5 pp.).—Fall in hardness was observed at 40% and 50% Sb in two series. Reported differences in hardness are ascribed to different thermal treatments.

CHEMICAL ABSTRACTS.

Structure of tin-antimony alloys. W. BRONIEWSKI and L. SLIVOVSKI (Compt. rend., 1928, 186, 1615—1616).—Measurements of the electrical conductivity, thermo-electric power, electrode potential, coefficient of expansion, and hardness, and of their respective temperature coefficients, for tin-antimony alloys reheated at 200° for 1200 hrs. suggest that Sn_3Sb_2 is the only compound formed. Thermal analysis confirms this result and shows that such crystals are deposited from a liquid of the composition Sn-Sb. This is said to explain the supposed formation of the compound SnSb in commercial alloys containing 25% of antimony.

J. GRANT.

Structure of silver-aluminium alloys with a high content of aluminium. M. HANSEN (Z. Metallk., 1928, 20, 217—222).—Examination of a series of silver-aluminium alloys containing 0—60% Ag by thermal and micrographic methods has confirmed the position of the liquidus and eutectic composition as found by Petrenko (A., 1905, ii, 635), but the m. p. of the eutectic is now found to be 558°. The solubility of silver in solid aluminium is about 0.45% at 20° and 0.75% at 200°; with further rise of temperature the solubility increases remarkably rapidly to a maximum of 48% Ag at the eutectic temperature. Thus all alloys containing more than about 0.5% Ag exhibit age-hardening properties when quenched from above 300° and tempered at a temperature below the solid solution line.

A. R. POWELL.

Solubilities and mol. wt. determinations in liquid chlorine. K. H. BUTLER and D. MCINTOSH

(Proc. Nova Scotian Inst. Sci., 1927, 16, 198).—The solubilities in liquid chlorine were obtained by measuring the rise in b. p. caused by addition of the solute. Fifty-nine of the commoner salts were found to be insoluble at the b. p. Sulphur, arsenic, silver, copper, and zinc did not react with the liquid chlorine, whilst aluminium, iodine, phosphorus, and tin reacted, but only the last caused any rise in b. p.

S. J. GREGG.

Grain growth in metals caused by diffusion. F. C. KELLEY (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 89, 7 pp.).—Rapid grain growth results from diffusion, the direction of grain being parallel to that of diffusion. The diffusion of chromium and manganese in iron is discussed. Iron diffuses into nickel, but not nickel into iron.

CHEMICAL ABSTRACTS.

Solubility of thalious chloride in water and aqueous solutions of magnesium sulphate and lanthanum nitrate at 25°. M. RANDALL and K. S. CHANG (J. Amer. Chem. Soc., 1928, 50, 1535—1536).—The solubility of thalious chloride is 0.01611 mol. per 1000 g. of water, the solution having sp. gr. 1.0034 and d 1.0004.

S. K. TWEEDY.

Vapour pressure of mixtures of benzene and cyclohexane. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 562—583).—Measurements of the vapour pressures of mixtures of benzene and cyclohexane at temperatures between 30° and 80° give values almost identical with those calculated from Antoine's formula (Compt. rend., 1888, 107, 681). At all temperatures mixtures of maximum vapour pressure exist, their composition depending on temperature. The vapour-pressure curves of benzene and cyclohexane cut at 50°; below this temperature the vapour pressure of the latter exceeds that of the former, whilst above 50° the contrary is the case. The 50° isotherm is strictly symmetrical, with a maximum value at 50% of benzene; at higher temperatures the summit is shifted in the direction of cyclohexane. This affords a confirmation of Kononov's law (J. Russ. Phys. Chem. Soc., 1884, 16, 11). The properties of the above mixture are not additive at temperatures below the b. p.

R. TRUSZKOWSKI.

Vapour pressures of mixtures of toluene and cyclohexane. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 584—593).—The vapour pressure of mixtures of toluene and cyclohexane rises steadily at all temperatures as the proportion of cyclohexane increases; at all concentrations the observed vapour pressure is greater than the arithmetic mean of those of the constituents. The observed vapour pressures agree well with Antoine's formula (Compt. rend., 1888, 107, 681).

R. TRUSZKOWSKI.

Equilibrium of solutions of barium and lead chlorides dissolved in aqueous hydrochloric acid. P. A. VOLKOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 704—724).—The solubility of lead chloride at 25° and at 0° has a minimum value when 7—8 mols. of barium chloride are present per 100 mols. of water and a maximum value at the saturation concentration of barium chloride. The first effect is due to the increase in concentration of chlorine ions and the second probably to the formation of complex salts.

Similar results have been obtained for the system lead chloride—hydrochloric acid—water (Ende, Z. physikal. Chem., 1903, 16, 162). In presence of concentrated hydrochloric acid the solubility of barium chloride is unaffected by the presence of lead chloride; the solubility of the latter salt is greatly increased by the addition of hydrochloric acid, whilst that of barium chloride becomes very small. The use of this reaction is recommended for the separation of traces of lead from radium. R. TRUSZKOWSKI.

Diffusion of hydrogen through iron. W. E. DEMING (Phil. Mag., 1928, [vii], 5, 1081—1084).—It is shown with the aid of the results of Borelius (A., 1927, 727) and of Bartlett (*ibid.*, 404, 927) that the rate of diffusion of hydrogen through iron is represented by an equation of the form $dP^{1/n}/dt = K_1/c\Delta^2P^{1/n}$, where P is the pressure of the gas and c the amount adsorbed per unit volume under unit pressure. For the steady state this becomes $dm = K_1A\Delta P^{1/n}dt$, where dm is the amount of hydrogen diffusing through an area A of thickness dx with pressures P and $P+dP$ in time dt . These equations are exactly similar in form to those representing the conduction of heat by metals. A. E. MITCHELL.

Solubility of oxygen in iron, and in ferrous oxide (oxoferrite, wüstite). C. BENEDICKS and H. LÖRQUIST (Z. anorg. Chem., 1928, 171, 231—238).—Schenck and Dingmann's value for the solubility of oxygen in solid iron (A., 1927, 1030) is much in excess of the values to be found in the literature, and also in their diagram for the system iron—oxygen the ferrous oxide region of homogeneity is displaced towards much higher concentrations of oxygen. It seems probable, however, that in these authors' experiments the mixture of metal and oxides became contaminated with alumina from the vessels used to contain it, so that the previously accepted values are possibly substantially correct. R. CUTHILL.

Fractional crystallisation of radioactive substances. III. Distribution of radium between solid crystalline barium chloride dihydrate and its saturated aqueous solution at 0° and 35°. W. CHLOPIN and A. POLESSITSKY (Z. anorg. Chem., 1928, 172, 310—320; cf. A., 1927, 1133).—The distribution of radium between solid barium chloride and its saturated solution is strictly in accordance with the simple partition law. The partition coefficient at constant temperature and concentration of the liquid phase remains constant for large variations in the relative quantities of the two solvents and also for large variations, e.g., 2.628×10^{-8} — $2.816 \times 10^{-5}M$, in the concentration of the radium salt. The distribution coefficient varies with temperature, the temperature coefficient being -0.516 per degree between 0° and 35° and -0.275 per degree between 35° and 57.5°. Hence fractional crystallisation of the chlorides, and also of the bromides, is the more effective the lower is the temperature at which the crystallisation takes place. There are considerable differences between the partition coefficients found by different investigators, but these may probably be explained by variations in temperature and acid concentration. M. S. BURR.

Influence of viscosity on the rate of absorption of carbon dioxide by neutral sodium carbonate. P. RIOU and P. CARTIER (Compt. rend., 1928, 186, 1727—1729).—An extension of the authors' viscosity experiments (this vol., 702) to ethylene glycol, methyl and ethyl alcohols, lactose and acetaldehyde has shown that although viscosity has a certain influence on the rate of absorption of a gas by a liquid, it is not the principal factor, the chemical nature of an added non-reacting organic crystalloid substance playing a far more important part and increasing the viscosity and rate of absorption to an extent which suggests a catalytic effect. J. GRANT.

Important factors in the investigation of adsorption from solutions. K. C. SEN (Z. anorg. Chem., 1928, 171, 275—280).—From the Freundlich adsorption isotherm $x/m = KC^n$, it follows that if K and n actually remain constant independently of the volume of the solution and the weight of adsorbent, m , then for a given concentration C of the solution, x/m should also be independent of m , and of the volume and initial concentration of the solution. For adsorptions in which there is no possibility of chemical reaction, e.g., the adsorption of acetic acid by animal charcoal (Pavlov, A., 1924, ii, 833), this is in agreement with the experimental results. Where, on the other hand, forces of a chemical nature may be involved, as in the adsorption of ions by colloids, this is no longer true. Thus in the adsorption of copper sulphate by manganese dioxide, the values of K and n are not independent of m and of the initial concentration of the solution. R. CUTHILL.

Adsorption from solution by ash-free adsorbent charcoal. V. Adsorption from buffer solutions as a means of determining the isoelectric point for charcoal. E. J. MILLER and S. L. BANDEMER (J. Physical Chem., 1928, 32, 829—842; cf. A., 1927, 929).—Adsorption from Sørensen's standard buffer solutions by blood, wood, and sugar charcoals, purified by treatment with hydrofluoric acid (A., 1926, 898), and by unpurified blood charcoal has been studied. Adsorption produces the changes in reaction which are to be expected from previously-established facts of adsorption by pure adsorbent charcoals (cf. A., 1926, 1090). Pure charcoal decreases the acidity of acid buffer mixtures by adsorption of acids and increases the alkalinity of less alkaline buffers by hydrolytic adsorption of acid from salts with the liberation of alkali. The alkalinity of highly alkaline buffers is not reduced. Unpurified blood charcoal reduces the alkalinity of the more alkaline buffers owing to the presence of acid impurities in the charcoal. Pure charcoal carrying adsorbed acids acts in a similar manner. Decomposition or elimination of acid impurities by ignition of the unpurified charcoal removes this effect. The method of adsorption from buffer solutions is unsuitable for the determination of the isoelectric point for charcoals, and the results bear no relation to the isoelectric point determined electrokinetically. Data are given. L. S. THEOBALD.

Adsorption in binary systems. (MLLE.) L. S. LÉVY (Compt. rend., 1928, 186, 1619—1621; cf. this vol., 118).—The adsorption from solutions containing

iron and nickel or copper and nickel has been studied with manganese dioxide as the adsorbent, the concentration of one metal being kept constant and the other varied. The results agree with Freundlich's adsorption formula. Values for the constants of the formula are obtained, and it is shown that equal concentrations of copper and nickel have the same influence on the adsorption of iron, but the concentration of iron which is required to produce the same effect on the adsorption of copper is only 0.0017 as great as the corresponding nickel concentration. J. GRANT.

Adsorption in solutions. XIII. Adsorption from mixed solutions of electrolytes. M. DUBININ (Z. physikal. Chem., 1928, 135, 24—35).—The adsorption by pure activated wood and sugar charcoal from mixed aqueous solutions of electrolytes has been studied quantitatively. A linear relationship exists between the quantities of each component adsorbed from a binary mixture. From the ratio between the number of molecules of each component in the adsorbed layer, the extent to which the adsorption of one component is diminished by the second may be calculated by a method applicable to such widely differing mixtures as hydrochloric and nitric acids, hydrochloric and oxalic acids, and hydrochloric acid and acetone; in the first case poisoning of the catalyst occurs, in the second there is ordinary partition, and in the third independent adsorption of the two components takes place. Such differences are purely qualitative, and all these cases are susceptible of the same general treatment. H. F. GILLBE.

Adsorption of electrolytes by crystalline surfaces. A. PINKUS and (MLLE.) L. DE BROUCKÈRE (Bull. Acad. roy. Belg., 1927, [v], 13, 415—440).—The adsorption of an electrolyte A_mB_n at a crystalline surface in contact with water has been investigated. The electrolytes chosen were hydrochloric acid, and the chlorides of potassium, lithium, copper, and nickel, whilst the surface consisted of microcrystalline, pure barium sulphate presenting a surface area of 8.45×10^5 cm.² per g. Solutions of the various electrolytes, saturated with barium sulphate, were agitated with known weights of barium sulphate for 5—10 hrs. at 25°, the solid was washed, and the amounts of adsorbed electrolytes were determined by various direct and indirect methods. The same equilibrium conditions could be obtained under defined conditions, starting either from pure barium sulphate or from crystals bearing an excess of adsorbed electrolyte.

The reversibility of the adsorption and the equivalent adsorption of cations and anions is quantitatively demonstrated. Errors arising from capillary absorption are negligible. Adsorption isotherms $\log x = f(\log c)$ are plotted, x being the equilibrium concentration in g.-equivalents per g. of barium sulphate, and c the equilibrium concentration of the solution in g.-equivalents per litre. The curves cease to be linear at higher concentrations.

The expression $x = p/Ax^v + Bp$ has been deduced theoretically and fully verified. The terms in the expression follow from $A = Na/S$, $B = 4N\theta/mnS$, and $f(x) = ax^v$, where a and v are constants, p is the

osmotic pressure, N is Avogadro's number, S is the adsorbing surface in cm^2 per g., and θ is the surface in cm^2 occupied by a single adsorbed particle. The verification does not apply to the nickel and copper chlorides, as the activity coefficients are not known.

R. A. MORTON.

Absorption of ammonia, carbon dioxide, and vapours of benzene and acetone by gels of titanium dioxide and stannic oxide. N. J. NIKITIN and W. J. JURÉEV (*Z. anorg. Chem.*, 1928, 171, 281—284).—The absorption of the above gases and vapours by titanium dioxide and stannic oxide at the ordinary temperature has been studied. Titanium dioxide readily absorbs ammonia, and at -16° under 1 atm. takes up about 8.5% of its weight of the gas; stannic oxide is less active, and several other oxides manifest very little activity. In respect of the absorption of benzene vapour, titanium dioxide gel is comparable with ordinary inactive silica gel.

R. CUTHILL.

Surface tension of a mixture of ethyl alcohol and water. I. K. I. ALEKSEEVA (*Z. physikal. Chem.*, 1928, 134, 467—474).—The surface tension of mixtures containing 99.7—87% of ethyl alcohol has been measured by the maximum bubble pressure method. The change in surface tension is directly proportional to the change in concentration.

O. J. WALKER.

Variation with time of surface tension of plasma. G. HOMÈS (*Bull. Acad. roy. Belg.*, 1927, [v], 13, 555—572).—A slow decrease in the surface tension of colloidal liquids over a period of about 2 hrs. has been demonstrated, and shown to be independent of evaporation. Both dynamic and static surface tension are little affected by the nature of the anticoagulant used. A full theoretical discussion is appended.

R. A. MORTON.

Capillary action of mercury in the absence of gas-grown skins. J. J. MANLEY (*Phil. Mag.*, 1928, [vii], 5, 958—962).—If the gas-grown skin which normally occurs on the surface of a charged barometer tube be removed, the convexity of the mercury surface is changed to concavity. The same effect is obtained with any mercury surface which has been treated, either by electric discharge or by boiling, so as to remove the gas-grown skin. The difference between the reduced reading of a standard barometer and that of a treated column was found to be +3.1 mm. This capillary effect is four times as great as that shown by water.

W. E. DOWNEY.

Surface action in chemical phenomena. R. DUBRISAY (*Bull. Soc. chim.*, 1928, [iv], 43, 625—641).—A lecture delivered on May 11, 1928.

Reflecting power and colour sequences shown by metals on activation. F. H. CONSTABLE (*Nature*, 1928, 122, 57).—It has been verified that a burnished metal surface becomes duller on activation, the accompanying colour phenomena being also less pronounced.

A. A. ELDRIDGE.

Formation of surface films on palladium by heating in air and by anodic polarisation. G. TAMMANN and J. SCHNEIDER (*Z. anorg. Chem.*, 1928, 171, 367—371).—The rate of increase with the time,

t , of the thickness of the surface film of oxide produced on palladium when heated at 500 — 750° in air is represented by the equation $t = ae^{by} - a$ (cf. A., 1922, ii, 831), y being the thickness of the equivalent film of air, and $\log b$ decreasing in an approximately linear manner with rise in temperature. The same relation applies to the anodic polarisation, but here when y has reached a certain magnitude, which depends on the current strength, both a and b abruptly assume new values.

R. CUTHILL.

Determination of surface-development of foaming drugs. R. DIETZEL and U. PANKOW (*Apoth. Ztg.*, 1928, 43, 44—45; *Chem. Zentr.*, 1928, i, 1076).—A photomicrographic method is described. The increase of surface caused by a spuman preparation was 260-fold at 20° , 390-fold at 37° .

A. A. ELDRIDGE.

New interference method of measuring the surface area of film catalysts. I. Theory. II. Nickel. Preparation of the film, apparatus for activation, and study of the surface area. F. H. CONSTABLE (*Proc. Roy. Soc.*, 1928, A, 119, 196—201, 202—213).—I. Spectrophotometric measurements of the intensity and wave-length of the light reflected from oxidised surfaces of iron, nickel, and copper show that interference is the main cause of production of the colour sequences, so that the colour of these films uniquely determines their thickness when the order of the colour and the refractive index of the film is known. This supplies a method of evaluating the surface area of metallic film catalysts if the full data are available. Five methods are outlined, involving (1) measurements of the mass of the film and spectrophotometric observations on the light reflected from the coloured film; (2) data on the spectrophotometric analysis of the reflected light and the conductivity of the film; (3) observation of the surface colour expressed in terms of the equivalent air thickness of the covering film and the mass of the film; (4) simultaneous observations of the surface colour and the electrical conductivity of the metallic film; and (5) determination of the initial values of the oxidation constants from observations of the surface colour, and of the mass of oxide produced, or the change in conductivity of the metallic film.

II. Experimental details are given for the preparation of uniform graphite films on china clay rods, and an electrical method of deposition of nickel on the graphite-coated rods is described. The metal films were activated by alternate oxidation and reduction at 580° , and then reduced at the lowest possible temperature by hydrogen. They were then oxidised at 330° , the conductivity of the film being measured at intervals during the oxidation, and the surface area was determined from spectrophotometric and visual observations of the surface colour. Curves show the relation between the fall of conductivity with time and the thickness of the oxide film. The area on activation passes through a minimum and then rises. This effect is accompanied by a fall in the conductivity due to cracking in the film, the strain set up by the alternate oxidation and reduction being sufficient to break up the film. Raising the

temperature to 563° after activation, with alternate oxidations and reductions, showed that two consecutive oxidations and reductions were necessary before the film would settle down to an equilibrium state. The terminal area was less than that shown by metal reduced at the lowest possible temperature.

L. L. BIRCUMSHAW.

Dialysis. III. Temperature coefficient of dialysis. H. BRINTZINGER and B. TRÖMER (*Z. anorg. Chem.*, 1928, **172**, 426—428).—The relation between c_0 and c_t , the concentration of a dialysable substance before and after dialysis for a time t , is expressed by the equation $c_t = c_0 \times e^{-\lambda t}$, where λ is a coefficient typical for each substance and dependent on the membrane, the size of surface, concentration, presence of other substances, temperature, etc. (this vol., 121). Experiments have been made at different temperatures, but under otherwise comparable conditions, and λ has thus been found to vary linearly with temperature. $\lambda_T = \lambda_{T'}[1 + a(T' - T)]$, where a is the temperature coefficient. a appears to be of the order of magnitude of the temperature coefficient for diffusion without a membrane. M. S. BURR.

Electro-osmosis and electrolytic transport of water in solutions of alkali chlorides. J. BABOROVSKÝ and J. VELÍŠEK (*Chem. Listy*, 1928, **22**, 265—267).—Measurements of the proportion of solutions of sodium, potassium, or lithium chloride transported by one faraday, of the electrolytic transport of water in these solutions, of the transport of these salts themselves, and finally of the transport numbers of their cations in normal solution show that these are linear functions of the concentration in g.-equivalents. This confirms the work of Hepburn on other electrolytes (*A.*, 1926, 1100; 1927, 422).

R. TRUSZKOWSKI.

Electro-osmosis and anion effect. A. RABINERSON (*Kolloid-Z.*, 1928, **45**, 122—129).—Experiments have been performed to determine the drop in electrokinetic potential at a surface of talc in various electrolyte solutions, and to determine the influence of various anions. Variations were noticed in the electro-osmotic velocity at high concentrations of electrolyte, a result which is ascribed to the great adsorbing surface of talc. At these concentrations, the Helmholtz formula is inapplicable and the falling branch of the curve relating electro-osmotic velocity with concentration does not give a true representation of the change of electrokinetic potential, and the antagonistic effect of mixtures of electrolytes cannot be studied quantitatively. Sulphate and citrate ions produce a higher negative charge than chloride ions, and similarly alkali salts give a higher negative charge than acids. Antagonistic effects were observed in experiments on the reversal of charge by addition of multivalent cations in presence of other electrolytes. The concentration of ferric chloride or of thorium nitrate required to reverse the charge was raised by addition of sulphate or citrate ions, but was unaltered by chloride or nitrate ions. E. S. HEDGES.

Electrodialysis of serum. G. ETTISCH, R. BRADFIELD, and W. EWIG (*Kolloid-Z.*, 1928, **45**, 141—145).—Undiluted serum can be rapidly electro-dialysed with a current density of 20—30 milliamp./

cm.² by using a parchment membrane for the cathode and a collodion membrane soaked in albumin from suitably treated serum for the anode. The latter may consist of a collodion membrane containing hæmoglobin. The liquid in the middle cell changes gradually from its initial hydrogen-ion concentration to the value p_H 5.0. Contrary to the views of Reiner (*A.*, 1926, 1205), immersion of a collodion membrane in serum-albumin for a short time is insufficient to cause it to behave as an albumin membrane, and the supposition that the albumin membrane acts as a valve cannot be maintained. During the course of the electrodialysis, the anode membrane is surrounded by a liquid with acid reaction, whilst the liquid round the cathode membrane has an alkaline reaction.

E. S. HEDGES.

Phenomenon of stratification in electrodialysis as an electrophoretic phenomenon. F. BLANK and E. VALKÓ (*Biochem. Z.*, 1928, **195**, 220—227).—The separation into layers during electrodialysis of colloidal solutions using Pauli's apparatus is explained as an electrophoretic phenomenon. The upper layer arises at the membrane and, owing to the migration of colloid particles, is colloid-free and of smaller density and therefore rises to the surface.

P. W. CLUTTERBUCK.

Influence of lipoids on the diffusion of acids and alkalis in gels. S. I. AFFONSKY (*Biochem. Z.*, 1928, **195**, 387—395).—Usually cholesterol accelerates and lecithin retards the diffusion process of acids and alkalis (sulphuric and acetic acids, sodium hydrogen carbonate and hydroxide, etc.) through agar and gelatin gels, but when the lipid concentration becomes high, then both cholesterol and lecithin inhibit, but the latter more strongly than the former.

P. W. CLUTTERBUCK.

Diffusion rings and regions of crystallisation. G. LINCK and E. KORINTH (*Z. anorg. Chem.*, 1928, **171**, 312—316).—If a solution of sulphur in carbon disulphide thickened with rubber or Canada balsam is allowed to evaporate, the sulphur first appears as a cloudiness consisting of globulites of about 1 μ in diameter. Some of these increase in size at the expense of their neighbours, and regions free from globulites are thus formed. When a crystal is formed it grows in the same way, the drops in its vicinity moving towards it, probably carried by the streaming of the more concentrated solution to the crystal. In the course of the crystallisation, the formation of a pale yellow tetragonal modification of sulphur has been observed, this passing spontaneously into a pale yellow liquid modification. The formation of diffusion rings in gases (cf. König, *A.*, 1920, ii, 594) does not occur in the dark and in absence of vibration.

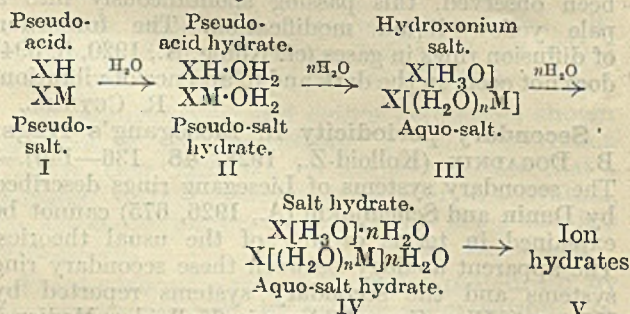
R. CUTHILL.

Secondary periodicity in Liesegang's rings. B. DOGADKIN (*Kolloid-Z.*, 1928, **45**, 136—140).—The secondary systems of Liesegang rings described by Dunin and Schemjakin (*A.*, 1926, 675) cannot be explained in terms of any of the usual theories. The apparent analogy between these secondary ring systems and the secondary systems reported by Küster ("Über Zonenbildung in Kolloiden Medien," Jena, 1913) is purely an outward resemblance. Experiments in gelatin purified by electrodialysis

showed that the secondary rings described by Küster are due to chlorides and phosphates present as impurities in the original gel. On the other hand, the secondary periodicity reported by Dunin and Schemjakin is due to the alteration of various external factors affecting the solubility of the product during the course of the diffusion. Such factors are changes in temperature, concentration of the diffusing electrolyte, consistency of the gel, and in some cases intensity of illumination. In the precipitation of silver chromate, secondary systems of rings have been produced by varying the intensity of illumination.

E. S. HEDGES.

Chemical changes of acids and salts in solution based on refractometric data. A. HANTZSCH and F. DÜRIGEN (Z. physikal. Chem., 1928, 134, 413—452).—The attempts to explain the change on dilution of the molecular refraction of electrolytes in aqueous or non-aqueous solution by physico-chemical theories, *e.g.*, dissociation, association, electrostriction, deformation, are rejected in favour of a chemical explanation in terms of Hantzsch's views (following abstract). The refractivity of acids and salts in aqueous solution is in general influenced by two chemical changes which have opposite effects—firstly, the conversion of homopolar substances into heteropolar substances, which brings about an increase in refraction, and secondly, hydration or solvation, which lowers the refraction. The observed molecular refraction gives the net result of these two processes, which may occur simultaneously in certain concentration regions. These changes may be followed by another optical method, *viz.*, by investigation of the absorption in the ultra-violet, and also by means of conductivity determinations. The latter method is applicable only to dilute solutions, whilst the optical methods are of value mainly for concentrated solutions. The chemical changes brought about by the action of water on acids are most readily observed in the case of nitric acid. The molecular refraction of this acid increases regularly up to a dilution of 90 mols. of water to 1 mol. of acid, and then remains constant. Similarly, the absorption reaches a constant value at this dilution. This is explained by a complete displacement of the equilibrium $[O_2N\cdot OH]_2 \rightleftharpoons 2[NO_3][H_3O]^+$ towards the right, *i.e.*, towards the side of the hydroxonium salt. The changes which homopolar acids and homopolar pseudo-salts undergo by the action of water can be represented by the general scheme:



The refraction and absorption may vary during the changes I→II→III→IV, but are not affected

during the change IV→V. True salts are converted on dissolution directly into aquo-salts, which may then become further hydrated according to the above scheme.

The foregoing conclusions are based partly on the refractometric data of other workers and partly on new observations.

O. J. WALKER.

Constitution of acids and salts, and their chemical changes in solvents. A. HANTZSCH (Z. physikal. Chem., 1928, 134, 406—412).—A further summary of the author's views on the constitution of acids and salts (*cf.* A., 1927, 327, 1011).

O. J. WALKER.

Dielectric constants of aqueous amino-acid solutions. G. HEDESTRAND (Z. physikal. Chem., 1928, 135, 36—48).—The increase of the dielectric constant of water produced by glycine, α - and β -alanines, and taurine is linearly proportional to the concentration of the solute; *o*-, *m*-, and *p*-amino-benzoic acids decrease the dielectric constant. Neutral salts decrease equally the dielectric constants of water and of aqueous glycine solutions.

H. F. GILLBE.

Unprotected uniform silver hydrosols. III J. VOIGT and J. HEUMANN (Z. anorg. Chem., 1928, 173, 27—44).—The effect on the sols of the addition of various quantities of sodium carbonate solution to the silver solutions before reduction was investigated. The reducing agents used to prepare the sols were hydrazine sulphate, hydrazine hydrate, and formaldehyde. The first gave the finest sol, the last the coarsest. The effect of addition of ammonia was also studied. It was found that the number of sub-microns per mm.³ of the sol varies with the amount of alkali added, the colour of the sol changing. If the number of particles in a definite volume of sol be plotted against the volume of alkali a curve is obtained which shows a peak. The position of this peak varies with the reducing agent used. The colour of the sol was investigated. Two samples of silver sol inoculated with gold, one containing 0.0005% of silver, the other 0.001%, were successfully concentrated by ultrafiltration. Whilst there was relatively no change in the number of particles present, there was a change of colour. The concentrated solution was diluted so as to contain about the same number of particles per unit volume as the original sol, and it was then compared with it as regards coagulation. It was shown that the ultrafiltered solution contained no protective colloid. The colour changes on coagulation of sols prepared in different ways were studied. It was found that uniform silver sols free from protective colloid, having a diameter less than 30 μ , pass through different series of colour changes on coagulation by electrolytes. This behaviour seems to depend to some extent on the mode of preparation of the sol and also on the electrolyte used. It appears that dilution of a pure silver sol is accompanied by an increase in the silver ion content of the sol.

A. J. MEE.

Colloid chemistry. XXIII. Physico-chemical investigation of thorium oxide sol. W. PAULI and A. PETERS (Z. physikal. Chem., 1928, 135, 1—23).—Pure concentrated thorium oxide sols, with

chlorine as contra-ion, have been prepared by peptisation in hot and cold solution. The chlorine and thorium oxide contents have been determined potentiometrically and measurements of the conductivities of the sols have been carried out. Sols obtained by hot peptisation yield very low values for the activity of the chlorine ion, an effect attributed to reciprocal interionic forces between the chlorine ions and the colloid particles. The activity coefficients and the dilution-equivalent conductivity relationship exhibit marked anomalies, which can be explained in terms of modern views, whereas the classical theory leads to very improbable values for the colloid-ion mobilities. Substitution of the contra-ion by the addition of various silver salts indicates that complex asymmetric univalent ions have a greater effect than simple ions in changing the activity coefficient.

H. F. GILLBE.

Electrochemistry of colloids. I. Colloidal silicic acid. A. J. RABINOVITSCH and E. LASKIN (*Z. physikal. Chem.*, 1928, 134, 387—405).—A quantitative investigation has been made of the increase in the dissociation constant of weak acids when these pass from the state of true solution to the colloidal state (cf. Rabinovitsch, A., 1925, ii, 778). Silicic acid sols containing from 0.25 to 0.53% SiO_2 were prepared by Graham's method. The total and the free hydrogen-ion concentration of these sols was determined from (a) conductometric and (b) potentiometric titration curves using alkali solutions. The results for the two methods agree satisfactorily. The dissociation constant of colloidal silicic acid derived from the potentiometric data is found to be 2×10^{-4} and is much higher than the value of 10^{-9} found by Hägg for true solutions (A., 1926, 924). This increase is probably due to the weakening of the attractive force between the hydrogen ion and the acid anion owing to adsorption of the latter by the colloidal particle. By diluting the silicic acid sols the number of free hydrogen ions increases and becomes greater than the total quantity of hydrogen ion of the undiluted sol. This effect is so large that the sol acts as a buffer solution, and is explained by a hydration of the silica molecules in the interior of the colloid particles.

O. J. WALKER.

Rôle of dielectric constants, polarisation, and dipole moments in colloid systems. II. Stability relations of weakly solvated pure organosols. W. OSTWALD (*Kolloid-Z.*, 1928, 45, 114—122).—A theory is advanced for the stability relations found experimentally by Svedberg for organosols prepared by electrical disintegration, according to which the orientation of polarisation of the dispersion medium is the chief factor in the stability. The theory agrees with all the known experimental details. The sols discussed are considered as examples of disperse systems which are stabilised, not by electrolytes, but by dipoles of a purely organic nature. The stability depends not only on the value of the dipole moment, but also on the number of dipoles present. The strong stabilising influence of small quantities of water on these systems is discussed and it is pointed out that water has a very high dipole moment and may confer

a polar property on a non-polar organic liquid. This view is extended to a consideration of the catalytic effect of water on gaseous chemical reactions and the change in the properties of liquids with intensive drying. In connexion with the latter, it is pointed out that all the liquids used by Baker have smaller dipole moments than water.

E. S. HEDGES.

Combined water of colloids. J. AMAR (*Compt. rend.*, 1928, 186, 1147—1149).—Measurements of the velocity of evaporation of aqueous solutions of ovalbumin (water content 85%) indicate that 47% of the total solvent is more firmly absorbed by the colloid. From these and similar figures (Davis and Eyre, A., 1923, ii, 838; Mayer and Plantefol, A., 1924, i, 809) the size of the water envelope (which is smaller when the continuous phase contains inorganic salts) surrounding the average colloid particle may be calculated.

G. A. C. GOUGH.

Influence of salts on the viscosity of linseed oil. M. S. DUNIN and F. M. SCHEMJAKIN (*Kolloid-Z.*, 1928, 45, 146—152).—The aqueous extract of linseed has a high viscosity, which is decreased by addition of the following salts at concentrations of 0.2—0.04*N*: sodium, potassium, and calcium chlorides, sodium and potassium sulphates and nitrates. Small quantities of magnesium sulphate (0.0001—0.1*N*) lower the viscosity, but a slow rise is produced by higher concentrations. Potassium, ammonium, and zinc sulphates, and calcium chloride behave similarly to magnesium sulphate, but to a smaller extent. The specific effect of magnesium sulphate is related not only to the rôle of magnesium in the chlorophyll of plants, but also to the effect of magnesium on the swelling of plant colloids.

E. S. HEDGES.

Alteration of hydrogen-ion concentration of stable kaolin suspensions by mechanical working in capillaries. A. JEPPESEN (*Kolloid-Z.*, 1928, 45, 156—158).—Suspensions of kaolin in water containing a small amount of sodium hydroxide showed on keeping an increase in viscosity and a decrease in hydroxyl-ion concentration. Experiments showed that the adsorption of hydroxyl ions is accelerated by the process of drawing through the capillary tube in the measurement of the viscosity.

E. S. HEDGES.

Form and structure of soil particles. G. I. POKROVSKI (*Kolloid-Z.*, 1928, 45, 158—161).—Particles of soil have a plate-like form and are consequently difficult to measure. An optical method of measurement is described; this shows that the particles in the soil are oriented, giving horizontal layers.

E. S. HEDGES.

Thermodynamic theory of the colloidal state. A. MARCH (*Kolloid-Z.*, 1928, 45, 97—112).—A theoretical paper in which thermodynamic principles are applied to systems of any degree of dispersion. The known laws relating to molecular solutions are derivable from the general theory, which is also applicable to colloids.

E. S. HEDGES.

Colloidal heat-indicator. R. E. LIESEGANG (*Kolloid-Z.*, 1928, 45, 112—114).—A temperature indicator can be made by dissolving 0.4 g. of novocaine

hydrochloride in 20 c.c. of 20% sodium sulphite solution. This solution is clear at the ordinary temperature, but becomes turbid at 32°. A less satisfactory indicator is obtained when quinine is used in place of novocaine. The indicator has been applied to the study of the temperature distribution in banded liquids. When a concentration gradient is set up in a tube (e.g., by placing solid sodium chloride at the bottom of a test-tube of water and leaving for some days) and the tube is subsequently plunged quickly into hot water, a series of bands or zones is observed, differentiated from each other by the refractive power. In presence of the temperature indicator, the experiment gives banded turbidities, which are shown to be rings, the cool contents of the middle of the tube remaining clear. The formation of layers is ascribed to the sinking of this middle liquid, which does not travel to the bottom of the tube, but stops when it reaches a warmer layer of higher concentration and the same density.

E. S. HEDGES.

Soaps as colloidal electrolytes. J. W. MCBAIN (J. Amer. Chem. Soc., 1928, 50, 1636—1640).—Linderström-Lang's view that soap solutions are completely dissociated is criticised (A., 1927, 109). Ultrafiltration, migration, viscosity, and hydration phenomena are directly at variance with this view. The data agree, however, with the author's micelle theory and show that the ionic micelle does not conform to the rule of ionic strength.

S. K. TWEEDY.

Relation between the properties and composition of soaps. IV. Surface tension and emulsifying power of palmitic, oleic, and lauric soaps. M. HIROSE (J. Soc. Chem. Ind. Japan, 1927, 30, 823—827).—The emulsifying powers in petroleum of the sodium salts of palmitic, oleic, and lauric acids have been compared by reference to the drop numbers using Hillyer's stalagmometer. The measured values for mixtures are much larger than those calculated from the simple mixture rule. In the case of the surface tension, the deviations of the measured from the calculated values are small; at 60—80° the two series are nearly coincident. At temperatures below 60°, the lowering of the surface tension is greater for the mixed soaps above mentioned than for the corresponding mixed soaps derived from stearic and oleic acids or from stearic, oleic, and lauric acids. At temperatures higher than 70°, the reverse is true.

Y. NAGAI.

Relation between the properties and composition of soaps. V. Drop number and the surface tension of lauric-oleic acid soaps. M. HIROSE (J. Soc. Chem. Ind. Japan, 1928, 31, 156—159).—A 0.5% solution of sodium oleate was mixed with a sodium laurate solution of the same concentration in various proportions and the drop number and surface tension were determined at 40°, 60°, and 80°. It was found that the drop number of the mixtures deviates markedly from the simple mixture rule, a maximum being obtained at 30% of laurate solution. This deviation is less at higher temperatures. The surface tension of a laurate solution is increased by the admixture of a small amount of oleate solution,

whilst the reverse holds when a small amount of laurate solution is added to the oleate solution.

Y. NAGAI.

Relation between the properties and composition of soaps. VI. Viscosity, lathering power, and washing power of stearic-oleic-lauric acid soap solutions. M. HIROSE (J. Soc. Chem. Ind. Japan, 1928, 31, 160—166).—The viscosity, lathering power, and washing power of 0.5% solutions of stearic-oleic-lauric acid soaps have been measured and compared. The relation between these properties, surface tension, and drop number is also discussed.

Y. NAGAI.

Soap. VII. Viscosity and hydration of soap solutions. M. NONAKA (J. Soc. Chem. Ind. Japan, 1927, 30, 828—835).—The viscosity at 25—30° of solutions of the sodium salts of oleic, palmitic, and stearic acid has been measured at various concentrations by means of an Ostwald-Auerbach pressure viscosimeter. At small pressures all the soap solutions show "structure viscosity," whilst at higher pressures turbulence occurs. The Hagen-Poiseuille rule holds only for mean pressures. Using the relation between viscosity and hydration suggested by Hatschek, the hydration of the micelle is calculated. Thus the concentration of the soaps in the micelle was found to be about 30%, about 1.7%, and about 2.0% for the solutions of the oleate at 25°, of the palmitate at 26°, and of the stearate at 30°, respectively.

Y. NAGAI.

Silica gels. P. BARY (Rev. Gén. Colloid., 1928, 6, 85—89).—Silica gels containing 27—35% of water suffer disintegration when placed in water. A similar, although much less marked effect is observed with ether, benzene, and toluene, but not with carbon tetrachloride. It is suggested that liquid is sucked into the pores of the gel by capillary attraction, which, by compressing the air they contain, engenders disruption.

F. J. WILKINS.

Structure of gels. I. Colloidal solutions of a photo-polymerisation product of vinyl chloride, giving solid, waxy masses and gels. G. FLUMIANI (Kolloid-Z., 1928, 45, 152—155).—A product of the photo-polymerisation of vinyl chloride gave either elastic gels or waxy, vaseline-like masses, according to the solvent from which it was obtained. The elastic gel was obtained from solutions in aniline, Peru balsam, rosemary oil, tetralin, bromoform, and ethylene dibromide, and the wax-like material from solutions in castor oil, cedar oil, terpentine, pine oil, origanum oil, camphor, and copaiba balsam. The principal difference between the two forms seems to be the order of magnitude of the smallest particles of the disperse phase, which determines the attraction between these particles and the solvent particles.

E. S. HEDGES.

Barophoresis in gels. H. SOBOTKA and A. B. SABIN (J. Amer. Chem. Soc., 1928, 50, 1561—1572).—Data are given in support of the relations $d = k\sqrt{t}$ and $(c_1/c_2)^n = k_1/k_2$, where d is the distance a coloured salt solution (concentration c) diffuses into a gelatinous medium in time t , k being a constant. Diffusion may occur with adsorption (methylene-blue) or without (picric acid, sodium dichromate). The temperature

coefficient of diffusion tends to rise when adsorption occurs. The rates of diffusion are usually greater when the diffusing salt moves against gravity ("barophoresis"; cf. Peskoff, *Kolloid-Z.*, 1924, **33**, 215), but at and above the "critical concentration" of the diffusing substance the sense of barophoresis is reversed, i.e., the diffusion becomes more rapid in the direction of gravity. The densities of the intermicellar liquids, indirectly determined, coincide with the densities of the solutions at the corresponding critical concentrations, thus demonstrating that the diffusion against gravity is really a convection current between the intermicellar liquid and the less dense solution.

S. K. TWEEDY.

Optical activity and colloidal behaviour of aqueous gelatin dispersions. E. O. KRAEMER and J. R. FANSELOW (*J. Physical Chem.*, 1928, **32**, 894—911; cf. A., 1925, ii, 1057; 1927, 621).—The influence of p_H , temperature, nature of electrolyte, and gelatin concentration on the optical rotation of dilute aqueous dispersions of electrodyalysed, de-ashed gelatin has been studied. Above 30°, the specific rotation is independent of these factors over somewhat wide limits, but minimal rotations may appear at p_H 1, 5, and 8.5, with rapid falls in rotation at the two extremes. Heating at 100° in sealed tubes results in irreversible changes in rotation owing to hydrolysis. Below 25°, maximal rotations occur near p_H 1, 5, and 8.5, and with low gelatin concentrations at low temperatures the maxima and minima are pronounced, but tend to disappear at higher concentrations. The specific influence of electrolytes is not marked at moderate concentrations. Above 30°, the adjustment of rotation to temperature is immediate, but below 25°, the speed of adjustment is measurable. Optical behaviour and colloidal behaviour run closely together. Gel formation is invariably accompanied by pronounced mutarotation and a high specific rotation, and any factor which prevents the latter prevents gel formation as well. This appears to be characteristic of optically active systems capable of forming gels. It is suggested that the intermicellar cohesion which accompanies the incipient precipitation responsible for gel formation modifies indirectly the intramolecular structure by exercising a "distributed stress," which in the special case of gelatin is more effective in controlling rotatory power than the more localised stresses associated with acid or base combination. Curves summarising the data obtained are given.

L. S. THEOBALD.

Ionic activity of gelatin. H. S. SIMMS (*J. Gen. Physiol.*, 1928, **11**, 613—628).—Titration curves have been determined for solutions of gelatin free of electrolytes and containing definite concentrations of sodium and magnesium chlorides and potassium and magnesium sulphates, and the influence of these salts on the dissociation constants of the gelatin and on its activity has thus been found. From the relation between the ionic strength and the activity of a multivalent ion, the dissociating groups of which are separated by finite distances, the average distance between like charges on the gelatin molecule has been calculated and is found to be 18 Å. The structure of the gelatin molecule is discussed (cf. A., 1926, 681).

W. O. KERMACK.

Nature of the ionisable groups in proteins. H. S. SIMMS (*J. Gen. Physiol.*, 1928, **11**, 629—640).—The titration curve for gelatin deaminised by treatment with nitrous acid has been determined. The resulting data are analysed along with the titration curves for gelatin and for ovalbumin. These curves are in general such as are to be expected from the amino-acid content of the protein except that the place of arginine appears to be taken by a group referred to as "prearginine" which shows itself at p_H 4.6 (cf. A., 1926, 681).

W. O. KERMACK.

Combination of salts and proteins. III. The combination of cupric, magnesium, calcium, aluminium, lanthanum, and potassium chlorides, silver nitrate, and sodium sulphate with gelatin. J. H. NORTROP and M. KUNITZ (*J. Gen. Physiol.*, 1928, **11**, 481—493).—A gelatin solution contained within a membrane is allowed to come into equilibrium with a salt solution on the other side of the membrane and the electrical potential between the liquids on two sides of the membrane is measured. The concentration of the salt ions in the liquid external to the membrane is found by analysis, and from this the concentration of the free salt ions within the membrane is calculated from the theory of the Donnan membrane equilibrium. The total concentration of ions within the membrane is found by analysis, so that the quantity of ions combined with the gelatin may be calculated by difference. In the case of cupric chloride 0.9 millimol. of copper combines with 1 g. of gelatin, but gelatin deaminised by treatment with nitrous acid combines with only 0.4—0.5 millimol. of copper per g. In presence of acid, less copper combines with gelatin, but the sum of the copper ions and hydrogen ions which combine with gelatin remains constant and equal to 0.9 millimol. per g. The chloride ion combines with gelatin whether deaminised or not. Similar results are found for aluminium, lanthanum, magnesium, and calcium chlorides, but in these cases deamination of the gelatin does not alter the power of combining with the cation. For lithium, sodium, and potassium chlorides no combination with the cations appears to take place, but only with the chloride ion, so that the gelatin is negatively charged and not positively as with the preceding salts. In the case of silver nitrate some combination with the silver ion takes place, but the nitrate ion is uncombined, whilst with sodium sulphate no combination occurs, the gelatin remaining unchanged.

W. O. KERMACK.

Influence of inorganic ions on the dispersion of ovalbumin and hæmoglobin at various hydrogen-ion concentrations. V. SCHRÖDER (*Biochem. Z.*, 1928, **195**, 210—219).—By counting the number of particles visible ultramicroscopically in solutions of ovalbumin and hæmoglobin, it is shown that at a definite p_H , the addition of salts (0.05—0.1M) displaces the precipitation optimum, anions displacing to the acid side in the order $SO_4 < HPO_4 < Cl, Br, I < SCN$ and the cations Ca^{++} and Mg^{++} to the alkaline side.

P. W. CLUTTERBUCK.

Lipin-protein complexes. I. Lecithin-caseinogen complexes. T. R. PARSONS (*Biochem.*

J., 1928, 22, 800—810).—The percentage of lecithin in precipitates obtained by the addition of a mixture of lecithin and caseinogen to buffer solutions of graded acidity increases with increasing hydrogen-ion concentration of the medium. When mixtures of caseinogen and progressively increasing quantities of lecithin are added to the same buffer solution the initially rapid increase in the percentage of lipin in the several precipitates becomes more and more gradual until a stage is reached at which very considerable further increase of the total proportion of lecithin added produces but slight increase in the percentage of the constituent in the precipitated complex. The results are explained in terms of the mutual precipitation of two colloids with opposite charges which vary in intensity with the hydrogen-ion concentration of the dispersion medium.

S. S. ZILVA.

Plasticity. IV. Plastic masses with silica. O. RUFF and B. HIRSCH (Z. anorg. Chem., 1928, 173, 14—26).—The preparation of plastic masses from which articles can be moulded from powdered quartz is described. The starting material was Swedish quartz of which the particles varied in size from 2μ to 8μ . By washing, centrifuging, etc. various fractions of the quartz were obtained. The effect of alkali on the plasticity was determined; it was not possible to make a vessel from this paste. One sample of a neutral paste, where the silica was merely mixed with water, was suitable for working, and a vessel was made, dried, and burnt. For acid pastes, the silica was first mixed with hydrochloric acid of various concentrations. The effect of acid concentration, size of particles, and temperature on the degree of plasticity was shown. Addition of acid improves the plastic properties of a quartz-water paste. Experiments were also carried out with pastes acidified with nitric, sulphuric, oxalic, phosphoric, or acetic acid, respectively, and with pastes to which solutions of neutral salts as well as hydrochloric acid had been added. The vessels moulded were burnt at about 1500° . The pastes contained in all cases a certain amount of quartz gel and sol. The assumption that the increased plasticity is due to adsorption of the acid, which has been put forward to explain the similar effects with alumina and zirconia, is tested, and it is found that the amount of hydrogen-ion adsorption is only small and is difficult to determine. The hydrogen-ion concentration of the quartz hydrated surface is p_H 4.85. A hypothesis is put forward to explain the facts, based on the assumption of a diffusion equilibrium between the hydrogen ions which find their way inside the quartz particle and those in the dispersion medium, and the formation of a polar layer of molecules on the surface of the quartz particle.

A. J. MEE.

Dispersoidological investigations. XVIII. General methods of obtaining fibrous precipitates of any substance; the structure of fibres in general and of cellulose fibres in particular. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1927, 8, 7—17).—Precipitates of a fibrous structure may be obtained by several methods. A precipitate AC, produced by the interaction of two very concentrated solutions of AB and

CD (Kolloid-Z., 1908, 2, 306), consists of fibres the walls of which represent a gelatinous membrane of the substance AC and the adsorbed soluble reaction product DB. Within the fibres is a solution of AB or CD. Similar fibres are obtained under suitable conditions if the solution becomes separated into two layers. The process is accompanied by the formation of practically insoluble membranes on the surface of streams arising during this separation, e.g., the effects observed during the separation into two layers of aqueous colloidal solutions of silk fibroin (A., 1927, 309) or casein by the addition of alcohol, salts, etc. A third method of obtaining fibrous precipitates depends on whether the crystals are "negative," i.e., drawn out to a large extent in one direction forming needles, or not. The ends of the microcrystals drawn out in one direction possess the greatest velocity of growth, and when in the mother-liquor easily grow together, forming long fibres. The movement of the mother-liquor from the crystals in a definite direction promotes the formation of such fibres. Cellulose fibres are more complex in structure than precipitate fibres. Microscopic and ultramicroscopic examination of cellulose fibres, under different conditions of swelling, shows that the fibre consists of a number of concentric tubes. The outer hard cuticle or skin consists of a mixture of wax-like and grease-like substances the chemical nature of which has not yet been clearly defined. Then follows a transition layer of cuticulated cellulose, a tube chiefly of cellulose, a second transition tube of plasmated cellulose, and finally an inner tube which contains the central canal or lumen and represents a plasmatic formation. The cellulose tube consists of a number of very thin concentric tubes the walls of which are of unequal thickness and consist of ultramicroscopically thin fibres arranged parallel to each other along the length of the tubes. During dispersion the fibre is divided into long thin fibrils which ultimately break up across the length of the fibre.

M. S. BURR.

Dispersoidological investigations. XX. Microscopic investigation of coarse-cellular or membranous jellies in polarised light. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1927, 8, 41—66).—The method of studying barium sulphate precipitates in polarised light is described, and a number of photomicrographs which have been taken are reproduced. The results support the conclusions reached in numerous earlier publications, viz., that the "aggregate fluid-crystalline" state is a perfectly universal state of matter. M. S. BURR.

Dispersoidological investigations. XXI. Caoutchouc-like state of matter in connexion with a microscopic investigation of silk coagula in natural and polarised light. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1927, 8, 67—80).—The microstructure of a silk coagulum and its action on polarised light have been examined during the changes in consistency and elastic properties which accompany dehydration and ageing; similar observations were also made with threads of natural silk during the process of swelling to a syrupy consistency in hot concentrated sodium iodide solu-

tion. As the threads swell they are seen to be composed of the thinnest ultramicro-fibrils, which, in the course of swelling, gradually become curled in spirals. When the thread has the consistency of a viscous syrup, several of these spiral curls coalesce into oblong drops. In the reverse process, threads drawn out of a silk coagulum, precipitated by a concentrated neutral aqueous solution of sodium citrate, ultimately display properties identical with those of natural silk threads, including the appearance of interference colours. In the state in which the curled fibrils are evident, the silk coagulum displays elastic caoutchouc-like properties. It is therefore inferred that the high elasticity of caoutchouc must be due to the presence of similar spirally curled fibrils in an interfibril, viscous, or plastic dispersion medium which permits the fibrils, after the stretching out of the system, to become more or less straightened, as well as to become curled again after the system has been released from tension. These conclusions have been confirmed by the examination, in polarised light, of a thread of rubber alternately stretched and contracted. In the precipitation of silk coagula the aggregate fluid-crystalline state is observed as in the case of barium sulphate (cf. preceding abstract). M. S. BURR.

Does the theory of complexity of micelles find application in the study of cellulose? I, II. M. CATOIRE (Bull. Soc. Chim. biol., 1928, 10, 714—726; 727—735; cf. A., 1927, 412, 511).—I. The deflocculation accompanied by swelling indicates that the structure of cellulose breaks down, through less complex polymerides, to the monoses in a number of stages. Fractional precipitation of an acetic acid solution of cellulose acetate with water shows that the inorganic matter (particularly silica) is probably present in a state of combination and not merely as an impurity. It is suggested that the smaller micelles contain less silica and that silica is essential to the polymerisation of the monoses. Partial removal of the mineral matter from cotton renders it more susceptible to deflocculation after conversion into cellulose nitrates, whilst the addition of various salts during, or after, treatment with nitric and sulphuric acids leads to the formation of a less soluble product. Treatment of cellulose acetates of small inorganic content (slightly soluble in acetone) with aqueous solutions of sodium hydroxide of increasing concentration leads first to an increase in the solubility and then to insolubility after drying.

II. The application of the theories of complexity and micelles is discussed. G. A. C. GOUGH.

Coagulation of strongly solvatised sols by organic substances and salts. I. B. JIRGENSONS (Biochem. Z., 1928, 195, 134—141).—A medium containing a mixture of an organic substance (isopropyl and ethyl alcohols, acetone) and an inorganic salt (calcium, strontium, potassium chlorides) coagulates caseinogen and albumin sols more rapidly than either substance added separately. When the mixture was added in large quantity (30—50 vols. % of alcohol with 0.2—1.2*M* solution of inorganic salt per litre) it was found that the coagulation time was lengthened with organic substances of small dielectric constant (isopropyl alcohol). The degree of stabilisation

increases with increasing concentration of the organic and inorganic substances. P. W. CLUTTERBUCK.

Coagulation of colloids by electrolytes. V. Pure silicic acid sols. E. LASKIN (Kolloid-Z., 1928, 45, 129—136).—Pure silicic acid was prepared by adding sodium silicate to hydrochloric acid, dialysing in a collodion thimble, and finally subjecting to electrodialysis and concentrating by evaporation. Such sols are very stable and strongly acid in reaction, having a p_H of about 3.5. The coagulation of the sol by electrolytes was followed by conductometric and potentiometric methods. In some preparations, coagulation can be brought about only by saturated potassium chloride solution, whilst in others, saturated solutions of lithium chloride, barium chloride, and acids are also effective. It is believed that the principal factor in the coagulation of the sols is the dehydration of the colloid particles by ions with strong hydrating tendencies. Basic colouring matters coagulate the sol readily, even when in very dilute solution, the cations of the substance being adsorbed by the colloid particles. Acid colouring matters are not adsorbed by the sol and do not effect coagulation. The degree of dispersion of the colouring matter plays no part. During coagulation the acidity of the sol increases, resembling in this respect the behaviour of mastic sols, but differing from that of sols of arsenious sulphide and tungstic acid.

E. S. HEDGES.

Coagulation. G. WIEGNER [with P. TIONTA and H. MÜLLER] (Z. Pflanz. Düng., 1928, A 11, 185—228).—The Smoluchowski rule for the rapid perikinetic coagulation of monodisperse systems may be considered as an extension of the laws governing the reactions of gold sols. Kaolin particles in monodisperse systems are coagulated according to the same rule. The slow perikinetic coagulation of monodisperse systems is examined by ultramicroscopic methods. Relationships between this process, ion hydration, and base exchange in colloids are examined and discussed. The Müller formula is applied to the rapid perikinetic coagulation of polydisperse systems and is applicable to clay particles. Polydisperse systems coagulate more rapidly than monodisperse systems involving the same number of ultimate particles. The mass of the particles in polydisperse systems is one thousand times as great as in corresponding monodisperse systems. Formulæ are developed which represent the course of rapid and slow orthokinetic coagulation. By the electrical discharge of the particles it is possible to differentiate between their sizes. Orthokinetic coagulation is frequently more important than perikinetic in soil analysis by sedimentation or elutriation methods. It is shown that the Wiegner elutriation apparatus may be arranged so that by observations of deposition curves at different heights the original dispersion characteristics can be calculated. A. G. POLLARD.

Stabilisation of albumins by globulins. V. BERGAUER (Bull. Soc. Chim. biol., 1928, 10, 576—580).—In order to determine whether the protecting action of natural globulin against the coagulation of serum-albumin by alcohol is due actually to the globin or to lipins contained in the usual preparation,

the coagulating actions of alcohol on (a) serum-albumin alone, (b) serum-albumin protected with globulin, with lipin-free globulin, and with a lipin emulsion have been investigated. Whilst globulin itself has a small effect, the lipin-containing globulin and the lipin emulsion show much greater protection. It is suggested that the protecting action of the lipin-free globulin is due to a small amount of chemically combined lecithin. G. A. C. GOUGH.

Colloidal dissolution of composite (high-molecular) compounds by means of substances which possess a large true solubility and are inclined to great solvation. P. P. VON WEIMARN (Japan. J. Chem., 1928, 3, 71—87).—See A., 1927, 725.

M. S. BURR.

Free energy and fugacity in gaseous mixtures of hydrogen and nitrogen. A. R. MERZ and C. W. WHITTAKER (J. Amer. Chem. Soc., 1928, 50, 1522—1526).—The fugacities and free energies of nitrogen and hydrogen in mixtures of these gases are calculated from the compressibility figures of Bartlett (A., 1927, 927). The maximum deviation from the behaviour of a perfect mixture does not exceed 20% for pressures up to 1000 atm. S. K. TWEEDY.

Strength of acetamide as an acid. G. E. K. BRANCH and J. O. CLAYTON (J. Amer. Chem. Soc., 1928, 50, 1680—1686).—By plotting the conductivities, Λ , at 25° of acetamide solutions of constant concentration (C) containing small, varying concentrations (c) of barium hydroxide against c , $L = (\partial\Lambda/\partial c)_C$ is obtained. The variation of L with C was measured, and, from conductivity measurements for acetamide solutions containing sodium chloride (for which L is a linear function of C), was corrected for the influence of acetamide on the mobilities of the acetamide and hydroxyl ions. The value 12 ± 2 is recorded for the hydrolysis constant of the acetamide ion, and $K = 8.3 \times 10^{-16}$ for the acid dissociation constant. Measurements with benzamide, which were unsatisfactory owing to the low solubility of this substance, gave K between 10^{-14} and 10^{-15} , in disagreement with the accepted value. S. K. TWEEDY.

Electrolytic dissociation of dibasic acids. IV. Dissociation constants of some thiolmonocarboxylic acids. E. LARSSON (Z. anorg. Chem., 1928, 172, 375—384).—As unsymmetrical dibasic acids monothiolmonocarboxylic acids, $\text{OH}\cdot\text{CO}\cdot\text{R}\cdot\text{SH}$, must have two first and two second dissociation constants, K_1' , K_1'' , and K_2' , K_2'' , respectively. These cannot be determined separately, but only the total values, $K_1 = [\text{H}^+] \times ([\text{O}\cdot\text{CO}\cdot\text{R}\cdot\text{SH}] + [\text{OH}\cdot\text{CO}\cdot\text{R}\cdot\text{S}^-]) \div [\text{OH}\cdot\text{CO}\cdot\text{R}\cdot\text{SH}]$ and $K_2 = [\text{H}^+] \times [\text{O}\cdot\text{CO}\cdot\text{R}\cdot\text{S}^-] / ([\text{O}\cdot\text{CO}\cdot\text{R}\cdot\text{SH}] + [\text{OH}\cdot\text{CO}\cdot\text{R}\cdot\text{S}^-])$. $K_1 = K_1' + K_1''$, and $1/K_2 = 1/K_2' + 1/K_2''$ or $K_2 = K_2'K_2'' / (K_2' + K_2'')$. Actually K_1 is practically equal to the dissociation constant of the carboxyl group of the acid and K_2 the dissociation constant of the thiol anion $\text{O}\cdot\text{CO}\cdot\text{R}\cdot\text{SH}$. K_1 has been determined at 25° by conductivity measurements, correction being made on the assumption that the activity coefficient of the ions may be calculated from the formula valid for acetic acid. K_2 has been determined colorimetrically by indicators, the degree of accuracy being approximately 0.1 of p_H . The values of K_1 for thioglycollic, α -thiol-lactic, β -thiol-

lactic, and α -thiolisobutyric acid are 2.1×10^{-4} , 2.0×10^{-4} , 0.46×10^{-4} , and 1.26×10^{-4} , respectively, and of K_2 , 2.1×10^{-11} , 2.0×10^{-11} , 2.9×10^{-11} , and 0.48×10^{-11} , respectively.

M. S. BURR.

Ionisation of solutions of hydrogen sulphide. M. AUMÉRAS (Compt. rend., 1928, 186, 1724—1726; cf. this vol., 711).—It is shown theoretically and confirmed by the experiments of the author and of others that the solubility product of cadmium sulphide in water corresponds with the equilibrium $\text{CdS} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{HS}^-$ and not with $\text{CdS} \rightleftharpoons \text{Cd}^{2+} + \text{S}^{2-}$. If this is taken into account, the second dissociation constant of hydrogen sulphide has a value of $0.59 - 0.37 \times 10^{-15}$ at 25° which is of the same order as that found by an independent method by Knox (A., 1906, ii, 608). J. GRANT.

Dilution and neutral salt errors of buffer mixtures. C. MORTON (J.C.S., 1928, 1401—1415).—Electrometric measurements have been made which show the influence of dilution and the addition of neutral salts on half-neutralised solutions of acetic and cacodylic acids, one fourth neutralised solutions of aspartic acid and of arginine, three fourths neutralised solutions of *o*-phthalic and α -monoglycerolphosphoric acids, and mixtures of sodium pyrophosphate and hydrochloric acid in the molecular proportions 2:3 and 2:1. The relations (between the p_H limits 4—10) are expressed by Debye and Hückel's equation, $p_H = p_K - \log [\text{acid}]/[\text{salt}] - A\sqrt{\mu} + B\mu$. The value of A is approximately $(n - 0.5)$, where n is the valency of the buffer electrolyte, and agrees with that calculated on Debye and Hückel's theory.

The Van Slyke (A., 1922, ii, 893) unit of buffer capacity describes only the resistance of the buffer solution to p_H changes on addition of alkali or acid. It is suggested that this unit should be supplemented by a factor $\pi = dp_H/d\sqrt{\mu} = 2\beta\sqrt{u} - A$ which is a measure of the dilution and neutral salt errors. As the second term is the greater, especially in dilute solution, π will increase rapidly with the valency of the buffer electrolyte. The values obtained for the thermodynamic dissociation constants are: aspartic acid, $pK_a = 3.895$; acetic acid, $pK = 4.735$; cacodylic acid, $pK_a = 6.247$; *o*-phthalic acid, $pK_2 = 5.333$; glyceryl-phosphoric acid, $pK_2 = 6.744$; pyrophosphoric acid, $pK_3 = 6.704$, $pK_4 = 9.880$; arginine, $pK_{s_1} = 5.178$.

F. J. WILKINS.

Influence of dilution on the p_H of buffer mixtures. I. M. KOLTHOFF (Biochem. Z., 1928, 195, 239—247).—The influence of dilution on the p_H of ordinary (phthalate, acetate, phosphate, and hydrogen carbonate-carbonate) buffer solutions may be accurately calculated using the equations of Debye and Hückel for the activity coefficients of the ions and assuming a mean ionic diameter of 4×10^{-8} cm. With citrate buffer, better results are obtained by assuming a diameter of 6.5×10^{-8} cm. With boric acid-borate mixtures, the calculation breaks down, due to formation of complex boric acid-borate ions.

P. W. CLUTTERBUCK.

Pinachrome as a one-colour indicator. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1928, 50, 1604—1608).—A solution of pinachrome in alcohol is a suitable indicator for use near the neutral point

(p_H 5.8—7.8). At low electrolyte concentrations the salt error is very small; at higher concentrations the acidity indicated is too great. Alkaline solutions of the indicator are unstable. A simple test is described whereby the adsorption of a substance at the air-water interface may be demonstrated.

S. K. TWEEDY.

Influence of the so-called higher terms in the Debye-Hückel theory of solutions of strong electrolytes. T. H. GRONWALL, V. K. LAMER, and K. SANDVED (Physikal. Z., 1928, 29, 358—393; cf. A., 1927, 314, 828).—The Debye-Hückel theory is discussed at length with special reference to the theoretical side of recent developments. An analytical integration is given for the Poisson equation forming the basis of the theory and determining the electrostatic potential ψ of an ion. This gives a complete statistical expression for the electrical density as a function of ψ , instead of using merely the first linear term as in the approximate calculation given by Debye and Hückel. Hence the free energy as well as the activity coefficient remain in the form of infinite series progressing in powers of $1/D$, D being the dielectric constant. For very low concentrations asymptotic expressions are obtained, from which it follows that the Debye limiting law is valid not only for the Debye approximation, but also quite generally. For the case of pairs of ions of equal valency, numerical values have been worked out for terms up to $1/D^5$ inclusive. Comparison with experimental data shows very good agreement even in the case of small ionic diameters where the Debye approximation fails.

R. A. MORTON.

Solubility of lead bromide in aqueous salt solutions and the calculation of the activity coefficient from solubility measurements. M. RANDALL and W. V. A. VIETTI (J. Amer. Chem. Soc., 1928, 50, 1526—1534).—The solubility at 25° of lead bromide in solutions of lead and barium nitrates and cadmium and potassium bromides is measured. The solubility in pure water is 0.02683 mol. per 1000 g. of water. A graphical method for calculating the Lewis and Randall "proportionality factor" from the graph of the log. of the reciprocal of the mean molality against the square root of the ionic strength is given, and illustrated by application to thallous chloride (*ibid.*, 1535) and lead bromide. The method is satisfactory when the saturating salt is "non-associated" in the Bjerrum sense, or when the solubility is very small, but it may lead to considerable errors with fairly soluble "associated" substances such as lead bromide.

S. K. TWEEDY.

Solubility of lead monoxide and basic lead carbonate in alkaline solutions. M. RANDALL and H. M. SPENCER (J. Amer. Chem. Soc., 1928, 50, 1572—1583).—The solubilities at 25° of the tetragonal (red) and orthorhombic (yellow) varieties of lead monoxide in dilute potassium hydroxide solution are recorded. The standard free energy change for the reaction $PbO + OH' = HPbO_2'$ is 1903 g.-cal. and 1740 g.-cal. for the red and yellow oxides, respectively. From the corresponding solubilities of hydrated lead monoxide and basic lead carbonate the standard

free energies are: $PbO, \frac{1}{2}H_2O(s) + OH' = HPbO_2' + \frac{1}{2}H_2O(l)$, 1512 g.-cal.; $Pb_3(CO_3)_2(OH)_2(s) + 7OH' = 3HPbO_2' + 2CO_3'' + 3H_2O(l)$, 6961 g.-cal. The activity coefficient of the plumbite ion is approximately equal to that of the nitrate ion in dilute solutions. Berl and Austerweil's work is criticised (A., 1907, ii, 457).

S. K. TWEEDY.

Reduction potential of selenious acid and the free energy of aqueous selenic acid. M. S. SHERRILL and E. F. IZARD (J. Amer. Chem. Soc., 1928, 50, 1665—1675).—The equilibrium $X_2 + H_2SeO_3 + H_2O = H_2SeO_4 + 2HX$, where $X = Cl$ or Br , was investigated. From the equilibrium constants the reduction potential of the reaction $H_2SeO_3 + H_2O(l) = 3H' + HSeO_4' + 2\ominus$ was calculated to be -1.088 volts. The free energy, ΔF , of $HSeO_4'$ is thus -107,710 g.-cal. at 25°. Data representing the solubility of gaseous chlorine in hydrochloric acid at 25° and 1 atm. and the distribution of bromine between carbon tetrachloride and aqueous hydrobromic acid solutions are recorded. The equilibrium constant $[Br_3']/[Br_2][Br']$ increases with rising hydrobromic acid concentration.

S. K. TWEEDY.

Thermomagnetic study of magnetic iron sesquioxide. J. HUGGETT and G. CHAUDRON (Compt. rend., 1928, 186, 1617—1619).—A thermomagnetic study of Malaguti's magnetic iron sesquioxide has shown that at a sufficiently high temperature it is transformed irreversibly into the non-magnetic form, with the liberation of heat. The reversibility obtained with the impure oxide is due to the elevation of this temperature above the point of magnetic transformation. The magnetic properties of the oxide therefore depend on the method of preparation.

J. GRANT.

Metallic nitrides and hydrides. I. I. SHUKOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 600—640; cf. *ibid.*, 1926, 3, 14).—The equilibrium pressures for hydrogen in contact with various metals at various temperatures have been determined. The following hydrides are formed: sodium hydride, NaH ; cerium hydride, CeH_2 , which is capable of dissolving hydrogen to yield a solid solution, and palladium hydride, Pd_2H . The curve for rhodium is similar to that for palladium, indicating a large absorptive power for hydrogen, but in the case of iridium, compound formation does not appear to occur although considerable quantities of hydrogen are absorbed.

R. TRUSZKOWSKI.

Systems iron-silicon, iron-chromium, and iron-phosphorus. C. KREUTZER (Z. Physik, 1928, 48, 556—566).—The influence of silicon and chromium on the α - γ and γ - δ changes of iron has been investigated by means of X-ray spectra. With silicon concentrations up to 2.2% the α -phase changes into the δ -phase through γ -iron. With 2.2—2.5% of silicon there is a region in which α - and γ -iron can coexist, but above 2.5% the α -phase changes directly into the δ -phase. Similarly, the α - δ change occurs directly in the presence of more than 15% Cr. With phosphorus up to 1.7%, mixed crystals are formed, but at greater concentrations the phosphides Fe_3P , Fe_2P , and a third of unknown composition are produced.

J. W. SMITH.

Critical points in chromium-iron alloys. A. B. KINZEL (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 100, 7 pp.).—With addition of chromium up to 10% the A4 transformation is gradually lowered from 1400° to 1250°; further addition causes more abrupt lowering, and at 12.25% the A4 and A3 transformations are practically coincident. The A3 transformation is not affected. The "austenite" loop in the chromium-iron system ends at 12.37% Cr.

CHEMICAL ABSTRACTS.

α -Phase boundary of the copper-nickel-tin system. W. B. PRICE, C. G. GRANT, and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 103, 12 pp.).—The ternary isotherm was determined for mixtures containing less than 25% Sn. The α -phase boundary fluctuates but little. A series of hardenable alloys is described.

CHEMICAL ABSTRACTS.

Aluminium-beryllium alloys. R. S. ARCHER and W. L. FINK (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 91, 27 pp.).—Brinell hardness numbers for chill-cast and heat-treated aluminium-beryllium (0.013–0.75%) alloys show an ageing effect, maximal for the alloy containing 0.75% Be. The solid solubility of beryllium is about 0.075% at 639°, 0.05% at 631°, and <0.013% at the ordinary temperature. The constitutional diagram was re-examined up to 1.7% Be; the eutectic point is at 0.87% Be and 645°. The density is additive. The effect of beryllium on the properties of aluminium-copper alloys was investigated; the corrosion resistance is not improved.

CHEMICAL ABSTRACTS.

Hydrates, transition temperatures, and solubility of sodium iodate. H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1928, [v], 16, 68–72).—The stable hydrates of sodium iodate are the penta- and mono-hydrates; the hydrate $\text{NaIO}_3 \cdot 1.5\text{H}_2\text{O}$ reported by Meerburg (A., 1905, ii, 508) could not be detected. The transition temperatures corresponding with $\text{NaIO}_3 \cdot 5\text{H}_2\text{O} \rightarrow \text{NaIO}_3 \cdot \text{H}_2\text{O}$ and $\text{NaIO}_3 \cdot \text{H}_2\text{O} \rightarrow \text{NaIO}_3$ are 19.85° and 73.4°, respectively. The change at 73.4° is slow enough to permit the solubilities of the metastable and stable forms to be determined. Solubility data for sodium iodate in water from 0° to 90.3° are given. The solubility, S , of the monohydrate from 20° to 50° is represented by the equation $\log S = 3.6344 - 802.8/T$ and that of the pentahydrate between 0° and 15° by $\log S = 7.7793 - 2019/T$.

L. S. THEOBALD.

System lithium perchlorate-water. J. P. SIMMONS and C. D. L. ROFF (J. Amer. Chem. Soc., 1928, 50, 1650–1653).—According to the solubility curve between 0° and 170° the tri- and mono-hydrates are the only compounds formed. The transition points are: $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (m. p. 95.1°) \rightleftharpoons $\text{LiClO}_4 \cdot \text{H}_2\text{O}$, 92.53°; $\text{LiClO}_4 \cdot \text{H}_2\text{O}$ (m. p. 149°) \rightleftharpoons LiClO_4 , 145.75°. The solubility of anhydrous lithium perchlorate is 37.48 g. per 100 g. of solution at 25°; the densities of the saturated solutions are recorded from 0° to 40°.

S. K. TWEEDY.

F. p. of ethyl alcohol-water mixtures. D. N. TARASSENKOW (Z. angew. Chem., 1928, 41, 704).—The f. p. of mixtures of ethyl alcohol and water containing from 5.1 to 74.7% of alcohol by weight

have been determined, the freezing-mixture being contained in a Dewar flask. With higher concentrations of alcohol the solution is too viscous for accurate measurement. The freezing curve indicates the separation of a crystalline hydrate.

The following data are recorded, the figures in parentheses being wt.-% of alcohol: (5.1) –2.1°, (9.3) –4.1°, (14.2) –6.7°, (17.8) –10.2°, (24.4) –15.2°, (29) –19.1°, (33.3) –24.2°, (37.6) –28.4°, (43.0) –33°, (46.7) –35.4°, (51.9) –38°, (56.3) –42°, (61.4) –45°, (66.1) –48°, (70.2) –56°, (74.7) –67°.

R. BRIGHTMAN.

System aluminium oxide-water. G. F. HÜTTIG and E. VON WITTGENSTEIN (Z. anorg. Chem., 1928, 171, 323–343).—The properties of various preparations of hydrated alumina and also of some of the naturally occurring forms have been investigated by gradually removing the water, and at each stage of the dehydration observing the temperature, t , at which the pressure of water vapour over the product is 10 mm. (cf. A., 1926, 798). Aluminium hydroxide precipitated in the cold with ammonia from solutions of the chloride and washed until almost free from chloride is a true amorphous colloid, and the curve representing the variation of t with the water content, N , is exactly similar to those for other oxides, not related chemically to alumina, in the same state. With increasing age, the dispersity decreases, the arrangement of the molecules becoming at the same time more orderly, and the system tends to pass into hydrargillite or its dehydration products. If hydrargillite crystals are dehydrated at 192°, decomposition is complete when the residue has the composition $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, this being the upper limit, in respect of water content, of the series of continuously homogeneous hydrates lying between $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and Al_2O_3 . If the cold-precipitated hydroxide, aged in air to the composition $\text{Al}_2\text{O}_3 \cdot 2.95\text{H}_2\text{O}$, is dehydrated to the composition $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the N - t diagram for the removal of the last molecule of water is essentially the same as that for the complete dehydration of the monohydrate prepared from hydrargillite, except that the water is retained rather more firmly, although not firmly as in bauxite. Both preparations seem to be amorphous colloids starting to change into bauxite. The curve for bauxite itself is closely similar to that for diaspor, so that the affinity of the transformation of one form into the other must be nearly zero. By ageing the precipitated hydroxide under water, a product is obtained which seems to contain the dihydrate (cf. Guichard, A., 1927, 475). A hydroxide prepared by precipitating aluminium sulphate at 48° with ammonia in presence of ammonium chloride and ageing for a long time in a closed vessel gives the X-ray interferences corresponding with the isomeride of hydrargillite discovered by Böhm (*ibid.*, 113), and "aloton" seems to be similar. Since, however, hydrargillite itself is the stable isomeride, the colloidal system alumina-water must ultimately pass into this form. The dehydration curve of diaspor is not greatly affected by variations in the fineness of division, and yields no indications of the existence of definite lower hydrates. If hydrargillite is heated at 370° under 20 atm. pressure of water vapour, it is converted into crystalline bauxite, whereas diaspor

undergoes no change when treated in this way. From a consideration of the general behaviour of the system aluminium oxide-water, it seems that here the laws of constant and multiple proportions may possess something of an ideal character, the chemical forces which give rise to compounds with strictly stoichiometric compositions being accompanied by forces of diffusion, which are independent of stoichiometric considerations. The usual stoichiometric formulæ do not, in general, therefore, represent the actual compositions, but only the limiting states which the system approaches more or less closely in the stable pure state. The activity of a preparation of aluminium oxide depends on the distance by which it is removed from the final equilibrium state.

R. CUTHILL.

Lowering of the eutectic temperature in binary mixtures. V. Determination of mol. wt. from the position of the eutectic temperature. E. KORDES (Z. anorg. Chem., 1928, 173, 1-13).—The formation of mixed crystals raises the position of the eutectic temperature. This may possibly be due to the attractive force tending to form a compound. The mol. wt. of a substance can be found if it is mixed with another of known mol. wt. and the position of the eutectic temperature and the composition of the eutectic mixture are determined. In applying the method, regard must be had to certain causes of error, such as the formation of mixed crystals etc. Many systems have been investigated by this method, the results giving approximate values for the mol. wts. of the same order of accuracy as might be obtained by vapour-density determinations. In many cases, polymerisation is indicated. Aluminium bromide appears to dissolve as $(\text{AlBr}_3)_2$ in arsenic tribromide. Sulphur dissolved in naphthalene and in iodine separates in the monoclinic form and gives for its mol. wt. values corresponding with the formulæ $\text{S}_{8.5}$ and S_9 , respectively. Since other determinations have given values corresponding with S_7 to S_9 for this form, it is highly probable that the correct formula is S_8 . For grey selenium a value corresponding with Se_4 is obtained. Experiments with water as one of the components indicate that the water is not polymerised. This does not agree with determinations by other methods. The method is of use for strong electrolytes. Since the mol. wt. is always found to be the same when the same crystalline form of a substance separates, it is assumed that the value obtained represents the mol. wt. of the substance in the crystalline state.

A. J. MEE.

Solid solutions and compound formation. A. LEHRMAN (Chem. News, 1928, 136, 401-403).—It is suggested that the vertical line drawn through the point corresponding with the composition of the compound in a f.-p. diagram consists of two lines, which represent two solid solutions, so close together that the ordinary methods of analysis do not permit of their separation. Similar considerations are applied to three-component systems.

C. W. GIBBY.

Separation of mixed crystals from solutions. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1928, 173, 73-80).—The conditions of separation of mixed crystals from a solution are discussed. Mixed

crystals are not in equilibrium with the solution from which they separate, so that special diagrams must be drawn to express conditions of separation. Three methods of drawing such diagrams are given, and the differences between hydrated and anhydrous mixed salts are demonstrated. The differences can be referred to a different type of growth of the two types of crystals. Protection of one component by the other is also studied. Experiments on protection were carried out by placing mixed crystals of potassium permanganate and potassium perchlorate in a saturated solution of potassium perchlorate. If the potassium permanganate content of the mixed crystal was less than 9% a small amount dissolved, but the composition of the residue was the same. If, however, the permanganate content was greater, more dissolved, and the amount of permanganate in the residue fell to 8-11%. Similar results were obtained by using mixed crystals of potassium chromate and potassium sulphate and a solution of potassium sulphate.

A. J. MEE.

Systems with retrograde melting curves. I. System sodium selenate-water. II. System magnesium sulphate-water. A. SMITS (Z. physikal. Chem., 1928, 135, 62-72, 73-84).—I. [With W. M. MAZEE.]—Theoretical.

II. [With J. RINSE and L. H. LOUWEEKOYMANS.]—The systems sodium selenate-water and magnesium sulphate-water have been investigated from 76° to 372° and from 60° to 95°, respectively. The former system has a continuous melting curve, partly retrogressive and having a vertical tangent, whilst the melting curve of the latter is retrogressive and has a critical end-point. A curve having two vertical tangents, a possibility discussed in I, has not yet been obtained experimentally.

H. F. GILLBE.

Equilibria between metals and salts in the molten state. X. Equilibria in the molten state with aluminium as one component. R. LORENZ and G. SCHULZ (Z. anorg. Chem., 1928, 171, 258-260; cf. this vol., 594).—The reactions $3\text{Mg} + 2\text{K}_3\text{AlCl}_6 = 2\text{Al} + 3(\text{MgCl}_2, \text{KCl}) + 3\text{KCl}$, $3\text{Ca} + 2(\text{AlCl}_3, 3\text{NaCl}) = 2\text{Al} + 3(\text{CaCl}_2, 2\text{NaCl})$, and $4\text{Al} + 3\text{Na}_2\text{SiF}_6 + 6\text{NaF} = 4\text{Na}_3\text{AlF}_6 + 3\text{Si}$ in the molten state seem to occur entirely from left to right.

R. CUTHILL.

Equilibria between metals and salts in the molten state. XI. Tin, cadmium, stannous chloride, cadmium chloride. R. LORENZ, W. FRAENKEL, and P. WOLFF (Z. anorg. Chem., 1928, 171, 355-363; cf. preceding abstract).—The equilibrium $\text{Sn} + \text{CdCl}_2 = \text{Cd} + \text{SnCl}_2$ at 600° (A., 1927, 518) is displaced slightly towards the right by the addition of bismuth, which is miscible with both metals and indifferent towards the salts; dilution of the salt phase with lithium chloride or an equimolecular mixture of sodium and potassium chlorides has the reverse effect. In respect of the applicability of the mass law, the systems containing bismuth are intermediate between condensed systems and dilute solutions.

R. CUTHILL.

Thermodynamics of iron oxides. M. TIGER-SCHÖLD (Jernkont. Annaler, 1923, 107, 67-105; Chem. Zentr., 1928, i, 886).—Equilibria in the systems

iron-oxygen-carbon and iron-oxygen-hydrogen are determined. Ferrous oxide decomposes below 534° into iron and ferrosiferrous oxide; ferrous and ferrosiferrous oxides are more readily reduced by carbon monoxide below 800° and by hydrogen above 800° . The dissociation pressures of ferrous, ferric, and ferrosiferrous oxides are computed. The reactions $3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ and $3\text{Fe}_2\text{O}_3 + \text{H}_2 = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ are practically irreversible. Heats of formation are calculated to be (kg.-cal.): ferrous oxide 66.3, ferrosiferrous oxide 217.0, ferric oxide 197.1. A. A. ELDRIDGE.

Equilibria in the reduction, oxidation, and carburization of iron. VI. R. SCHENCK and T. DINGMANN (Z. anorg. Chem., 1928, 171, 239—257).—Experiments in which iron was caused to take up oxygen by being heated in carbon dioxide, under conditions admitting no possibility of contamination of the reacting system with substances derived from the containing vessel, have given values for the solubility of oxygen in iron which approximate to that previously obtained by the reduction method (A., 1927, 1030). Benedicks and Löfquist's explanation of the discrepancy between this value and values to be found in the literature (Z. anorg. Chem., 1928, 171, 231) is therefore to be regarded as untenable; it is probably the latter values which are affected by the material of the containing vessel. Further, a comparison of the diagram for the cementation of iron with carbon monoxide calculated from the data for cementation with methane and the diagram obtained directly by experiment shows that in the latter the austenite area is depressed by about 130° , and is different in form, which can be explained only by postulating a considerable solubility of oxygen in iron. R. CUTHILL.

Heterogeneous equilibrium $\text{CdBr}_2 + \text{H}_2\text{S} = \text{CdS} + 2\text{HBr}$ at higher temperatures. K. JELLINEK and L. ZUCKER (Z. anorg. Chem., 1928, 171, 271—274).—The above equilibrium has been studied at 300 — 500° by the method applied to other sulphides (cf. following abstract). Except at the highest temperature, the values of the equilibrium constant are in fairly good agreement with Nernst's approximate formula. R. CUTHILL.

Heterogeneous equilibrium between metallic chlorides and hydrogen sulphide, and between metallic sulphides and hydrogen chloride at higher temperatures. K. JELLINEK and G. VON PODJASKI (Z. anorg. Chem., 1928, 171, 261—270).—The following equilibria have been measured over the temperature ranges indicated in parentheses: $\text{CdCl}_2 + \text{H}_2\text{S} = \text{CdS} + 2\text{HCl}$ (232 — 352°), $\text{MnCl}_2 + \text{H}_2\text{S} = \text{MnS} + 2\text{HCl}$ (407 — 583°), and $2\text{AgCl} + \text{H}_2\text{S} = \text{Ag}_2\text{S} + 2\text{HCl}$ (230 — 419°), by passing hydrogen sulphide over the chloride or hydrogen chloride over the sulphide at various rates, and extrapolating the composition of the emergent mixture of gases to zero rate of flow. The values of the equilibrium constants are not in agreement with Nernst's approximate formula, the reason being that it is not permissible to neglect the molecular heats. Vologdin and Penkivitsch's value of 62,900 g.-cal. for the heat of formation of mangan-

ous sulphide (A., 1914, ii, 247) is irreconcilable with the present results. R. CUTHILL.

Reduction of silver sulphide by means of carbon. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 367—369).—The tension of carbon disulphide in the reaction $2\text{Ag}_2\text{S} + \text{C} = 4\text{Ag} + \text{CS}_2$ at 1015° and 1050° has been calculated (a) from determinations of the sulphur tension and of the ratio $p_{\text{S}_2}/p_{\text{CS}_2}$ (cf. this vol., 480, 594), and (b) from the equilibrium data obtained from the reduction of silver sulphide by hydrogen and the dissociation constant of carbon disulphide. The agreement between the two methods is satisfactory. O. J. WALKER.

Chemical equilibrium and space [geometry]. N. S. KURNAKOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 525—552).—The application of three-dimensional geometry to chemical problems is discussed and illustrated. R. TRUSZKOWSKI.

[Equilibrium models.] V. I. NIKOLAEV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 553—561).—The space-model for the four-component system H_2O — N_2O_5 — Na_2O — EtOH in the form of a triangular prism is described; solutions saturated with sodium nitrate are represented by two curved surfaces which intersect at the median line of the triangle and run parallel to the axis of the prism. R. TRUSZKOWSKI.

Generalisation of the method of residues; determination of hydration of solid phases in the equilibrium of systems. V. P. SHISHOKIN (Ann. Inst. Anal. Phys. Chem., 1927, 3, 746—749).—Schreinemakers' residue method (A., 1893, ii, 260) for the determination of the composition of solid phases in heterogeneous systems may be extended to any number of solid phases. This is illustrated by reference to the system magnesium chloride, sodium sulphate, water. R. TRUSZKOWSKI.

Method of radiation calorimetry, and the heat of fusion or of transition of certain substances. L. E. STEINER and J. JOHNSTON (J. Physical Chem., 1928, 32, 912—939).—A method is described for determining the heats of fusion or transition of substances, or the heat of reaction of certain irreversible processes. The new, electrically-heated, radiation calorimeter permits the time-temperature curves for small amounts of poorly-conducting materials to be rapidly obtained, and the heat of reaction can then be found by graphical methods preferably from the heating curve with an error not greater than 5% from the mean of a series. The heats of fusion of phenol and benzophenone found are 2690 and 4600 g.-cal., respectively, and those of the polymorphous forms of monochloroacetic acid are α 4630, β 4450, and γ 3790 g.-cal. The heat of transition of red-yellow mercuric iodide is 640 g.-cal. and of ammonium nitrate III—II 310, and II—I 980 g.-cal., respectively. The interpretation of time-temperature curves and the theoretical basis of the method are fully discussed and details of the apparatus are given. L. S. THEOBALD.

Heat of formation of partly miscible water-alcohol mixtures. P. BRUN (Compt. rend., 1928, 186, 1729—1731).—Mixtures of ethyl and isoamyl

alcohols and water intended to simulate fusel oils have been studied calorimetrically by Berthelot's method, exothermic and endothermic mixtures being associated with a decrease and an increase in volume, respectively (cf. A., 1926, 895). Biron's law is found to apply except for mixtures near the miscibility limit. The thermal diagrams show breaks characteristic of the critical miscibility and an attempt is made to explain the contradictory results of Mondain-Monval (Bull. Soc. chim., 1928, [iv], 43, 145) on the assumption of molecular association which modifies the thermal properties of certain mixtures. J. GRANT.

Ratio of the heats of combustion of benzoic acid and salicylic acid. P. E. VERKADE and J. COORS, jun. (Rec. trav. chim., 1928, 47, 709—714).—By means of combustions of naphthalene, methyl racemate, and hydrobenzoin it has been confirmed that the heats of combustion determined by Berner (A., 1926, 116) contain a small systematic error. The heat of combustion of salicylic acid found by him is too low. A redetermination of this quantity gave the value 5241.3 g.-cal. (15°) per g. (air) at constant volume, in agreement with the authors' previous determination (A., 1925, ii, 39). O. J. WALKER.

Effect of certain corrections on the results obtained for the heat of combustion of organic compounds. W. SWIENTOSLAWSKI and H. STARCZEWSKA (Rocz. Chem., 1928, 8, 195—209).—Corrections for the isothermal heat of combustion of a number of organic substances are given, as well as for the temperature coefficient. These corrections are so small as to be negligible except in those cases where the heat of combustion of the given compound is small; in the latter case the correction is negligible where the temperature variation is of the order of 1°. If the combustions take place within the temperature limits 15—21°, the correction for the temperature coefficient may also be neglected. When an ice-calorimeter is used, or when the deviations from the usual calorimetric temperature of 15—21° are considerable, the application of the correction for the temperature coefficient du/dt is necessary.

R. TRUSZKOWSKI.

Swientoslawski's method for the correction of the older thermochemical data. P. E. VERKADE and J. COORS, jun. (Rec. trav. chim., 1928, 47, 701—708; cf. this vol., 712).—A further criticism of Swientoslawski's method for correcting the thermochemical data of Zubow, Swarts, Richards, and others. It is considered that the only result of these corrections is to replace incorrect data by data the trustworthiness of which is doubtful. O. J. WALKER.

Characteristics of homogeneous, exothermic gas reactions. R. N. PEASE and P. R. CHESEBRO (Proc. Nat. Acad. Sci., 1928, 14, 472—475).—Although it is usually found that a glass surface acts as a catalyst, experiments are described which point to inhibition by glass surfaces. A 1:1 methane-oxygen mixture was passed through a pyrex tube poisoned with potassium chloride, heated at 650°. It was found that 5% of the mixture was oxidised in a contact time of 3 secs. When, however, the tube was packed with broken pyrex glass, poisoned as before with potassium chloride, only 10% oxidation

occurred in a contact time of 20 sec. It thus appears that the glass packing inhibited the reaction. It is inferred that the reaction is homogeneous. The potassium chloride is not essential for this inhibiting effect. Clean glass fragments have a similar, but smaller, effect. Other reactions, such as the oxidation of hydrogen and of isobutane, have been shown to be inhibited in similar circumstances. It is suggested that reaction centres are developed in the body of the gas, these centres being associated with extremely large amounts of energy. Some of the energy of the reaction centres will be absorbed by the glass walls, and hence a tube packed with broken glass limits the development of the reaction centres by decreasing the volume available for their formation, and the glass acts as a temporary reservoir for their excessive energy. This accounts for the inhibition of the reaction. A. J. MEE.

Conductivities of sodium and potassium derivatives of β -ketonic compounds in alcoholic solution. (Miss) E. WHITE (J.C.S., 1928, 1413—1415).—The molecular conductivities of sodium and potassium derivatives of ethyl acetoacetate, acetylacetone, benzoylacetone, ethyl isobutyl- and isoamyl-acetoacetate, and also of sodium and potassium ethoxides and potassium iodide have been determined in alcoholic solution at 25° at dilutions of 4—1024 litres. The conductivities of the β -ketonic derivatives are only slightly less than that of potassium iodide.

F. J. WILKINS.

Liquid hydrogen sulphide as an ionising medium. H. R. CHIPMAN and D. McINTOSH (Proc. Nova Scotian Inst. Sci., 1927, 16, 189—195).—Of the fifteen substances examined, iodine, triisobutylamine, tripropylamine, and antimony trichloride were found to give solutions in liquid hydrogen sulphide which possessed appreciable conductivity over a considerable concentration range. The conductivity of iodine increased on dilution, indicating that it ionises into positive and negative ions, whilst that of the other three increased on concentration, indicating the formation of compounds with the solvent which then dissociate. In the case of antimony trichloride the compound SbS_2Cl_3 is probably formed.

S. J. GREGG.

Electrical conductivity of calcite. W. J. JACKSON (Proc. Nova Scotian Inst. Sci., 1927, 16, 46—53).—A constant *E.M.F.* of the order of 300 volts was applied to a crystal of calcite and the current was found to vary approximately exponentially with temperature; a displacement current and a conduction current were both indicated and there was a polarisation effect due possibly to a space charge near the electrodes or throughout the crystal. The conductivity is directional. Exposure of the crystal to X-rays increases the conductivity, but it returns to a normal value in 1—2 hrs.

S. J. GREGG.

Electrical conductivity of solids. G. MAYR (Nuovo Cim., 1927, 4, cxxv—clvi; Chem. Zentr., 1928, i, 885).—A review. A. A. ELDRIDGE.

Electrical conductance of nickel sulphate solution. Ionic conductance of nickel. K. MURATA (Tech. Rep. Tôhoku, 1928, 7, 1—7).—See this vol., 595.

Electrode potential of nickel. I. Measurements in an atmosphere of hydrogen and reduced nickel powder. K. MURATA (Tech. Rep. Tôhoku, 1928, 7, 9—25).—See this vol., 596.

Electrometric titration curves of dibasic acids.

I. Normal acids. R. GANE and C. K. INGOLD (J.C.S., 1928, 1594—1600).—The chemical evidence supporting the theory that the angles between the valencies of a carbon atom are modified by the space requirements of the attached groups may be confirmed by the measurement of the second dissociation constant of normal dibasic acids. Bjerrum's relation (cf. A., 1923, i, 1059) connecting the first and second dissociation constants of symmetrical dibasic acids with the distance between the ionising groups is not adequate for all purposes. It is important to measure both dissociation constants by the same method and in the same experiment. The first and second dissociation constants and the apparent distance between the ionising centres are calculated for homologous normal dibasic acids from oxalic acid to azelaic acid. The causes of the systematic deviations of the apparent from the real distances are discussed, and it is shown that in glutaric acid and in the higher acids, but not in malonic acid or succinic acid, deviations due to internally propagated polar effects are negligible.

R. A. PRATT.

Limiting potential of sugar solutions. R. WURMSER and J. GELOSO (Compt. rend., 1928, 186, 1842—1844; cf. A., 1927, 316).—At p_H 7 the limiting potential (E) of a gold or platinum electrode in a solution of pure dextrose is attained after 30 days at 40°, 9 hrs. at 75°, and 2 hrs. at 90°, and corresponds with the expression $E = -0.0002T_pK$. The constant K includes the term r_H , which has a temperature coefficient of ± 0.5 in a phosphate buffer. In the absence of buffers the potential first passes through a minimum. Dyes (up to a maximum concentration of 6×10^{-4} g./100 c.c.) do not affect the final potential but influence the rate at which it is attained, the leuco-compounds of janus-green and phenosafranine, which are more electronegative than dextrose, being oxidised by the latter.

J. GRANT.

Volta effect. E. DUBOIS (Compt. rend., 1928, 186, 1832—1833).—The Volta effect, measured in water vapour, between a fixed, electrically heated, cylindrical spiral electrode of the metal studied, and a cool mobile cylindrical electrode, shows differences of about 0.1 volt for iron, nickel, molybdenum, aluminium, or copper, but none for gold, silver, or platinum (cf. A., 1927, 832). The metal becomes more electropositive, and the change is a qualitative indication of the action of water vapour on the metal.

J. GRANT.

Solid cells, particularly thermoelectric cells with solid electrolytes. H. REINHOLD (Z. anorg. Chem., 1928, 171, 181—230).—Measurements with the cells $Ag|AgCl|Cl_2$, $Ag|AgBr|Br_2$, $Pb|PbCl_2|Cl_2$, and $Pb|PbCl_2|AgCl|Ag$ with solid electrolytes at temperatures up to about 500° show that the $E.M.F.$ may be calculated from the thermal data for the processes occurring at the electrodes with the aid of the Gibbs-Helmholtz equation and Nernst's heat theorem. It thus follows that the heat theorem is

valid over the whole range of temperature investigated, and it becomes possible to represent as a function of the temperature the heat effects and affinities of the reactions $Ag + \frac{1}{2}Cl_2 = AgCl$, and $\frac{1}{2}Pb + \frac{1}{2}Cl_2 = \frac{1}{2}PbCl_2$ up to the m. p. of the chlorides, and of the reaction $\frac{1}{2}Pb + AgCl = \frac{1}{2}PbCl_2 + Ag$ up to the eutectic temperature of the mixture of chlorides. In the thermoelectric cells $Ag|AgI|Ag$, $Ag|AgCl|Ag$, $Ag|AgBr|Ag$, $Pb|PbCl_2|Pb$, $Cl_2|AgCl|Cl_2$, $Br_2|AgBr|Br_2$, and $Cl_2|PbCl_2|Cl_2$, in which a difference of temperature is maintained between the electrodes, it appears that the changes which occur are of exactly the same nature as in the above isothermal cells, so that here also the heat theorem is true, and may be used to calculate the $E.M.F.$ resulting from the chemical changes which take place in the cells. The values calculated in this way, however, prove, in general, to be different from the actually observed values, except in cases in which the electrolyte is a purely anionic conductor, as with lead chloride, where there is fairly satisfactory agreement. With the cells containing silver halides, indeed, the direction of the current is the reverse of what would be expected. It seems therefore that there is a component of the $E.M.F.$ of the thermoelectric cells with cationically conducting electrolytes which is opposite in sign to the $E.M.F.$ calculated from the electrode processes and exceeds this in magnitude; for cells with anionic conductors any such $E.M.F.$ is negligible. This residual $E.M.F.$ may be considered as arising from a Benedicks effect, i.e., an $E.M.F.$ produced in a homogeneous conductor by a temperature gradient, these effects for the metal and electrolyte respectively being of the same order of magnitude, and in opposite directions for cells containing anionic conductors and in the same direction for cells containing cationic conductors. The Benedicks effect in metals is calculated to be equal to about half the residual $E.M.F.$ in the latter type of cell. It seems that the methods used in calculating the $E.M.F.$ of the above thermoelectric cells may also be applied to cells in which both anions and cations conduct the current, provided that the transport numbers are known.

R. CUTHILL.

Magneto-electrolytic potentials. E. O. HOLMES, jun. and A. HANDY (J. Amer. Chem. Soc., 1928, 50, 1303—1314).—When a salt solution is allowed to flow through a constant magnetic field, a $P.D.$ is set up at right angles both to the direction of flow and to the field. These magneto-electrolytic potentials are investigated for copper and zinc sulphate solutions (Scarpa, A., 1925, ii, 128). The $P.D.$ is independent of the nature and concentration of the electrolyte, but is proportional to the velocity of flow and the field strength. Experiment shows that the magnetic field produces neither dissociation nor ionic displacement. An equation for the $P.D.$ is derived, which is shown to correspond with the equation representing the electro-magnetic effects which are involved in the operation of the dynamo, with the addition of a very small osmotic term.

S. K. TWEEDY.

Reduction of niobic acid. I. S. J. KIEHL and D. HART (J. Amer. Chem. Soc., 1928, 50, 1608—1620).—The solubility at 25° of niobic acid is 8.34 g. of niobium pentoxide per 100 g. of solution containing

88.11% of sulphuric acid, or 15.43 g. in 100 c.c. of solution. The solution must contain at least 3*M*-sulphuric acid and not more than 0.038*M*-niobium pentoxide to remain stable for 3 days; higher oxide concentrations require greater acid concentrations. Niobium, in 0.00032*M*-solution, may be detected in presence of tantalum by the blue or pale green colour obtained on reducing a dilute solution of "niobic acid" with zinc. At a mercury cathode niobic acid in sulphuric acid solution is almost completely reduced to the trivalent state. In 3*M*-sulphuric acid the reduced solution is blue; in 6*M*- and 10*M*-sulphuric acid it is reddish-brown, but turns blue on dilution with water, indicating complex formation rather than valency change. S. K. TWEEDY.

Theory of combustion. N. SEMENOV (Z. Physik, 1928, 48, 571—582).—From a higher development of the Arrhenius theory expressions are deduced for the velocity of chemical reactions and for the conditions of explosion. These are found to be in agreement with experimental observation (A., 1927, 122; this vol., 483). J. W. SMITH.

Gaseous combustion at high pressures. X. The co-volume corrections, maximum temperatures, and dissociation of steam and carbon dioxide in explosions. D. M. NEWITT (Proc. Roy. Soc., 1928, A, 119, 464—480).—A review of data accumulated in researches on high-pressure explosions of hydrogen-air, carbon monoxide-air, etc. mixtures, relating to the effects of density and temperature on the internal energies of gaseous media and the dissociation of steam and carbon dioxide (cf. Bone, Newitt, and Townend, A., 1924, ii, 398; 1925, ii, 800). A revision of the previous estimates of maximum temperatures and dissociation has been carried out. The revised figures for the maximum temperatures reached in theoretical hydrogen- and carbon monoxide-air explosions are almost identical with those estimated previously in cases where the initial pressure (P_i) did not exceed 25 atm., but for all higher pressures the revised figures are lower than the old, the divergence increasing with increase of P_i . This is due to the fact that a co-volume correction is now applied to the maximum pressure (P_m) attained during explosion. The revised figures in general confirm the original estimates for the dissociation of steam and carbon dioxide. The fact that the "corrected" P_m/P_i ratios were found to show an unexpectedly large increase with the initial pressure was previously ascribed to the increasing opacity of the gaseous medium to the radiation emitted during the explosion. It is now found that about 50% of the effect in the case of the carbon monoxide explosions, and about 75% in the hydrogen explosions, may be accounted for by the probable increase in the co-volume factor with temperature and pressure. L. L. BIRCUMSHAW.

Inflammability of hydrogen. VI. Influence of tin tetramethyl and lead tetramethyl on the limits of inflammability of hydrogen. Y. TANAKA and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1928, 31, 20—23; cf. A., 1927, 1145).—Tin tetramethyl and lead tetramethyl have mol. refraction for the *D* line 36.40 and 40.13, respectively; the atomic refractions of tin and lead are 13.53 and 17.26, respectively. S. OKA.

Least energy required to ignite mixtures of air and ethyl ether vapour. Y. NAGAI and M. FURUHATA (J. Soc. Chem. Ind. Japan, 1927, 30, 781—786).—See A., 1927, 943.

Effect of ethyl bromide on the least energy required to ignite mixtures of air and ethyl ether vapour. Y. NAGAI and M. FURUHATA (J. Soc. Chem. Ind. Japan, 1927, 30, 786—791).—See A., 1927, 943.

Carbonyl bromide. I. Thermal decomposition. S. LENHER and H. J. SCHUMACHER (Z. physikal. Chem., 1928, 135, 85—101).—At the ordinary temperature the equilibrium $\text{CO} + \text{Br}_2 \rightleftharpoons \text{COBr}_2$ is established in the dark very slowly, and only about 10% of carbonyl bromide is formed. In the light equilibrium is established in a few hours, at a bromine concentration of about 200 mm. and a carbon monoxide concentration of about 560 mm. The thermal decomposition is a surface reaction of the first order, and is independent of added gases. The decomposition velocity is greater in borosilicate glass than in soda glass, and greater still in quartz vessels. Carbonyl bromide is stable at temperatures up to 150°. Between 210° and 230° the temperature coefficient of the reaction velocity in borosilicate vessels is 1.8 for 10° rise of temperature.

H. F. GILLBE.

Kinetics of nitrous acid. III. Kinetics of the decomposition of nitrous acid. E. ABEL and H. SCHMID (Z. physikal. Chem., 1928, 134, 279—300).—A method and an apparatus are described for the investigation of the decomposition of nitrous acid according to the equation $3\text{HNO}_2 = \text{H}^+ + \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O}$. The reverse reaction is neglected. The velocity is proportional to the fourth power of the concentration of undissociated acid, and inversely proportional to the square of the concentration of nitric oxide. Considering the distribution equilibrium between gas and liquid phases, the velocity of decomposition was inversely proportional to the square of the partial pressure of nitric oxide. The velocity coefficient rises with increasing ionic concentration, the relationship between the two being almost linear. Mathematical expressions are given for the velocity coefficient. Since the concentration of nitrous acid appears in the velocity expression to the fourth power the degree of dissociation of the acid appears particularly great if there is no excess of hydrogen and nitrite ions present which depress the dissociation. If sulphate ions are also present the reaction is still further complicated. An expression is deduced for the case where the nitrous acid is practically undissociated. The mechanism of the decomposition is discussed. The reaction involves the hydrolysis of nitrogen tetroxide as a part-reaction. The velocity of this reaction can be expressed by the equation $-d[\text{N}_2\text{O}_4]/dt = 2 \times 10^4 p_{\text{N}_2\text{O}_4}$, where $p_{\text{N}_2\text{O}_4}$ represents the partial pressure of the gas. A. J. MEE.

Absorption kinetics for molecules attached at more than one point. R. E. BURK and D. C. GILLESPIE (Proc. Nat. Acad. Sci., 1928, 14, 470—472).—A theoretical paper in which the kinetics of desorption of molecules attached to the surface by two linkings are considered and compared with the

kinetics of desorption of molecules attached by only one linking. By considering the probability that a molecular vibration would break one or both linkings, the rate of desorption is calculated. It is shown that singly and doubly attached molecules would come off at the same rate if $M(\alpha + \beta) = 2$, where M is the number of vibrations of the underlying surface atoms (assumed all alike) per second, α is the average time after breaking one linking that the end of the molecule thus set free returns to the surface, and β is the corresponding time for the other end of the molecule.

A. J. MEE.

Reaction velocity at a liquid-liquid interface.

R. P. BELL (J. Physical Chem., 1928, 32, 882—893).—The velocity of reaction at the liquid-liquid interface between a solution of benz-*o*-toluidide in benzene and of potassium permanganate in water has been measured at 14–90° and 25° (approx.) for varying concentrations of the reactants, and the interfacial tension between water and benzene solutions of benz-*o*-toluidide has been measured by the drop-weight method. The reaction results from collisions between the permanganate ions and an adsorbed layer of benz-*o*-toluidide, and the velocity is independent of diffusion from solvent to solvent. Comparison of surface tension with velocity confirms the Gibbs-Helmholtz adsorption equation.

L. S. THEOBALD.

Reaction regions. XVIII. Velocity of propagation of the reaction in iron-sulphur mixtures. W. P. JORISSEN and C. GROENEVELD. XIX. Reaction regions in which one of the substances is gun cotton. W. P. JORISSEN and H. A. STARINK (Rec. trav. chim., 1928, 47, 737—742, 743—751).—XVIII. The velocity of propagation of the reaction between iron and sulphur induced by a piece of burning magnesium ribbon in a finely-divided mixture of these two elements shows a maximum when plotted against the composition of the mixture. The top of the curve, which is somewhat uncertain, appears to lie to the right of the ratio for complete transformation, i.e., 1S:1Fe (100% sulphur being on the left).

XIX. The reaction regions of mixtures of gun cotton (12.12% N) with salts and with organic substances have been investigated. It is shown that mixtures with definite times of reaction can be prepared.

O. J. WALKER.

Mechanism of hydrogen-ion catalysis. E. MÜLLER (Z. physikal. Chem., 1928, 134, 190—192).—By making use of the electronic theory of the structure of the molecule, the mechanism of hydrogen-ion catalysis of ester formation is investigated. According to Goldschmidt the hydrogen ion forms a complex ion by addition to a neutral molecule. It is shown that in the uncatalysed reaction it is necessary for 4 atoms to come into contact at the same time, whereas if the catalysis takes place according to the theory of Goldschmidt, it is sufficient if 2 atoms in the molecules collide. The probability of the second reaction occurring is therefore many times greater than that of the first.

A. J. MEE.

Rate of oxidation of hydrogen peroxide by bromine and its relation to the catalytic decom-

position of hydrogen peroxide in a bromine-bromide solution. W. C. BRAY and R. S. LIVINGSTON (J. Amer. Chem. Soc., 1928, 50, 1654—1665).—Experimental results are recorded which prove that the rate of oxidation follows the equation: $-d[\text{H}_2\text{O}_2]/dt = K[\text{Br}_2][\text{H}_2\text{O}_2]/[\text{Br}'][\text{H}']$. An apparatus is described for measuring reaction rates having half-times of 0.5—6 sec.; the solutions are mixed at two jets and the reaction is stopped by adding to the mixture a third solution which reacts with, and so removes, one of the reacting components with great rapidity. The hypobromous acid mechanism for the reaction between hydrogen peroxide and bromine and for the catalytic decomposition of hydrogen peroxide is in agreement with experimental results. The hypobromite-ion mechanism suggested by Christiansen (A., 1927, 1035) is unsatisfactory. Hydrogen peroxide may be determined by pipetting a quantity into potassium iodide solution containing 0.2*N*-sulphuric acid, and, after keeping in the dark for 40 min., titrating with thiosulphate.

S. K. TWEEDY.

Oxidation of some dicarboxylic acids by hydrogen peroxide in the presence of certain catalysts. J. H. WALTON and D. P. GRAHAM (J. Amer. Chem. Soc., 1928, 50, 1641—1648).—A continuation of previous work (A., 1926, 918). Owing to the large number of uncontrollable factors a quantitative relation between structure and ease of oxidation could not be deduced. Experiments were carried out with oxalic, succinic, malic, lactic, and tartaric acids, and also glycerol, formic acid, and ethylene glycol. The carbon dioxide content of the solution has a large influence on the nature of the reaction, and increase in acidity tends to increase the decomposition rate of the peroxide and the oxidation rate of the acid. Oxalic acid forms a stable complex containing equimolecular quantities of ferric and oxalate ions. In presence of the lactic acid structure the concentration of the copper salt catalyst has practically no influence on the oxidation or the rate of decomposition of hydrogen peroxide. Introduction of hydroxyl groups into succinic acid increases the rate of oxidation of the acid but decreases the power to inhibit the decomposition of hydrogen peroxide. Primary alcohol groups exert a protective action on formic acid and reduce the rate of oxidation.

S. K. TWEEDY.

Theory of acid and basic catalysis. Mutarotation of dextrose. J. N. BRÖNSTED and E. A. GUGGENHEIM (J. Amer. Chem. Soc., 1927, 49, 2554—2584).—The conception, previously advanced (A., 1926, 797), that molecules, independently of their electric charge, should be regarded as acids or bases according as they tend to lose or to unite with a hydrogen nucleus is developed to include acid and basic catalysis. The new theory ascribes the catalytic effect not particularly to hydrogen and hydroxyl ions, but generally to acid and basic molecules as defined above. Dilatometric measurements at 18° of the mutarotation of dextrose under the influence of acids and bases of various electrically-charged types support the new theory. The velocity coefficient at 18° when water only is present has the value $(5.30 \pm 0.10) \times 10^{-3}/\text{min.}$ at p_{H} 4—6, the range of minimum

velocity, and the neutral salt effect is negligible for salts up to an ionic strength of 0.2. The effect of the oxonium ion (OH_3^+), determined in aqueous solutions of perchloric acid, is proportional to its concentration and primary salt effect is again undetectable. Data for 13 weak, monobasic, organic acids buffered to p_{H} 4—6 by their corresponding salts show the anions of these acids to be catalytically active in proportion to their concentrations. With the strongest bases, the trimethylacetate, propionate, and acetate ions, the effect is greater than one fifth that of the oxonium ion. Catalysis by the undissociated acid is established in the case of formic, glycollic, and mandelic acids; with weaker acids, the smallness of the catalytic effect makes its detection uncertain. Catalysis by acid and basic molecules increases regularly with an increase in strength of the acid or base. A mechanism for the mutarotation of dextrose is suggested, and previous work is discussed. Finally, it is pointed out that the laws of mutarotation conform to those previously discovered for the decomposition of nitroamide (A., 1925, ii, 982). L. S. THEOBALD.

Autoxidation and antioxygenic action. Catalytic properties of phosphorus. C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (Compt. rend., 1928, 186, 1673—1677).—It has been shown by manometric determinations of the oxygen absorbed that about 1% of white phosphorus inhibits the autoxidation of furfuraldehyde, but increases that of benzaldehyde, styrene, or turpentine. Elaborate precautions were taken and in the last case it is shown that the oxygen absorption obtained was not due to oxidation of the phosphorus, although it may have been due partly or completely to the catalytic effect of one of its oxidation products. Red phosphorus has analogous but less marked effects, and inhibits or accelerates the oxidation of sodium sulphite solution according as the latter is slightly alkaline or acid, respectively. J. GRANT.

Heterogeneous catalysis and adsorption. II. C. F. VAN DUIN [in part with H. G. SNIJDER] (Rec. trav. chim., 1928, 47, 715—736; cf. A., 1921, ii, 392).—The acceleration of the reaction between $\alpha\beta$ -dibromopropionic acid and inorganic iodides by the addition of carbon, previously observed by Kruyt and the author, has been confirmed. An acceleration was also observed for the sodium salt of the acid. The velocities of hydrolysis of methyl *m*- and *o*-sulphobenzoate, methyl isovalerate, monoacetin, methyl hydrogen succinate, methyl hydrogen *d*-tartrate, and methyl mesotartrate, and of the inversion of sucrose are all retarded by the addition of carbon. The unimolecular reaction *r*-dibromosuccinic acid \rightarrow bromofumaric acid + hydrobromic acid is also retarded by addition of carbon, a result which supports the hypothesis that adsorbed molecules are in a less favourable condition to meet other molecules and to take part in a reaction. On the other hand, the velocity of the termolecular reactions *r*-(or meso-) dibromosuccinic acid + 2KI = maleic (or fumaric) acid + 2KBr + I_2 is greatly increased by the presence of carbon. This result supports the hypothesis that adsorption can cause positive catalysis only where the orientation of the adsorbed molecules is such that the

reacting groups are turned away from the adsorbent and towards the surrounding liquid. This orientation must be so favourable that the primary decrease of the velocity of the reaction, caused by the adsorption itself, is overcome. Experiments were also carried out using a colloidal suspension of tin oxide as adsorbent. The velocity of hydrolysis of methyl hydrogen *d*-tartrate is decreased in presence of tin oxide, but with methyl mesotartrate the velocity is unaffected. In the former case the retarding influence due to the adsorption itself preponderates, whereas in the latter case this retarding influence is just compensated by the accelerating influence due to the favourable orientation of the molecules.

O. J. WALKER.

Catalytic activity of titania in the reduction of nitro-compounds. G. ETZEL (J. Physical Chem., 1928, 32, 852—860).—The catalytic activity of titania obtained by reduction in hydrogen of the hydroxide, prepared from the chloride by precipitation with ammonia, on the reduction of nitrobenzene has been studied. The yield of amines increases with the amount of catalyst; the optimum temperature for reduction to aniline is 282° and the best yield obtained was 94.4% with a catalyst reduced at 302° . A higher temperature of reduction favours the formation of azobenzene and hydrazobenzene, whilst a lower (260°) increases the yield of cyclohexylamine and diphenylamine formed. The optimum rates of flow of hydrogen and nitrobenzene for production of aniline are 14 litres/hr. and 4.05 g./hr., respectively. Continuous or intermittent feeding of the latter has little effect. The activity of the catalyst is poor initially, but soon increases to a constant value, and the use of asbestos as a support had no effect. Small amounts of manganese (5%) in the titania do not increase the yield of aniline, but prevent the formation of azobenzene and give a product of a better colour. The aniline produced was slightly yellow with the catalyst reduced at 260° and cherry-red with those reduced at higher temperatures. L. S. THEOBALD.

Catalytic oxidation of aromatic hydrocarbons and their derivatives by means of air. E. B. MAXTED.—See B., 1928, 473.

Catalytic oxidation of nitro- and halogen derivatives of toluene by means of air. E. B. MAXTED and A. N. DUNSBY (J.C.S., 1928, 1439—1442; cf. A., 1907, ii, 273).—The catalytic oxidation of *p*-nitrotoluene, *o*-nitrotoluene, *o*-bromotoluene, and *o*-chlorotoluene, using tin vanadate as catalyst, is described. Air was passed at a known speed through a suitably heated wash-bottle containing the substance to be oxidised before entering the catalyst tube, and the products were collected in a weighed receiver. The products from *p*-nitrotoluene were *p*-nitrobenzoic acid, *p*-nitrobenzaldehyde, and unchanged *p*-nitrotoluene, the maximum yield of acid being 16% at a catalyst temperature of 285° and a carburettor temperature of 93° . With *o*-nitrotoluene, much decomposition occurred and practically no acid was isolated. With *o*-bromotoluene, the maximum yield of *o*-bromobenzoic acid was 24.3% at a catalyst temperature of 290° and a carburettor temperature of 60° . With *o*-chlorotoluene, the maximum yield of *o*-chlorobenzoic

acid was 13.8% with a catalyst temperature of 287° and a carburettor temperature of 60°.

R. A. PRATT.

X-Ray examination of iron catalysts for the ammonia synthesis. O. EISENHUT and E. KAUPP (*Z. physikal. Chem.*, 1928, 133, 456—471).—The X-ray diagram of the catalyst for the ammonia synthesis prepared from ferrosferri oxide according to G.P. 249,447 shows that when the activity is maximal the lattice is identical with that of α -iron. Similarly it seems that in the formation of a catalyst from potassium aluminium ferrocyanide (cf. Mittasch and Kuss, this vol., 605) α -iron is present actually from the commencement of the reduction, although where local excessive temperatures occur γ -iron may be formed. The admixture of potassium chloride with the ferrocyanide has no appreciable effect on the process of formation. Even in catalysts prepared according to B.P. 253,122 (B., 1927, 481) or Norwegian Patent 43,263 α -iron is still the essential constituent.

R. CUTHILL.

Ammonia synthesis with catalysts obtained from complex cyanides of iron. A. MITTASCH and E. KUSS.—See B., 1928, 522.

Influence of arsenic on the catalytic activity of platinum for the oxidation of sulphur dioxide. E. B. MAXTED and A. N. DUNSBY (*J.C.S.*, 1928, 1600—1603; cf. A., 1903, ii, 639; 1926, 365).—The activity of a progressively poisoned platinum catalyst and its arsenic content are correlated. Dry electrolytic oxygen and sulphur dioxide were allowed to react at $300^{\circ} \pm 2^{\circ}$ in the presence of platinum prepared by the reduction of platinic chloride with hydrogen. Unconverted sulphur dioxide was collected and determined iodometrically. The catalyst was progressively poisoned with a standard arsenic solution and the corresponding decreases in activity were recorded. The poisoning curve showed that, in the first stages of poisoning, the catalytic activity varies approximately linearly with the arsenic content. This initial portion is followed by a region in which the continued addition of arsenic affects the activity to a far smaller degree. The addition of about 0.0016 g. of arsenic reduced the activity of 1 g. of platinum to half its original value, but a total arsenic content of about 0.03 g. per g. of platinum reduced this only to 26% of its original activity.

R. A. PRATT.

Catalytic action in the oxidation of sulphides and arsenides. F. CARMICHAEL (*Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min.*, 1927, No. 24, 47—53).—Chalcocite, pyrrhotite, and nickeliferous pyrrhotite were not oxidised more rapidly in presence of platinum-black, pyrite, or manganese dioxide. Polydymite gave 11.4% S, and a residue of iron hydroxide. The reaction was accelerated by platinum-black. The oxidation of rammelsbergite was promoted by each of the catalysts.

CHEMICAL ABSTRACTS.

Hygroscopic and catalytic properties of gelatinated electrolytic copper. C. MARIE and P. JACQUET (*Compt. rend.*, 1928, 187, 41—43).—The desiccation and moisture-absorption curves of copper deposited electrolytically in the presence of gelatin (A., 1927, 840) have the same slope as that of gelatin

alone under the same conditions. Such deposits will catalyse the synthesis of water at 100°, and have an activity and structure (as shown by X-ray examination) comparable with those of finely-divided copper obtained by the reduction at 220° of copper oxide prepared from the nitrate.

J. GRANT.

Reduction of sodium sulphate to sulphide, particularly by hydrogen and carbon monoxide in presence of catalysts. P. P. BUDNIKOV and E. SHILOV.—See B., 1928, 481.

Catalytic refining of bromine. P. T. DANILITSCHENKO and M. RAVITSCH.—See B., 1928, 482.

Electrodeposition of tellurium. F. C. MATHERS and H. L. TURNER (*Amer. Electrochem. Soc.*, Sept. 1928, 54. Advance copy. 8 pp.).—Tellurium can be deposited in smooth, thick layers with theoretical current efficiency from a bath containing 300 g. of tellurium dioxide (49.6% TeO_2 , 46.1% Na_2TeO_3), 500 g. of 48% hydrofluoric acid, and 200 g. of sulphuric acid per litre at the ordinary temperature, using 1.6 amp./dm.² at a lead cathode. With tellurium anodes the bath voltage was about 1 volt, and 0.9% of selenium contained in the anodes remained entirely in the slimes, showing that this bath can be used for refining tellurium. The deposited tellurium is light grey and very brittle. Baths consisting of hydrochloric-sulphuric acid solutions of tellurium dioxide gave somewhat less satisfactory deposits.

H. J. T. ELLINGHAM.

Electrolytic preparation of the borides of calcium, strontium, and barium. L. ANDRIEUX (*Compt. rend.*, 1928, 186, 1537—1539).—In the method previously described (A., 1927, 216, 844) the electrolytic bath may be replaced by a mixture in suitable proportions of powdered boric anhydride with the oxide or carbonate, and the fluoride, of the corresponding alkaline-earth metal, heated at 1000°. Direct electrolysis of the metallic borates gives amorphous boron, and a much smaller yield of boride, particularly in the case of barium.

J. GRANT.

Electrolytic separation of copper from cuprous chloride solutions. P. P. FEDOTÉV [with N. P. FEDOTÉV] (*Z. anorg. Chem.*, 1928, 173, 81—91).—The form of deposit obtained by electrolysing cuprous chloride solution under various conditions is examined. Incidentally the solubility of cuprous chloride in hydrochloric acid and in sodium chloride solution at 19° was found, and also the solubility in cupric chloride solution. The solutions of cuprous chloride in hydrochloric acid and in sodium chloride were electrolysed under different conditions. Using solutions of cuprous chloride in hydrochloric acid and a current density of 80 amp./m.², with increase of cuprous chloride content the deposit became more uniform and had a fine crystal structure. The same was observed for solutions of the salt in sodium chloride. On the whole, using the same conditions, the deposit from the acid solution was more uniform and of finer structure than that from the sodium chloride solution. The effects of other conditions such as current density, temperature, stirring, and addition of colloids were also studied. The crystal form of the deposit was investigated. It is quite

possible to obtain a compact cathode deposit of copper from cuprous chloride solutions at the ordinary temperature and with ordinary current densities.

A. J. MEE.

Effect of colloids in the electro-deposition of silver from silver nitrate solutions. S. WERNICK (Trans. Faraday Soc., 1928, 24, 361—366).—The "silver numbers" of a number of colloids commonly used to reduce grain-size were determined. Silver deposits were obtained from neutral silver nitrate solutions containing the different colloids, and photomicrographs of these deposits were taken. The number of crystals per unit area was determined, and taken as a measure of the fineness of the deposit. With the exception of dextrin, it was found that there was a rough relationship between silver number and fineness of deposit; the larger the silver number the more closely grained was the deposit.

L. F. GILBERT.

Precipitation of gold and silver from their dilute solutions. M. YASUDA (Bull. Chem. Soc. Japan, 1928, 3, 113—118).—A coherent plate is obtained by compressing and hammering a mixture of powdered lead and manganese. When immersed in dilute solutions of gold or silver, such as sea water, the precious metals are deposited on the surface and recovered by cupellation. From solutions containing 37 mg. of gold per m.³ the yield was 10⁻⁶ g./cm.² of surface in 100 hrs. A plate containing 5% Mn is most suitable.

C. J. SMITHELLS.

Crystallographic X-ray study of the structure of simultaneous electrolytic depositions of two metals. A. ROUX and J. COURNOT (Compt. rend., 1928, 186, 1733—1736).—The X-ray diffraction spectra of simultaneous electrolytic deposits of copper with zinc on steel, and of cadmium with silver, tin, or nickel on duralumin are not due to the superposition of the spectra of the constituent metals, and therefore indicate that these have either combined or formed solutions.

J. GRANT.

Electrolytic production of heavy metals from fused electrolytes. II. G. NEUENDORFF and F. SAUERWALD.—See B., 1928, 526.

Electro-deposition of iron-nickel alloys. II, III. S. GLASSSTONE and T. E. SYMES (Trans. Faraday Soc., 1928, 24, 370—372, 372—378; cf. A., 1927, 633).—II. Anions and cations appear to exert little influence on the relative tendencies for iron and nickel to deposit from solutions containing simple ions of both metals.

III. Experiments performed at higher temperatures than previously employed confirm the conclusion that the relative tendencies of iron and nickel to deposit in the form of an alloy are independent of the hydrogen-ion concentration of the electrolyte. In accordance with a previous theory (A., 1927, 24), at higher temperatures the deposits from a given solution contain less iron than at lower temperatures, and the increase of the proportion of iron with increase of current density is much more gradual. The influence of dilution and stirring is similar to that observed at the ordinary temperature, but is not so marked, on account of the increased rate of diffusion. Diffusion of the ions is so rapid at 90° that depletion of the

electrolyte near the cathode probably does not occur to any appreciable extent. There is a minimum iron content of the electrolyte from which the initially deposited alloy contains relatively less iron than does the electrolyte. This minimum is decreased as the temperature is raised.

L. F. GILBERT.

Application of electrical resistance measurements to the study of atmospheric corrosion of metals. J. C. HUDSON.—See B., 1928, 488.

Experimental technique of photochemistry. V. Reflexion losses in the optical system of the Hilger ultra-violet monochromatic illuminator. H. N. RIDYARD and D. W. G. STYLE (J. Physical Chem., 1928, 32, 861—867; A., 1925, ii, 809).—The apparatus and method used in measuring the reflexion of mercury lines by the mirror in this illuminator are described. The reflexion losses at the various quartz surfaces in this instrument have been calculated together with the total transmissions of the mercury lines. Factors by which galvanometer deflexions should be multiplied to reduce all lines to the standard of 579 $\mu\mu$ are also given.

L. S. THEOBALD.

Photo-decomposition of an iron-carbon monoxide compound and the law of photochemical equivalence. O. WARBURG and E. NEGELEIN (Naturwiss., 1928, 16, 387).—Cremer has shown that aqueous solutions of ferrocysteine absorb 2 molecules of carbon monoxide for every atom of iron in the complex. Irradiation of the solution effects the dissociation of the compound formed. The use of monochromatic light (mercury) shows that Einstein's law is valid, since 4 molecules of carbon monoxide are liberated per quantum absorbed over the region 366—580 $\mu\mu$. The photochemical effects supply a method of obtaining the absorption spectrum which yields data in excellent agreement with direct measurements. The work is of value in confirming the validity of other work on the absorption spectrum of the respiratory enzyme (cf. this vol., 537).

R. A. MORTON.

Chemical actions of radiations. P. VILLARD (Compt. rend., 1928, 186, 1669—1673).—The author compares his experiments and theories with those of Belliot (B., 1927, 174; A., 1927, 323) and claims priority. Experimental evidence favours the hypothesis that the impressions produced on a plate by radiations of very different frequencies have not the same properties and can co-exist independently on the same plate. The relation between solarisation and the slight blackening which accompanies it in the case of silver bromide is also discussed. Solarisation is probably a relative effect, the theory of atomic levels indicating that a plate solarised for one frequency cannot be acted on by another which affects a lower atomic level.

J. GRANT.

Effect of light on indigo-dyed [cotton] fabric. R. HALLER, J. HACKL, and M. FRANKFURT.—See B., 1928, 479.

Purification of potassium dihydrogen phosphate. R. HOLCOMB and R. R. MCKIBBIN (J. Amer. Chem. Soc., 1928, 50, 1695—1696).—The sediment produced on keeping potassium dihydrogen phosphate solutions consists of a mixture of colloidal aggre-

gated aluminium and ferric compounds, sometimes accompanied by alkaline-earth metal salts. The phosphate may be purified by keeping a 0.2*M* solution at 75–85° for 24 hrs. in a sealed flask. After filtration, the liquid is either evaporated to dryness and the residue recrystallised, or is concentrated and precipitated with alcohol. S. K. TWEEDY.

Dehydration of gypsum. A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 24–27).—Gypsum loses >99% of water when heated at 115° for 22 hrs. A study of the optical properties and water content in all stages of the manufacture of plaster of Paris shows that this is not a definite compound but a mixture of bassanite and gypsum (3–2:1). The hemihydrate was prepared only by wet methods. CHEMICAL ABSTRACTS.

Behaviour of calcium carbide towards free halogens and sulphur. E. BIESALSKI and H. VAN ECK (Z. angew. Chem., 1928, 41, 720–723; cf. B., 1928, 522).—Bromine and calcium carbide react slowly at the ordinary temperature, about 80–90% of hexabromoethane being formed after 3.5 months. At higher temperatures little or no hexabromoethane is formed, the carbide being decomposed with production of free carbon. Low temperature favours the production of hexachloroethane from calcium carbide and chlorine, although the yield is small (3–5%). A certain amount of carbon is produced, but the carbide is attacked very slowly, 80–90% remaining after 6 months. Very little reaction occurs between iodine and calcium carbide at the ordinary temperature, but 35–37% of tetraiodoethylene, together with considerable amounts of free carbon, is obtained after heating at 100–160° in sealed tubes for some hours. A 20% yield of carbon disulphide and much carbon are obtained when calcium carbide and sulphur are heated at 270°. Traces only of carbon disulphide are formed at 500°.

The first reaction, which is probably preceded by adsorption, is the formation of calcium halide or sulphide and carbon. The latter can either polymerise or react with the agent to form halogen compounds or carbon disulphide. The yield of halogen compound or carbon disulphide is determined by the rates of the three reactions concerned. If the polymerised carbon accumulates the carbide becomes coated with a layer of carbon and the first reaction is prevented. The formation of a layer of calcium halide may also prevent further attack on the carbide. This latter effect is not of considerable magnitude with bromine and iodine, since these readily form complex compounds with the corresponding halides. J. S. CARTER.

Composition of the precipitate formed by the action of potassium ferrocyanide on calcium salts in presence of acetic acid. I. TANANAEV (Z. anorg. Chem., 1928, 172, 403–406).—In presence of a sufficient quantity of acetic acid a saturated solution of potassium ferrocyanide forms a precipitate even with a very dilute solution of a calcium salt. The nature of this precipitate has been examined when formed in presence of (1) excess of ferrocyanide and (2) excess of calcium salt. The complex salt obtained could be completely decomposed by

repeated evaporation to dryness with concentrated nitric acid. In both cases the composition of the precipitate agreed with the formula $K_2CaFe(CN)_6$. An oxalate method for the determination of potassium in the presence of calcium is described. M. S. BURR.

Action of aqueous ammonia on mercurous chloride. H. S. KING (Trans. Nova Scotian Inst. Sci., 1927, 16, 115–125).—The formula Hg_2Cl_2 is preferred for mercurous chloride since the formula $HgCl$ cannot be reconciled with the electron structure of the mercury atom. The unsymmetrical form $Hg\cdot HgCl_2$ agrees best with the chemical properties of the compound. The mechanism of the reaction is described as follows: $Hg\cdot HgCl_2 \rightleftharpoons Hg + HgCl_2$; $HgCl_2 + NH_3^+ = Cl\cdot Hg\cdot NH_3^+ + Cl^-$; $Cl\cdot Hg\cdot NH_3^+ + NH_3 = Cl\cdot Hg\cdot NH_2 + NH_4^+$; $\alpha Cl\cdot Hg\cdot NH_2 = (Cl\cdot Hg\cdot NH_2)_x$.

It is impossible to separate the isotopes of mercury by this reaction. S. J. GREGG.

Preparation of boric anhydride and its efficiency as a drying agent. J. H. WALTON and C. K. ROSENBAUM (J. Amer. Chem. Soc., 1928, 50, 1648–1650).—The oxide is prepared by dehydrating boric acid at not above 800°; the mass is poured into carbon tetrachloride at 0° and powdered. If the dehydration temperature exceeds 800°, the product exhibits an induction period, probably due to the formation of molecular complexes. The oxide is a rapid and efficient drying agent until it contains 25% of its weight of water (metaboric acid stage).

S. K. TWEEDY.

Elucidation of [the nature of] hydrated alumina by the ammonia extraction method. W. BILTZ and G. A. LEHRER [with K. MEISEL] (Z. anorg. Chem., 1928, 172, 292–309).—The action of liquid ammonia on samples of hydrated alumina of different origin has been studied, and the results have been compared with those obtained by Willstätter (A., 1924, ii, 615; 1926, 34) by acetone drying. An X-ray examination of the different products has also been made. The results may be explained by dividing the hydrates into two classes. Hydrates of the first class have a special lattice distinguished by its great stability. They therefore occur as minerals. Only two of this type have been examined, viz., hydrargillite, $Al_2O_3\cdot 3H_2O$, and bauxite, $Al_2O_3\cdot H_2O$. These substances cannot unite directly with water or ammonia. There are, however, bauxite compounds of the second kind which may be called bauxite hydrates and bauxite ammines, and most of the compounds examined belong to this class. In addition to other hydrates, a bauxite dihydrate, $[Al_2O_3\cdot H_2O]\cdot 2H_2O$, may be obtained isomeric with hydrargillite. It will take up a molecule of ammonia with which it is only loosely combined. Hydrates of the second class, formed by precipitation from aluminium salt solutions, do not consist of completely formed crystals, but of crystals in process of formation. By varying the conditions, intermediate forms, more or less similar to hydrargillite in water content and lattice structure, are obtained. M. S. BURR.

Indium. III. A. THIEL and H. LUCKMANN (Z. anorg. Chem., 1928, 172, 353–371; cf. A., 1904, ii, 618; 1906, ii, 169; 1910, ii, 413).—It has been shown by dialysis against an indium-free ammonia solution

that the solution of precipitated indium hydroxide in concentrated ammonia solution is not colloidal. Pure metallic indium can be obtained by electrolysis in sulphuric or tartaric acid solution, but the separation is not quantitative. The determination of indium as In_2O_3 , by precipitating and calcining the hydroxide, has been shown to be inexact, since, if the oxide is heated at a sufficiently high temperature to remove all traces of water, partial decomposition takes place. Satisfactory results may, however, be obtained by heating the oxide in a current of carbon dioxide and hydrogen sulphide, and weighing the resulting sulphide, In_2S_3 . The purest form of the oxide, In_2O_3 , is obtained by heating the hydroxide at 850° to constant weight, and then heating for 0.5 hr. in air at 1000° ; it has $d\ 6.75 \pm 0.01$. The oxide is yellow, but usually appears white, due to a thin superficial layer of the volatile oxide In_2O . The latter has been obtained by the action of a reducing gas on In_2O_3 at 500° , followed by sublimation in a high vacuum at 650 – 700° . In thin transparent layers the lower oxide is yellow, black in thicker ones, brittle and hard. It is stable towards cold water, but dissolves readily in hydrochloric acid with evolution of hydrogen. When heated in air it glows suddenly and passes into the yellow In_2O_3 ; it has $d\ 6.31 \pm 0.03$. In the preparation of In_2O a residue not readily volatile is left behind as a dirty white, bulky powder. Its composition agrees with the formula InO . Since, unlike In_2O_3 , it is not hygroscopic, and is also light-coloured, it cannot be a mixture of the other two oxides. The sulphide, In_2S_3 , is yellow or brown according to its method of preparation. At 850° it is markedly volatile and, in a closed tube, has m. p. $1050 \pm 3^\circ$. The fused product is black or, when finely powdered, red; $d\ 4.90 \pm 0.01$. The sulphide In_2S_3 is prepared similarly to the corresponding oxide, and is also similar in appearance and properties; it has m. p. $653 \pm 5^\circ$, $d\ 5.92 \pm 0.01$. By heating together atomic proportions of indium and sulphur at 650° a slate-grey powder of the approximate composition InS is obtained. At 850° , in a vacuum, it rapidly volatilises, giving In_2S and sulphur. Sintering points and m. p. of mixtures of indium and sulphur have been plotted against composition, and the form of the curve points to the existence of a compound InS and suggests also the possibility of the formation of a sulphide In_4S_5 . In_2O and In_2S are fairly strongly paramagnetic, InO and InS are less so, and In_2O_3 and In_2S_3 are indifferent. An X-ray examination of the different products has also been made, but the differences in the interference diagrams are not sufficient to settle the question of the individuality of InO and InS .

M. S. BURR.

Fractional separation of neodymium and samarium. L. ROLLA and L. FERNANDES (Atti R. Accad. Lincei, 1928, [vi], 7, 370–372).—The separation and purification of neodymium from samarium and *vice versa* can be readily carried out by fractional crystallisation of the double nitrates with magnesium and manganese, which have the composition $2\text{R}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ and $2\text{R}(\text{NO}_3)_3 \cdot 3\text{Mn}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, R representing an atom of the rare element.

O. J. WALKER.

Reduction of metallic sulphides by carbon. N. PARRAVANO and G. MALQUORI (Gazzetta, 1928, 58, 279–289; cf. this vol., 479, 480, 594, 844).—The reaction $2\text{MS} + \text{C} = 2\text{M} + \text{CS}_2$ is considered from the static point of view in comparison with the analogous reduction of metallic oxides by carbon. Since with the sulphides the reducing gas, carbon monoxide, is absent, it is necessary that the particles of carbon must be immersed in the mass to be reduced and that the sulphide must diffuse into this mass with a certain velocity in order that they may reach the carbon. These considerations explain the greater difficulty of reduction of metallic sulphides.

T. H. POPE.

Separation on iron of carbon from carbon monoxide and light petroleum. U. HOFMANN (Ber., 1928, 61, [B], 1180–1195).—Thermal decomposition of hydrocarbons does not permit the preparation of the “series of black, crystalline carbons” at temperatures below 700° (cf. Hofmann and Hofmann, B., 1927, 802; Koch-Holm, this vol., 464). This may be effected by passing carbon monoxide over reduced or powdered iron, electrolytic iron, or reduced cobalt; wrought iron and steel foil are ineffective. Below 400° , activity is too small, whilst above 700° the equilibrium $2\text{CO} = \text{C} + \text{CO}_2$ is so far displaced towards the left that little separation of carbon occurs. Between 700° and 900° , light petroleum is a suitable source of carbon. The reaction commences at some particular spot at which, probably, the iron is particularly finely divided. Thence the catalyst becomes continuously disaggregated, so that the rate of separation attains a maximum and then falls until the catalyst becomes exhausted. The carbon thus prepared contains about 4–5% of iron which can be removed completely only by repeated extraction with boiling, 10% nitric acid. The pure, black carbon is pronouncedly crystalline, the size of the crystallites increasing uniformly with the temperature of production independently of the source of the carbon. Chemical properties, density, and general behaviour show no sudden change when light petroleum is substituted for carbon monoxide. The individual crystallites are only loosely arranged, so that the carbon, prepared at low temperatures, is a loose, voluminous powder resembling soot. Above 700° , it becomes more compact and granular, whilst at 900° it is noticeably hard. Parallel with the temperature of preparation, the density of the compressed product increases from 2.00 to 2.17. Simultaneously the resistance to oxidising agents increases, although all specimens ultimately yield graphitic acid. Carbon, prepared at 400° and activated by carbon dioxide, has an adsorptive power of 8–10% measured towards 1% phenol; this decreases with rising temperature of preparation to 0.5% at 900° . The unusually large size of the crystallites and the observation that in the same porcelain tube lustre carbon can be prepared from light petroleum at 900° and a much more coarsely crystalline carbon product formed on iron indicate that the metal does not play merely the part of an accelerator. Röntgen examination of finely-divided iron which has been treated with carbon monoxide at 400° until deposition of carbon has just commenced establishes the presence

of cementite. In the intermediate and final preparations of unpurified carbon, lines are observed due to some unidentified product, termed provisionally "carbide X." These lines disappear when the carbon is purified with dilute nitric acid. The change probably consists in the initial production of cementite, $2\text{CO} + 3\text{Fe} = \text{Fe}_3\text{C} + \text{CO}_2$, which with more carbon monoxide affords carbide X; decomposition of the latter substance yields carbon. This change controls the rate of the total reaction. When, as with carbon monoxide at 400° or light petroleum at 700° , the carbide X is itself very stable, the rate of separation of the carbon is remarkably small. H. WREN.

Elucidation of [the nature of] silica hydrates by the ammonia extraction method. W. BILTZ and E. RAHLFS (Z. anorg. Chem., 1928, 172, 273—291).—By tensimetric methods (cf. A., 1927, 1157), the action of liquid ammonia on non-gelatinous silica hydrates, obtained by treating with acid, under varying conditions, solid crystalline synthetic alkali silicates, vitreous alkali silicates, and silicate minerals respectively, has been examined. In the case of the hydrated silica obtained from crystalline sodium metasilicate, the nature of the resulting products suggests that the ammonia first exerts a dehydrating action on the hydrate, removing two thirds of the water. Ammonia molecules are then added on to the silica molecule in stages, the resulting products being $6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ with 1, 2, 3, or 4 molecules of ammonia, and the smallest molecular entity of the original product appears to be $6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$. The latter is crystalline and gives a definite X-ray pattern. Dehydration under reduced water vapour pressure gives only the metasilica trihydrate, $6\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, which has the same composition as disilica hydrate, but, unlike it, loses a molecule of water on treatment with liquid ammonia. The metasilica hydrate from vitreous metasilicate differs from the one described, since, although it is dehydrated by liquid ammonia to the same extent, it does not take up ammonia in stages but continuously, and the smallest molecule has the composition $3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. It is an amorphous powder with no X-ray pattern. The disilica hydrate, from crystalline sodium disilicate, is not dehydrated by ammonia, but takes up in a continuous manner an amount of ammonia equivalent to the water present. It gives water up in stages when the pressure is isothermally reduced and is crystalline with a definite X-ray pattern. Its least molecule is $6\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. The product obtained from vitreous disilicate is similar, but gives up water continuously and not in stages, under suitable conditions. It is a powder with no X-ray pattern and its least molecule is $2\text{SiO}_2 \cdot \text{H}_2\text{O}$. The disilica hydrate from the mineral heulandite is identical with a loosely aggregated disilica hydrate from crystalline sodium disilicate. Silica gels prepared in various ways have also been examined. They may perhaps be definite hydrates, but it is doubtful. At low temperatures large adsorption of ammonia takes place. As the gel ages the adsorptive power diminishes. M. S. BURR.

Hydroxysiloxens. H. KAUTSKY and H. THIELE (Z. anorg. Chem., 1928, 173, 115—124).—Directions are given for the preparation of monohydroxysiloxen,

$\text{Si}_6\text{O}_3\text{H}_5 \cdot \text{OH}$, by the hydrolysis of monobromosiloxen with alcohol containing 20% of water. The hydrolysis is a reversible reaction. The higher hydroxysiloxens can be obtained similarly, except the penta-derivative, which does not appear to have been prepared. Monohydroxysiloxen is yellow; the dihydroxy-derivative, $\text{Si}_6\text{O}_3\text{H}_4(\text{OH})_2$, is brownish-red; the trihydroxy-derivative, $\text{Si}_6\text{O}_3\text{H}_3(\text{OH})_3$, is red; the tetrahydroxy-derivative, $\text{Si}_6\text{O}_3\text{H}_2(\text{OH})_4$, is brownish-violet; and the hexahydroxy-derivative, $\text{Si}_6\text{O}_3(\text{OH})_6$, is black. The hydroxysiloxens function as weak bases. They can also be obtained by the action of sulphur dioxide dissolved in acetone on siloxen. Hexahydroxysiloxen is extremely explosive in air; the tendency to explode increases in this series of compounds with increasing number of SiOH groups, and with increasing number of Si-Si linkings. A. J. MEE.

Preparation and properties of a boride of cerium. L. ANDRIEUX (Compt. rend., 1928, 186, 1736—1738; cf. this vol., 850).—Cerium boride (CeB_2) is best prepared by the electrolysis for 2 hrs. at 950 — 1000° by a current of 20 amp. of a molten bath having the composition $0.1\text{CeO}_2 + 2\text{B}_2\text{O}_3 + \text{Li}_2\text{O}(\text{Li}_2\text{CO}_3) + \text{LiF}$. Lower yields are obtained with the oxides and/or fluorides of other alkali or alkaline-earth metals, whilst borax alone gives compounds richer in boron. The boride forms aggregates of small, hard, violet-blue, cubic or prismatic crystals, $d^{15} 4.6$, and is attacked only by dilute or concentrated nitric acid, concentrated sulphuric acid, or by fused alkalis. It burns with difficulty in air, but reacts violently in the hot with lead or sodium peroxides and is similar in properties to the borides of the alkaline-earth metals. J. GRANT.

Electrical synthesis of hydrazine. G. BREDIG and A. KOENIG (Naturwiss., 1928, 16, 493).—By passing pure gaseous ammonia through a strongly cooled high-tension arc, and cooling the vapour at once with liquid air, hydrazine is formed in appreciable quantities, and has been detected by the formation of weighable quantities of benzylideneazine. The reaction mechanism is the union of NH_3 and $-\text{NH}$, rather than the union of two NH_2 groups, because the probability of collision between two NH_2 groups (with ammonia in great excess) can only be very small. In support of this view, Raschig's detection of hydrazine among the products obtained by burning oxygen in ammonia is cited. Further support is forthcoming from the catalytic synthesis of hydrogen cyanide from carbon monoxide and ammonia at 600 — 700° , which may occur as follows: $2\text{CO} \longrightarrow \text{C} + \text{CO}_2$; $\text{NH}_3 \longrightarrow \text{NH} + \text{H}_2$; $\text{C} + \text{NH} \longrightarrow \text{HCN}$. R. A. MORTON.

Nitrogen trifluoride. O. RUFF, J. FISCHER, and F. LUFT (Z. anorg. Chem., 1928, 172, 417—425).—Nitrogen trifluoride has been obtained by electrolysis of fused anhydrous ammonium hydrogen fluoride. It is a colourless gas at the ordinary temperature, and, according to analysis and density measurements, has a formula NF_3 . It is condensed by liquid air to a colourless mobile liquid which boils under atmospheric pressure at -119° and freezes below -210° . Vapour-pressure measurements have been made between

—125° and —194°, and the molecular heat of vaporisation is calculated to be 2400 g.-cal. Nitrogen trifluoride is insoluble in water and unattacked by water or hydrogen, but a reaction takes place if an electric spark is passed through a mixture of the gas with water vapour, and hydrogen fluoride and oxides of nitrogen are formed. With hydrogen under the same conditions the reaction is very violent, nitrogen and hydrogen fluoride being obtained. The gas is remarkably stable; it does not react with mercury, manganese dioxide, potassium hydroxide solution, or glass at the ordinary temperature. M. S. BURR.

Reduction of nitrites, nitrates, and nitric acid with magnesium amalgam: a new method of preparing hyponitrites. P. NEOGI and B. L. NANDI (J.C.S., 1928, 1449—1455; cf. A., 1899, ii, 656; 1900, ii, 16; 1903, ii, 426).—The reducing action of magnesium amalgam on metallic nitrates and nitrites affords a convenient method for the preparation of hyponitrites. The following *hyponitrites* have not hitherto been described: cadmium, zinc, lithium, rubidium, and caesium; magnesium hyponitrite was identified in solution only. The reduction of nitrates by this amalgam proceeds in stages to produce nitrites, hyponitrites, ammonia, and hydroxylamine, the last-named being often produced in considerable quantities. Sodium and potassium hyponitrites were prepared by reducing the corresponding nitrites, but all the others by reduction of nitrates. In general, magnesium amalgam was added slowly to a concentrated solution of the salt, at 5° or below. After a short time, magnesium hydroxide was removed, and the reduction similarly repeated until the solution was free of nitrate and nitrite. Concentration is carried out in a vacuum desiccator containing sulphuric acid, and the product generally extracted with alcohol. The zinc salt was obtained by reduction in acid solution. During the preparation of cadmium hyponitrite (d_4^{20} 2.121) the explosive *oxyhyponitrite*, $\text{Cd}(\text{OH})\text{NO}$, was formed. When heated in a vacuum, cadmium hyponitrite suddenly decomposes at 185° with formation of cadmium oxide and nitrous oxide. Oxyhyponitrite was also formed in the reduction of lead nitrate. The reduction of nitric acid in the presence of sulphuric acid resulted in a 60% yield of hydroxylamine sulphate of 97.8% purity. No hyponitrites were formed on reducing mercuric and mercurous nitrates and the nitrates of copper, cobalt, nickel, silver, and ammonium. R. A. PRATT.

Nitronium or nitracidium salts and the cationic migration of nitric acid. A. HANTZSCH and K. BERGER (Ber., 1928, 61, [B], 1328—1334; cf. A., 1925, ii, 634).—The formation of additive compounds from perchloric and nitric acids gives rise to compounds previously designated nitronium mono- and di-perchlorate in analogy with the hydroxonium perchlorate from perchloric acid and water. As the nomenclature is liable to lead to confusion with azylium and oxylium compounds, it is proposed to term cations formed by addition of hydrogen atoms to acids acidium cations, e.g., nitracidium, acetacidium, etc. Multivalent cations formed by further addition of hydrogen atoms are distinguished by the

addition of "hydro-". Thus, nitronium perchlorate and nitronium diperchlorate are to be termed nitracidium perchlorate and hydronitracidium perchlorate.

The structure $\left[\text{O}_2\text{N}-\text{O}-\overset{\text{H}}{\underset{|}{\text{N}}} \right]^+$ is assigned to the acidium ion, since it exhibits much more feeble absorption than the corresponding acid. Electrochemical evidence of the salt-like nature of nitracidium and hydronitracidium perchlorate is deduced from observations of their electrical conductivity in nitromethane, freed from water and hydrocyanic acid by distillation over mercury oxide and freshly sublimed phosphoric oxide. The limiting conductivity of the two salts is of the order of magnitude required for a binary and ternary electrolyte, respectively. Further analyses of the anodic and cathodic solutions after electrolysis of solutions of the salts establishes the cathodic wandering of the nitric acid. H. WREN.

Application of the spectrographic and spectrophotometric methods to the study of the hydrolysis of some alkaline salts. P. JOB (Compt. rend., 1928, 186, 1546—1548).—The author's spectrographic and spectrophotometric methods (A., 1926, 791) for the study of the formation of complexes may be applied to any reaction between substances in solution, so long as the absorption spectrum of the reaction products differs sufficiently from that of the reactants. The hydrolysis constants of phenol, *p*-chlorophenol, and the nitrophenols have been determined approximately, and the principal reaction between solutions of sodium chromate and sulphuric acid has been shown to be $\text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HCrO}_4^-$, which in strong solutions is probably followed by the reaction $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$. J. GRANT.

Migration of masked sulphate groups in chrome alum liquors. W. SCHINDLER and K. KLANFER.—See B., 1928, 533.

Chrome tanning. VI. Properties and behaviour of various pretreated chromium sulphate solutions. E. STIASNY and O. GRIMM.—See B., 1928, 494.

Chrome tanning. VII. Hydrolysis and tanning action of sulphatochromium sulphates. E. STIASNY and D. BALÁNYI.—See B., 1928, 495.

Selenium tetrafluoride. E. B. R. PRIDEAUX and C. B. COX (J.C.S., 1928, 1603—1607).—Lebeau's preparation of selenium tetrafluoride (A., 1907, ii, 540) may have contained the hexafluoride, oxyfluoride, and even the dioxide dissolved in hydrofluoric acid (cf. A., 1907, ii, 613, 679). The authors have prepared selenium tetrafluoride (yield 73.5%) by the action of selenium tetrachloride on silver fluoride, thus precluding the presence of water, hydrofluoric acid, or a higher fluoride. The compound has d_4^{20} 2.77, b. p. 93°, and m. p. —13.2°, and hence is clearly distinct from the oxyfluoride. The tetrafluoride reacted immediately with silicon in the cold to give silicon tetrafluoride and a red deposit of selenium. Sulphur did not react in the cold. Some tetrafluoride containing a little oxyfluoride reacted strongly with red phosphorus to give selenium dioxide, selenium, and apparently a mixture of phosphorus fluoride and oxyfluoride. A comparison of the

properties of the lower fluorides of selenium and of a solution of the dioxide in hydrofluoric acid showed that, although the tetrafluoride and the oxyfluoride are similar in their chemical reactions, they are not identical.

R. A. PRATT.

Double salts of selenic acid. J. MEYER and W. AULICH (Z. anorg. Chem., 1928, 172, 321—343).—The properties of the selenates of potassium, sodium, magnesium, and calcium, and the solubility isotherms at 25° of the double salt systems potassium-magnesium, sodium-magnesium, potassium-calcium, sodium-calcium, and potassium-sodium selenates have been investigated and compared with those of the corresponding sulphates. The simple selenates are very similar to the simple sulphates, except that potassium selenate is very much more soluble than potassium sulphate. No magnesium selenate dodecahydrate was obtained, but there is, apparently, a dihydrate. Unstable forms of both selenate and sulphate heptahydrates are obtained. Calcium selenate, in addition to the hemihydrate which behaves similarly to plaster of Paris, forms also a hydrate, $\text{CaSeO}_4 \cdot 1.5\text{H}_2\text{O}$. Sodium selenate resembles sodium sulphate very closely. The transition temperature of the decahydrate to the anhydrous form is 31.8°. The sodium selenate decahydrate effloresces similarly to Glauber's salt, and the solubility falls with rise of temperature after the transition point is reached. The potassium selenate-magnesium selenate solubility isotherm at 25° indicates the existence of selenate-schönite, $\text{K}_2\text{SeO}_4 \cdot \text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$, and there is transition to the tetrahydrate, selenate-leonite, at 33.1°. At 25° sodium and magnesium selenates do not form a double salt, but at 28.1° a mixture of equimolecular proportions of the two salts gives selenate-astrakhanite, $\text{Na}_2\text{SeO}_4 \cdot \text{MgSeO}_4 \cdot 4\text{H}_2\text{O}$. Potassium and calcium selenate form a compound, $\text{K}_2\text{SeO}_4 \cdot \text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$, whereas the double sulphate is a monohydrate. The sodium calcium double selenate contains 2 molecules of water, but by drying at 100° the anhydrous selenate-glauberite is obtained. No double salt of sodium and potassium selenate has been obtained. The sulphates, however, form glaserite, $2\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$.

M. S. BURR.

Different states of iron in relation to its chemical behaviour. O. BAUDISCH (Naturwiss., 1928, 16, 542—545).—Earlier work is summarised. Ferrous hydroxide, precipitated by hydrolysis or by the action of hydroxyl ions from a solution of ferrous hydrogen carbonate reacts in the nascent state with molecular oxygen to form a compound exhibiting a very high oxidation and reduction potential. The reduction has been studied in detail for the system potassium nitrate-potassium nitrite.

R. A. MORTON.

Existence of ferrous chloride hexahydrate. G. AGDE and F. SCHIMMEL (Z. anorg. Chem., 1928, 173, 111—114).—A neutral solution of ferrous chloride saturated at 10° was cooled to -15°, when the hexahydrate $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ separated. The transition temperature between the hexahydrate and the tetrahydrate is 12.3°. Lesceur's observation that when hydrogen chloride is passed into ferrous chloride solution only the tetrahydrate crystallises is not confirmed.

A. J. MEE.

Ferric nickel acetate and similar compounds ; a lower basic ferric acetate. R. WEINLAND and H. HOLTMEIER (Z. anorg. Chem., 1928, 173, 49—62).—Salts of the type $\text{Fe}_3\text{Ni}(\text{OAc})_8(\text{OH})_3 \cdot 6\text{H}_2\text{O}$ have been prepared in which the nickel is replaced by cobalt, manganese, zinc, cadmium, and magnesium. They may be obtained by mixing solutions of ferric chloride or nitrate, a salt of the metal to be introduced, and sodium acetate in the right proportions. Directions are given for the preparation of the following acetates : $\text{Fe}_3\text{Ni}(\text{OAc})_8(\text{OH})_3 \cdot 6\text{H}_2\text{O}$; $\text{Fe}_3\text{Co}(\text{OAc})_8(\text{OH})_3 \cdot 8\text{H}_2\text{O}$; $\text{Fe}_3\text{Mn}(\text{OAc})_8(\text{OH})_3 \cdot 5\text{H}_2\text{O}$; $\text{Fe}_3\text{Zn}(\text{OAc})_8(\text{OH})_3 \cdot 5\text{H}_2\text{O}$; $\text{Fe}_3\text{Cd}(\text{OAc})_8(\text{OH})_3 \cdot 7\text{H}_2\text{O}$; $\text{Fe}_3\text{Mg}(\text{OAc})_8(\text{OH})_3 \cdot 10\text{H}_2\text{O}$; $\text{Fe}_3\text{Ni}_4(\text{OAc})_{26}(\text{OH})_9 \cdot 23\text{H}_2\text{O}$; $\text{Fe}_3\text{Co}_4(\text{OAc})_{26}(\text{OH})_9 \cdot 23\text{H}_2\text{O}$;

$\text{Fe}_3\text{Zn}_4(\text{OAc})_{26}(\text{OH})_9 \cdot 18\text{H}_2\text{O}$. Salts of the second type will combine with pyridine, and isomorphous compounds of the formulae $\text{Fe}_6\text{Ni}_3\text{O}_3(\text{OAc})_{17}(\text{OH})_{12}\text{C}_5\text{H}_5\text{N}$ and $\text{Fe}_6\text{Co}_3\text{O}_3(\text{OAc})_{17}(\text{OH})_{12}\text{C}_5\text{H}_5\text{N}$ are described. The benzoates $\text{Fe}_6\text{Mg}_3(\text{OBz})_{18}(\text{OH})_6 \cdot 12\text{C}_5\text{H}_5\text{N}$ and $\text{Fe}_6\text{Ni}_3(\text{OBz})_{18}(\text{OH})_6 \cdot 12\text{C}_5\text{H}_5\text{N}$ are also described. If sodium perchlorate solution is added to a solution of the salt $\text{Fe}_3\text{Mg}(\text{OAc})_8(\text{OH})_3 \cdot 10\text{H}_2\text{O}$ a yellowish-brown basic ferric acetate, $\text{Fe}_3\text{O}(\text{OAc})_4(\text{OH})_3 \cdot 7\text{H}_2\text{O}$, is obtained.

A. J. MEE.

[Hydrate of cobaltic fluoride.] E. BIRK (Z. anorg. Chem., 1928, 171, 372).—A reply to Barbieri and Calzolari (this vol., 495).

R. CUTHILL.

Cyanogen compounds of the platinum metals.

II. Cyanogen compounds of ruthenium. F. KRAUSS and G. SCHRADER (Z. anorg. Chem., 1928, 173, 63—72).—The blue cyanide of ruthenium of which the constitution was previously supposed to be $\text{Ru}(\text{CN})_2$ or $\text{Ru}(\text{CN})_3$ is shown to be a complex compound of the formula $\text{Ru}_2(\text{CN})_5 \cdot \text{H}_2\text{O}$. Directions are given for the preparation of this compound from $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. It is practically insoluble in the usual solvents. With concentrated ammonia solution, however, it gives a complex salt of the formula $\text{NH}_4[\text{Ru}_2(\text{CN})_5 \cdot 4\text{NH}_3]$, which dissolves in water with a yellowish-brown colour. By the addition of solutions of salts of heavy metals to a solution of this ammonium compound, precipitates are obtained with characteristic colours. In this way the nickel and copper compounds, $\text{Ni}[\text{Ru}_2(\text{CN})_5 \cdot 4\text{NH}_3] \cdot 7\text{H}_2\text{O}$ and $\text{Cu}[\text{Ru}_2(\text{CN})_5 \cdot 4\text{NH}_3] \cdot 5\text{H}_2\text{O}$, respectively, were prepared. The cyanide $\text{Ru}(\text{CN})_3 \cdot 5\text{H}_2\text{O}$ can be obtained from $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ by the action of chlorine, and then sulphuric acid. This also gives a complex compound, $\text{Ru}(\text{CN})_3 \cdot \text{H}_2\text{O} \cdot 2\text{NH}_3$, with ammonia. Both these compounds, in which the ruthenium is tervalent, are probably non-electrolytes, the co-ordination numbers being 4 and 6. Their constitutions are discussed.

A. J. MEE.

Recovery of pure platinum. E. H. REERINK (Z. anorg. Chem., 1928, 173, 45—48).—The fact that when a current of carbon monoxide is passed over heated platinum chloride a volatile platinum carbonyl chloride is formed is employed in the separation of platinum from other metals of the same series which do not form such compounds under the same conditions. The platinum carbonyl chloride decomposes at about 300° with the formation of platinum, carbon

monoxide, chlorine, and carbonyl chloride. In order to obtain the platinum in the compact form, a platinum wire is heated at about 600° in the vapour of the compound, when the platinum formed grows round the wire. A. J. MEE.

Use of filters of known weight in quantitative analysis. B. ORMONT (Ukraine Chem. J., 1928, 3 [Sci.], 47—58).—If 9 cm. filter papers weighing from 0.4 to 0.6 g. are dried to constant weight, the mean error in the latter amounts to 1.2 mg. Such dry filters are exceedingly hygroscopic, so that if, after drying to constant weight at 100—105°, they are left at 75°, they absorb 3.7 mg. of moisture within 90 min., and 0.4 mg. at 95°. If the moisture content be made constant by drying in a desiccator, calcium chloride cannot be used, as it acts too slowly. Phosphorus pentoxide is better, but it also does not give constant weight within 48 hrs., although less moisture remains than after drying at 75° for 1 hr. or at 105° for 30 min. Leaving in the desiccator for a further 48 hrs. leads to a loss of 0.3—0.7% more than after the first 48-hr. period, a mean absolute error of 0.23% as compared with 0.12% for the method of drying to constant weight. Under experimental conditions, however, and in the presence of precipitates the former method is preferable. R. TRUSZKOWSKI.

Use in analysis of the mercury dropping cathode. E. BAYLE and L. AMY (Compt. rend., 1928, 186, 1610—1612).—Heyrovsky's mercury dropping cathode (A., 1927, 1159) has been improved for the purposes of analysis by the use of a fine capillary tube allowing the flow of 4—5 c.c. of mercury/min., the oscillations and other fluctuations in current being thereby eliminated. The end of the tube is kept at a constant distance from the mercury level. Since the current intensity is independent of the concentration of one of a mixture of two salts, so long as the *P.D.* is less than a critical value (beyond which the intensity is a linear function of concentration so long as the latter is small), it is possible to determine each salt in succession, using suitable *P.D.* An accuracy of 1% was obtained for mixed solutions of bismuth and cadmium sulphates using 0.25 mg. of salt. J. GRANT.

Following the course of the reaction in potentiometric titrations. F. L. HAHN, M. FROMMER, and R. SCHULZE (Z. physikal. Chem., 1928, 133, 390—396).—It may be shown mathematically that in a potentiometric titration the turning point on the titration curve occurs before or after the true end-point according as the number of molecules, *U*, of the substance being titrated which react with one molecule of the reagent is greater or less, respectively, than 1. This error may be quite appreciable even when *U* diverges only moderately from 1. By the method previously described (A., 1927, 743), however, it is possible to calculate from the potentials at various stages of the titration both the true end-point and the value of *U*. R. CUTHELL.

Apparatus for measuring hydrogen-ion concentrations. P. HANSEN.—See B., 1928, 505.

Colorimetric determinations. II. Hydrogen-ion concentration and p_H . A. L. CALDWELL (J. Amer. Pharm. Assoc., 1928, 17, 529—534).

Determination of hydrogen-ion concentrations in phosphate and borate mixtures by means of the quinhydrone electrodes. E. BILLMANN, A. KLIT, and T. SWAETICHIN (Biochem. J., 1928, 22, 845—854).—The simple quinhydrone, the quinoquinhydrone, and the hydroquinhydrone electrodes have been examined and compared with hydrogen electrodes by determining the potentials for phosphate mixtures of p_H 5.90—8.04 and for borate mixtures of p_H 7.34—8.05. The simple quinhydrone electrode gave correct p_H values in phosphate mixtures up to 7.73 and still very good values at p_H 8.04; in borate mixtures it gave correct values. The quinoquinhydrone electrode gave correct values in phosphate mixtures up to p_H 7.38. In more alkaline phosphate mixtures and in the borate mixtures the potentials were very drifting. The hydroquinhydrone electrode gave very stable potentials in the phosphate mixtures but too low p_H values, because of the acid influence of the hydroquinhydrone. Owing to the acid influence of quinol, corrections must be introduced in the measurements of Billmann and Katagiri (A., 1927, 516) with hydroquinhydrone electrodes in phosphate and hydrogen carbonate solutions. The acid influence of quinol may affect the measurements of Grossman (A., 1927, 488) in phosphate and borate in such a manner that the correction formula introduced may hold only for special cases. S. S. ZILVA.

Behaviour of indicators in certain titrations. R. T. THOMSON (Analyst, 1928, 53, 315—321).—In the titration of ammonia, methyl-orange is the only satisfactory all-round indicator, particularly for determining the acidity or alkalinity of ammonium salts. For sodium and calcium phosphates the alkalinity of the pyrophosphate corresponds with that of the dibasic phosphate with bromophenol-blue, methyl-orange, methyl-red, or bromothymol-blue, but a large increase was shown with the other indicators, and in using phenolphthalein, for example, hydrolysis by boiling must be carried out before titrating. Calcium phosphate cannot be accurately determined by titration methods, since basic phosphate is produced both when sodium hydroxide is used with excess of calcium chloride, and when no excess of calcium is present. Methyl-orange is the best indicator for methylamines in the presence of carbonic acid, since the general behaviour of indicators is the same as with ammonia. Congo-red was used as a satisfactory indicator for alkalinity in pyridine. Other indicators did not give very good end-points; thymol-violet gave an acid result (0.24% sulphuric acid). Sofnol No. 1 is seriously affected by carbonic acid, and where larger quantities of boric acid than 0.2 g. are being titrated methyl-orange is preferable. D. G. HEWER.

Use of the centrifuge in quantitative analysis. [Determination of sulphur.] A. GUNDER (Z. anal. Chem., 1928, 73, 441—444).—The precipitation with barium chloride is carried out in a weighed silica tube and the precipitate separated from the solution by centrifuging and decanting. Washing is effected also by centrifuging. The tube with the precipitate adhering tightly to its walls is dried in a steam oven, heated to redness, and weighed. Separation of the mother-liquor and washings from the precipitate after

treatment for 5 min. in the centrifuge is readily effected without loss by the use of a small siphon. A similar procedure is useful for collecting silver chloride, calcium oxalate, ammonium phosphomolybdate, etc. Platinum tubes must be used if calcium oxalate is to be converted into oxide for weighing. A. R. POWELL.

Determination of sulphur dioxide in small amounts in the atmosphere. R. J. MCKAY and D. E. ACKERMAN.—See B., 1928, 482.

Volumetric determination of sulphate in potable water. F. G. GERMUTH.—See B., 1928, 504.

Determination of ammonia. K. TAUFEL and C. WAGNER.—See B., 1928, 522.

Analysis of a mixture of water, nitric acid, and sulphuric acid by thermometric titration. T. SOMIYA (Chem. News, 1928, 137, 14).—Addition of fuming sulphuric acid to a mixture of water, nitric acid, and sulphuric acid results in a well-defined temperature maximum when the water is converted into sulphuric acid and the nitric acid into $\text{OH}\cdot\text{SO}_2\cdot\text{ONO}_2$. Further addition of the fuming acid gives a less well-marked temperature maximum when the nitric acid is converted into $(\text{SO}_3)_4\text{N}_2\text{O}_5$. A. R. POWELL.

Analysis of [natural] phosphates [according to the official French method.] A. SANFOURCHE and F. BLÉ (Bull. Soc. chim., 1928, [iv], 43, 680—683).—Sources of error inherent in the official method are pointed out. Individually these errors are small, but their cumulative effect may lead to final errors of the order of 1%. Since decomposition of the phosphate with hydrochloric acid is not followed by evaporation to dryness to fix silica, the resulting solution is apt to contain appreciable amounts of silicic acid, part of which is usually contained in the precipitate of magnesium ammonium phosphate. This and other errors leading to high results may be avoided when ammonium citrate is present in amounts greater than those indicated by the official method. When precipitation and washing are carried out at 35° the amount of pyrophosphate finally weighed is appreciably less than when these are effected at 18—20°. The ignited pyrophosphate is often grey, due to the presence of carbon, but no appreciable error is thereby introduced. The practice of treating grey pyrophosphate with nitric acid to remove carbon is condemned. There appears to be a lack of uniformity regarding the conversion factor to be applied. J. S. CARTER.

Determination of small amounts of arsenic. H. KLEINMANN (Deut. Z. ges. gerichtl. Med., 1927, 11, 61—71; Chem. Zentr., 1928, i, 945).—The arsenic is converted, after separation as trichloride, into a nearly neutral solution of the pentoxide, and the precipitate formed on addition of a reagent containing cocaine and molybdic acid is determined nephelometrically. A. A. ELDRIDGE.

Rapid method for determination of carbon in iron and steel. N. M. MILOSLAVSKY and V. F. VEPRTZKA (Ukraine Chem. J., 1928, 3 [Tech.], 31—35).—A description of de Nolly's method for the determination of carbon in iron and steel (Bull. Soc. Ind. Min., 1910, 13, 4). R. TRUSZKOWSKI.

Volumetric determination of carbon and carbon dioxide in rock products by electrical incandescence. W. J. PRITT (Chem. Eng. Min. Rev., 1928, 20, 167—170).—The substance, together with an oxidiser if necessary, is placed in a transparent quartz tube the rubber stopper of which carries (a) a nickel tube reaching nearly to the bottom and carrying a resistance wire, (b) a tube for the ingress of oxygen or air, (c) a gas-exit tube. The substance is mixed with a catalyst and heated at 950°; the carbon dioxide is absorbed preferably in barium hydroxide, and determined volumetrically, water also being absorbed in the usual way. The method is applicable to the determination of carbon and hydrogen in organic material. CHEMICAL ABSTRACTS.

Complete gas analysis by the simultaneous oxidation of methane, carbon monoxide, and hydrogen. H. VON JÜPTNER (Instruments, 1928, 1, 55—57).—Of the residual gas after determination of the carbon dioxide, heavy hydrocarbons, and oxygen, 15 c.c. are exploded with 75 c.c. of air, and the carbon dioxide and excess of oxygen determined. The calculation is discussed. CHEMICAL ABSTRACTS.

Determination of hydrocyanic acid in gaseous mixtures. G. E. SEIL, J. S. SKELLY, and H. A. HELIGMAN (Gas Age Rec., 1927, 60, 179—180, 223—224, 259—260).—The most satisfactory method consists in removal of ammonia with 10% sulphuric acid, conversion of hydrogen cyanide into ammonium hydrogen sulphate by concentrated sulphuric acid, and determination of the nitrogen by Kjeldahl's method. CHEMICAL ABSTRACTS.

Helium. I. Detection of very small quantities of helium [and neon]. F. PANETH and K. PETERS (Z. physikal. Chem., 1928, 134, 353—373).—By a systematic investigation of the sources of error the apparatus for the spectroscopic detection of helium and neon has been improved so that 10^{-10} c.c. of either of these gases can be detected with certainty. A table is given showing the single spectral lines which are observed using quantities of helium and neon from 10^{-5} to 10^{-10} c.c. The smallest quantity of air which can be detected by this means from the appearance of the neon lines is 10^{-5} c.c. With this method it is possible to detect spectroscopically the formation of helium from the invisible active deposit of thorium. O. J. WALKER.

Zirconium sulphate as a reagent for the detection of potassium. R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1928, 50, 1515—1522).—To the solution at 0° an equal volume of concentrated (20.96%) zirconium sulphate solution is added. Solutions containing in the absence of sodium 0.53 mg. of potassium, and in the presence of sodium 1.76 mg. of potassium, yield a white precipitate. In more concentrated solutions large amounts of sodium sulphate retard the reaction. The test is as delicate as the sodium cobaltinitrite test only when the solution is kept for 1—2 hrs. At certain dilutions comparison blank tests are necessary. Zirconium sulphate solutions of half the above strength are equally sensitive in the absence of sodium, and in the presence of the latter will detect 0.7 mg. of potassium. S. K. TWEEDY.

Volumetric determination of potassium. O. PFUNDT (*Z. anal. Chem.*, 1928, 73, 439—440).—To obtain accurate results by titration with sodium perchlorate (Jander and Pfundt, A., 1927, 1046) a motor-driven glass propeller should be used to keep the solution stirred thoroughly during the addition of the reagent. A convenient form of apparatus is illustrated.

A. R. POWELL.

Determination of potassium as chloroplatinate. M. McCURDY (*Proc. Nova Scotian Inst. Sci.*, 1927, 16, 142—143).—The precipitate of potassium chloroplatinate can be ignited to platinum over a Fischer-Meker burner instead of being dried at 100°, without any loss of accuracy.

S. J. GREGG.

Determination of potassium ferrocyanide. P. P. BUDNIKOV.—See B., 1928, 522.

Specific reagent for the rapid gravimetric determination of sodium. H. H. BARBER and I. M. KOLTHOFF (*J. Amer. Chem. Soc.*, 1928, 50, 1625—1631).—Experiments are described demonstrating the use of uranyl zinc acetate reagent (Kolthoff, A., 1927, 436) for the gravimetric determination of sodium in the form of the compound $(\text{UO}_2)_2\text{ZnNa}(\text{OAc})_9 \cdot 6\text{H}_2\text{O}$ (not $9\text{H}_2\text{O}$). Less than 50 mg. of potassium chloride in the solution causes only a small error; lithium and strontium must be absent. Barium, calcium, magnesium, and zinc do not interfere. Phosphoric acid, and large amounts of oxalic and tartaric acids, must be absent.

S. K. TWEEDY.

Decomposition of silicates by strontium salts in metals. J. KAVINA (*Chem. Listy*, 1928, 22, 267—270).—Strontium chloride or a mixture thereof with ammonium chloride is used for fusion with silicates in the determination of alkali metals in the latter. This fusion mixture corrodes platinum vessels; nickel crucibles cannot be used. Precipitation of strontium as carbonate from aqueous extracts of the fused mass is not as complete in the presence of alkali chlorides as in their absence, 0.1 mg. of strontium being, however, readily precipitable from 3 c.c. of a solution containing 0.2 g. of alkali chlorides. Strontium chloride used alone does not yield satisfactory results.

R. TRUSZKOWSKI.

Qualitative analysis of the group magnesium, sodium, potassium. H. S. KING (*Proc. Nova Scotian Inst. Sci.*, 1927, 16, 30—34).—The filtrate from the alkaline-earth group is evaporated until crystals appear, and 4*N*-phosphoric acid and excess of ammonia solution are added; the precipitate is extracted with dilute sulphuric acid and alcohol and the magnesium again precipitated as magnesium ammonium phosphate. The filtrate is evaporated to dryness, ignited, dissolved in water, and the last traces of ammonium salts are eliminated (as nitrogen) by passing in a mixture of nitric oxide and nitrogen peroxide (from the interaction of starch and nitric acid). After boiling, portions of the solution are tested for potassium and sodium with sodium cobaltinitrite and potassium antimonate, respectively.

S. J. GREGG.

Potentiometric determination of silver as ferrocyanide. W. SPEYER (*Z. anal. Chem.*, 1928,

74, 108—113).—The potentiometric titration of silver with potassium ferrocyanide gives results which are more than 1% too low, but reasonably accurate results are obtained with lithium or sodium ferrocyanide, although the potential limits between which the steepest fall in the curve occurs vary in different tests.

A. R. POWELL.

Rapid method for the determination of calcium and magnesium present together. N. M. MILOSLAVSKY and E. A. VILENKO (*Ukraine Chem. J.*, 1928, 3 [Tech.], 37—41).—Willstätter and Waldschmidt's-Leitz's method (A., 1923, ii, 258) for the determination of calcium and magnesium present together is verified and certain slight improvements are suggested.

R. TRUSZKOWSKI.

Qualitative separation of the metals of the alkaline-earth group. C. B. NICKERSON (*Proc. Nova Scotian Inst. Sci.*, 1927, 16, 25—29).—The filtrate after separation of barium as chromate from the solution of acetates is treated with acetic acid, ammonium sulphate, and a large excess of ammonia solution, whereby the strontium (*e.g.*, 3 mg.) is precipitated as sulphate. The calcium (*e.g.*, 400 mg.) is precipitated from the filtrate as oxalate.

S. J. GREGG.

Modification of the Schneider-Finkener method for the determination of zinc. I. MAJDEL (*Arhiv Hemiju Farm.*, 1928, 2, 127—136).—The solution, which should contain a moderate amount of ammonium sulphate and be distinctly acid, is neutralised with ammonia, using Congo-red paper as indicator. After addition of 4 c.c. of *N*-sulphuric acid the solution is diluted to 300 c.c. and treated for $\frac{1}{2}$ hr. at 70° with hydrogen sulphide. After 1 hr. the solution is filtered. The washed precipitate is heated with sulphur in a Rose crucible in a current of hydrogen. The method is applicable to quantities of zinc not exceeding 0.2—0.3 g. The presence of chlorides in the solution is not desirable.

J. S. CARTER.

Quantitative spectral analysis of lead in gold, and a new method of analysis by emission spectra. IV. W. GERLACH and E. SCHWEITZER (*Z. anorg. Chem.*, 1928, 173, 92—103).—A method is described by which as little as 0.001% of lead can be detected and determined in a mixture of lead and gold. Various errors are described. It is necessary to spark between new electrodes for 1—2 min. before taking a photograph. For the analysis the 3684 and 2614 lines of lead can be used, the intensities of the lines being compared with those given by standard mixtures. In a preferable method the spectrogram of the gold containing lead is photographed a number of times in succession with equal exposures, and then a secondary spectrogram of cadmium with 10% of tin is photographed, with exposures increasing in geometrical progression. The secondary spectrogram is photographed superposed on that of the gold-lead mixture. The tin lines are relatively near those of gold. The photograph in which the 3684 lead line is equivalent in intensity to the 3656 tin line is found, and then by comparison of lines of gold and tin in this photograph the lead content can be calculated from a table. The effect of heating the electrodes on the intensity of the

lines when only a small percentage of lead is present is investigated by finding how the intensity varied with the time of passing the spark. A. J. MEE.

Spectroscopic method of finding the position of an impurity in a metal. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1928, 173, 104—110).—The spectro-analytical method described in the preceding abstract can be used to discover the location of an impurity in a metal, and consequently whether it is distributed uniformly or not. The method applied to a lead-gold mixture shows that for concentrations of lead between 0.04% and 1% the impurity lies on the boundary of the gold crystal.

A. J. MEE.

Microtitration of lead cations and of chromic anions by centrifugo-volumetry. R. F. LE GUYON and R. F. AURIOL (Compt. rend., 1928, 186, 1551—1553).—The author's centrifugo-volumetric method (A., 1926, 927) has been applied to the determination of lead or chromium by precipitation of solutions of lead nitrate by solutions of potassium chromate, the end-point being denoted by the appearance of a yellow colour and the failure to produce a precipitate when the latter is added drop by drop to the former and centrifuged. A slight error is introduced for solutions which are not exactly equivalent, but otherwise quantitative results are obtained in neutral or acetic acid solutions and in the absence of other ions which might be precipitated with the lead.

J. GRANT.

Potentiometric determination of copper as cupric ferrocyanide. S. TAKEGAMI (Z. anal. Chem., 1928, 74, 39—41; cf. this vol., 499).—Following the unsatisfactory results obtained by the potentiometric titration of copper with potassium and lithium ferrocyanides, the corresponding salts of sodium and magnesium were examined. On plotting *P.D.* against concentrations, neither the sodium nor the magnesium salt gave a sharply marked turning point corresponding with any known stoichiometric proportion. Results with the magnesium salt in alcohol gave characteristic maxima corresponding fairly well with the equivalent-line for cupric ferrocyanide, but the method was not sufficiently accurate or convenient to be of practical importance. Small hope was seen of extension of the method in any simple way by use of other ferrocyanides.

R. A. PRATT.

Electrolytic apparatus for determination of copper in insecticides and fungicides. E. B. HOLLAND and G. M. GILLIGAN.—See B., 1928, 498.

Determination of mercuric cyanide and oxycyanide. E. RUPP and F. LEWY (Apoth.-Ztg., 1928, 43, 228).—A modification of the official German procedure for determining mercuric cyanide in oxycyanide tablets.

CHEMICAL ABSTRACTS.

Determination of traces of mercury. III. Determination of mercury in urine and faeces and the influence of medication. N. E. SCHREIBER, T. SOLLMANN, and H. S. BOOTH (J. Amer. Chem. Soc., 1928, 50, 1620—1625).—The method previously described (A., 1926, 929) may be used to determine mercury in urine; the result is usually about 0.01 mg. too low. Prolonged keeping of the urine at 0° without

freezing does not affect the method, and the following may be present: bismuth, chloral hydrate, salvarsan, "barbital," and small amounts of bromides and hexamethylenetetramine. Sodium salicylate, "cinchophen," and large amounts of hexamethylenetetramine should be absent. Bromides in large quantities and iodides must be removed by addition of sodium nitrite after oxidation. The organic matter in faeces must be destroyed by oxidation with potassium permanganate and concentrated nitric acid.

S. K. TWEEDY.

Ceric sulphate in volumetric analysis. IV. Potentiometric titration of vanadyl ion alone or in presence of ferric and chromic ions. Stability of vanadyl solutions. N. H. FURMAN (J. Amer. Chem. Soc., 1928, 50, 1675—1680; cf. this vol., 499).—Vanadyl salt solutions at 50—60° may be titrated potentiometrically with ceric sulphate, even in the presence of large quantities of ferric and chromic salts. When ferrous iron is present, the first end-point obtained on titrating in the cold corresponds with the quantitative oxidation of the iron, and the second end-point, in the hot, to that of the vanadium. Dilute vanadyl salt solutions containing free acid are quite stable for 1 year.

S. K. TWEEDY.

Cerium salts as oxidising agents in electro-metric titrations. II. J. A. ATANASIU and V. STEFAYESCU (Ber., 1928, 61, [B], 1343—1347).—An acid 0.1M-solution of ceric sulphate, obtained by electrolytic oxidation of the mixture of cerium sulphates derived by dissolution of cerium oxide in concentrated sulphuric acid, is used. Such a solution can be preserved unchanged for months if reducing agents are excluded. It is a very energetic and useful reagent for oxidative reactions when potentiometric methods are employed. In 0.1M- to 0.01M-solution ceric sulphate is remarkably insensitive to external physical influences and chemical reagents which frequently induce errors in titrations with permanganate. Experiments with nitrites, oxalic acid, ferrocyanides, hydrogen peroxide, ferrous iron, arsenic, tin, and titanium are described.

H. WREN.

Silicate analysis. J. ROBITSCHKE (Chem. Obzor, 1927, 2, 325—326; Chem. Zentr., 1928, i, 1074).—8-Hydroxyquinoline is used for the precipitation of aluminium and magnesium. The precipitate, $M(C_9H_6ON)_3$, may be weighed or titrated with bromine in hot hydrochloric acid: $C_9H_7ON + Br_2 = C_9H_5ONBr_2 + 2HBr$.

A. A. ELDRIDGE.

Use of mercury ammonium salts in quantitative analysis. I. Quantitative separation of aluminium and nickel. B. ŠOLAJA (Arhiv Hemiju Farm., 1928, 2, 136—142).—Aluminium is precipitated quantitatively from solutions of its salts by addition of "fusible white precipitate," $HgCl_2(NH_3)_2$. The precipitate is ignited to alumina. In presence of sulphates aluminium and nickel may be separated by the use of this reagent.

J. S. CARTER.

Quantitative separations and determinations by volatilisation with hydrogen chloride. VI. Determination of oxide in aluminium alloys. G. JANDER and W. BRÖSSE (Z. angew. Chem., 1928, 41, 702—704).—The method recently described (B.,

1927, 527) for the separation of aluminium, silicon, and magnesium etc. in aluminium alloys can be used for the accurate determination of the aluminium oxide present in such alloys, if not less than 0.02% is present. Under the prescribed conditions of drying, moisture is sufficiently eliminated from the gaseous hydrogen chloride, and further drying by cooling to -78° to -80° with ether and solid carbon dioxide is unnecessary. An internal reaction temperature of about 275° is used instead of $200-220^{\circ}$ as originally recommended. R. BRIGHTMAN.

Potentiometric determination of gallium. H. D. KIRSCHMAN and J. B. RAMSEY (*J. Amer. Chem. Soc.*, 1928, **50**, 1632—1636).—The potentiometric ferrocyanide titration in presence of ferri-cyanide previously described is applicable to slightly acid gallium chloride solutions (cf. Bray and Kirschman, this vol., 38). The precipitate has the composition $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$. The accuracy is about 0.3%.

S. K. TWEEDY.

Determination of ferrous iron in silicate rocks. I. B. A. SOULE (*J. Amer. Chem. Soc.*, 1928, **50**, 1691—1694).—Improvements in Cooke's method are described. The sample may be dissolved in boiling hydrofluoric and sulphuric acids in a Pyrex flask, and the solution titrated with permanganate (observing the usual precautions) without transference to a second vessel. The method of determining the factor necessary to correct for the reduction caused by material dissolved from the glass is given.

S. K. TWEEDY.

Volumetric determination of ferrous ion by means of potassium iodate. G. B. HEISIG (*J. Amer. Chem. Soc.*, 1928, **50**, 1687—1691).—To the ferrous salt solution 6 c.c. of iodine chloride solution (Jamieson, "Volumetric Iodate Methods," 1926, 8), 6 c.c. of carbon tetrachloride, and excess of hydrochloric acid are added in turn. After cooling, the mixture, which must contain 50 vol.-% of hydrochloric acid, is titrated with standard potassium iodate solution until the carbon tetrachloride layer is decolorised. If the end-point is exceeded, the excess of potassium iodate may be determined by a potassium iodide solution which has been standardised against potassium iodate; in fact, this back-titration method may be used to carry out the determination. The determination is unaffected by acetic, succinic, and tartaric acids, ethyl alcohol, formaldehyde, and filter paper.

S. K. TWEEDY.

Gravimetric determination of molybdenum. E. WENDEHORST (*Z. anal. Chem.*, 1928, **73**, 452—457).—In neutral or slightly alkaline solutions the mercurous molybdate method gives slightly high results due to adsorption of alkali salt. In acid solutions the results are more nearly correct by compensation of errors. The barium molybdate method gives low results owing to the solubility of the salt (1 : 14,000 of water). Precipitation of molybdenum as trisulphide and conversion into disulphide for weighing gives poor results, but conversion into trioxide yields excellent results. A. R. POWELL.

Potentiometric analysis of binary, ternary, and quaternary tin alloys. H. BRINTZINGER and F. RODIS.—See B., 1928, 488.

Use of liquid amalgams in volumetric analysis. X. Determination of vanadium, chromium, and nitro-compounds. K. SOMEYA (*Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 131—139).—See this vol., 387.

Potentiometric analysis of the hardening elements in special steels. II. Determination of chromium and vanadium in iron alloys and superior steels. E. ZINTL and P. ZAIMIS.—See B., 1928, 525.

Determinative mineralogy. IV. P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (*Amer. J. Sci.*, 1928, [v], **15**, 455—460).—Micro-methods for the determination in minerals of gold and sulphur respectively are described. The method for gold is based on the formation of pleochroic crystals of gold pyridine bromide. The test is specific for this element (limit, 0.02 μg .), some forty elements as ions being examined for interference. Special instructions are given for minerals containing cadmium, zinc, and lead.

Two tests are described for sulphur. The first depends on the colour change of an alkaline solution of bromocresol-green by the action of sulphurous acid formed during the heating of the metallic mineral in a specially designed tube. The second test, applied to non-metallic or to metallic minerals, depends on the decolorisation of a starch-iodine solution by the sulphur dioxide evolved on heating the mineral. The test is specific for sulphur. The limit in each case is 0.2 μg .

R. A. PRATT.

Separation of the platinum metals. ANON. (*Chem. Eng. Min. Rev.*, 1928, **20**, 142—143, 170—171).—Concentrated hydrochloric acid (7—8 c.c.) is added to the chloride solution (100 c.c., 0.3 g. of each metal, but less of osmium) and the palladium precipitated with 1% alcoholic dimethylglyoxime; the precipitate is collected, washed with cold, very dilute hydrochloric acid, dried at 105° , and ignited (finally in hydrogen). The filtrate is boiled for 30 min. with furildioxime (2% solution) and alcohol (10%), the precipitate being washed with very dilute alcohol, and after ignition weighed as platinum. The filtrate is evaporated to one third of its volume and boiled with 5 c.c. of concentrated hydrochloric acid and 5 g. of sodium chlorate for each 100 c.c. After addition of an equal volume of alcohol to the chlorine-free solution, rhodium is precipitated with potassium nitrite, the precipitate being washed with 50% alcohol and the filtrate used for determining ruthenium, osmium, and iridium. The precipitate is dissolved in aqua regia, the excess of acid removed, the chloride reduced with magnesium or zinc, and the rhodium washed with dilute hydrochloric acid and ignited in hydrogen. The filtrate is evaporated to remove nitrous fumes, and concentrated hydrochloric acid (10 c.c. per 100 c.c.) is added, and evaporation continued until solids separate, when 2—3 vols. of water are added, followed by sodium hydroxide to alkalinity, and alcohol to 33 vol.-%. The precipitated ruthenium oxide is dissolved in hydrochloric acid, the metal precipitated with magnesium or zinc, and ignited in hydrogen. The filtrate is evaporated to remove alcohol; the osmium and iridium are precipitated with zinc dust and washed with very dilute

hydrochloric acid. The iridium is dissolved from the filter in sodium hypochlorite solution, the osmium being ignited in hydrogen. Zinc and hydrochloric acid are added to the iridium solution, the iridium being dried at 190° before being heated in hydrogen.

CHEMICAL ABSTRACTS.

Ultra-violet light filter. F. SAUNDERS (J. Opt. Soc. Amer., 1928, 16, 362).—One mm. of a solution of potassium hydrogen phthalate containing 40.836 g. per litre transmits uniformly up to 3000 Å., and cuts off sharply at that wave-length. The salt should be recrystallised several times. C. W. GIBBY.

Experiments on Geiger ion counters. R. D. BENNETT (J. Opt. Soc. Amer., 1928, 16, 339—354).—The sensitivity of this instrument has been investigated with varying dimensions, voltage, and gas pressure. It is very sensitive for detecting single ions, but only moderately so for ultra-violet light, as its efficiency is low. Quantitative use is possible only if the sensitivity can be kept constant over long periods. C. W. GIBBY.

Projection electroscope for standardising radium preparations. L. F. CURTISS (J. Opt. Soc. Amer., 1928, 16, 363—366).—For standardising strong radium preparations the ordinary gold-leaf electroscope observed through a microscope involves danger to the operator, and eyestrain. An instrument is described in which a quartz fibre attached to the gold leaf is projected ($\times 100$) on a ground-glass scale. C. W. GIBBY.

Vacuum stopcock. A. P. H. TRIVELLI (J. Opt. Soc. Amer., 1928, 16, 367—369).—Greater security in mercury sealed stopcocks for vacuum work may be obtained by having a ring of mercury round the centre of the barrel, filled from a small funnel sealed on the outside. C. W. GIBBY.

Automatic colorimeter. G. BAGANZ (Chem. Fabr., 1928, 358).—The apparatus is designed for the control of the chlorination of town's water by the use of benzidine and potassium iodide as colorimetric indicators, but is capable of adaptation. It consists of an electrical arrangement for the taking of samples, addition of indicators, and washing out of the apparatus at regular time intervals, the observation only being left to the attendant. C. IRWIN.

Selenium cells as colorimeters. A. MICKWITZ (Z. anorg. Chem., 1928, 171, 285—311).—In order to study the absorption of light by a solution, the effect of the transmitted light on the resistance of a selenium cell, measured by the current passing when a constant *P.D.* is applied, may be compared with the effect obtained by using as absorbent a layer of water of the same thickness, and the same source of light. In order to eliminate the effect of variations in the properties of the cell with the time and also hysteresis effects in the resistance, the cell is exposed to the light transmitted by the water and the light transmitted by the solution for alternate periods of 20 sec. each, each period of illumination being separated from the following period by 40 sec. of darkness, and this is continued until the current corresponding with each kind of light becomes constant. The absorption by the solution is then expressed numerically by the ratio x of the quantity (current passing through the cell

when illuminated by the light transmitted by the solution — current passing in darkness) to the corresponding quantity for the water. Absorption curves constructed in this way for solutions of copper sulphate and copper nitrate may be used for the colorimetric determination of these salts, the mean error with the sulphate being $\pm 1.5\%$. As the value of x is affected considerably by variations in the *P.D.* applied to the cell, this should be kept constant for all the measurements. Iron may be determined colorimetrically in the form of colloidal ferrous sulphide, the oxidation of which, with consequent change of colour, is delayed by addition of sodium sulphite; the mean error is $\pm 2.5\%$. Experiments of this kind show that a saturated solution of ferrous sulphide at the ordinary temperature contains 0.0028 g. of iron/litre.

R. CUTHILL.

Still for preparation of pure water. H. S. KING (Proc. Nova Scotian Inst. Sci., 1927, 16, 176).—A simple adaptor for fitting a tin condenser on to the neck of an ordinary flask is described. S. J. GREGG.

Application of an electromagnetic force to the thermobalance. Z. SHIBATA and M. FUKUSHIMA (Bull. Chem. Soc. Japan, 1928, 3, 118—123).—If the sensitivity of Honda's thermobalance (cf. Sci. Rep. Tôhoku Imp. Univ., 1915, 4, 97) is increased its range is reduced and errors due to hysteresis in the spring are increased. This is overcome by attaching an iron rod, on the axis of a solenoid, to the wire connecting the beam to the spring. Movement of the beam is counteracted by passing a current through the solenoid, the change in weight being calculated from the value of the current. Accuracy equal to that of a chemical balance is obtained.

C. J. SMITHELLS.

Apparatus for analysis of solutions, especially bleach liquors containing chlorine. K. HINTZMANN.—See B., 1928, 478.

Physical methods in chemical laboratories. III. **Production of intense magnetic and electric fields.** H. GEHLEN (Z. angew. Chem., 1928, 41, 714—716).—Modern methods for the production of intense magnetic and electric fields are briefly described. J. S. CARTER.

Pumice impregnated with anhydrous magnesium perchlorate as a drying agent. J. H. YOE, R. W. MCGAHEY, and W. T. SMITH (Ind. Eng. Chem., 1928, 20, 656—657).—Pumice granules are soaked for 24 hrs. in 35% magnesium perchlorate solution, heated at 175° to dehydration, and further heated at about 240° in a slow current of dry (P_2O_5) air, at rates of flow from 1.5 to 3.5 litres per hr. The material has greater capacity than phosphorus pentoxide; it can be repeatedly reactivated and does not become sticky on handling or form channels through use. It contracts on absorbing water and is neutral. At rates higher than 5 litres per hr. the agent is less effective than phosphorus pentoxide.

D. G. HEWER.

Automatic apparatus for determination of small concentrations of sulphur dioxide in air. M. D. THOMAS and R. J. CROSS (Ind. Eng. Chem., 1928, 20, 645—647).—The air sample is drawn continuously by a Nelson pump delivering about 30 litres in

2 min., corresponding with approximately 1 g.-mol. vol. under conditions of operation, and the absorber consists of a standard "salvarsan tube" containing about 1 g. of starch, 2 g. of potassium iodide per litre, and the necessary iodine. Its strength is determined by titration with 0.002*N*-sodium thiosulphate, 1 c.c. of which corresponds with 1 in 10^6 of sulphur dioxide for 1 g.-mol. vol. of air. The method is automatic to the point of titration; a diagram of the apparatus is given. A modification for field work uses the intake manifold of the conveying motor-car for obtaining suction. The method was tested by comparison with the Selby method with satisfactory results, and concentrations of sulphur dioxide as low as 1 in 10^7 of air were dealt with since a 0.000075*N*-solution of iodine did not change when 400 litres of air were aspirated through it. With high concentrations of iodine incomplete absorption of sulphur dioxide and volatilisation of iodine may occur, but the method is trustworthy up to 6 in 10^5 . D. G. HEWER.

Regulation of flow of carbon dioxide through a combustion train. J. C. RICE (Ind. Eng. Chem., 1928, 20, 627).—A positive pressure may be impressed on a small Kipp apparatus by fixing a slightly inflated rubber balloon to a small glass tube through the top orifice of the generator. Backing of the acid in the Kipp apparatus is thus avoided and the slightest pressure on the balloon will counterbalance the suction caused by the column of mercury in the nitrometer. D. G. HEWER.

Apparatus for determining m. p. S. AVERY (Ind. Eng. Chem., 1928, 20, 570).—A Thiele tube, lengthened for the use of an Anschütz total-immersion thermometer and modified to permit mechanical circulation by a propeller driven by a small fan motor, is used for the determining of m. p. It is suitable for use with petrolatum, glycerol, or with a glass propeller and shaft and lead bearing for sulphuric acid. The tube is heated in the same way as a Thiele tube, and the temperature can be very accurately regulated, fluctuation of the thermometer with slow heating being avoided. D. G. HEWER.

Extraction apparatus especially for use with liquids. P. H. PRAUSNITZ (Chem. Fabr., 1928, 346—347).—The use of a perforated glass filter in the extraction of aqueous solutions with ether in the bottom of the extraction tube is of great value in producing effective distribution. The extraction tube should be cylindrical and the space beneath the filter plate as small as possible. Several different

arrangements of extraction apparatus are described and times required for complete extraction of a given solution determined. C. IRWIN.

Stand for electrolysis with a rotating electrode. A. GUNDER (Z. anal. Chem., 1928, 73, 444—445).—The stand comprises a heavy cast-iron tripod with enlarged foot pieces and a thick glass central rod carrying a movable cast-iron arm on one side of which are the driving pulleys and on the other the rotating gear operating in a mercury contact cup on one branch of the arm. A. R. POWELL.

Moving flames. W. PAYMAN (J.C.S., 1928, 1738—1740; cf. this vol., 729).—A "flame-speed" camera and a "wave-speed" camera are described. These are used in determining the speeds of flames, and examining their mode of propagation, use being made of the abrupt change in refractive index of a gas mixture at the surface of a flame passing through it. R. A. PRATT.

Equilibrator; device for determination of the distribution ratio of a volatile solute between two miscible solvents. G. JONES and B. B. KAPLAN (J. Amer. Chem. Soc., 1928, 50, 1600—1603).—Two closed bulbs are so mounted and connected together by tubes that on rotation gas or vapour is forced to bubble continuously and consecutively through two separated liquids. S. K. TWEEDY.

Nomography. III. Logarithmic and exponential functions. O. LIESCHE (Chem. Fabr., 1928, 359—361, 392—394).—The use of logarithmic scales facilitates the graphical solution of numerous problems. Various examples are given of the combination of a logarithmic scale and an equally divided scale or of two logarithmic scales arranged either parallel or "projectively" at an angle for the graphical determination of the breaking down of mesothorium, the variation of a reaction velocity with the temperature, the iodometric determination of antimony, etc. C. IRWIN.

Visual method of showing high temperature coefficient of resistance of metals as compared with alloys. P. ROOD (J. Opt. Soc. Amer., 1928, 16, 357—359).—An experiment suitable for lectures. C. W. GIBBY.

Rational nomenclature of chemical compounds. A. SEMENTZOV (Ukraine Chem. J., 1928, 3 [Sci.], 39—45).—It is proposed to base Ukrainian chemical nomenclature on international names, as opposed to national. R. TRUSZKOWSKI.

Geochemistry.

Spectroscopic proof of the presence of boron in the sun. S. B. NICHOLSON and N. G. PERRAKIS (Compt. rend., 1928, 186, 1523—1524; cf. this vol., 340).—Boron has been shown to be present in the sun by the identification of 26 out of 81 of the most intense rays in the spark spectrum of boric acid in the region 4645—5137 Å., the remainder being unidentifiable on account of the proximity of other strong solar rays, some of which showed the Zeeman

effect. The mean and maximum disagreements were 0.005 and 0.013 Å., respectively. J. GRANT.

Nocturnal fluctuations of ozone. D. CHALONGE (Compt. rend., 1928, 186, 1856—1858; cf. this vol., 389).—Daily and nightly determinations at Paris of the thickness of the layer of ozone in the upper atmosphere from October 1927 to April 1928 have shown that when suitably corrected for the absorption

coefficients of ozone for the spectral regions used, the results confirm those of other workers (cf. Buisson, this vol., 611). A mean nightly value of 3.35 mm. (under conditions of normal temperature and pressure) was obtained, there being no seasonal variation and very little deviation from determinations made in the daytime. J. GRANT.

Chemical characters of waters of Florida. W. D. COLLINS and C. S. HOWARD (U.S. Geol. Survey, Water-Supply Paper 596 G, Feb. 17, 1928, 177—233).

Organic content of the water of small lakes. E. A. BIERGE and C. JUDAY (Proc. Amer. Phil. Soc., 1927, 66, 357—372).—A study of lakes in N.E. Wisconsin. A low proportion of inorganic matter is associated with a low content of organic matter, but a high proportion of inorganic matter may be associated with a low or high organic matter content.

CHEMICAL ABSTRACTS.

Radioactivity of water from various sources in Poland. S. GRABIANKA (Rocz. Chem., 1928, 8, 183—194).—The radioactivity of water from nine different sources of mineral water varies from 1.98 to 9.72 Mache units. R. TRUSZKOWSKI.

Necessity of the physical-chemical study of the reaction $2\text{CaCO}_3 + \text{MgSO}_4 \rightleftharpoons \text{CaCO}_3 + \text{MgCO}_3 + \text{CaSO}_4$. B. P. KROTOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 662—682).—The importance of Heydinger's reaction (Trans. Roy. Soc. Edinburgh, 1827, 36) for the study of the formation of deposits in salt lakes is pointed out. Dolomite and magnesite may be among the ultimate products of this reaction, the direction of which depends on the concentration of other salts in solution, as well as on that of its substrates, and on the temperature of the water.

R. TRUSZKOWSKI.

Systematics of salt lakes. B. P. KROTOV (Ann. Inst. Anal. Phys. Chem., 1927, 3, 641—662).—An historical and theoretical review of the reactions taking place in salt lakes, on the basis of which a new classification of such lakes is proposed.

R. TRUSZKOWSKI.

Sulphur-bearing waters of Helouan-les-Bains; their composition and therapeutic value. S. NARKIER (J. Egypt. Med. Assoc., 1928, 11, 57—72, 114—128).

Base exchange and the formation of coal. E. McK. TAYLOR.—See B., 1928, 509.

Occurrence of iodine in phosphate beds. E. WILKE-DÖRFURT, J. BECK, and G. PLEPP (Z. anorg. Chem., 1928, 172, 344—352).—In continuation of previous work (A., 1927, 642), the iodine in a very large number of phosphate minerals has been determined, using several different methods. The results are recorded. Attempts to prepare an iodoapatite have been unsuccessful, and no appreciable quantity of iodine has been found in apatites from different sources. The iodine found in the different phosphate beds is attributable to a biological origin. The large variations in iodine content are no doubt due to differences in geological history and climatic conditions since formation. M. S. BURR.

Tremolite, clinohumite, stromeyerite, natron, and hexahydrite. T. L. WALKER and A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 15—24).—Tremolite, *d* 2.96, from Faraday, Ont., contained (analyses by RICKABY): SiO_2 57.36, TiO_2 0.14, Al_2O_3 1.04, Fe_2O_3 0.21, FeO 0.72, CaO 12.41, MgO 25.22, Na_2O 1.49, K_2O 0.47, H_2O 0.44, total 99.50%. Clinohumite from Chaffey's Locks, *d* 3.17, contained SiO_2 37.42, TiO_2 1.14, Fe_2O_3 0.46, FeO 1.27, MgO 56.32, MnO 0.10, H_2O 0.56, F 5.04, less O 2.12, total 100.19%. Stromeyerite from Cobalt and Gorvanda, Ont., *d* 6.26, contained Cu 31.00, Ag 53.31, S 16.02, total 100.33%. Natron from Clinton, B.C., *d* 1.34, contained Na_2O 21.23, CO_2 15.46, H_2O 63.59, total 100.28%. Hexahydrite from Oroville, Washington, *d* 1.71, contained MgO 17.88 ($\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$) 0.10, SO_3 34.64, H_2O 47.32, insol. 0.03, total 99.97%.

CHEMICAL ABSTRACTS.

Bytownite and huronite. T. L. WALKER and A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 5—11).—Bytownite (crushed and granulated anorthosite) contains SiO_2 54.30, Al_2O_3 27.49, Fe_2O_3 1.27, CaO 10.21, MgO 0.50, Na_2O 4.77, K_2O 0.84, H_2O 0.79, total 100.17%. Huronite (75% muscovite and some zoisite) contains SiO_2 46.70, Al_2O_3 31.60, Fe_2O_3 1.41, FeO 0.57, CaO 6.90, MgO 0.64, MnO 0.05, K_2O 6.96, Na_2O 1.45, H_2O 3.63, CO_2 0.40, total 100.31%. (Analyses by RICKABY.)

CHEMICAL ABSTRACTS.

Cohenite from Ovivak, Greenland. E. THOMSON (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 41—43).—Cohenite contains Fe 78.12, S 16.40, insol., 3.86%, corresponding with the formula Fe_2S , but the residue examined was not a pure mineral.

CHEMICAL ABSTRACTS.

Serpentine and chlorite. N. KURNAKOV and V. CERNYH (Mem. Soc. Russ. Min., 1926, 55, 183—194; Chem. Zentr., 1928, i, 1013—1014; cf. this vol., 268).—The formula $\text{H}_2\text{Mg}_3\text{Si}_2\text{O}_8$ fairly accurately expresses the composition of many serpentines; if alumina (up to 8.2%) is present, the chlorites are approached. The nature of the heating curves is discussed. With increase in the alumina content the orthochlorites show conversion into corundophilite and amesite. A. A. ELDRIDGE.

Crystallography of aurichalcite, danburite, cerussite, etc. H. BUTTGENBACH (Mém. Soc. Roy. Sci. Liège, 1924, [3], 12, No. 9).—A review is given of the literature on the crystallography and optics of aurichalcite. A new crystal-form is noted on danburite from Switzerland. Twinned crystals of cerussite from Tunisia are figured and described. Crystallographic data are given for *m*-xylylhydrocotarnine, *o*-, *m*-, and *p*-tolylhydrocotarnine, tin dibromodip-tolyl, tin tetratolyl (*o*-, *m*-, and *p*-), tin tetra- α -naphthyl. L. J. SPENCER.

Louisite. T. L. WALKER (Proc. Nova Scotian Inst. Sci., 1927, 16, 35—37).—Louisite consists of an aggregate of radiating spherules of quartz in cleavable apophyllite. S. J. GREGG.

Anorthoclase in caucasites. D. S. BELIANKIN (Bull. Acad. Sci. Russ., 1927, 1115—1123).—The author classifies the anorthoclases with orthoclases

and distinguishes the four series: potassium and sodium anorthoclases, either with low or medium values of $2V$, or with high values of $2V$. It is suggested also that the anorthoclases with low or medium $2V$ be termed potassium sanidine (or simply sanidine) and sodium sanidine respectively. Potassium sanidine occurs widely in igneous rocks, principally in intruded materials and mostly in those of recent age.

T. H. POPE.

Minerals from new veins in Belgian Congo.

H. BUTTGENBACH (Mém. Soc. Roy. Sci. Liège, 1927, [3], 14, No. 4).—Accounts are given of several minerals from veins of copper ore in limestone near intrusive rocks recently discovered at several places along the tributaries of the Lubi river. Massive stromeyerite contains Cu 20.45, Ag 60.00, S 15.65, Fe 0.26, insol. 2.56, total 98.92%. Planchette intermixed with shattuckite and chrysocolla gave SiO_2 41.24, CuO 50.67, CaO trace, H_2O 5.54, moisture 0.85, insol. 1.36, total 99.66%. Crystals of willemite, baryte, libethenite, and volborthite are figured and described.

L. J. SPENCER.

New mineral [berthonite] from Tunis. H. BUTTGENBACH (Ann. Soc. geol. Belg., 1927, 46, 212; Chem. Zentr., 1928, i, 1013).—Berthonite, d 5.49, hardness 4—5, contains Pb 21.83, Cu 23.68, Sb 32.45%, corresponding with the formula $5\text{PbS}_9\text{Cu}_2\text{S}_7\text{Sb}_2\text{S}_3$.

A. A. ELDRIDGE.

Two scapolites from the banks of the Slioudianka River. S. SMIRNOV (Mem. Soc. Russe Min., 1927, 55, 354—361; Chem. Zentr., 1928, i, 1014).

Mineralogy of the bauxites of the Fenouillet region. J. DE LAPPARENT (Compt. rend., 1928,

186, 1560—1561; cf. *ibid.*, 1927, 185, 658).—The bauxites examined were all essentially of the diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) type, and contained about 50% in the form of numerous, very small, flat macleated crystals situated along the optical axes, the macles being similar to those of manganite. The crystals were distributed throughout the mass of the rock, sometimes in the pure state, but usually associated with clays, gibbsite, or vegetable tissues and then forming a succession of crusts. Boehmite, which is often associated with diaspore, was not observed.

J. GRANT.

Apophyllite. S. DI FRANCO (Atti Acc. Gioenia Sc. Na. Catania, 1926, 15, No. 7; Chem. Zentr., 1928, i, 1013).—A specimen of apophyllite contained SiO_2 52.75, CaO 25.43, K_2O 4.73, Na_2O 0.43, H_2O 16.8% and had d^{15} 2.375.

A. A. ELDRIDGE.

Analcime. S. DI FRANCO (Boll. Soc. Geol. Ital., 1926, 45, 1; Chem. Zentr., 1928, i, 1013).—A specimen of analcime contained H_2O 8.22, SiO_2 54.10, Al_2O_3 23.68, CaO 0.45, Na_2O 13.40, K_2O 0.34%, and had d 2.249.

A. A. ELDRIDGE.

Successive treatment of mined platinum from Tagil with dilute aqua regia. B. C. KARPOV (Ann. inst. platine, 1927, 5, 363—364).—Successive treatment of a grain of crude platinum with portions of aqua regia showed that the outer layers contained more iron and copper than the nucleus.

CHEMICAL ABSTRACTS.

Minerals. H. COLLINS (Chem. News, 1928, 136, 385—387).—Data for twelve minerals are given (see this vol., 613).

Organic Chemistry.

Cholesterol as parent of petroleum. II. N. D. ZELINSKI and K. P. LAVROVSKI (Ber., 1928, 61, [B], 1291—1294; cf. B., 1927, 865).—The various fractions of the hydrocarbons obtained by the action of aluminium chloride on cholesterol (*loc. cit.*) have been subjected to catalytic dehydrogenation and the products treated with fuming sulphuric acid. The "artificial petroleum" is shown to consist of a complicated mixture of hydrocarbons containing only very small amounts of aromatic substances. It consists chiefly of paraffins and cycloparaffins, mainly derivatives of cyclohexane. The fractions are readily dehydrogenated and the products, after removal of the aromatic hydrocarbons, consist either exclusively of compounds, $\text{C}_n\text{H}_{2n+2}$ (octanes, nonanes, decanes), or mixtures of these with cycloparaffins (naphthenes) of hexahydroaromatic character.

H. WREN.

Electrosynthesis. M. Z. YOVITCHITCH (Bull. Acad. roy. Belg., 1927, [v], 13, 365—370; cf. A., 1925, ii, 406).—The sum of the percentages of carbon and hydrogen in the products obtained by the action of a silent electric discharge on ethylene and benzene (both normally, but not rigorously purified and dried) is considerably below 100. Since these products, unlike those previously investigated, lose in weight on

exposure to air it is assumed that this deficiency is due entirely to the action of the electric discharge itself. A similar deficiency is found in the case of the products from acetylene which has been in contact with the air only for the minimum possible time. J. W. BAKER.

Polymerisation of olefines. R. VAN WINKLE (J. Amer. Pharm. Assoc., 1928, 17, 544—547).—The harmful impurities in propylene for anaesthetic purposes are probably higher ethylenic hydrocarbons formed during the dehydration of isopropyl alcohol. It was hoped to remove these by polymerisation; contrary to the view of Lebedev, however, propylene also polymerises in the cold when under pressure in contact with activated floridin (a commercial silicate). After 2 months, a liquid containing bi- and ter-molecular polymerides, b. p. about 70° and 100°, respectively, is obtained. After a year a mixture of products is obtained, of which three volatile fractions and a residue are examined by the depression of f. p. of benzene; the empirical formulæ are $(\text{C}_3\text{H}_6)_3$, b. p. 35.5—37.5°/7 mm. (15%); $(\text{C}_3\text{H}_6)_4$, b. p. 60—64.5°/7 mm. (30%); $(\text{C}_3\text{H}_6)_5$, b. p. 82—85°/3 mm. (15%), and higher polymerides (40%).

isoButylene when passed through a short column of catalyst forms some dimerides; with a long

column, only $(C_4H_8)_3$, b. p. 43—46°/7 mm. (62.5%); $(C_4H_8)_4$, b. p. 75—79°/5 mm. (13.3%), and higher polymerides (24.2%) are formed. E. W. WIGNALL.

Action of the silent electric discharge on hydrocarbons of the ethylene series. N. D. PRIANSCHNIKOV (Ber., 1928, 61, [B], 1358—1363; cf. A., 1927, 336).—The most volatile fractions obtained by the polymerisation of isobutylene under the action of the silent electric discharge contain more hydrogen than is required for the composition C_nH_{2n} , so that the process is accompanied by re-distribution of the hydrogen atoms. The saturated hydrocarbons are concentrated in the fractions of lower b. p. Polymerisation is also accompanied by fission and rearrangement of alkyl groups, thus explaining the production of fractions, b. p. 32—52° and 75—85°, with mol. wt. corresponding with C_6 and C_7 compounds in which about 20—30% of hydrocarbons C_nH_{2n} and 70—80% of compounds C_nH_{2n+2} are present. Addition of bromine and reduction of permanganate prove the presence of unsaturated linkings, but polymethylene derivatives can be present only in small amount. The low b. p. and density of the C_6 fraction indicate a highly-branched structure of the hydrocarbons. The first fraction probably contains $\beta\beta$ -dimethylbutane and $\beta\beta$ -dimethylbutylene, whilst $\beta\delta$ - and $\beta\beta$ -dimethylpentanes and $\beta\beta\gamma$ -trimethylbutane are probably present in the second fraction. The products of higher b. p. are notably richer in unsaturated hydrocarbons and contain also naphthenes. After treatment with chromic acid mixture their composition corresponds with 60% of C_nH_{2n} and 40% of C_nH_{2n+2} ; lack of additive power indicates the presence of naphthenes. The presence of aromatic compounds appears unlikely. The action of the silent electric discharge on ethylenic hydrocarbons is closely similar to that of high temperature and pressure. The character of the products depends largely on conditions, prolongation of the action causing increase in the quantity of highly-polymerised, non-volatile substances. Increase in electric tension does not influence the process to the same degree, whereas the structure of the original hydrocarbon greatly affects the rate of reaction. H. WREN.

Action of bromine water on certain olefinic hydrocarbons and ethers. J. READ and W. G. REID (J.C.S., 1928, 1487—1493).—The action of bromine water on styrene, a number of related aromatic ethers, and other ethylene derivatives has been investigated. With styrene, anethole, safrole, and isosafrole the yield of bromohydrin (determined by titration of the hydrobromic acid produced with sodium hydrogen carbonate solution) is increased and that of the dibromide decreased by raising the temperature to 90° and by dilution. At concentrations between about 0.1 and 0.2 mol./litre the percentage yields of the bromohydrin at 90° and at the ordinary temperature are as follows: styrene 77.9 and 96.7, anethole 47.9 and 76.1, safrole 65.2 and 69.2, isosafrole 67.0 and 72.8, amylene (trimethylethylene) 78.9,—, *dl*- Δ^3 -menthene 62.9,—; yields of more than 90% with ethylene, sodium maleate and fumarate, indene, itaconic, cinnamic, methylcoumaric, and methylcoumarinic acids, more than 85% with maleic

acid and allyl alcohol, and 51.5% with oleic acid. By application of this method are obtained β -hydroxy- β -phenylethyl bromide, b. p. 109—110°/2 mm., n_D^{20} 1.5800, d_4^{20} 1.4994, which when shaken with concentrated ammonia for 10 hrs. yields β -hydroxy- β -phenylethylamine; *dl*- β -hydroxy- β -p-methoxyphenyl isopropylamine, m. p. 84° (hydrochloride, m. p. 182°; benzoyl derivative, m. p. 159°; benzylidene derivative, syrup; *d*- α -bromocamphorsulphonate, crude, m. p. 103°), is similarly obtained by the action of ammonia on anethole bromohydrin. This base is resolved by fractional crystallisation of the *d*-camphorsulphonate, the *d*- β -hydroxy- β -p-methoxyphenylisopropylamine *d*-camphorsulphonate, m. p. 194—195°, $[\alpha]_D^{20}$ +20.5°, separating, from which is obtained *d*- β -hydroxy- β -p-methoxyphenylisopropylamine, m. p. 80—81°, $[\alpha]_D^{20}$ +4.6° (water), +13.9° (methyl alcohol), +18.4° (ethyl alcohol), +22.9° (benzene), +21.7° (acetone) (hydrochloride, m. p. 171—172°, $[\alpha]_D^{20}$ +14.7°; benzoyl derivative, m. p. 153—154°). From safrole is obtained the dibromide, m. p. 87°. *iso*Safrole bromohydrin, when treated with ammonia, yields β -amino- α -hydroxydihydroisosafole, $CH_2O:C_6H_3:CH(OH):CHMe:NH_2$ (hydrochloride, m. p. 154°), whilst amylene bromohydrin similarly yields γ -amino- β -hydroxy- β -methylbutane, b. p. 60—62°/16 mm. (chloroplatinate, m. p. 186°; benzoyl derivative, oil; *p*-nitrobenzoyl derivative, m. p. indefinite about 65°; *d*- α -bromocamphorsulphonate, m. p. 170°; *d*-camphorsulphonate, m. p. 144°). When amylene bromohydrin is heated with aqueous potassium hydroxide for 0.5 hr. it is converted into trimethylethylene oxide, which is converted by the action of dilute sulphuric acid into methyl isopropyl ketone and the corresponding glycol, the ketone being best obtained by heating the bromohydrin with litharge and lead chloride in a sealed tube at 200° for 7 hrs. *dl*- Δ^3 -Menthene is conveniently prepared by the action of phosphorus trichloride on *dl*-menthol at 80° for 1 hr. (Robertson). J. W. BAKER.

Reactions of simultaneous reduction and oxidation, and isomeric transformations. A. E. FAVORSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 369—414).—The alcoholic fermentation of dextrose (cf. A., 1926, 500) appears to consist of a series of associated reactions of reduction and oxidation, occurring in the following sequence. A molecule of dextrose decomposes, giving two molecules of glyceraldehyde, one carbon atom at the point of attack being reduced to give a primary alcoholic group and the other oxidised to give an aldehydic group. The glyceraldehyde, like α -glycol, gives up water and forms methylglyoxal. With the participation of water (1 mol.), glyceraldehyde (1 mol.) and methylglyoxal (1 mol.) yield glycerol (1 mol.) and pyruvic acid (1 mol.), the last decomposing to form acetaldehyde and carbon dioxide. With the aid of water (1 mol.), acetaldehyde (1 mol.) and methylglyoxal (1 mol.) react, giving ethyl alcohol and pyruvic acid.

[With VASILIEV.]—Favorski (A., 1913, i, 12) showed that, when treated with phosphorus pentachloride, ketones give, according to their structure, either products formed by replacement of the carbonyl oxygen atom by chlorine or, with preliminary enolisation, chloroketones. Pinacolin reacts in the

first way, and ethyl *tert.*-butyl ketone in the second, giving α -chloroethyl *tert.*-butyl ketone, b. p. $84^{\circ}/53$ mm., d_4^{20} 0.9814, d_4^{30} 0.9993, which reduces Fehling's solution and, when heated with potassium formate and methyl alcohol, is converted into (1) trimethylacetylmethylcarbinol, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CMe}_3$, which is mostly isomerised into acetyl-*tert.*-butylcarbinol, $\text{OH}\cdot\text{CHAc}\cdot\text{CMe}_3$, b. p. 108 — $111^{\circ}/100$ mm., d_4^{20} 0.9523, d_4^{30} 0.9352 (cf. Aschmarin, A., 1913, i, 15), in the conditions of the experiment; conversion of the last-named compound into the glycol, $\beta\delta\delta$ -trimethylpentane- $\beta\gamma$ -diol (cf. Prileschaeff, A., 1904, i, 795), m. p. 64.5 — 65° , may be effected by treatment with magnesium methyl bromide, and oxidation of this diol yields oxotanol; (2) $\delta\delta$ -dimethylpentane- $\beta\gamma$ -diol, m. p. 54° . [V. V. DOLIVO-DOBROVLSKI. $\beta\delta\delta$ -Trimethylpentane- $\beta\gamma$ -diol forms crystals of two types, one in small plates of quadratic outline incapable of measurement, and the other in prismatic crystals of the monoclinic system, $a:b:c = 2.306:1:0.675$, $\beta = 97^{\circ}$.] Treatment of trimethylacetylmethylcarbinol with magnesium phenyl bromide gives γ -phenyl- $\delta\delta$ -dimethylpentane- $\beta\gamma$ -diol, m. p. 94° , and β -phenyl- $\delta\delta$ -dimethylpentane- $\beta\gamma$ -diol, m. p. 82.5° .

[With A. I. UMNova.]—The action of alcoholic potassium hydroxide on isopropyl α -bromoisopropyl ketone (cf. A., 1913, i, 13) yields isobutyryldimethylcarbinol (*semicarbazone*, m. p. 178 — 179°); treatment of the carbinol with magnesium phenyl bromide gives γ -phenyl- $\beta\delta$ -dimethylpentane- $\beta\gamma$ -diol, m. p. 75 — 76° , oxidation of which yields phenyl isopropyl ketone and acetone. *iso*Butyryldimethylcarbinol, also obtained from isopropyl α -chloroisopropyl ketone (*loc. cit.*), undergoes isomerisation on prolonged treatment with alcoholic potassium hydroxide or when heated with alcoholic sulphuric acid, yielding acetylmethylisopropylcarbinol, b. p. 161 — 164° , d_4^{20} 0.9045— 0.9230 , which is also formed by oxidation of dimethylisopropylethylene. When heated in a sealed tube with alcohol and a small quantity of sulphuric acid, oxotanol is converted into acetylmethyl-*tert.*-butylcarbinol, $\text{OH}\cdot\text{CMeAc}\cdot\text{CMe}_3$, b. p. 176 — $178^{\circ}/746$ mm., d_4^{20} 0.9505, d_4^{30} 0.9362 (*semicarbazone*, m. p. 190 — 190.5°), which yields pinacolin and acetic acid on oxidation.

[With E. KOTSCHERGINA.]—When either heated in a sealed tube with alcohol and a small amount of sulphuric acid or introduced into a sucrose solution undergoing fermentation by brewers' yeast, benzoylmethylcarbinol isomerises into acetylphenylcarbinol. The author considers that the formation of acetylphenylcarbinol from benzaldehyde in a fermenting liquid, observed by Neuberg (*Biochem. Z.*, 1920, 115, 282), is due to isomeric change of benzoylmethylcarbinol formed from the benzaldehyde.

[With E. D. VÉnus-DANILOVA.]—Bromination of dipropyl ketone yields propyl α -bromopropyl ketone, $\text{CHBrEt}\cdot\text{COPr}$, b. p. 82 — $83^{\circ}/17$ mm., d_4^{20} 1.2717, d_4^{30} 1.2433, which attacks the mucous membrane, and the di- α -bromopropyl ketone, b. p. 100 — $101^{\circ}/17$ mm., d_4^{20} 1.5572, d_4^{30} 1.5234. Treatment of the monobromocompound with aqueous potassium hydroxide or with water and freshly precipitated calcium or barium carbonate yields (1) butyrylethylcarbinol, b. p. 181 — 182° , or 75 — $76^{\circ}/18$ mm., d_4^{20} 0.9488, d_4^{30} 0.9309 (*semicarbazone*, m. p. 117 — 118°), and (2) propionylbutyryl

diketone [*disemicarbazone*, m. p. 253 — 255° (decomp.)]. Reduction of butyrylethylcarbinol by means of magnesium *tert.*-butyl (or amyl) chloride yields *s*-ethylpropylethyleneglycol, $\text{OH}\cdot\text{CHEt}\cdot\text{CHPr}\cdot\text{OH}$, m. p. 98 — 99° , b. p. 117.5 — $118^{\circ}/21$ mm. Butyrylethylcarbinol undergoes decomposition when distilled, even under diminished pressure, giving a compound, $\text{C}_7\text{H}_{12}\text{O}_2$, b. p. 146 — 148° or 58 — $61^{\circ}/25$ mm. [*semicarbazone*, m. p. 253° (decomp.)], together with compounds of higher b. p. which could not be separated, and a precipitate, which does not distil. The last evidently represents a condensation product and when subjected to prolonged heating with continuous stirring with 2% sulphuric acid solution on a water-bath, yields propionylpropylcarbinol (*semicarbazone*, m. p. 121 — 122°) and the anhydride, $\text{O}(\text{CHEt}\cdot\text{COPr})_2$, b. p. 151 — $152^{\circ}/20$ mm., which gives a *semicarbazone*, $\text{C}_{16}\text{H}_{32}\text{O}_3\text{N}_6$, m. p. 178 — 179° . When heated with alcohol in presence of sulphuric acid, butyrylethylcarbinol undergoes isomerisation into propionylpropylcarbinol, which, by treatment with magnesium methyl bromide, is converted into α -methyl- α -ethyl- β -propylethylene glycol (β -ethylhexane- $\beta\gamma$ -diol), b. p. 101 — $102^{\circ}/12$ mm., d_4^{20} 0.9548, d_4^{30} 0.9404. Oxidation of the latter with chromic acid yields methyl ethyl ketone, butyrylmethylcarbinol, b. p. 93 — $96^{\circ}/30$ mm. (*semicarbazone*, m. p. 143 — 144°), butyric acid, and a small amount of acetic acid, apparently formed by further oxidation of the methyl ethyl ketone.

[With E. D. VÉnus-DANILOVA.]—When heated with alcohol in presence of sulphuric acid, propionylmethylcarbinol undergoes isomeric change to acetyl-ethylcarbinol, b. p. 147 — $148^{\circ}/761.5$ mm., d_4^{20} 0.9673, d_4^{30} 0.9500, which gives a *semicarbazone*, m. p. 216 — 217° , and, on treatment with magnesium methyl bromide, yields $\alpha\alpha$ -dimethyl- β -ethylethylene glycol, b. p. $122^{\circ}/112$ mm., d_4^{20} 0.9764, d_4^{30} 0.9627. Oxidation of the latter gives acetone and propionic acid, together with a small amount of acetic acid, probably formed by oxidation of the acetone. T. H. POPE.

Transformation of propionylmethylcarbinol into acetylmethylcarbinol. [MME.] E. VÉnus-DANILOVA (*Bull. Soc. chim.*, 1928, [iv], 43, 582—586).—Ethyl α -bromoethyl ketone, b. p. 62 — $64^{\circ}/28$ mm. (from diethyl ketone, yield 67%), with barium carbonate is converted into propionylmethylcarbinol, b. p. 60 — $60.5^{\circ}/20$ mm., $152.5^{\circ}/761$ mm., d_4^{20} 0.9742 [*semicarbazone*, m. p. 208 — 209° (decomp.)] (cf. Pechmann, A., 1890, 1234), together with traces of a diketone and a glycol anhydride. (See also preceding abstract.) R. BRIGHTMAN.

Transformation of butyrylethylcarbinol into propionylpropylcarbinol. [MME.] E. VÉnus-DANILOVA (*Bull. Soc. chim.*, 1928, [iv], 43, 575—592).—See above (Favorski and Vénu-Daniilova).

Action of polyhydric alcohols on periodic acid. L. MALAPRADE (*Bull. Soc. chim.*, 1928, [iv], 43, 683—696).—See this vol., 269.

α -Glucuheptulitol. G. BERTRAND and G. NITZBERG (*Compt. rend.*, 1928, 186, 1773—1776).— α -Glucuheptulitol (this vol., 620) has $[\alpha]_D^{20} -2^{\circ} 42'$, in 5% aqueous solution. The value is much greater in the absolute sense than that for heptitols in general.

Acetylation with acetic anhydride and zinc chloride at the b. p. yielded an *acetyl* derivative, m. p. 116—117°, α_D about +2° in chloroform ($l=2.2$). Theoretically α -glucoheptulose should yield on reduction the two active β -glucoheptitols, but proof of the identity of α -glucoheptulitol with one of the β -glucoheptitols is lacking. The rotation value of the *d*-form of the latter (A., 1912, i, 607) is not in agreement with that for α -glucoheptulitol.

J. D. FULTON.

Derivatives of glycerol containing sulphur. E. FROMM, R. KAPPELLER, and I. TAUBMANN (Ber., 1928, 61, [B], 1353—1358).—The compound obtained by the action of sodium hydrogen sulphite on epichlorohydrin and regarded as derived from the sulphonic acid, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, yields sodium sulphite when boiled with sodium hydroxide and hence is the *sulphurous* ester, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{H}$. Normal sodium sulphite and epichlorohydrin, however, afford sodium β -hydroxypropyl- $\alpha\gamma$ -disulphonate.

Benzyl mercaptan, sodium hydroxide, and epichlorohydrin or dichlorohydrin afford $\alpha\gamma$ -dibenzylthiolisopropyl alcohol, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\text{Ph})_2$, m. p. 59°. The products derived from it by the action of hydrogen chloride, benzoyl chloride, or acetic anhydride are non-crystalline, but the *acetate* is oxidised to $\alpha\gamma$ -dibenzylsulphonylisopropyl β -acetate, m. p. 159—160°. Oxidation of $\alpha\gamma$ -dibenzylthiolisopropyl alcohol by potassium permanganate unexpectedly affords $\alpha\gamma$ -dibenzylsulphonylisopropyl alcohol, m. p. 208° (monohydrate, m. p. 215°); conversion of the alcohol into the corresponding ketone is not effected by potassium dichromate and concentrated acids, which substantially cause loss of water of crystallisation and separation of the anhydrous alcohol. $\alpha\gamma$ -Dichloroacetone and benzyl mercaptan in presence of alcoholic sodium hydroxide afford $\alpha\gamma$ -dibenzylthiolacetone, oxidised by permanganate in acid solution to $\alpha\gamma$ -dibenzylsulphonylacetone, m. p. 182°; the ketone is transformed by alcoholic sodium hydroxide and subsequent treatment with benzyl chloride into dibenzyl sulphone, m. p. 148°. $\alpha\gamma$ -Dibenzylsulphonylacetone is indifferent towards phenylhydrazine, hydroxylamine, or hydrazine hydrate. The presence of the carbonyl group is established by treatment with benzyl mercaptan and hydrogen chloride and oxidation of the mercaptol to the crystalline *tetrasulphone*, $(\text{SO}_2\cdot\text{CH}_2\text{Ph})_2\text{C}(\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\text{Ph})_2$, m. p. 198°.

H. WREN.

Quantitative study of the oxidation of methyl oleate and elaidate by hydrogen peroxide in presence of acetic acid. T. P. HILDITCH and C. H. LEA (J.C.S., 1928, 1576—1583).—Methyl oleate and elaidate were oxidised in glacial acetic acid with 35% hydrogen peroxide solution at 15—20°, 75—80°, and 95° and the products investigated quantitatively. Three types of oxidation products are formed: (1) a methyl dihydroxystearate, (2) a monoacetyl derivative of (1) formed by the addition of peracetic acid and not by acetylation, and (3) an oily product which liberates iodine from acidified potassium iodide solution, and when heated at 100° under reduced pressure evolves an acrid, acid vapour (not peracetic acid) and the iodine absorption of the resulting product is

increased. This oily product is probably a very unstable molecular or peroxide complex, $-\text{CH}-\overset{\text{O}_2}{\text{CH}}-$, formed by the direct combination of molecular oxygen with the unsaturated system. No oxido-compounds (cf. Böseken, A., 1927, 39) could be detected. The κ -dihydroxystearic acid derivatives produced from methyl oleate are exclusively those of the acid of m. p. 95°, whilst methyl elaidate yields only derivatives of the corresponding acid, m. p. 132°. These results combined with those previously obtained (A., 1926, 938) suggest that various oxidising agents yield the dihydroxystearic acid directly related to the ethylene derivative oxidised without change of configuration, whilst the formation of the isomeric acid, m. p. 132°, by oxidation of oleic acid with potassium permanganate results from inversion during oxidation in the excessively alkaline medium which is essential for the quantitative production of this dihydroxystearic acid.

J. W. BAKER.

Cerebrosides. VII. Hydroxy-acids of brain cerebrosides. E. KLENK (Z. physiol. Chem., 1928, 174, 214—232; cf. A., 1927, 691).—Besides cerebronic acid there is present in cerebroside fractions an unsaturated hydroxy-acid which on catalytic hydrogenation takes up two atoms of hydrogen and yields cerebronic acid. Oxidation of cerebronic acid with potassium permanganate yields a tricosoic acid, $\text{C}_{23}\text{H}_{46}\text{O}_2$, and not lignoceric acid, $\text{C}_{24}\text{H}_{48}\text{O}_2$, as stated by Levene and Taylor (A., 1922, i, 714). The hydroxy-acid yields pelargonic acid, $\text{C}_9\text{H}_{18}\text{O}_2$ on oxidation with ozone, and on further oxidation of the other products with potassium permanganate, dodecane- α -dicarboxylic acid, $\text{C}_{14}\text{H}_{26}\text{O}_4$, is produced. The unsaturated hydroxy-acid is probably $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}:\text{CH}\cdot[\text{CH}_2]_{12}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ and cerebronic acid is probably $\text{C}_{24}\text{H}_{48}\text{O}_3$ and not $\text{C}_{25}\text{H}_{50}\text{O}_3$ as usually given. There are evidently several fatty acids with C_{21} in cerebrosides and phosphatides. Since kephalin contains acids of the C_{18} series, the fatty acids of brain lipins appear to be multiples of C_6 .

A. WORMALL.

Conversion of pyruvic acid into alanine. AUBEL and BOURGUEL (Compt. rend., 1928, 186, 1844—1846).—The conversion has been effected by stirring pyruvic acid (1 mol.) and ammonia (2 mols.) in an atmosphere of hydrogen for 5—6 days, and employing colloidal palladium stabilised by starch paste as catalyst. Previous attempts with platinum-black proved unsuccessful. The fixation of hydrogen is very slow. On evaporation of the reaction mixture in a vacuum, the catalyst and starch are precipitated by boiling alcohol, the whole being then filtered and evaporated to a small volume. Hot absolute alcohol is again added, followed by ether, which slowly precipitates the alanine in crystalline form. Further purification is effected by adding a concentrated aqueous solution of alanine to boiling absolute alcohol, when a pure, crystalline product is obtained.

J. D. FULTON.

Properties of conjugated compounds. V. Hydrogenation of certain extended heterogeneous systems. J. T. EVANS and E. H. FARMER (J.C.S., 1928, 1644—1650).—Reduction of ethyl

muconate with aluminium amalgam in moist ether yields exclusively the Δ^8 -dihydro-ester (cf. Farmer, J.C.S., 1923, 123, 2531). Crotylideneacetone, by reduction with the same reagent, yields mainly (80%) a substance, b. p. 169—178°/23 mm., which is regarded as 5-acetyl-1-methyl-3:4-dipropenylcyclopentan-1-ol (yielding acetaldehyde on ozonolysis and succinic acid on oxidation with chromic acid), together with an unsaturated pinacol-like substance (not identified). Reduction of sorbic acid with sodium amalgam in glacial acetic acid, or of sodium sorbate in aqueous solution with aluminium amalgam or with sodium amalgam, with or without the passage of carbon dioxide, yields a mixture of Δ^8 - and Δ^7 -dihydrosorbic acids, the proportion of the Δ^7 -acid under the three conditions mentioned being 40, 35, and 30%, respectively. J. W. BAKER.

Colouring matter from saffron. IV. P. KARRER and H. SALOMAN (Helv. Chim. Acta, 1928, 11, 711—713).—The formula for α -crocetin is now deduced to be $C_{17}H_{20}(CO_2H)_2$ (A., 1927, 571; this vol., 644). Hydrogenation of γ -crocetin yields tetradeca-hydro- γ -crocetin, thus demonstrating the presence of seven conjugated double linkings and not eight as previously assumed. α -Crocetin is formulated as $\gamma\gamma\lambda$ -trimethyltetradecaheptaene- $\alpha\alpha'$ -dicarboxylic acid. H. BURTON.

Conjugated unsaturated compounds. VI. Colouring matter from Chinese *Gardenia*. Occurrence of conjugated unsaturated colouring matters in plants. R. KUHN, A. WINTERSTEIN, and W. WIEGAND (Helv. Chim. Acta, 1928, 11, 716—724).—Gardenidin, the colouring matter of *Gardenia grandiflora*, L. (cf. Munesada, A., 1923, i, 77), and α -crocetin (Karrer, preceding abstract) are identical. α -Crocetin has been isolated from the petals of *Crocus luteus*, and is probably identical with nyctanthin (Hill, J.C.S., 1907, 91, 1501; Perkin, *ibid.*, 1912, 101, 1538). α -Crocetin ($\gamma\gamma\lambda$ -trimethyltetradecaheptaene- $\alpha\alpha'$ -dicarboxylic acid) is postulated as being derived from three isoprene residues and 2 mols. of glyoxylic acid, whilst bixin, $C_{25}H_{30}O_4$, m. p. 198° (corr.), is formulated as $\gamma\gamma\lambda\sigma$ -tetramethyloctadecanonaene- $\alpha\alpha'$ -dicarboxylic acid, derived from four isoprene units and 2 mols. of glyoxylic acid. A list of the colour reactions of bixin and gardenidin with various acids is given. H. BURTON.

Physical and chemical properties of bismuth sodium citrate and bismuth sodium tartrate. W. F. VON OETTINGEN, T. SOLLMANN, and H. H. SCHWEID (J. Amer. Pharm. Assoc., 1928, 17, 540—543).—Solutions of bismuth sodium citrate are neutral, are not precipitated by p_H changes within physiological limits, are precipitated by calcium chloride (but stabilised by sodium citrate), and may be sterilised by boiling. Solutions of bismuth sodium tartrate are alkaline (p_H of 10% solution, 8.2—8.4), are precipitated by acidity above p_H 7.6, by many salts, by Locke's solution, by serum, and by heating. E. W. WIGNALL.

Walden inversion. XII. Oxidation of β -thiolvaleric and γ -thiolvaleric acids. P. A. LEVENE and T. MORI (J. Biol. Chem., 1928, 78, 1—22).—The sulphonic acids obtained by oxidation of *l*- β - and *l*- γ -

thiolvaleric acids show the same change in rotation on passing into the salts as do the corresponding thiol-acids; the anomalous behaviour of *l*- β -thiol- and *l*- β -sulpho-butyrac acids in this respect (A., 1926, 1225) remains, therefore, an isolated phenomenon. The present work confirms the hypothesis that substitution of halogen by a hydroxyl or thiol group is accompanied by Walden inversion. *d*- β -Hydroxyvaleronitrile, with thionyl chloride or phosphorus pentachloride, gave *l*- β -chlorovaleronitrile, b. p. 69—70°/10 mm., $[\alpha]_D^{20}$ -10.5° in ether, and, with alcoholic hydrogen chloride, *ethyl l*- β -hydroxyvalerate, b. p. 77—79°/10 mm., $[\alpha]_D^{20}$ -14.7° in ether; the latter ester, with thionyl chloride or phosphorus pentachloride, yielded *ethyl d*- β -chlorovalerate, b. p. 66—67°/10 mm., $[\alpha]_D^{20}$ +6.65°, and, with phosphorus pentabromide, *ethyl d*- β -bromovalerate, $[\alpha]_D^{20}$ +16.1°, which, on hydrolysis with fuming hydrobromic acid in the cold, gave *d*- β -bromovaleric acid, b. p. 117—119°/10 mm., $[\alpha]_D^{20}$ +11.0°, sodium salt $[\alpha]_D^{20}$ +8.5°, both in 35% alcohol. *Ethyl d*- β -bromovalerate, with potassium hydrogen sulphide, gave *ethyl l*- β -thiolvalerate, b. p. 72—76°/10 mm., $[\alpha]_D^{20}$ -5.2° in ether, which, however, could not be hydrolysed; *d*- β -bromovaleric acid yielded *l*- β -thiolvaleric acid, b. p. 112—113°/10 mm., $[\alpha]_D^{20}$ -15.5° (sodium hydrogen salt, $[\alpha]_D^{20}$ -8.75°; sodium salt, $[\alpha]_D^{20}$ -11.2°, all in 20% alcohol); *ethyl l*- β -thiolvalerate, on oxidation, yielded *l*- β -sulphovaleric acid, $[\alpha]_D^{20}$ -7.87° (barium hydrogen salt, $[\alpha]_D^{20}$ -7.16°; barium salt, $[\alpha]_D^{20}$ -5.06°, all in water). *Ethyl l*- γ -chlorovalerate, b. p. 71—73°/9 mm., $[\alpha]_D^{20}$ -19.7° in ether, with potassium hydrogen sulphide, gave a mixture of lactone and ester from which, by hydrolysis with potassium hydroxide, was obtained *d*- γ -thiolvaleric acid, b. p. 121—122°/10 mm., $[\alpha]_D^{20}$ +5.14° (sodium hydrogen salt, $[\alpha]_D^{20}$ +1.56°; sodium salt, $[\alpha]_D^{20}$ +1.36°, all in 20% alcohol). On treatment with dilute sulphuric acid, this acid yielded *l*- γ -thiolvalerolactone, b. p. 69—70°/10 mm., $[\alpha]_D^{20}$ -78.3° in ether, and, on oxidation, *l*- γ -sulphovaleric acid, $[\alpha]_D^{20}$ -1.94° (barium hydrogen salt, $[\alpha]_D^{20}$ -1.31°; barium salt, $[\alpha]_D^{20}$ -1.68°, all in water). C. R. HARRINGTON.

Disulphosuccinic acid. H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1928, 47, 776—781).—When potassium acetylenedicarboxylate is heated at 100° in a sealed tube with 2 mols. of potassium hydrogen sulphite, and the solution treated with hydrochloric acid, an 80% yield of tripotassium hydrogen disulphosuccinate (+1H₂O, decomp. 180°) is obtained. The free acid (+4H₂O), which loses water at 120—130° and decomposes at 163°, yielding carbon dioxide and sulphur dioxide, is probably the $\alpha\alpha'$ -disulpho-acid. The following normal salts are described: potassium (+4H₂O), sodium (+2H₂O), thallium (anhydrous, decomp. 285°; cf. A., 1927, 856), calcium, dehydrated at 190°, barium (+3H₂O, lost at 240—250°), silver, and lead. With silver nitrate the tetrapotassium and tetrasodium salts yield double salts, the composition of which depends on the excess of silver nitrate present. In the preparation of acetylenedicarboxylic acid from dibromosuccinic acid, yields of 92% of the potassium hydrogen salt are obtained if absolute alcohol is used; dibromosuccinic acid is prepared from fumaric acid in 87% yield by the action of bromine (5% excess) in aqueous

solution in sunlight: maleic acid is previously transformed (yield 93%) by treatment with bromine water in sunlight.

R. BRIGHTMAN.

Aldehydes from acetylenic carbinols. II. $\beta\zeta$ -Dimethyloctenaldehyde, β -methyl- β -*tert*-butylacetaldehyde, and experiments with the acetylenic carbinol from acetophenone. H. RUPE and L. GIESLER (Helv. Chim. Acta, 1928, 11, 656—669).—Treatment of methyl isohexyl ketone with sodamide in ether and subsequent reaction of this product with acetylene affords methylisohexylethynylcarbinol, which is converted by hot formic acid (cf. this vol., 640) into a mixture of $\beta\zeta$ -dimethyl- Δ^8 -octenaldehyde (I), b. p. 94°/13 mm. (90%; semicarbazone, m. p. 170°; oxime, b. p. 131—132°/11 mm.; phenylhydrazone), and $\beta\zeta$ -dimethyl- Δ^8 -octenaldehyde, b. p. 98—100°/11 mm. (10%; semicarbazone, m. p. 122°). Oxidation of (I) with alkaline potassium permanganate affords isohexanoic acid (*p*-toluidide, m. p. 61—62), whilst catalytic reduction yields $\beta\zeta$ -dimethyloctenaldehyde, b. p. 78—79°/11 mm. (semicarbazone, m. p. 97°; oxime, b. p. 131—132°/17 mm.). Similar treatment of methyl-*tert*-butylethynylcarbinol (cf. Wouseng, A., 1924, i, 823) gives β -methyl- β -*tert*-butylacetaldehyde, d_4^{20} 0.8822, n_D^{20} 1.46718 [semicarbazone, m. p. 193° (cf. Wouseng, loc. cit.); oxime, b. p. 131°/10 mm.], together with $\gamma\gamma$ -dimethyl- β -methylenevaleraldehyde, b. p. 150° (semicarbazone, m. p. 148—149°). If sodamide is used in the preparation of sodium acetophenone the product of the reaction with acetylene is phenylmethylethynylcarbinol (10%), b. p. 102—103°/12 mm., m. p. 49°, but when sodium is employed the product is acetophenonepinacol. Treatment of the carbinol with formic acid gives a small amount of β -methylcinnamaldehyde, b. p. 122—130°/12 mm. (semicarbazone, m. p. 201°). H. BURTON.

Catalytic hydrogenation of oximes and their conversion into β -hydroxylamines. G. VAVON and M. KRAJČINOVIĆ (Arhiv Hemiju Farm., 1928, 2, 119—127).—See this vol., 398.

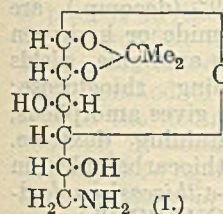
Determination of methylglyoxal in alkaline iodine solution, and the mechanism of the reaction. F. FISCHLER and R. BOETTNER (Z. anal. Chem., 1928, 74, 28—32; cf. A., 1926, 1170).—The ability of methylglyoxal to form iodoform is used as a basis for its determination. The reaction has been expressed by the equation $\text{CH}_3\cdot\text{CO}\cdot\text{CHO} + 3\text{I}_2 + 5\text{KOH} = \text{CHI}_3 + 2\text{H}\cdot\text{CO}_2\text{K} + 3\text{KI} + 3\text{H}_2\text{O}$; the possible formation of oxalic acid is, however, accounted for by a reaction $\text{CH}_3\cdot\text{CO}\cdot\text{CHO} + 4\text{I}_2 + 7\text{OH}^- = \text{CHI}_3 + \text{C}_2\text{O}_4^{2-} + 5\text{I}^- + 5\text{H}_2\text{O}$. A volumetric method was devised to determine the correct relationship of methylglyoxal to iodine. The substance was treated with a known excess of 0.1*N*-potassium iodide solution followed by a known amount of *N*-sodium hydroxide solution, agitated, kept for 30 min., acidified with an amount of *N*-hydrochloric acid equal to 25% in excess of the alkali added, and the excess of iodine was titrated with thiosulphate. The excess of acid remaining was found by back titration using phenolphthalein. The method of calculating the result is explained. The amount of oxalic acid and iodoform produced and the increase in alkalinity indicate that the relationship was $\text{CH}_3\cdot\text{CO}\cdot\text{CHO} = 8\text{I}$. R. A. PRATT.

Polymerisation and condensation. III. Acetocondensation of dihydroxyacetone. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1928, 78, 23—33).—An old sample of dihydroxyacetone was extracted first with a mixture of equal parts of alcohol and ether and then with acetone. The alcohol-ether-soluble portion was distilled up to 110°/0.2 mm., and yielded volatile fatty acids, methylglyoxal, unimolecular dihydroxyacetone, m. p. 82°, and a residue which, on acetylation, yielded diacetyl-dihydroxyacetone and diacetyldihydroxyacetonyldihydroxyacetone, b. p. 138—150°/0.5 mm. The acetone-soluble portion was similarly distilled and gave again unimolecular dihydroxyacetone, together with a residue from which was isolated a substance, $\text{C}_9\text{H}_{14}\text{O}_7$, m. p. 258°. From the insoluble residue was obtained a crystalline substance, $\text{C}_6\text{H}_{10}\text{O}_5$, m. p. 164°. It thus appears that, when kept at the ordinary temperature, dihydroxyacetone undergoes true autocondensation; whether this is preceded by polymerisation remains uncertain. C. R. HARRINGTON.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. II. Ring-chain tautomerism in its relation to the mutarotation of the sugars. J. W. BAKER (J.C.S., 1928, 1583—1593).—Carefully purified specimens of tetra-acetyl- and tetramethyl-glucose which show an arrest of mutarotation (Lowry and Richards, A., 1925, i, 886) in pure ethyl acetate and acetone at 24° and 44° mutarotate rapidly in the fused state under identical aseptic conditions. The effect of structural influences on the velocity of mutarotation of a series of *p*-substituted tetra-acetylglucose anilides, containing the ring-chain tautomeric system $\text{O}=\text{C}\cdot\text{NHR} \rightleftharpoons \text{HO}-\text{C}\cdot\text{NR}$, in ethyl acetate $\text{L}(\text{C}_4)\text{—}$ $\text{L}(\text{C}_4)\text{—}$ containing either hydrochloric or acetic acids as a catalyst at 24° has been studied. As R is varied the unimolecular velocity coefficient (*k*) decreases in the order $\text{C}_6\text{H}_4\text{OMe}(p) > \text{C}_6\text{H}_4\text{Me}(p) > \text{C}_6\text{H}_5 > \text{C}_6\text{H}_4\text{Cl}(p) > \text{C}_6\text{H}_4\text{Br}(p)$. The value of the ratio k/K_b , where K_b is the dissociation constant of the substituted anilide RNH_2 as a base, approximates to a common value. These results are in agreement with the predictions of the electronic interpretation of the ring-chain mechanism of mutarotation (Baker, Ingold, and Thorpe, A., 1924, i, 262), but are opposed to those of an extension of the duplex theory of catalysis suggested by Lowry (A., 1925, i, 886). The mechanism of the action of the catalyst is discussed. The tetra-acetylglucose *p*-substituted anilides are prepared by the action of the appropriate substituted aniline on tetra-acetylglucosidyl bromide and thus are obtained: *p*-toluidide, m. p. 147°, *p*-anisidide, m. p. 129°, *p*-bromoanilide, m. p. 160°, *p*-chloroanilide, m. p. 147°; *N*-methylanilide, m. p. 102°. The last does not exhibit mutarotation even in the presence of acid catalysts. J. W. BAKER.

Acetone [isopropylidene] compounds of sugars and the products of their transformations. IX. Transformation of monoacetoneglucose [glucose isopropylidene ether]. H. OHLE and L. VON VARGHA (Ber., 1928, 61, [B], 1203—1208; cf. A., 1926, 151).—*p*-Toluenesulphonylglucose isopropylidene

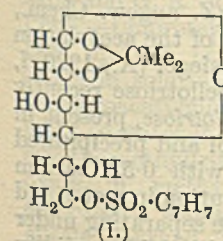
ether, m. p. 108°, readily loses its acyl group under the influence of alkali hydroxide, giving only traces of glucose isopropylidene ether. With methyl-alcoholic ammonia it is transformed into a nitrogen-free, non-crystalline material and a mixture of ammonium *p*-toluenesulphonate and the *p*-toluenesulphonate of ζ -aminoglucose isopropylidene ether, m. p. 176–177° (decomp.), $[\alpha]_D^{20}$ -7.02° in water. The isolation of the last compound is best effected by treating the crude mixture with sodium carbonate, thus giving the carbamate, $C_{19}H_{34}O_{12}N_2[R \cdot CH_2 \cdot NH \cdot CO_2H, NH_2 \cdot CH_2R]$, m. p. 80° (decomp.) when rapidly heated, $[\alpha]_D^{20}$ 0° to -6.25° in water during 2 days, which is subsequently acted on by *p*-toluenesulphonic acid. The amino-sugar is converted by nitrous acid into glucose isopropylidene ether. The carbamate is transformed by dilute sulphuric acid into ζ -amino-*d*-glucose, which yields a non-crystalline carbonate, m. p. 96–98° (decomp.), $[\alpha]_D^{20}$ $+12.5^\circ$ in water, a very hygroscopic *p*-toluenesulphonate, $[\alpha]_D^{20}$ $+31.68^\circ$ in water, and a well-defined picrate, incipient decomp. 140°, $[\alpha]_D^{20}$ $+7.4^\circ$ in water; it is most definitely characterised as the *p*-toluenesulphonate of its phenylhydrazone, m. p. 182–183°, $[\alpha]_D^{20}$ $+6.8^\circ$ to $+1.3^\circ$ in alcohol during 16 hrs. The position of the amino-group follows from the identity of this salt with that prepared from the aminomethylglucoside hydrobromide of



Fischer and Zach (A., 1911, i, 117). The constitution (I) is therefore ascribed to ζ -aminoglucose isopropylidene ether. Since γ -*p*-toluenesulphonylglucose isopropylidene ether is already known, its crystalline isomeride, m. p. 108°, must have the acyl group in position ϵ or ζ , unless it be assumed that the oxygen bridge forms the α and ζ carbon atoms. A decision between these possibilities cannot at present be made.

H. WREN.

Acetone [isopropylidene] compounds of sugars and the products of their transformations. X. New *p*-toluenesulphonylglucose diisopropylidene ether. H. OHLE and L. VON VARGHA (Ber., 1928, 61, [B], 1208–1210; cf. preceding abstract).—Repetition of the work of Ohle and Dickhäuser (A., 1926, 151) shows that *p*-toluenesulphonylglucose isopropylidene ether, if purified by means of toluene instead of light petroleum, does not react with acetone in presence of copper sulphate. If sulphuric acid is used, *p*-toluenesulphonylglucose diisopropylidene ether, m. p. 87°, $[\alpha]_D^{20}$ $+27.1^\circ$ in chloroform, is produced, which differs from the γ -*p*-toluenesulphonyl derivative of Freudenberg and Ivers (A., 1922, i, 523). If

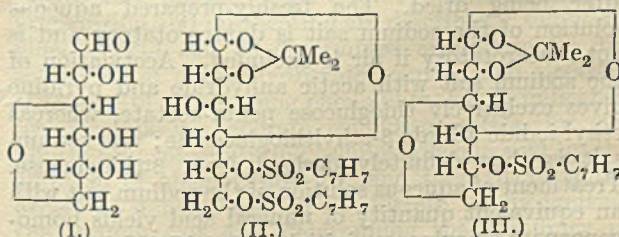


the constitution (I) be assigned to the monoisopropylidene ether, the action of the acid involves the shifting of the oxygen bridge, whereas if the isomeric form with the acyl group attached to the ϵ -carbon atom is adopted, acyl migration must necessarily occur. The compound obtained by Ohle and

bromide in glacial acetic acid is not 6-*p*-toluenesulphonyl-2:3-triacetyl- β -methylglucoside, since it is not identical with the product isolated by Helferich and others (A., 1927, 1174); hydrolysis of it gives ill-defined compounds. There is no evidence to show that hydrogen bromide and glacial acetic acid cause structural changes similar to those produced by sulphuric acid, since the new *p*-toluenesulphonylglucose diisopropylidene ether, when treated with the reagent and subsequently with methyl alcohol and silver carbonate, does not yield *p*-toluenesulphonyltriacyl- β -methylglucoside, m. p. 155°.

H. WREN.

Acetone [isopropylidene] compounds of sugars and the products of their transformations. XI. Conversion of glucose isopropylidene ether into γ -anhydro-*d*-glucose. H. OHLE, L. VON VARGHA, and H. ERLBACH (Ber., 1928, 61, [B], 1211–1216; cf. preceding abstracts).—Di-*p*-toluenesulphonylglucose isopropylidene ether, m. p. 160° (cf. Ohle and Dickhäuser, A., 1926, 151), is converted by treatment with 1 mol. of alkali hydroxide or by restricted treatment with an excess of the reagent into the compound, m. p. 132°, obtained in limited yield by treatment of glucose isopropylidene ether with 3 mols. of *p*-toluenesulphonyl chloride in pyridine at 100° (*loc. cit.*) and erroneously regarded as a third *p*-toluenesulphonylglucose isopropylidene ether. Fresh analyses show the compound to contain 1 mol. of water less than required by theory. It is hydrolysed by alkali hydroxide to anhydro-*d*-glucose isopropylidene ether, m. p. 56–57°, $[\alpha]_D^{20}$ $+29.33^\circ$ in water, from which it is smoothly regenerated by *p*-toluenesulphonyl chloride in pyridine; the corresponding benzoyl compound, m. p. 58–59°, $[\alpha]_D^{20}$ $+22.28^\circ$ in chloroform, and acetyl derivative, b. p. 125–130°/0.05 mm., $[\alpha]_D^{20}$ $+35.7^\circ$ in chloroform, are described. Hydrolysis of anhydro-*d*-glucose isopropylidene ether by acids affords the anhydro-*d*-glucose of Fischer and Zach (A., 1912, i, 678), identified also as the phenylhydrazone and phenylosazone. The production of the anhydro-sugar by this and Fischer's methods leads to the structure (I) (expressed as the aldehydic form). The readily removable *p*-toluenesulphonyl group of di-*p*-toluenesulphonylglucose isopropylidene ether must be present in the ζ -position (II). The constitution (III) is ascribed to the *p*-toluenesulphonylanhydro-*d*-glucose isopropylidene ether. Di-*p*-toluenesulphonylglucose isopropylidene ether behaves towards alcoholic ammonia in much the same manner as towards alkali hydroxide, but in certain circumstances appears to yield an amino-compound in small amount.



The toluenesulphonyl group appears to affect the properties of the sugar residue more deeply than the

benzoyl or acetyl group and to render possible reactions which do not otherwise occur; similar results are to be expected from the biochemically important sulphuric and phosphoric acid residues. H. WREN.

Thio-sugars and their derivatives. XII. Xanthoglucose and its fission to glucothiose [α -thioglucose]. W. SCHNEIDER, R. GILLE, and K. EISFELD (Ber., 1928, 61, [B], 1244—1259; cf. A., 1914, i, 668, 669, 977).—Acetobromoglucose is converted by potassium ethyl xanthate in anhydrous alcohol into *ethylxantho-d-glucose tetra-acetate*, $C_6H_7O_5Ac_4 \cdot S \cdot CS \cdot OEt$, $[\alpha]_D^{20} +30.8^\circ$ in *s*-tetrachloroethane, which also exists in an unstable *modification*, slender needles, lowest observed m. p. $74-76^\circ$, with a somewhat lower specific rotation. It is hydrolysed by a saturated solution of hydrogen chloride in methyl alcohol at 0° to *ethylxantho-d-glucose*, $C_6H_{11}O_5 \cdot S \cdot CS \cdot OEt$, m. p. $92-98^\circ$ after softening at 87° , $[\alpha]_D^{20} -50.5^\circ$ in water (*dihydrate*, m. p. $63-65^\circ$, $[\alpha]_D^{20} -45.4^\circ$ in water). Hydrolysis of the tetra-acetate by ammonia gives α -thioglucose with the properties recorded previously, but invariably containing a low percentage of sulphur; acetylation of the products thus obtained yields only amorphous substances from which thioglucose penta-acetate cannot be isolated, so that mixtures of acetyl derivatives are present. Under certain conditions the acetate of diglucosyl disulphide is obtained; its formation is presumably due to atmospheric oxidation, but even when air is completely excluded the sulphur content of the product remains low. Optical observation of the course of hydrolysis shows the xanthate residue to be considerably more readily removed than the acetyl groups. Thioglucose tetra-acetate must therefore be formed initially; its isolation in substance has not been effected, but acetylation of the product of incomplete hydrolysis affords thioglucose penta-acetate in almost quantitative yield (cf. Schneider and Wrede, A., 1914, i, 977). Hydrolysis of the latter compound by alcoholic ammonia gives products similar to those obtained from the xantho-compound. On the other hand, Zemplén's method affords smoothly the *sodium* compound, $C_6H_{11}O_5 \cdot SNa \cdot 2H_2O$, m. p. $173-174^\circ$ (decomp.) after darkening. The salt is stable in air when dry and unexpectedly stable in aqueous solution in the absence of air. It can be titrated with acid in the presence of methyl-orange but not of phenolphthalein. In aqueous solution it is oxidised slowly by air, or immediately by hydrogen peroxide, to diglucosyl disulphide. The corresponding silver compound, prepared by means of ammoniacal silver acetate, resembles that described previously, but loses its ability to dissolve in water after being dried. The freshly-prepared aqueous solution of the sodium salt is dextrorotatory and is not mutarotatory if air is excluded. Acetylation of the sodium salt with acetic anhydride and pyridine gives exclusively thioglucose penta-acetate, whereas ethyl iodide affords β -ethylthioglucoside; the sodium salt is thus definitely derived from β -thioglucose. Treatment of aqueous solution of the sodium salt with an equivalent quantity of mineral acid yields homogeneous β -thioglucose, initial $[\alpha]_D^{20} +17.62^\circ$ in water. The specific rotation increases slowly during about 10 days, during which sufficient decomposition occurs

to influence the final value even when air is excluded. If a slight excess of mineral acid is used, this decomposition is excluded and the equilibrium value for the α - and β -forms ($[\alpha]_D^{20} +58.4^\circ$ in water) is observed. If the solution is evaporated and the residue acetylated in pyridine, the product can be separated by crystallisation into β -thioglucose penta-acetate and α -thioglucose penta-acetate, m. p. $126-127^\circ$, $[\alpha]_D^{20} +120.2^\circ$ in *s*-tetrachloroethane. It follows therefore that α -thioglucose must have a high, positive specific rotation and hence that sinigrin, which according to Wrede gives an initially laevorotatory thioglucose, cannot be derived from it. The nature of the thioglucose from sinigrin remains unexplained.

H. WREN.

Thio-sugars and their derivatives. XIII. Addition of acetobromoglucose to thiocarbamides; *S*-glucosido- ψ -thiocarbamides. W. SCHNEIDER and K. EISFELD (Ber., 1928, 61, [B], 1260—1263; cf. preceding abstract; Fischer, A., 1914, i, 662; Helferich and Kosche, A., 1926, 273).—Acetobromoglucose reacts with thiocarbamide in boiling toluene yielding *tetra-acetyl-d-glucosido- δ -thiuronium bromide*, $C_6H_7O_5Ac_4 \cdot S \cdot C(NH_2)(NH) \cdot HBr$, m. p. 192° , $[\alpha]_D^{20} -8.72^\circ$ in water; the corresponding, unstable *hydrogen carbonate*, $C_{16}H_{24}O_{12}N_2S$, m. p. 92° (decomp.) after softening at 84° , and the *hydrogen oxalate*, $C_{17}H_{26}O_{13}N_2S$, m. p. 159° (decomp.), are described. Hydrolysis of the bromide or hydrogen carbonate with methyl-alcoholic ammonia yields non-crystalline products containing thioglucose; methyl-alcoholic hydrogen chloride gives amorphous, very hygroscopic materials containing dextrose. Acetobromoglucose and phenylthiocarbamide in boiling benzene afford *phenyl- ψ -thiocarbamido-d-glucose tetra-acetate*, $C_6H_7O_5Ac_4 \cdot S \cdot C(NH_2)(NPh)$, m. p. 150° , $[\alpha]_D^{20} \pm 0^\circ$ in *s*-tetrachloroethane, $[\alpha]_D^{20} +19.15^\circ$ in ethyl acetate (*hydrogen oxalate*, m. p. 146° , $[\alpha]_D^{20} -15.55^\circ$ in 50% alcohol). Hydrolysis by methyl-alcoholic ammonia gives thioglucose, whereas the use of sodium methoxide leads to the sodium derivative of the thio-sugar. The product obtained by use of methyl-alcoholic hydrogen chloride contains notable amounts of the *hydrochloride* of phenyl- ψ -thiocarbamido-*d*-glucose, from which the free glucoside or other of its salts could not be obtained. Acetobromoglucose does not appear to react with thiocarbamide; with allylthiocarbamide it gives amorphous, non-homogeneous products. H. WREN.

Preparation, by sorbose bacteria, of a new reducing sugar with seven carbon atoms. G. BERTRAND and G. NITZBERG (Bull. Soc. chim., 1928, [iv], 43, 663—667).—See this vol., 510.

New isocellotriose. H. Ostr (Z. angew. Chem., 1928, 41, 696—698).—The product of the acetylation of cotton cellulose by Ostr and Prosielgel (A., 1920, i, 423) contains in addition to the cellotriose recently described (A., 1926, 1127) an *isocellotriose*, present in the portion freely soluble in alcohol and precipitated with isocellobiose on hydrolysis with 0.5*N*-barium hydroxide. It is purified by dissolution in water and precipitation with alcohol, the triose separating under these conditions as oily drops which rapidly solidify to a mass having $[\alpha]_D^{20} +15.6^\circ$, reducing power 29

(dextrose 100), ash 0.75%. It contains about 0.5 mol. of water of crystallisation (lost at 115–120°), forms no osazone, has no sweet taste, and is not fermented by yeast. It is only slowly hydrolysed to dextrose by 2.5% hydrochloric acid, conversion being incomplete after 8–10 hrs. and considerable amounts of humic substances formed. Acetylation with acetic anhydride and zinc chloride affords an *undeca-acetate*, m. p. 120–150°, $[\alpha]_D^{20} +2.4^\circ$ (chloroform), which is somewhat more soluble than the similarly prepared *undeca-acetate* of the isomeric cellotriose, m. p. 200–220°, $[\alpha]_D^{20} +2.2$ to 6.2° , the latter being contaminated with a little of the octa-acetates, m. p. 222° and 192°, of the isomeric cellobiose. *isoCellobiose acetate*, m. p. 115–125°, $[\alpha]_D^{20} +4^\circ$ in chloroform, was similarly prepared from *isocellobiose*, being much more readily soluble than the cellobiose octa-acetate, m. p. 220°, which is also formed.

R. BRIGHTMAN.

Konjmannan. T. OHTSUKI (Acta Phytochim., 1928, 4, 1–39).—The carbohydrates present in the mannan prepared from “konjak powder” have been investigated. *d*-Mannose and *d*-glucose are present only in the ratio 2:1, confirming the results of Mayeda (A., 1922, i, 694). The results of Miyake (J. Coll. Agr. Imp. Univ. Hokkaido, 1927, 12, 164), who finds that *lævulose*, *dextrose*, and *mannose* are present in the ratio 1:2:3, are criticised. *Lævulose* is present in the crude “konjak powder,” but not in the purified mannan, whilst the calculations of Miyake are based on the assumption that the hypiodite method of Willstätter and Schudel is applicable to the determination of all aldoses; *mannose*, however, is oxidised to the extent of 59.42% only, and Miyake’s figures when corrected support the view that *lævulose* is absent. By the action of *takadiastase* on *konjakmannan*, a product, “*lævidulinose*,” has been isolated and this is probably identical with Mayeda’s trisaccharide “*lævidulin*” obtained by the action of bacteria on mannan (*loc. cit.*). This trisaccharide contains *mannose* and *dextrose* in the ratio 2:1. The nature of the micelle of the mannan has been studied by heating the substance with anhydrous glycerol at 235° and by acetylation, and the conclusion is reached that *d*-mannose anhydride and *d*-glucose anhydride (in the ratio 2:1) are parent substances of the mannan micelle. The preparation, purification, and the properties of the mannan and the properties of “*lævidulinose*” and of various derivatives formed by liquefaction (by *takadiastase*, dried yeast, and acetylation) and by heat dissociation, are given.

A. WORMALL.

Preparation of glucosides of the α -series. Crystalline α -methylfructoside. H. H. SCHLUBACH and G. A. SCHRÖTER (Ber., 1928, 60, [B], 1216–1222).—Chlorotetra-acetyl-*lævulose* (cf. Brauns, A., 1920, i, 713), $[\alpha]_D^{20} -155.5^\circ$ in chloroform, is more stable in solution but less stable in substance than β' -chloroacetylglucose. On account of its susceptibility to water it cannot be satisfactorily transformed into the methylfructoside by silver carbonate and silver oxide in methyl alcohol, although addition of anhydrous sodium sulphate or copper sulphate effects marked improvement. When its ethereal solution is added to a methyl-alcoholic solution of

silver nitrate in the presence of silver carbonate or, preferably, pyridine (to unite with the liberated nitric acid), silver chloride is immediately and almost quantitatively precipitated and *tetra-acetyl- α -methylfructoside*, m. p. 112°, $[\alpha]_D^{20} +45^\circ$ in chloroform, is obtained. Hydrolysis of the latter compound is best effected with barium hydroxide; crystalline products are obtained with difficulty or not at all when methyl-alcoholic ammonia or sodium methoxide is employed. Crystallisation of α -methylfructoside is difficult, the most suitable solvent being *isobutyl* or *isoamyl* alcohol; the data, m. p. 96–97°, $[\alpha]_D^{20} +44^\circ$ in water, must therefore be regarded as provisional. The adherence of α -methylfructoside to the stable fructose series is established by methylation with methyl sulphate and alkali hydroxide and subsequent hydrolysis of the pentamethylfructoside to $\gamma\delta\epsilon$ -tetramethylfructose.

A satisfactory explanation of the course of the reaction between silver nitrate and alkyl halides in the presence of alcohols cannot yet be given, but the occurrence of a Walden inversion in the case recorded above appears to exclude further the possibility of a double exchange.

H. WREN.

New constitutional formula for cellulose. G. ODDO (Gazzetta, 1928, 58, 301–309).—The suggested formula for cellulose is based on the uniform concatenation of four molecules of *dextrose* with elimination, also uniform, of four molecules of water. The mechanism of the union of the *dextrose* molecules is that already suggested for polysaccharides, and consists in addition of a *dextrose* molecule by means of the alcohol group of the ϵ -carbon atom, as in *cellobiose*, to the aldehydic group of the next molecule, with formation of the alcoholate or semi-acetal, with subsequent closure of the hydrofuran nucleus in the sugar molecule where the addition occurs, by elimination of 1 mol. of water from the α - and δ -carbon atoms. The formula is considered to interpret simply and completely the fundamental facts concerning cellulose and its physical and chemical behaviour.

T. H. POPE.

Acetic ester of cellulose xanthate. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1928, 31, 94–100).—The acetic ester of cellulose xanthate was produced by the treatment of viscose with chloroacetic acid, and its properties and method of analysis are given.

Y. TOMODA.

Metallic complexes of cellulose nitrates. A. APARD (Mém. Poudres, 1928, 23, 63–68).—See this vol., 276.

Celluloseglucolic acid. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1928, 31, 67–73).—Methods of preparation and purification are described. Celluloseglucolic acid can be determined accurately by dissolving it in alkali hydroxide solution and titrating the excess of alkali, using phenolphthalein as indicator, by decomposing sodium celluloseglucolate by sulphuric acid, precipitating celluloseglucolic acid by the addition of alcohol, filtering, and then titrating the excess of mineral acid in the filtrate, or by igniting the sodium salt and determining the alkalinity of the ash. Conductometric titration can also be used, whereas potentiometric titration does not give a sharp

end-point. Celluloseglucolic acid is insoluble in water or organic solvents. Hydrolysis does not occur when the acid is heated with acid and alkali. Its sodium salt is soluble in water and forms a homogeneous solution with viscose. With barium chloride, zinc or copper sulphate, or silver nitrate the corresponding salt was precipitated. Celluloseglucolic acid can be dyed using basic dyes. Y. NAGAI.

Additive compounds of halides of bivalent metals with organic bases. V. G. SCAGLIARINI and E. BRASI (Atti R. Accad. Lincei, 1928, [vi], 7, 411—413; cf. A., 1927, 137).—By the action of mercuric halides on hexamethylenetetramine in acetone solution the following compounds have been obtained: (with excess of the base) $2\text{HgCl}_2 \cdot \text{C}_6\text{H}_{12}\text{N}_4$; $\text{HgBr}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$; $\text{HgI}_2 \cdot \text{C}_6\text{H}_{12}\text{N}_4$, and (with excess of the halide) $3\text{HgCl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$; $\text{HgBr}_2 \cdot \text{C}_6\text{H}_{12}\text{N}_4$, and $3\text{HgI}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ (yellow). O. J. WALKER.

General reaction of amino-acids. H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, 78, 91—105).—On warming α -amino-acids with acetic anhydride and pyridine, carbon dioxide is eliminated and two acetyl groups are introduced, one attaching itself to nitrogen and the other to the α -carbon atom so that the product is an α -acetamido-ketone; the reaction is not confined to amino-acids, since, e.g., phenylacetic acid yields similarly benzyl methyl ketone, and it is thought that, as in the case of the reaction observed by Perkin (J.C.S., 1886, 49, 317), it proceeds through intermediate formation of a β -ketonic acid. Proline, alkylamino-acids, and amino-acids which contain no replaceable hydrogen in the α -position undergo simple acetylation only. Phenylalanine gave acetamidobenzylacetone, m. p. 98—99° (semicarbazone, m. p. 103—104°), tyrosine yielded acetamido-*p*-hydroxybenzylacetone, m. p. 135—136° (O-acetyl derivative, m. p. 123°; semicarbazone, m. p. 230—231°; phenylhydrazine hydrochloride, m. p. 195—197°; picrate, m. p. 125—126°; benzylidene derivative, m. p. 170—180° after sintering). Phenylaminoacetic acid gave α -acetamido- α -phenylacetone, m. p. 103—104°. Leucine gave α -acetamido- α -isobutylacetone (amidoguanidine derivative, m. p. 182—183°). Alanine yielded α -acetamido- α -methylacetone (amidoguanidine derivative, m. p. 183—184°); both glycine and hippuric acid yielded acetamidoacetone, identified by formation of methylglyoxalbisisnitrophenylhydrazine on boiling with *p*-nitrophenylhydrazine in dilute sulphuric acid, and by formation of 2:5-dimethylpyrazine on acid hydrolysis followed by distillation with mercuric chloride and alkali.

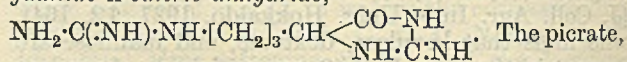
C. R. HARRINGTON.

Separation of the α -amino-acids resulting from the hydrolysis of proteins. G. W. MUEHLEMAN (Diss., Geneva, 1927, No. 817, 5—31).—The amino-acids are benzoylated at a specified alkaline reaction; the by-products include the mixed anhydrides of benzoic and amino-acids, whether benzoylated or not, the anhydrides being readily hydrolysed by sodium ethoxide. Benzoic acid is removed by sublimation. The benzoylated amino-acids are esterified with diazomethane. Separation of the esters by fractional distillation is only approximate. The corresponding benzoylated acids, obtained

by hydrolysis with sodium ethoxide, are more easily purified and identified. CHEMICAL ABSTRACTS.

Amino-acids. V. Synthesis of *N*-alkylglutamic acids. S. SUGASAWA (J. Pharm. Soc. Japan, 1927, [550], 1041—1043; cf. *ibid.*, 1927, [545], 359).—The semialdehyde of succinic acid or its ethyl ester reacts with potassium cyanide and alkylamines in alcoholic solution or their hydrochlorides in aqueous-alcoholic solution, yielding *N*-alkylglutamic acids or their esters. The following individuals are described: *N*-methylglutamic acid, m. p. 156—158° (ethyl ester, b. p. 108—109°/2 mm.); hydrochloride, m. p. 159—160°; *N*-dimethylglutamic acid, m. p. 155—156° (ethyl ester, b. p. 101—103°/0.5 mm.); *N*-ethylglutamic acid, m. p. 159—160° (ethyl ester, b. p. 109—110°/2 mm.).

Transformations of substances resembling peptides. XXV. So-called "arginyllarginine" of E. Fischer, an $\alpha\delta$ -diguano-*n*-valeric anhydride. L. ZERVAS and M. BERGMANN (Ber., 1928, 61, [B], 1195—1203).—The uncertainties regarding the nature of "arginyllarginine" are removed by the observation that it is optically inactive $\alpha\delta$ -diguano-*n*-valeric anhydride,



m. p. 218°, of Fischer and Suzuki (A., 1906, i, 73) is largely and the dinitrate entirely derived from this anhydride. This conception is founded on repeated elementary analysis of the nitrate and the picrate derived therefrom and the absence of nitrogen determinable by the formaldehyde or Van Slyke methods. Secondly, the condensation of *d*-arginine with *S*-ethylisothiocarbamide hydrobromide affords *d*- $\alpha\delta$ -diguano-*n*-valeric anhydride dinitrate, m. p. 189° (corr.), $[\alpha]_D^{20}$ −28.6° in water [corresponding picrate, m. p. 228° (corr.)], which readily suffers racemisation, with formation of a product identical with Fischer's "arginyllarginine dinitrate." In the auto-condensation of arginine ester according to Fischer and Suzuki (*loc. cit.*), the liberation of the ester from its hydrochloride is immediately followed by interaction of the guanido-group of one molecule with the ester group of a second molecule, giving the methyl ester of an arginyllarginine which is too unstable to permit isolation. In the second stage of the change, the peptide guanido-group reacts with the vicinal α -amino-group with ring closure, producing $\alpha\delta$ -diguano-*n*-valeric anhydride and ornithin methyl ester or a closely related product (separated from the mother-liquors of $\alpha\delta$ -diguano-*n*-valeric anhydride picrate as *d*-ornithuric acid). The observations of Kossel and Staudt (this vol., 81) and of Edlbacher and Bonem (A., 1925, i, 863) are based on experiments involving the use of a non-homogeneous picrate, m. p. 218°; when purified through the nitrate, the picrate has m. p. 228°. The unusually ready autoracemisation of *d*- $\alpha\delta$ -diguano-*n*-valeric anhydride is shared by *d*-phenylalanyl-*d*-arginine anhydride (Bergmann and Köster, unpublished work) and appears to be due to the presence of the asymmetric centre in a ring system and the basicity of the guanido-group.

Attempts to condense arginine ester with glycine

ester lead only to a greatly accelerated formation of glycine anhydride.

H. WREN.

Characterisation of the $-OMgX$ group. H. GILMAN and F. SCHULZE (Rec. trav. chim., 1928, 47, 752—760).—To discover a general reagent capable of replacing the $-MgX$ group in compounds of the type $R \cdot O \cdot MgX$ and characterising the $-OMgX$ group by giving a readily identifiable compound (cf. A., 1920, i, 483), a number of reactions of the $R \cdot O \cdot MgX$ compounds have been examined. No general reagent has been discovered, the effectiveness of a given reagent depending also on the type of Grignard reagent used, the nature of the halogen atom, the size of the group R , and the temperature of replacement. The $-OMgCl$ group is replaced more readily than $-OMgBr$, the latter than $-OMgI$, but the magnesium organochlorides are not always accessible. Media of higher b. p. than toluene should not be used and it is suggested than acyl halides or anhydrides or alkyl halides be tried first and then the phenylcarbimide, phenylcarbamine chloride, or phenylcarbamine bromide, which last are highly effective with certain types of $-OMgX$ compounds. Cases in which replacement appears impossible may be due to the use of an insufficiently reactive reagent or the formation of a comparatively unstable product. In these cases the sulphur analogue may be used (cf. A., 1924, i, 382; 1926, 1132), or an organo-metallic compound containing a more positive element, e.g., sodium alkyls or aryls, the reaction being almost certainly parallel to that with the Grignard reagent. Since, however, the $-MgX$ group attached to carbon, nitrogen, and sulphur is readily replaced, failure to replace the $-MgX$ group admits of the conclusion with some confidence that the $-MgX$ group is attached to oxygen.

No appreciable replacement took place in the following cases: benzyl chloride with magnesium phenoxybromide; phenylcarbimide with bromomagnesium benzoate; phenylthiocarbimide with magnesium ethoxyiodide and *n*-butoxyiodide; diphenylcarbamine chloride with magnesium ethoxybromide; chloro- and bromo-acetophenone with magnesium phenoxy-chloride and -bromide; ammonia with magnesium phenoxyiodide; allyl iodide with magnesium *n*-butoxyiodide; ethylene oxide with magnesium *n*-butoxy- and phenoxy-iodide; zinc diethyl with magnesium diphenylmethoxybromide; ethyl sulphate with magnesium phenoxy- and triphenylmethoxy-bromides and with calcium or zinc diphenylmethoxy- and triphenylmethoxy-iodides.

With magnesium triphenylmethoxybromide and acetic anhydride, triphenylcarbinol is the only solid product, the acetate being easily hydrolysed. Benzoic anhydride is the only reagent of those tried which replaces the $-MgBr$ group in magnesium diphenylmethoxybromide, affording 44—50% of benzhydryl benzoate. Benzyl bromide with magnesium diphenylmethoxybromide in cymene at 180° affords in small yield a substance, m. p. 176°, which is not benzyl benzhydryl ether; with the triphenylmethoxybromide in ether and toluene a 50% yield of triphenylmethane is obtained, a 70% yield resulting when the magnesium triphenylmethoxybromide is heated alone, together

with a light brown viscous oil, probably in consequence of the reactions: $CPh_3 \cdot O \cdot MgBr + Et_2O \rightarrow CPh_3 \cdot COEt + EtO \cdot MgBr$; $CPh_3 \cdot COEt \rightarrow CHPh_3 + Me \cdot CHO$ (cf. Gomberg, A., 1913, i, 257; Norris and Young, A., 1925, i, 20). With magnesium phenoxy- or benzyloxy-bromides, benzyl bromide yields only a little distillate of high b. p. Magnesium phenoxybromide and triphenylmethyl chloride in benzene give some *p*-hydroxytetraphenylmethane.

Phenylcarbimide reacts smoothly with $R \cdot O \cdot MgX$ compounds derived from a primary alcohol, but not from *sec.*- or *tert.*-alcohols of high mol. wt. Thus magnesium *n*-butoxybromide gives 80% of *n*-butylphenylcarbamate, magnesium phenoxyiodide, 70% of phenyl phenylcarbamate, and a small amount of a polymeride, m. p. 275° (probably triphenyl isocyanurate), magnesium benzyloxybromide, 70% of benzyl phenylcarbamate, but magnesium diphenylmethoxybromide gives only carbanilide, triphenyl isocyanurate, and unchanged benzhydrol, and the triphenylmethoxybromide only the original carbinol. Phenylthiocarbimide is unreactive.

Phenylcarbamine chloride and magnesium benzyloxybromide in ether give 70% of benzyl phenylcarbamate; magnesium diphenylmethoxybromide appears to react, but only carbanilide and benzhydrol could be isolated. With phenylcarbamine bromide in benzene the result was similar. Carbonyl chloride and magnesium benzyloxybromide in toluene yield a white precipitate, but no urethane on treatment with ammonia (cf. Yoder, A., 1923, i, 309).

Benzoyl bromamide and magnesium phenoxy- or ethoxy-bromide in benzene react vigorously, but only benzamide and benzoylphenylcarbamide can be isolated.

Thionyl chloride and α -chloromethyl ether react with magnesium phenoxybromide in benzene, but no definite products were isolated; diazomethane reacts vigorously, giving anisole and insoluble material.

Bromomethyl ethyl ether and magnesium benzyloxybromide appear to give the benzylethylacetal. Ketene and magnesium phenoxybromide in acetone yield about 15% of phenyl acetate and a little liquid of higher b. p. Phosphorus trichloride and magnesium diphenylmethoxybromide give some diphenylmethyl chloride, but mainly tetraphenylethylene.

Phenyl benzyl ether and magnesium *n*-butoxybromide in benzene or magnesium bromide in ether do not react; in benzene, magnesium bromide yields a little benzyl bromide and liquid of high b. p. The general order of reactivity of the $R \cdot O \cdot MgX$ compounds is the reverse of the order of solubility, the iodides being the most, the chlorides the least soluble. Solubility decreases with increasing size of the alkyl group. Magnesium benzyloxy- and phenoxy-halides have practically the same solubility.

R. BRIGHTMAN.

Action of hypochlorous acid on benzene hydrocarbons. F. W. KLINGSTEDT [with G. WIESE and G. RUDBÄCK] (Acta Acad. Aboensis math. phys., 1927, 4, No. 2, 1—36; Chem. Zentr., 1928, i, 503—505).—Hypochlorous acid yields with benzene α - and β -benzene hexachloride, monochlorobenzene, and a compound, $C_6H_5OCl_4$; with naphthalene naphthalene dichloride and tetrachloride, 1-chloronaphthalene,

and 1:4-dichloronaphthalene; with toluene, *m*- and *p*-xylene, and *p*-isopropyltoluene only monosubstitution products were obtained. With dilute acid substitution is the chief reaction, and with more concentrated acid, addition; also only substitution derivatives are obtained in the dark. Modifications in the course of the reaction are observed when the acid reacts in presence of mercury oxide or oxychloride (cf. Carius and Neuhoﬀ, *Annalen*, 1865, 136, 323, 342).

A. A. ELDRIDGE.

Action of niobium and tantalum pentachlorides on organic compounds. II. H. FUNK and K. NIEDERLÄNDER (*Ber.*, 1928, 61, [B], 1385—1388; cf. this vol., 408).—Under suitable conditions the pentachlorides of niobium and tantalum react with aromatic hydrocarbons evolving hydrogen chloride and leaving intensely coloured, non-crystalline residues which become carbonised when heated, and when decomposed with aqueous ammonia give coloured products in which the organic residue is attached to the metal. It is remarkable that substitution in the nucleus occurs, whereas this does not happen with the more active phenols (*loc. cit.*). Tantalum pentachloride and boiling benzene give the compound $\text{TaCl}_4 \cdot \text{C}_6\text{H}_6$, whereas with niobium pentachloride the substance $3\text{NbCl}_5 \cdot \text{C}_6\text{H}_6$ and, probably, $\text{NbCl}_5 \cdot \text{C}_6\text{H}_6$ and $2\text{NbCl}_5 \cdot \text{C}_6\text{H}_6$ are formed. According to the intensity of the reaction, tantalum pentachloride and naphthalene yield the compounds $\text{TaCl}_5 \cdot \text{C}_{10}\text{H}_8$, $\text{TaCl}_4 \cdot \text{C}_{10}\text{H}_7$, and $\text{TaCl}_3(\text{C}_{10}\text{H}_7)_2$, whereas from niobium pentachloride the substances $\text{NbCl}_4 \cdot \text{C}_{10}\text{H}_7$ and $\text{NbCl}_3(\text{C}_{10}\text{H}_7)_2$ are derived. Tetrahydronaphthalene gives the compounds $\text{TaCl}_4 \cdot \text{C}_{10}\text{H}_{11}$ and $\text{TaCl}_3(\text{C}_{10}\text{H}_{11})_2$. From anthracene the following substances are derived: $\text{TaCl}_5 \cdot \text{C}_{14}\text{H}_{10}$; $\text{TaCl}_4 \cdot \text{C}_{14}\text{H}_9$; $\text{TaCl}_3(\text{C}_{14}\text{H}_9)_2$; $\text{NbCl}_4 \cdot \text{C}_{14}\text{H}_9$. The additive compounds are completely decomposed by aqueous ammonia, giving colourless products. The compounds $\text{NbCl}_4 \cdot \text{C}_{14}\text{H}_9$ and $\text{TaCl}_3(\text{C}_{10}\text{H}_7)_2$ when similarly treated lose the expected quantity of chlorine and give a yellow, halogen-free product which, when evaporated with hydrogen chloride, leaves ammonium chloride in quantity corresponding with 1 mol. of NH_3 for one atom of niobium and two atoms of tantalum.

H. WREN.

Laws of aromatic substitution. VIII. B. FLÜRSCHHEIM and E. L. HOLMES (*J.C.S.*, 1928, 1607—1616).—The nitration of toluene derivatives of the type PhCX_3 , where $\text{X}_3 = \text{H}_2\text{Cl}$, $\text{H}_2(\text{CO}_2\text{Et})$, HCl_2 , $\text{HCl}(\text{CO}_2\text{Et})$, $\text{H}(\text{CO}_2\text{Et})_2$, Cl_3 , $\text{Cl}_2(\text{CO}_2\text{Et})$, $(\text{CO}_2\text{Et})_3$, H_2Br , and $\text{Br}(\text{CO}_2\text{Et})$, with nitric acid (*d* 1.52) at -10° or, in the case of compounds containing a mobile halogen atom, with a mixture of this acid and acetic anhydride at temperatures close to the ordinary, has been investigated. The ratio *m*/(*o*+*p*), determined by oxidation to the corresponding mixture of nitrobenzoic acids which were analysed by the method previously described (this vol., 403), for the above derivatives is, respectively, 13.6 (Holleman, *A.*, 1914, i, 511, found 4.4), 13.6 (Baker and Ingold, *A.*, 1927, 558, found 9.9), 52.25 (Holleman, *loc. cit.*, 51.05), 43.35, 34.05 (Baker and Ingold, *loc. cit.*, 25), 160.1 (Holleman, *loc. cit.*, 181.7), 156.8, 132.6, 130.1, 7.45, and 65.05%. The nature of chemical polarity and

polar effects is discussed from the point of view of the authors' theory of aromatic substitution. *Ethyl phenylmethanetricarboxylate*, b. p. $154-155^\circ/1.5$ mm., is obtained by the action of ethyl chloroformate on dry ethyl phenylsodiummalonate in dry ether for 7 hrs. It is very resistant to both hydrolysis and oxidation, and from the nitrated fraction most resistant to oxidation is isolated *ethyl o-nitrophenylmethanetricarboxylate*, m. p. $83-84^\circ$. *Ethyl phenylchloromalonate*, b. p. $143-144^\circ/2-1.5$ mm., is obtained by saturating a solution of ethyl phenylmalonate in carbon tetrachloride with dry chlorine at 0° and leaving the solution for 16 hrs.

J. W. BAKER.

Nitration of *m*-acetamidobenzotrifluoride. H. ROUCHE (*Bull. Acad. roy. Belge*, 1927, [v], 13, 346—357).—Nitration of *m*-acetamidobenzotrifluoride with a mixture of nitric and sulphuric acids at -5° and subsequent hydrolysis of the acetyl group with sodium hydroxide yields a mixture of (I) 6-nitro-, m. p. 129° (84%), and (II) 4-nitro-, m. p. 101° (6%), *m*-aminobenzotrifluoride. The structure of (I) is proved by reduction with tin and hydrochloric acid to 3:6-diaminobenzotrifluoride, m. p. 58° (sulphate; hydrochloride). This is hydrolysed with 20% hydrochloric acid to 3:6-diaminobenzoic acid, converted by distillation into *m*-phenylenediamine. Deamination of (I) with ethyl nitrite and alcoholic sulphuric acid yields *o*-nitrobenzotrifluoride, b. p. $216.3^\circ/765$ mm., m. p. 32.5° (III), reduced with tin and hydrochloric acid to *o*-aminobenzotrifluoride, b. p. $73^\circ/21$ mm., m. p. -34.7° (anilide, m. p. 94°), which yields successively the corresponding *o*-cyano-derivative, m. p. 7.5° , and phthalic acid. Deamination of (II) yields *p*-nitrobenzotrifluoride, m. p. 41.5° . When nitration of the original substance is effected with acetyl nitrate at -5° the products obtained after hydrolysis are (II) (61%) and 2-nitro-*m*-aminobenzotrifluoride, m. p. 64° (24.7%), which by deamination is converted into (III). Thus the use of acetyl nitrate appears to favour the formation of the vicinal derivative. The results are compared with those of Wender (*A.*, 1890, 884) on the nitration of *m*-nitroacetanilide, and of Kaiser (*A.*, 1886, 149) on *m*-acetamidobenzoic acid. The carboxyl group exhibits a greater tendency to the formation of the vicinal derivative than does the trifluoromethyl group.

J. W. BAKER.

Alkylation and acylation in the presence of titanium tetrachloride. G. STADNIKOV and L. KASCHTANOV (*Ber.*, 1928, 61, [B], 1389—1391).—The action of titanium tetrachloride on a solution of benzyl ethyl ether in boiling benzene yields primarily benzyl chloride which reacts with the benzene, giving diphenylmethane, and *p*- and *m*-dibenzylbenzene. Similar products are obtained when benzyl ethyl ether is replaced by benzyl chloride. *iso*Amyl acetate or benzoate does not react with benzene in presence of titanium tetrachloride, whilst *diiso*amyl ether is unaffected. Benzophenone could not be obtained from benzoyl chloride and benzene in presence of titanium tetrachloride, whereas the benzoyl group is readily introduced into thiophen. Benzene is unaffected by titanium tetrachloride.

H. WREN.

Action of sulphur compounds on 1-chloro-2:4-dinitronaphthalene, 1-chloro-2:4:5-trinitronaphthalene, and 1-chloro-2:4-dinitrobenzene. H. W. TALEN (Rec. trav. chim., 1928, 47, 782—795; cf. this vol., 405).—1-Chloro-2:4-dinitronaphthalene and 1 mol. of sodium sulphide or disulphide in alcohol afford only 2:2':4:4'-tetranitrodinaphthyl sulphide, m. p. 283° (decomp.) (cf. Zincke and Krollpfeiffer, A., 1913, i, 455); with excess of sulphide a small quantity of dark red substance, probably a reduction product, separates. If the sodium sulphide is added rapidly and, after dilution with water, iodine in aqueous potassium iodide is added to the red solution, 2:2':4:4'-tetranitrodinaphthyl disulphide, decomp. 230° after darkening at 225°, is obtained; the 2:4-dinitro- α -thionaphthalene, m. p. 117—118°, may be isolated by acidifying the red solution. With 1 mol. and with 2 mols. of thiocarbamide in alcohol 1-chloro-2:4-dinitronaphthalene yields only 2:2':4:4'-tetranitrodinaphthyl sulphide, the reaction with 1 mol. of sodium xanthate giving in addition a little sodium 2:4-dinitro- α -naphthalate and *ethyl* 2:4-dinitronaphthyl disulphide, m. p. 85°, the formation of the latter substance being in accordance with Weeldenburg's suggestion that in xanthate solutions there is an equilibrium between the isomeric *O*- and *S*-esters. The corresponding disulphide, decomp. 230°, was never produced.

Potassium thiocyanate also yields the monosulphide, m. p. 283° (decomp.), 2:4-dinitronaphthyl thiocyanate, m. p. 116° (decomp.), being obtained in a crude form only by the use of alcoholic ammonium thiocyanate. With alcoholic sodium sulphide or disulphide, 1-chloro-2:4:5-trinitronaphthalene yields only 2:4:5:2':4':5'-hexanitrodinaphthyl sulphide, decomp. 323°. These results are opposed to those obtained with 1-chloro-2:4-dinitrobenzene, the latter affording with 1 mol. of sodium xanthate mainly 2:4:2':4'-tetranitrodiphenyl disulphide with some of the corresponding monosulphide, whilst with 0.5 mol. of sodium xanthate the monosulphide is practically the sole product. Similarly 1 mol. of thiocarbamide affords mainly disulphide and monosulphide in approximately equal amounts; with 0.5 mol. of thiocarbamide the disulphide is the principal product. Thiocarbanilide (1 mol.) and 1-chloro-2:4-dinitrobenzene (2 mols.) yield 2:4-dinitro-1-anilino-benzene and a little tetranitrodiphenyl sulphide, the formation of the sulphide being increased by addition of sodium ethoxide to the acid mother-liquors. With 2 mols. of thiocarbanilide and 1 mol. of 1-chloro-2:4-dinitrobenzene the proportion of sulphide formed is considerably increased. These results confirm the observations of Blanksma (A., 1902, i, 281) that the proportion in which the mono- and di-sulphides are formed from 1-chloro-2:4-dinitrobenzene depends on the proportions of sulphur compounds to the chlorodinitrobenzene present in the reaction mixture.

R. BRIGHTMAN.

Reactivity of halogens in aromatic combination. H. LINDEMANN and A. PABST (Annalen, 1928, 462, 24—46).—A number of experiments have been carried out in order to test some of the theories of the cause of reactivity in halogeno-nitro-compounds

of the benzene series. It is shown that the decomposition of the well-defined additive compound formed between α -naphthylamine and 1-chloro-2:4-dinitrobenzene is not a unimolecular reaction, from which it is concluded that this particular type of additive compound is not a necessary intermediary in the displacement of halogen by the arylamino-group.

Methyl groups have been introduced into the molecule of 1-chloro- or 1-bromo-2:4-dinitrobenzene, in order to test the reality or otherwise of a Flürscheim or Vorländer effect. Thus, 2-halogeno-3:5-dinitrotoluenes should, according to the Flürscheim or Vorländer theories, be less reactive than the corresponding 1-halogeno-2:4-dinitrobenzenes, which should be less reactive than the 5-halogeno-2:4-dinitrotoluenes or the 3-halogeno-2:6-dinitrotoluenes on the same theories. Actually, as is now shown, the 5-halogeno-derivatives (chloro- and bromo-) are less reactive than the corresponding simple halogenodinitrobenzenes, but considerably more reactive than the 2-halogeno-derivatives, whilst the 3-halogeno-derivatives have no reactivity at all when the reactivity is measured, as in the present work, using boiling alcoholic solutions of aniline. Even boiling aniline itself reacts only gradually with 3-halogeno-2:6-dinitrotoluenes. These results are regarded as disproving the validity of the Flürscheim or Vorländer explanations of reactivity causes.

The explanation of reactivity in terms of conjugation effects is considered, and it is concluded that the depressant effects of the methyl groups in the above compounds is due to the disturbance of conjugation by these groups, a conclusion reached as the result of measuring the optical exaltation of the substances concerned. The exaltation of the 5- and 2-chlorodinitrotoluenes is similar in magnitude to that of chlorodinitrobenzene, and much higher than that of the non-reactive 3-chlorodinitrotoluene. The difference in reactivity between *o*- and *p*-chloronitrobenzene can also be explained on the disturbance of conjugation theory.

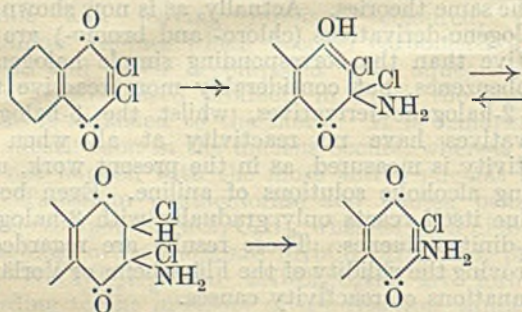
The fact that a methyl group depresses the activating effect of two nitro-groups when it is between the latter explains why 2-bromo-3:5-dinitro-*p*-xylene is non-reactive towards aniline and explains the now observed non-reactivity of 3-halogeno-2:6-dinitro-aceto-*p*-toluidides (below). The non-reactivity of halogen in 3-halogeno-2:6-dinitro-*p*-toluidines (below) is to be expected merely in view of the known depressant effect of amino-groups.

5-Bromo-2:4-dinitrotoluene, m. p. 114°, is obtained by nitrating *m*-bromotoluene. Details are given for the preparation of 3-bromo-*p*-tolunitrile, m. p. 52° (lit., 47°), from 3-bromo-*p*-toluidine. Nitration of the nitrile affords 3-bromo-2:6-dinitro-*p*-tolunitrile, m. p. 165°. 3-Bromo-2:6-dinitro-*p*-toluic acid, m. p. 235°, is best obtained, not by the (difficult) hydrolysis of the above nitrile, but by nitrating 3-bromo-*p*-toluic acid. The acid chloride, m. p. 111°, is converted by sodium azide in aqueous acetone into the corresponding azide, m. p. 101°, which when heated in aqueous acetic acid at 100° passes into 3-bromo-2:6-dinitro-*p*-toluidine, m. p. 170° (acetyl derivative, m. p. 151°; ethylurethane, from the azide and boiling alcohol, m. p. 122°). Elimination of the amino-group

from the toluidine affords 3-bromo-2:6-dinitro-toluene, m. p. 86°.

3-Chloro-2:6-dinitro-*p*-toluic acid, obtained by a method similar to that used for the 3-bromo-analogue, forms a *chloride*, m. p. 106°, convertible into an *azide*, m. p. 97° (decomp.), which when heated in dilute acetic acid at 100° is converted into 3-chloro-2:6-dinitro-*p*-toluidine, m. p. 173° (*acetyl* derivative, m. p. 154°). Deamination of the latter gives 3-chloro-2:6-dinitrotoluene, m. p. 77°.

The depressant action of the amino-group on the additive reactivity of conjugated systems is also shown in the case of 2-chloro-3-amino- α -naphthaquinone, which is readily prepared from 2:3-dichloro- α -naphthaquinone but is itself unaffected by ammonia. The annexed formulæ explain these facts:



In this case acetylation of the amino-group causes reappearance of reactivity on the part of the chlorine atom (Fries and Ochwat, A., 1923, i, 842).

Again, it is known that one chlorine atom in 2:3-dichloroindone is much more reactive than the other. If the present theory is correct, the 3-chlorine atom should be the reactive one (cf. Brass and Mosl, A., 1926, 838), and this is established by the fact that catalytic reduction of the chlorohydroxyindone obtained by the action of alkali on the dichloro-compound affords indane-1:3-dione (cf. annexed formula, showing the conjugation of only one chlorine atom in dichloroindone). E. E. TURNER.

Preparation of dimethylaminodiaryl sulphones. E. GEBAUER-FÜLNEGG and P. SCHWARZ (Ber., 1928, 61, [B], 1307—1308; cf. Bergel and Döring, this vol., 626).—*p*-Dimethylaminophenyl *p*-tolyl sulphone, m. p. 212°, and *p*-dimethylaminodiphenyl sulphone, m. p. 178°, are prepared by heating *p*-toluenesulphonyl chloride or benzenesulphonyl chloride dissolved in carbon disulphide with twice the molar quantity of dimethylaniline and the molar amount of aluminium chloride. H. WREN.

Aromatic compounds containing fluorine.

II. 4:4'-Difluoro-3-aminodiphenyl and 3:4:4'-trifluorodiphenyl. G. SCHIEMANN and E. BOLSTAD (Ber., 1928, 61, [B], 1403—1409; cf. Balz and Schiemann, A., 1927, 654).—Tetrazotisation of benzidine and treatment of the solution with borofluoric acid afford the bisdiazonium borofluoride, decomp. 137—138°, in 95% yield, which is converted by thermal decomposition into 4:4'-difluorodiphenyl, b. p. 115—116°/11 mm., in more than 80% yield. It is not readily nitrated by fuming nitric acid, nitric and

acetic acids, potassium nitrate, or ethyl nitrate, but is converted by nitric acid of *d* 1.4 into 4:4'-difluoro-3-nitrodiphenyl, m. p. 94.6° (corr.), together with ill-defined products. Reduction of the nitro-compound with tin and concentrated hydrochloric acid affords 4:4'-difluoro-3-aminodiphenyl, b. p. 293°/766 mm., 159—160°/13 mm., m. p. 27.5° (corr.) [*acetyl* derivative, m. p. 96.2°; *benzoyl* compound, m. p. 122—123°], which is readily diazotised and then couples with β -naphthylamine, β -naphthol, Schaeffer's acid, *G* and *R* acids, *p*-toluidine, and benzidine. Conversely, the amine couples with tetrazotised benzidine. Treatment of diazotised 4:4'-difluoro-3-aminodiphenyl with borofluoric acid gives 4:4'-difluorodiphenyl-3-diazonium borofluoride, decomp. 88°, which is transformed into 3:4:4'-trifluorodiphenyl, m. p. 88.8°, *d*₄²⁵ 1.43. H. WREN.

Thermal decomposition of nitrites; nitrites of triphenylethylamine and diphenylethylamine. L. HELLERMAN, M. L. COHN, and R. E. HOEN (J. Amer. Chem. Soc., 1928, 50, 1716—1729).— $\beta\beta$ -Triphenylethylamine nitrite (cf. A., 1927, 875) is stable at the ordinary temperature, but decomposes at 128° into triphenylethylene and a little $\beta\beta$ -triphenylethylamine nitrate, decomp. 239°. In hot aqueous solution it gives mainly triphenylethylene. It is suggested that $\beta\beta$ -triphenyldiazoethane is first formed and then decomposed into nitrogen and the free radical, $\text{CPh}_3\cdot\text{CH}_2$, which rearranges to triphenylethylene. A similar mechanism explains the anomalous behaviour of other primary amines with nitrous acid (cf. Freund and Lenze, A., 1891, 1172). Diphenylacetone nitrile is obtained quantitatively from diphenylacetamide and thionyl chloride at 90—105°. A mixture of $\beta\beta$ -diphenylethylamine hydrochloride and sodium nitrite gives $\alpha\beta$ -diphenylethylene when heated at 195° and phenylbenzylcarbinol in hot aqueous solution. In the latter case it is assumed that the radical, $\text{CHPh}_2\cdot\text{CH}_2$, passes into an active form of stilbene, which then combines with water. Since $\beta\beta$ -diphenyldiazoethane, which may be prepared from the oily nitroso-derivative of $\beta\beta$ -diphenylethylurethane (cf. Sieglitz, A., 1922, i, 828) and sodium ethoxide, is probably an intermediate in this reaction, its thermal decomposition has been studied. In acid solution it gives $\alpha\beta$ -diphenylethylene, but when heated alone or in alkaline or neutral solution it gives diphenylacetaldehyde. Further evidence for the intermediate formation in the above reactions of free bivalent radicals is afforded by the oxidation of triphenylammonium nitrite by mercuric oxide at 135° to triphenylacetaldehyde. Similarly, benzoylphenyldiazomethane and moist mercuric oxide give benzil, but no diphenylketen (cf. Schroeter, A., 1909, i, 617). H. E. F. NOTTON.

Velocity measurements of intramolecular changes in arylacylhalogenoamines. (Miss) C. C. J. FONTEIN.—See this vol., 716.

Purification of 3:4-dichloroaniline. A. E. PARMELEE, ASSR. TO E. I. DU PONT DE NEMOURS & Co.—See B., 1928, 474.

Manufacture of water-soluble dinitroarylaminodiarylamines. I. G. FARBERIND. A.-G.—See B., 1928, 516.

Reduction of hydroxyazo-compounds to aminophenols by means of phenylhydrazine. II. 5-Aminosaligenin and its oxidation by phenylhydrazine. G. ODDO and A. GIACALONE (*Gazzetta*, 1928, 58, 290—297; cf. A., 1905, i, 842).—Phenylhydrazine acts on benzenesazosaligenin, both on the azo-group as a reducing agent, giving 5-aminosaligenin, $C_7H_9O_2N$, m. p. 139° (tribenzoyl compound, m. p. 187°), and on the primary alcohol group as an oxidising agent, giving 5-aminosalicylaldehydephenylhydrazone (benzoyl derivative, m. p. 265°).

Benzenesazosaligenin, m. p. 145° (cf. Tummeley, A., 1889, 779), forms a diacetyl compound, m. p. 54°, and a dibenzoyl compound, m. p. 120°.

T. H. POPE.

Rearrangement of toluenediazoaminobenzene in aniline solution. M. FUKAMI and N. YOKOJIMA (*J. Soc. Chem. Ind. Japan*, 1928, 31, 116—117).—The rearrangement of toluenediazoaminobenzene in aniline solution in the presence of aniline hydrochloride results in the formation of 70% of tolueneazoaniline and 30% of aminoazobenzene.

Y. TOMODA.

Diaminotriphenylmethane and similar substances. H. WEIL, E. SAPPER, E. KRÄMER, K. KLÖTER, and H. SELBERG (*Ber.*, 1928, 61, [B], 1294—1307).—The poor yields recorded previously for the preparation of diaminotriphenylmethane from aniline, benzaldehyde, and aniline hydrochloride are due to the use of too large a proportion of the latter reagent, which induces phenylation of the diamino-compound. The aniline compound of diaminotriphenylmethane, m. p. 126°, is remarkably stable, can be crystallised unchanged from alcohol, and loses aniline slowly and incompletely when distilled with steam. When the compound is crystallised from benzene, the aniline is replaced by 1 mol. of benzene; the reverse change can be similarly effected. With various solvents, diaminotriphenylmethane appears to form two types of additive compounds. Thus if the products containing benzene and aniline respectively are dissolved in cold glacial acetic acid and treated with cold acetic anhydride under similar conditions, the diacetyl derivative, m. p. 240—241°, separates quantitatively from the former within 4 hrs., whereas from the latter the production is approximately complete after about 24 hrs. Acetylation is not inhibited when the acetylating mixture is poured into water or dilute hydrochloric acid, but the periodic differences then disappear. Retardation of the activity of the amino-groups in the aniline complex is also observed towards formaldehyde and benzaldehyde, but the differences are less marked than with acetic anhydride. It is, therefore, not surprising that the aniline compound, although containing an additional basic group, is less basic than the aniline-free substance. It is assumed that the affinity of diaminotriphenylmethane towards benzene is due to the accumulation of phenyl groups and towards aniline to the multiplicity of aniline residues. It has not been possible to prepare a compound of leuco-malachite-green and dimethylaniline, although the two compounds are only incompletely separable by distillation with steam. Very distinct indications of the existence of a compound of dimethylaniline and

hexamethyltriaminotriphenylmethane are, however, obtained.

Transitions are observed between the extremes, diaminotriphenylmethane-aniline and leuco-malachite-green-dimethylaniline. Thus 3-chlorodiaminotriphenylmethane ($+1C_6H_6$, m. p. 79°; $+1C_6H_5Me$, m. p. 73—75°) gives a crystalline additive compound with aniline, m. p. 92—93°, which loses the aniline when crystallised from alcohol; substitution of the third nucleus therefore affects the additive power of the other nuclei in marked degree. The following compounds are described: m-nitrodiaminotriphenylmethane, m. p. 157° (also $+1C_6H_6$, m. p. 76°, and $+1NH_2Ph$, m. p. 108°), of which the additive compound with benzene suffers slow acetylation and the diacetyl derivative, m. p. 204° (also $+1AcOH$, m. p. 166° with evolution of acetic acid), retains acetic acid so obstinately that it cannot be completely freed therefrom by crystallisation from alcohol; p-chlorodiaminotriphenylmethane ($+1NH_2Ph$, m. p. 109°; $+1C_6H_6$, m. p. 96—98°); o-hydroxydiaminotriphenylmethane, m. p. 150° ($+1NH_2Ph$, m. p. 125°; $+1C_6H_6$, m. p. 76°); m-hydroxydiaminotriphenylmethane, m. p. 172° (sulphate; $+1NH_2Ph$, m. p. 138°; $+1C_6H_6$, m. p. 106°); diacetyl derivative, m. p. 216°; p-hydroxydiaminotriphenylmethane, m. p. 178° [$+1NH_2Ph$, m. p. 153°; $+1C_6H_6$, m. p. 121°]; diacetyl derivative, m. p. (indef.) 194°, and its sodium salt; acetylation of the hydroxyl group in the foregoing compounds does not take place. Diaminotriphenylmethane forms compounds with aromatic bases which do not contain a substituent in the para-position. Compounds with the following bases are described: o-toluidine, m. p. 130°; m-toluidine; p-toluidine, m. p. 135—137°; m-chloroaniline, m. p. 92°; m-phenylenediamine, m. p. 46·5°; dimethylaniline, m. p. 142·5°; pyridine, m. p. 142°; piperidine, m. p. 112—116°, according to the rate of heating. o-Phenylenediamine, the three nitroanilines, aminobenzoic acid, the naphthylamines, diphenylamine, and benzyaniline do not unite with diaminotriphenylmethane. Similarly, benzene can be replaced by other non-basic substances, thus yielding compounds with the following: toluene, m. p. 100—101°; chlorobenzene, m. p. 108—109°; o-chlorotoluene, m. p. 108—112°, according to the rate of heating; thiophen, m. p. 110° (decomp.) after softening at 86° and second m. p. 139°; phenol, m. p. 110°; o-cresol, m. p. 97—98°. All para-disubstituted compounds, m-chlorotoluene, benzonitrile, diphenyl, benzenesulphonic acid, and nitrated hydrocarbons do not form compounds.

H. WREN.

Chloriodophenols obtained from 5-chloro- and 3:5-dichloro-salicylic acids. P. BRENANS and C. GIROD (*Compt. rend.*, 1928, 186, 1553—1555).—Iodine in the presence of sodium hydroxide reacts with 5-chlorosalicylic acid to afford 4-chloro-2:6-diiodophenol, m. p. 108° (ethyl ether, m. p. 69°; acetyl derivative, m. p. 127·5°). In a similar way 3:5-dichlorosalicylic acid yields 2:4-dichloro-6-iodophenol, m. p. 63° (ethyl ether, b. p. 290—294°; acetyl derivative, m. p. 66°).

G. A. C. GOUGH.

Tri-iodophenol from 5-iodo-, and 3:5-di-iodo-salicylic acid. P. BRENANS and C. GIROD

(Compt. rend., 1928, 186, 1851—1852).—To 5-iodosalicylic acid (A., 1923, i, 797) in very dilute aqueous sodium hydroxide (sodium carbonate gives smaller yields) is added a solution of iodine in potassium iodide. The solution is partly decolorised and after 1 hr. excess of dilute sulphuric acid is added and excess of iodine is removed by sulphur dioxide. The white precipitate is purified through its soluble barium salt. Tri-iodophenol has m. p. 157° (cf. A., 1901, i, 322, 643). Excess of hydrochloric acid added to the barium salt yielded another substance, m. p. 140° and above. 3:5-Di-iodosalicylic acid is similarly converted by iodine (1 mol.) into 2:4:6-tri-iodophenol. Using 2 mols. of iodine and 4 mols. of sodium hydroxide a red substance, $C_6H_4OI_2$, was obtained.

J. D. FULTON.

Action of light on colouring matters containing the nitro-group. A. SEYEWETZ and D. MOUNIER (Bull. Soc. chim., 1928, [iv], 43, 648—654).—See this vol., 167.

Reactions of activated magnesium. A. P. TERENTIEV and A. RUBINSTEIN (J. Russ. Phys. Chem. Soc., 1928, 60, 95—101).—*o*-Anisidine reacts with activated magnesium, analogously to other aromatic amines, forming the magnesium aniside with liberation of hydrogen, the former substance giving with carbon dioxide the corresponding carbamate. This salt when heated at 250—270° decomposes with formation of the aniside of 3-amino-2-methoxybenzoic acid, which on hydrolysis with alkalis gives 3-amino-2-methoxybenzoic acid. A. RATCLIFFE.

Mechanism of the reaction between pyrocatechol and phosphorus trichloride. L. ANSCHÜTZ and W. BROEGER (Ber., 1928, 61, [B], 1264—1267).—The initial product of the action of phosphorus trichloride on pyrocatechol is phosphorus pyrocatechyl monochloride, $C_6H_4\langle O \rangle PCl$, b. p. 80°/10 mm., which yields successively *o*-hydroxyphenyl *o*-phenylene phosphite, $C_6H_4\langle O \rangle P \cdot O \cdot C_6H_4 \cdot OH$, b. p. 155°/12 mm., m. p. 112—113°, and *o*-phenylene phosphite, $(C_6H_4)_3(PO_3)_2$, b. p. 242—248°/14 mm.; the three compounds can be isolated when reaction is effected in boiling benzene. *o*-Phenylene phosphite is obtained from *o*-hydroxyphenyl *o*-phenylene phosphite and phosphorus pyrocatechyl monochloride at 120°, whilst the latter compound results from *o*-phenylene phosphite and phosphorus trichloride at 160° in a sealed tube. The *thiochloride*, $C_6H_4\langle O \rangle PSCL$, b. p. 106°/1 mm., m. p. 49—50°, is obtained from the monochloride and sulphur at 195°. H. WREN.

Action of nitrosodimethylaniline on unsaturated compounds. A. QUILICO (Gazzetta, 1928, 50, 317—325; cf. Bruni and Geiger, A., 1927, 1080).—When mixed in equimolecular proportions, safrole and nitrosodimethylaniline do not react in the cold, but at 120° violent reaction occurs, with formation of azo-dimethylaniline (cf. Lippmann and Lange, A., 1881, 161) and a highly stable Schiff's base, $CH_2O_2 \cdot C_6H_3 \cdot CH \cdot CH \cdot CH \cdot N \cdot C_6H_4 \cdot NMe_2$, m. p. 160°, which yields piperonylic acid and a small proportion of an unidentified acid when treated with alkaline

permanganate; dissolves readily in mineral and acetic acids to deep red solutions; with dilute sulphuric acid gives a red salt, $C_{18}H_{18}O_2N_2 \cdot 2H_2SO_4$; gives piperonyl-acetaldehyde (cf. Ladenburg and Scholtz, A., 1895, i, 42) when boiled with sulphuric acid; yields a mixture of two isomeric oximes, $CH_2O_2 \cdot C_6H_3 \cdot CH \cdot CH \cdot N \cdot OH$, and dimethyl-*p*-phenylenediamine when treated with hydroxylamine; and may be obtained also by the interaction of piperonyl-acetaldehyde and dimethyl-*p*-phenylenediamine in alcoholic solution. The mechanism of the reaction is discussed. T. H. POPE.

Introduction of thiocyno-groups into organic compounds. I. G. FARBERIND. A.-G., ASSEES. OF H. P. KAUFMANN.—See B., 1928, 516.

Benzyl chloromethyl ether and dibenzylformal. P. CARRÉ (Compt. rend., 1928, 186, 1629—1630).—When benzyl alcohol is treated with excess of formaldehyde in presence of hydrogen chloride (cf. Hill and Keach, A., 1926, 271), there are formed in addition to benzyl chloromethyl ether, some benzyl chloride and dibenzylformal, $CH_2(O \cdot CH_2Ph)_2$. This last compound is produced also by heating a mixture of benzyl alcohol and benzyl chloromethyl ether. When dibenzylformal is heated at 330° (cf. Delépine, A., 1900, i, 164), formaldehyde, toluene, and benzaldehyde are formed. H. BURTON.

Oxidation of alcohols by means of phenylhydrazine. G. ODDO and A. GIACALONE (Gazzetta, 1928, 58, 298—300).—The formation of phenyl-osazones from phenylhydrazine and monosaccharides represents the only known instance of oxidation by means of phenylhydrazine, with partial conversion of the latter into aniline and ammonia. The results now described show that 5-aminosaligenin, saligenin, benzyl alcohol, and cinnamyl alcohol are readily oxidised by phenylhydrazine with formation of the phenylhydrazones of the corresponding aldehydes.

T. H. POPE.

Mobile anion tautomerism. II. Mechanism of anionotropic change, with special reference to the fate of the mobile anion. H. BURTON (J.C.S., 1928, 1650—1657; cf. Burton and Ingold, this vol., 634).—The possible fate of the mobile anion X (=Br, OAc, OH) in the anionotropic system $R \cdot CHX \cdot CH \cdot CHR' \rightleftharpoons R \cdot CH \cdot CH \cdot CHXR'$ is discussed. Two chief alternatives are proposed: (I) the simultaneous elimination of X at one end of the molecule and introduction of its equivalent, e.g., from HX, at the other end, or (II) the elimination of X^- in combination with a catalyst and its subsequent return to an electromeric cation. In the latter case four possibilities are suggested, since X^- might take part in covalent interaction or molecular association with the catalyst and dissociation of the anion and cation might occur or not. The hypotheses were tested in the case of the conversion of α -phenylallyl *p*-nitrobenzoate into cinnamyl *p*-nitrobenzoate (cf. *loc. cit.*). Weak or strong acids did not catalyse the change. Isomerisation took place smoothly in acetic anhydride. The possibility of a mechanism in which *p*-nitrobenzoic-acetic anhydride reacted with cinnamyl acetate was excluded by an experiment in which use of the mixed anhydride yielded a mixture of esters, and by the absence of double decomposition between the acetate

and the mixed anhydride. Benzonitrile, of similar dielectric constant to acetic anhydride, but with less tendency to form covalent compounds, was an equally good catalyst. Isomerisation occurred smoothly in chlorobenzene (dielectric constant 11). In *p*-xylene slow isomerisation occurred, attributed to the effect of products of decomposition. In acetic anhydride with an equivalent of tetramethylammonium acetate, the product was a mixture of cinnamyl acetate and *p*-nitrobenzoate. It is concluded that X^{\ominus} undergoes ionic dissociation dependent on the dielectric constant of the solvent, and probably combines electrostatically with it.

α -*p*-Chlorophenylallyl alcohol, b. p. 122–123°/10 mm., was prepared from *p*-chloriodobenzene and acetaldehyde by the Grignard reaction. The *p*-nitrobenzoate, m. p. 81–82°, was accompanied by a substance, m. p. 170°. The conversion of the alcohol into *p*-chlorocinnamyl alcohol, m. p. 56–58° (*p*-nitrobenzoate, m. p. 130–131°), by way of the acetate, b. p. about 155°/11 mm., by acetic anhydride, is described. *p*-Chlorocinnamyl bromide, m. p. 62–63°, was obtained from either alcohol with hydrobromic acid. α -*m*-Tolylallyl alcohol, b. p. 115–117°/11 mm. (*p*-nitrobenzoate, m. p. 53°), which yielded 3-methylcinnamyl alcohol, b. p. 137–140°/11 mm. (*p*-nitrobenzoate, m. p. 63–64°), by way of the acetate, b. p. about 145°/13 mm., is described, and the bromide, b. p. 138–140°/11 mm., derived from it. R. K. CALLOW.

Comparative stability of different isomerides according to their absorption spectra. Rearrangements in α -aryl- β -phenyl- β -ethylbutan- α -ols. (MME.) RAMART-LUCAS and ANAGNOSTOPOULOS (Compt. rend., 1928, 186, 1626–1629).—When alcohols of the type $CPhEt_2CHArOH$, are dehydrated by passing the vapour over kieselguhr at 300–350° under reduced pressure, unsaturated hydrocarbons of the form $CPhAr.CEt_2$, are obtained, whilst at 400–450°, the products have the general formula $CPhEt.CEtAr$. The absorption curves of the latter hydrocarbons are situated nearer the visible region than those of the former. The following compounds are described: *p*-tolyl α -phenyl- α -ethylpropyl ketone, m. p. 86°, b. p. 205°/15 mm. (oxime, m. p. 205°; semicarbazone, m. p. 169°); anisyl α -phenyl- α -ethylpropyl ketone, m. p. 56°, b. p. 222°/15 mm. (oxime, m. p. 180°); *p*-tolyl α -phenylpropyl ketone, m. p. 35°, b. p. 185°/11 mm. (semicarbazone, m. p. 161°); anisyl α -phenylpropyl ketone, m. p. 45°, b. p. 215–220°/20 mm. (oxime, m. p. 154°; semicarbazone, m. p. 118°); $\alpha\beta$ -diphenyl- β -ethylbutan- α -ol, b. p. 209°/20 mm. (phenylcarbimide derivative, m. p. 166°); β -phenyl- α -anisyl- β -ethylbutan- α -ol, b. p. 234°/20 mm. (phenylcarbimide derivative, m. p. 122°); $\alpha\alpha$ -diphenyl- β -ethylbutan- α -ol, b. p. 186°/15 mm.; δ -phenyl- γ -*p*-tolylhexan- γ -ol, b. p. 190°/15 mm.; $\alpha\alpha$ -diphenyl- β -ethyl- Δ^a -butylene, b. p. 160°/11 mm.; α -phenyl- α -*p*-tolyl- β -ethyl- Δ^a -butylene, b. p. 172°/11 mm.; α -phenyl- α -anisyl- β -ethyl- Δ^a -butylene, b. p. 190°/11 mm.; $\gamma\delta$ -diphenyl- Δ^a -hexene, b. p. 168°/14 mm.; δ -phenyl- γ -*p*-tolyl- Δ^a -hexene, b. p. 170°/11 mm., and δ -phenyl- γ -anisylhexene, b. p. 204°/12 mm. H. BURTON.

Degradation of high-molecular unsaturated acids. Degradation of chaulmoogric acid to

homohydnocarpylamine. Modified Curtius reaction. C. NÄGELI and G. STEFANOVITSCH (Helv. Chim. Acta, 1928, 11, 609–656).—Chaulmoogryl chloride reacts with excess of hydrazine hydrate to form the secondary hydrazide, $C_{36}H_{64}O_2N_2$, m. p. 127°, of chaulmoogric acid, although under regulated conditions the primary hydrazide (I), $C_{18}H_{34}ON_2$, m. p. 92°, $[\alpha]_D^{25}$ in chloroform +28.34° (hydrochloride, decomp. 130° after previous sintering; benzoyl derivative, m. p. 114°; benzylidene derivative, m. p. 89.5–91°; salicylidene derivative, m. p. 109°), is obtained also. Ethyl chaulmoograte and hydrazine hydrate react under various conditions, yielding a mixture of (I) and 4-amino-3:5-dihomohydnocarpyl-1:2:4-triazole, m. p. 132–133°, $[\alpha]_D^{25}$ in chloroform +21.54°. This last compound is formed when (I) is heated at 160° for 5 hrs., and does not form condensation products with aldehydes. When (I) is converted into the azide, and this is treated with alcohol, ethyl homohydnocarpylcarbamate (II), m. p. 48.5°, $[\alpha]_D^{25}$ in chloroform +47.62°, is obtained. This is hydrolysed by concentrated hydrochloric acid at 100° to homohydnocarpylamine, decomp. 90–120° (hydrochloride, decomp. 160°, $[\alpha]_D^{25}$ in alcohol +54.9°; picrate, m. p. 112°; chloroplatinate), also formed by the action of heat on a mixture of *s*-dihomohydnocarpylcarbamide (III), m. p. 113.5°, $[\alpha]_D^{25}$ in chloroform +54.96°, and moist calcium hydroxide. When chaulmoogryl chloride is treated with sodium azide in ether, and the product decomposed by boiling alcohol, (II) is the main product together with a small amount of (III). If the decomposition is carried out with water (III) is the sole product. Treatment of a methyl-alcoholic solution of chaulmoogramide with aqueous sodium hypochlorite (cf. Rinkes, A., 1927, 45) gives a substance, m. p. 81.5°, having the composition of methyl homohydnocarpylcarbamate, but showing an abnormally high mol. wt. in camphor. H. BURTON.

Action of sulphuric acid on aromatic acids: sulphonated aromatic acids. J. B. SENDERENS and J. ABOULENC (Compt. rend., 1928, 186, 1497–1499).—*m*-Sulphobenzoic acid may be prepared by heating benzoic acid at 200–210° with sulphuric acid of *d* 1.84, which readily sulphonates the toluic acids at 150–160°, or better with fuming sulphuric acid (20% SO_3) at 200°. *p*-Sulphophthalic acid is best prepared from phthalic anhydride by sulphonation with excess of fuming sulphuric acid at 215°. Sulphuric acid of *d* 1.84 decomposes phenylacetic acid at 180° without effecting sulphonation. Similar decompositions occur together with partial sulphonation by treatment with the fuming acid in the cold. G. A. C. GOUGH.

Sodium salts of aromatic nitriles. I. M. M. RISING and T.-W. ZEE (J. Amer. Chem. Soc., 1928, 50, 1699–1707).—Further evidence (cf. A., 1927, 359; this vol., 638) for the existence of the tautomeric forms, $CRPh.C'NNa$ (I), and $CRPh(CN)Na$ (II), of the sodio-derivatives of aromatic nitriles is discussed. These react in form (I) with acids, and in form (II) with acyl or alkyl halides. Thus yellow, amorphous sodio-phenylacetone nitrile gives with 50% sulphuric acid, 49% of the theoretical amount of hydrogen cyanide and 52% of benzyl alcohol. Sodio- α -phenylbutyronitrile gives, similarly, 100% of hydrogen cyanide and

69% of $\gamma\delta$ -diphenyl- Δ^7 -hexene. These reactions are ascribed to the formation from (I) of the free radical, CRPh \cdot , which then combines with itself or with water. These sodio-derivatives behave analogously to ethyl sodioacetacetate and are probably present as intermediates in the aldol-type condensation of 2 mols. of a nitrile in presence of sodium (von Meyer, A., 1895, i, 582). H. E. F. NOTTON.

Oxidative degradation of carboxylic acids. S. SKRAUP and E. SCHWAMBERGER (Annalen, 1928, 462, 135—158).—An investigation designed to discover whether oxidation of acids in an homologous series shows periodicity as regards type of degradation, periodicity being known to occur in other similar cases. A number of acids have been oxidised at 100° with alkaline permanganate, using the latter in amount corresponding with 3 atoms of oxygen per 1 mol. of acid (in some cases less permanganate).

Phenylacetic acid (1 mol.) gives 0.28 mol. of benzoic acid and, usually, some benzoylformic acid (permanganate added to acid) with 10 and 0.89 mol. of benzoic acid with 30. Mandelic acid is not an intermediate stage in the oxidation, since it undergoes oxidation to benzoylformic acid, which is more stable towards permanganate than phenylacetic acid itself (slow oxidation, 10 giving benzoic acid, 0.74 mol.).

When permanganate is added slowly to benzoylacetic acid dissolved in potassium carbonate, steam being introduced at the same time, benzoic and oxalic acids are the main products, only traces of benzoylformic acid and acetophenone being formed. When the solution of the acid is slowly added to the permanganate, benzoic acid and benzoylformic acid are the chief products, together with traces of oxalic acid. The former oxidation is presumably that of the enolic form of benzoylacetic acid, the latter that of the keto-form. In the latter case carbon dioxide loss on the part of the keto-form produces acetophenone, which is then oxidised to benzoylformic acid (giving benzoic acid in turn). Since the oxidation of β -phenylpropionic acid gives benzoylformic, but no oxalic acid, oxidation probably occurs in accordance with the scheme $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{COPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{COPh}\cdot\text{Me} \rightarrow \text{COPh}\cdot\text{CO}_2\text{H} \rightarrow \text{Ph}\cdot\text{CO}_2\text{H}$. Accompanying this β -oxidation is almost certainly some α -oxidation: $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$. In any case, neither cinnamic acid nor phenylglyceric acid is formed during the oxidation of β -phenylpropionic acid, since both of these acids are oxidised to benzaldehyde and oxalic acid, neither of which is produced in the oxidation referred to.

The oxidation of γ -phenylbutyric acid to benzoic and benzoylformic acids and of δ -phenylvaleric acid to benzoic and oxalic acids is not readily interpretable. Investigation of the oxidation of β -benzoylpropionic and γ -benzoylpyruvic acids throws no light on the problem, since these acids do not give malonic and succinic acids, respectively, when oxidised, but benzoic, and benzoic and oxalic acids, respectively.

β -Phenylpropionic acid is only slowly oxidised; similarly, β -*p*-tolylpropionic acid is readily oxidisable only to β -*p*-carboxyphenylpropionic acid. On the other hand, γ -phenylbutyric acid (prepared by

heating the *hydrazone-anhydride*, m. p. 153°, of β -benzoylpropionic acid with alcoholic sodium ethoxide at 160—170°) and δ -phenylvaleric acid (obtained by Skita reduction of cinnamylideneacetic acid; cf. Staudinger and Müller, A., 1923, i, 363) are readily oxidised.

Chlorobenzene and succinic anhydride condense in presence of aluminium chloride to give β -*p*-chlorobenzoylpropionic acid, m. p. 131°, the *hydrazone-anhydride*, m. p. 178°, of which may be converted into γ -*p*-chlorophenylbutyric acid, m. p. 62°, b. p. 185°/12 mm. Reduction of β -*p*-chlorobenzoylpropionic acid affords γ -*p*-chlorophenylbutyrolactone, b. p. 140—150°/1—2 mm. or 210°/15 mm.

n-Valeric, *n*-hexoic, *n*-heptoic, and *n*-octoic acids give only oxalic acid when oxidised under the present conditions. Suberic and azelaic acid show no appreciable difference in behaviour, such as might have been expected with two acids of even and odd carbon content, respectively. Both give oxalic acid as the only oxidation product. Neither fatty-aromatic nor fatty acids, therefore, exhibit periodicity as regards oxidation under the conditions now employed.

In extension of work done by Skraup and Nieten (A., 1924, i, 1185), *phenyl margarate*, m. p. 37°, b. p. 240—250°/11 mm. (decomp.), obtained from the acid by the thionyl chloride method, was heated for 72 hrs. at 328° in a sealed tube. The products are phenol and *n*-tetradecane, m. p. 5°, b. p. 130°/15 mm., some ester being recovered. Thus, since phenyl palmitate and stearate decompose, respectively, to give *n*-tridecane and *n*-pentadecane, no periodicity appears in such reactions either.

A general method is suggested for the preparation of straight-chain carboxylic acids, viz., by the oxidative degradation of the next higher homologue. Thus, methyl stearate is converted by magnesium phenyl bromide into diphenylheptadecylcarbinol, $\text{C}_{17}\text{H}_{35}\cdot\text{CPh}_2\cdot\text{OH}$, which without being purified is distilled under diminished pressure. The distillate (repeated distillation for pure product) contains a 75% yield of $\alpha\alpha$ -diphenyl- Δ^8 -octadecene, m. p. about -1°, b. p. 282—283°/18 mm., and this substance, when oxidised with chromic anhydride in dilute acetic acid, affords margaric acid (40 g. per 100 g. of stearic acid originally used).

Similarly, from methyl palmitate, $\alpha\alpha$ -diphenyl- Δ^6 -hexadecene, m. p. 17—18°, b. p. 265—270°/13 mm., and pentadecoic acid, b. p. 220—240°/15 mm., are obtained (25 g. of last-named acid from 100 g. of palmitic acid). Methyl oleate gives rise to $\alpha\alpha$ -diphenyl- Δ^8 -octadecadiene, $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_6\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_6\cdot\text{CH}\cdot\text{CPh}_2$, b. p. 285—286°/15 mm., oxidised to Δ^7 -heptadecenoic acid, m. p. -1°, b. p. 226—227°/20 mm. The latter acid is reduced (Skita method) to margaric acid, does not undergo the oleic-elaidic acid change (nitrous fumes) smoothly, and is oxidised by hydrogen peroxide in acetic acid (Hilditch, A., 1926, 938) to $\eta\delta$ -dihydroxymargaric acid, m. p. 94°. Methyl Δ^7 -heptadecenoate, b. p. 195°/15 mm., when oxidised by the method of Armstrong and Hilditch gives pelargonic and suberic acids (proof of constitution as a Δ^7 -acid). The new degradative method affords a possible means of determining the constitution of an acid which is

otherwise difficult to deal with. Two examples are chosen: (1) *cyclohexylacetic acid* is converted into its methyl ester (b. p. 105°/20 mm.), and the latter by means of the Grignard reagent into α -*diphenyl- β -cyclohexylethylene*, $C_6H_{11} \cdot CH : CPh_2$, b. p. 210—215°/15 mm., which on oxidation gives *cyclohexanecarboxylic acid*. (2) 4-Methylcyclohexanecarboxylic acid is esterified and then converted into 1-methyl-4-diphenylmethylenecyclohexane, $C_7H_{13} \cdot CPh_2$, b. p. 200°/12 mm., m. p. 65°, which is oxidised to 4-methylcyclohexanone. E. E. TURNER.

Isomeric 2-amino- α -arylcinnamic acids. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1928, 1478—1486).—2-Amino-3:4:2':5'-tetramethoxy- α -phenylcinnamic acid is found to exist in two interconvertible isomeric forms similar to those of 2-amino- α -phenylcinnamic acid (Pschorr, A., 1896, i, 303; Stoermer and Prigge, A., 1915, i, 683). The form *A* (+0.5H₂O), m. p. 219°, is colourless and sparingly soluble, whilst the form *B*, m. p. 167°, is yellow. In camphor solution, *A* is bimolecular and *B* unimolecular. Both are associated in azobenzene, but *A* has twice the mol. wt. of *B*. Both are unimolecular in acetic acid. In acid or alkaline solutions the form *B* predominates, and is precipitated by sodium acetate or acetic acid, respectively. The form *B* is converted into the form *A* fairly rapidly in azobenzene or benzene. The solid form *A* is produced also by sudden addition of the calculated amount of acetic acid to a solution in dilute ammonia of either form, and appears to be the stable form in neutral solution.

The acids were synthesised as follows: 2:5-dimethoxybenzaldehyde, prepared by introducing the aldehydo-group into *p*-dimethoxybenzene by the method of Adams and Levine (A., 1924, i, 860; cf. this vol., 654), was condensed with hippuric acid, yielding the azlactone, 5-keto-2-phenyl-4-(2':5'-dimethoxybenzylidene)-4:5-dihydro-oxazole, m. p. 170—172°, which yielded on hydrolysis with dilute acid or alkali α -benzamido-2:5-dimethoxycinnamic acid, m. p. 195—196°, or, on prolonged alkaline hydrolysis, 2:5-dimethoxyphenylpyruvic acid, m. p. 166—170° (decomp.), which yielded with *o*-phenylenediamine 3-hydroxy-2':5'-dimethoxy-2-benzylquinoxaline, m. p. 179—180° (+0.5EtOH). Oxidation of the pyruvic acid yielded 2:5-dimethoxyphenylacetic acid, the sodium salt of which, condensed with 2-nitroveratraldehyde, yielded *trans*-2-nitro-3:4:2':5'-tetramethoxy- α -phenylcinnamic acid, m. p. 204°, accompanied by *trans*-2-nitro-3:4-dimethoxycinnamic acid. By reduction with ferrous sulphate and ammonia, the reaction product being just acidified with acetic acid, a mixture of the forms *A* and *B* of the amino-acid was obtained. The form *A* separated from the alcoholic solution of the mixture, and the form *B* was found in the mother-liquors, the proportion of *B* to *A* increasing with the amount of acetic acid used in the precipitation. Either form yielded, on boiling the methylalcoholic solution of the diazonium sulphate, 3:4:5:8-tetramethoxyphenanthrene-9-carboxylic acid, m. p. 190—198°, which yielded 3:4:5:8-tetramethoxyphenanthrene, m. p. 118—120° (picrate, m. p. 158°).

cis-2-Nitro-3:4:2':5'-tetramethoxy- α -phenylcinnamic acid, m. p. 186°, was obtained by exposure of the sodium salt of the *trans*-acid to ultra-violet light, and on reduction yielded a solution from which acid precipitated 7:8:2':5'-tetramethoxy-3-phenylcarbostyryl, m. p. 189°. The same carbostyryl was formed from the *trans*-amino-acids, either by exposing an alcoholic solution of form *B* to ultra-violet light, or by heating either *A* or *B* with acetic anhydride and a trace of sulphuric acid. R. K. CALLOW.

Amides of thio- and dithio-salicylic acid. A. REISSERT and E. MANUS (Ber., 1928, 61, [B], 1308—1316).—Dithiosalicylic acid is converted successively into the chloride, m. p. 153°, and amide, m. p. 239°; the anilide, m. p. 243°, and methylamide, m. p. 216.5°, are described. The amide is converted by 2*N*-sodium hydroxide into benzoisothiazolone,

$C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown S \end{array} NH$, m. p. 158° (sodium salt), dithiosalicylamide, and thiosalicylamide (*o*-thiobenzamide).

The primary action therefore yields the compounds $NH_2 \cdot CO \cdot C_6H_4 \cdot SNa$ and $NH_2 \cdot CO \cdot C_6H_4 \cdot S \cdot ONa$, the latter of which immediately loses water with closure of the ring. Dithiosalicylanilide and 33% sodium hydroxide afford thiosalicylanilide, m. p. 110°, and, probably, the corresponding sulphinic acid. Benzoisothiazolone is most conveniently prepared by the successive action of bromine in carbon tetrachloride and boiling glacial acetic acid on dithiosalicylamide; 2-phenylbenzoisothiazolone, m. p. 143—144°, and 2-methylbenzoisothiazolone, m. p. 54° [hydrochloride, m. p. 130° (decomp.)], are analogously prepared. The silver salt of benzoisothiazolone is converted by methyl iodide into a mixture of 3-methoxybenzoisothiazole and 2-methylbenzoisothiazolone, m. p. 54°, separated by taking advantage of the volatility of the former and non-volatility of the latter with steam. Oxidation of the benzoisothiazolones with hydrogen peroxide affords the corresponding saccharins. Benzoisothiazolone is transformed by benzoyl chloride into its *N*-benzoyl derivative, m. p. 167°, converted by treatment with sodium hydroxide in acetone followed by oxidation of the product with air into *di-N*-benzoylbenzamide *oo'*-disulphide, $[NHBz \cdot CO \cdot C_6H_4 \cdot S]_2$, m. p. 191°, identical with that derived from dithiosalicylamide and 2 mols. of benzoyl chloride. Thiosalicylamide (*o*-thiolbenzamide), m. p. 140°, and thiosalicylanilide, m. p. 110°, are obtained by reduction of the corresponding dithio-compounds with zinc dust and dilute hydrochloric acid. *S*-Benzoylthiosalicylamide, $NH_2 \cdot CO \cdot C_6H_4 \cdot SBz$, m. p. 135°, is obtained when the dry sodium salt of thiosalicylamide is treated with benzoyl chloride in boiling benzene. Benzoylation of dithiosalicylamide by the Schotten-Baumann method affords a mixture of *N*-benzoylbenzoisothiazolone and *N*-benzoylthiosalicylamide formed by isomerisation from the primary *S*-derivative; when 2 mols. of the chloride are used for 1 mol. of the amide the compound cannot be isolated, but its formation is established by the oxidative production of the corresponding disulphide, $[NHBz \cdot CO \cdot C_6H_4 \cdot S]_2$. If benzoylation is effected by an excess of benzoyl chloride and sodium hydroxide, the *dibenzoyl* derivative,

NHBz·CO·C₆H₄·SBz, m. p. 138°, and the tribenzoyl compound, NBz₃·CO·C₆H₄·SBz, m. p. 220—222°, are obtained. The latter substance is converted into the former by boiling glacial acetic acid. Treatment of thiosalicylanilide with an excess of benzoyl chloride affords *S*-benzoylthiosalicylanilide, m. p. 140°, and *NS*-dibenzoylthiosalicylanilide, m. p. 164°.

H. WREN.

Synthesis of tropic acid. M. CHAMBON (Compt. rend., 1928, 186, 1630—1631).—When ethyl phenylbromoacetate is treated with trioxymethylene and zinc filings in presence of benzene, and the resulting product hydrolysed with alcoholic barium hydroxide, tropic acid, m. p. 118°, is obtained in 50% yield.

H. BURTON.

Optical activity and polarity of substituent groups. IX. Menthyl esters of methoxynaphthoic and of diphenyl-2-carboxylic acids. E. BRETSCHER, H. G. RULE, and J. SPENOE (J.C.S., 1928, 1493—1504; cf. this vol., 765).—When their rotatory powers are compared with those of benzoates, there is found to be a lowering in the case of 1-naphthoates and a marked increase in the case of 2-naphthoates, consistent with the former being regarded as 2:3-substituted benzoates with an *o*-directive group in the 2-position and the latter as 3:4-substituted benzoates. The introduction of the methoxyl group has an effect on the naphthoates similar to that on the benzoates. Menthyl 1- and 3-methoxy-2-naphthoates show a depression in rotatory power, less marked in the former, possibly owing to a screening effect. Of the 1-naphthoates, menthyl 2-methoxy-1-naphthoate shows the maximum effect, the rotatory power being reversed in sign. A marked diminution is found in the 8-methoxy-1-naphthoate, suggesting that the effect of *o*-substituents is transmitted through space and not through the carbon chain. In the 4-position the rotatory power is raised; in the 5-position it is unaffected. In menthyl 2'-methoxydiphenyl-2-carboxylate the methoxyl group increases the rotation on account of its general polar effect, whilst in the unsubstituted ester the phenyl group has the usual depressant effect of an *o*-*p*-directive substituent.

2-Methoxy-1-naphthoic acid, m. p. 176°, was prepared from 1-bromo-2-methoxynaphthalene by reaction with magnesium and carbon dioxide. The menthyl ester, m. p. 122—123°, was prepared from the acid chloride and menthol in presence of pyridine. 4-Methoxy-1-naphthoic acid was obtained by oxidation of the aldehyde (from α -naphthyl methyl ether by Gattermann's reaction) and yielded a chloride, b. p. 210—215°/15 mm., and menthyl ester, m. p. 114—115°. Methylation of 1:8-naphtholactone yielded methyl 8-methoxy-1-naphthoate, m. p. 51—52°, and the acid, m. p. 162—163° (corr.). The menthyl ester, m. p. 96—96·5°, was obtained by esterification at 120° in the presence of hydrogen chloride. Menthyl 5-methoxy-1-naphthoate, m. p. 90·3°, menthyl diphenyl-2-carboxylate, b. p. 175°/0·4 mm., and menthyl 2'-methoxydiphenyl-2-carboxylate, b. p. 171—173°/0·3 mm., are also described. The values of $[M]^{20}$ for the menthyl esters at different wavelengths and in different solvents are tabulated.

R. K. CALLOW.

Constitution of phenolphthalein. I. Preparation of compounds of phthalein type. H. LUND (J.C.S., 1928, 1569—1575).—Condensation of phloroglucinol trimethyl ether with terephthalaldehydic acid under the influence of hydrogen chloride yielded 2':4':6':2'':4'':6''-hexamethoxytriphenylmethane-4-carboxylic acid, m. p. 258—260° (corr.), which was converted by oxidation with lead tetra-acetate in acetic acid into 4-carboxy-2':4':6':2'':4'':6''-hexamethoxytriphenylcarbinyl acetate, violet (perchlorate, decomp. on heating). The carbinol acid and its anhydride were unstable. Condensation of phloroglucinol trimethyl ether with *o*-phthalaldehydic acid yielded only 2':4':6'-trimethoxyphenylphthalide, m. p. 200° (corr.). Phthalyl chloride and phloroglucinol trimethyl ether in the presence of zinc chloride yielded phloroglucinolphthalein hexamethyl ether, m. p. 175—176° (corr.), colourless, but violet in dilute hydrochloric acid. This readily split off a molecule of phloroglucinol trimethyl ether on treatment with acid. Esterification and hydrolysis yielded 2':4':6'-trimethoxybenzoyl-*o*-benzoic acid, m. p. 184—185° (corr.). Resorcinolphthalein tetramethyl ether, m. p. 153° (corr.), colourless, reddish-violet in hydrochloric acid, was prepared by a new method of condensation, the action of sulphuric acid in anhydrous ether, from 2':4'-dimethoxybenzoyl-*o*-benzoic acid and resorcinol dimethyl ether. Phenolphthalein monomethyl ether (+0·5C₇H₇, from toluene) was obtained by the action of methyl sulphate on phenolphthalein and also by condensing 4'-methoxybenzoyl-*o*-benzoic acid with phenol in anhydrous ether and sulphuric acid. Resorcinolphthalein 2':4'-dimethyl ether, m. p. 220° (corr.), was prepared in the same way from 4'-hydroxybenzoyl-*o*-benzoic acid and resorcinol dimethylether. Phloroglucinolphthalein 2':4':6'-trimethyl ether, m. p. 200° (corr.), was obtained similarly from phloroglucinol trimethyl ether.

The phenol group in the phthaleins

$\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}\cdot\text{CR}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, where R is a methoxy-substituted phenyl group, displayed an increasing acidity with increasing substitution in R. The

phthaleins of the type $\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}\cdot\text{R}_2$ showed increasing basicity with increasing methoxy-substitution in the two groups R. R. K. CALLOW.

Iodo-derivatives of phthaleins. F. R. GREENBAUM (Amer. J. Pharm., 1928, 100, 374—384).—Halogenated phthaleins used in cholecystography are found on intravenous injection to be highly toxic. A high iodine content is essential to render the drugs efficient. A number of new iodo-derivatives of various phthaleins, and xanthen derivatives, have been prepared. 1:2:3:4-Tetraiodophenolphthalein, prepared by heating tetraiodophthalic anhydride (1 mol.), phenol (2 mols.), and stannic chloride (2 mols.) at 200°, is amorphous, soluble in alkalis with a pink to red colour which disappears on further addition of alkali. It is iodinated by iodine in sodium hydroxide solution at the b. p. to octaiodophenolphthalein, yellow, and is readily soluble in dilute alkalis with a pale green colour. Dinitrophenolphthalein iodinated as above yielded di-iododinitrophenol-

phthalein, yellow, m. p. 249—250°, giving an orange colour in sodium hydroxide. Dinitrofluorescein yielded *di-iododinitrofluorescein*, orange-red, dissolving in sodium hydroxide with a blue colour. *m-Cresolphthalein* is yellowish-brown, and dissolves with a purple colour in dilute sodium hydroxide. On iodination in alkaline solution by iodine in potassium iodide followed by acidification with hydrochloric acid, *di-iodo-m-cresolphthalein*, brown, m. p. 214°, is obtained; it is only slightly soluble in dilute sodium hydroxide. Rhodamine-*B* from diethyl-*m*-aminophenol and phthalic anhydride, treated with iodine in potassium iodide gives a *monoiodo*-derivative and with iodine trichloride and hydrochloric acid a reddish-brown *di-iodo*-derivative, insoluble in dilute alkalis. Thymolphthalphthalein gave a *monoiodo*-derivative soluble in dilute alkalis with a blue colour.

J. D. FULTON.

Configuration of polymethylenedicarboxylic acids. III. *cis-cyclobutane-1:2-dicarboxylic acid*. R. KUHN and A. WASSERMANN (Helv. Chim. Acta, 1928, 11, 600—609).—Thermal decomposition of *cyclobutane-1:1:2:2-tetracarboxylic acid* gives a mixture of *cis*- and *trans-cyclobutane-1:2-dicarboxylic acids*, having m. p. 97—98° and 130° (uncorr.), respectively (cf. Perkin, J.C.S., 1887, 51, 25; 1894, 65, 583). The mixture is separated by dissolution in concentrated hydrochloric acid, in which solvent the *cis*-acid is more soluble. When the *cis*-acid is heated with concentrated hydrochloric acid at 190°, it is converted into the *trans*-form. The two dissociation constants, K_1 and K_2 , of the *cis*- and *trans*-acids have been determined in water and 50% methyl alcohol. The values for the ratio K_1/K_2 for the *cis*- and *trans*-acids in water are 98 and 66, and in 50% methyl alcohol 186 and 140, respectively. H. BURTON.

Condensation of ketones with ethyl acetoacetate. L. G. JUPP, G. A. R. KON, and E. H. LOCKTON (J.C.S., 1928, 1638—1644).—Condensation of *cyclohexanone* with ethyl acetoacetate by the method of Merling and Welde (A., 1909, i, 479) yielded only *cyclohexenylcyclohexanone*. With ethyl sodioacetoacetate the desired *ethyl Δ^1 -cyclohexenylacetoacetate*, b. p. 135°/20 mm. (*semicarbazone*, m. p. 141°), was obtained only in minute amount. The chief product was the *acid*, m. p. 121° (decomp.) (*semicarbazone*, m. p. 196°), accompanied by *cyclohexenylcyclohexanone* and an equilibrium mixture of *cyclohexylideneacetone* and *Δ^1 -cyclohexenylacetone* (cf. this vol., 887). Addition of water to the reaction mixture after 24 hrs. furnished a method of preparation of the last. The action of heat on *Δ^1 -cyclohexenylacetoacetic acid* yielded a mixture of *cyclohexylideneacetone* and *Δ^1 -cyclohexenylacetone* containing the former in great excess of the equilibrium quantity. The acid could not be esterified. The silver salt and methyl iodide yielded a substance, $C_{10}H_{14}O_3$, m. p. 177°. Methyl-alcoholic hydrogen chloride yielded an isomeric substance, m. p. 80°. An attempt to prepare the desired ester from ethyl sodio*cyclohexenylmalonate* and acetyl chloride yielded *ethyl Δ^1 -cyclohexenylacetylmalonate*, b. p. 181°/19 mm. (*semicarbazone*, m. p. 178°), and other methods

hexenylacetone; conversion of ethyl *cyclohexenylmalonate* into the acid-chloride-ester and reaction with zinc methyl iodide; condensation of *cyclohexenylacetone* and sodium ethoxide) also failed.

Condensation of *cyclopentanone* with ethyl sodioacetoacetate yielded *cyclopentylidenecyclopentanone* and a minute amount of *cyclopentylideneacetoacetic acid*, m. p. 137° (decomp.). Pulegone and ethyl sodioacetoacetate yielded *Δ^1 -pulegenylacetone*, b. p. 149—153°/21 mm. (cf. Barbier, A., 1899, i, 299) (*semicarbazone*, m. p. 187°), the structure of which was demonstrated by the formation of acetone and α -methylglutaric acid by ozonolysis. The ketone yielded with sodium and methyl iodide *α -methyl- Δ^1 -pulegenylacetone*, b. p. 150°/21 mm., d_{4}^{20} 0.94694, n_D^{20} 1.49347, $[R_L]_D$ 64.39 (*semicarbazone*, m. p. 191°), and with ethyl sodiomalonate a *dihydroresorcinol* derivative, m. p. 130°. Piperitone and ethyl sodioacetoacetate yielded a *ketone*, b. p. 155°/20 mm., d_{4}^{20} 0.95821, n_D^{20} 1.49610, $[R_L]_D$ 60.59 (*semicarbazone*, m. p. 217°), probably of analogous structure. Ethyl isopropylidenecetoacetate, b. p. 103°/18 mm., d_{4}^{20} 0.96308, n_D^{20} 1.45583, $[R_L]_D$ 46.52 (*semicarbazone*, m. p. 247°), could not be methylated with the aid of sodium powder, and the methylated ester decomposed in the presence of alcohol, giving ethyl trimethylacrylate, d_{4}^{20} 0.97812, n_D^{20} 1.45802, $[R_L]_D$ 41.02, the structure of which was confirmed by ozonolysis, acetone being obtained. R. K. CALLOW.

Methyl phthalate and other esters of *o*-phthalic acid. J. A. HANDY and L. F. HOYT (J. Amer. Pharm. Assoc., 1928, 17, 458—461).—The chemical, physical, and pharmacological properties of some commercial esters of *o*-phthalic acid, especially the methyl ester, are compared with those of ethyl phthalate.

E. H. SHARPLES.

Action of phosphorus pentachloride on homophthalic acid. W. DAVIES and H. G. POOLE (J.C.S., 1928, 1616—1620).—A method is described for preparing homophthalic acid in quantity by the oxidation of tetrahydronaphthalene with potassium permanganate (cf. von Braun, A., 1924, i, 48; Cornillot, A., 1927, 1069), and reduction of the phthalonic acid by hydriodic acid and red phosphorus. Homophthalyl chloride could not be prepared from the acid or the anhydride. When homophthalic anhydride was heated with phosphorus pentachloride (2.2 mols.) in excess of phosphoryl chloride, a smooth reaction occurred, yielding 3-chloroisocoumarin, m. p. 98.5—99°, b. p. 150°/5 mm. The anhydride reacts in the enolic form, the existence of which in solution is demonstrated by production of a coloration with ferric chloride under strictly specified conditions (cf. Dieckmann, A., 1914, i, 690). 3-Chloroisocoumarin is stable towards neutral or acid hydrolytic agents. From the product of reaction with ammonia in benzene *o*-carboxyphenylacetone nitrile, m. p. 126°, was isolated. It reacts with aniline to yield *homophthalanilide*, m. p. 231.5°, and dissolves in sodium hydroxide to a yellow solution which reduces permanganate and yields homophthalic acid on acidification or boiling. When homophthalic acid is heated with phosphorus pentachloride and phosphoryl chloride, 3:3:4:4-tetrachloro-3:4-dihydroisocoumarin, m. p.

122°, is obtained, which reacts with aniline to produce a chlorine-free *anilide*, m. p. 225°. The chlorine atoms are remarkably inert, and hydrolysis in boiling aqueous-alcoholic sodium hydroxide, which yielded phthalonic acid (*compound*, m. p. 239°, with *p*-nitrophenylhydrazine), was very slow.

R. K. CALLOW.

Action of dibromotetracarboxylic esters on sodium derivatives of ethyl malonate, ethyl ethanetetracarboxylate, and analogous substances. J. J. LENNON and W. H. PERKIN, jun. (J.C.S., 1928, 1513—1526).—Compounds of the type of $\alpha\gamma$ -dibromopropane- $\alpha\gamma\gamma$ -tetracarboxylic esters (Perkin and Prentice, J.C.S., 1891, 69, 822; cf. Gregory and Perkin, *ibid.*, 1903, 83, 782; 1905, 87, 358) react with sodium derivatives intramolecularly rather than intermolecularly, yielding, in this case, with ethyl sodiomalonate, ethyl cyclopentane-1:1:2:2-tetracarboxylate and ethyl ethanetetracarboxylate. A number of reactions of this type have now been investigated. Ethyl dibromomalonate and ethyl disodioethanetetracarboxylate interact in alcoholic solution with formation of ethyl ethylene-tetracarboxylate in good yield. Ethyl $\alpha\gamma$ -dibromopropane- $\alpha\gamma\gamma$ -tetracarboxylate, m. p. 55°, and ethyl sodiomalonate yield ethyl cyclopropane-1:1:2:2-tetracarboxylate and ethyl ethanetetracarboxylate. Ethyl $\alpha\gamma$ -dibromopropane- $\alpha\gamma\gamma$ -tetracarboxylate and ethyl disodioethanetetracarboxylate yield ethyl cyclopropane-1:1:2:2-tetracarboxylate and ethyl ethylene-tetracarboxylate. Ethyl $\alpha\delta$ -dibromobutane- $\alpha\delta\delta$ -tetracarboxylate, m. p. 83—85°, and ethyl sodiomalonate yield ethyl ethanetetracarboxylate and ethyl cyclobutane-1:1:2:2-tetracarboxylate, *cis*-cyclobutane-1:2-dicarboxylic anhydride, b. p. 165—170°/20 mm., m. p. 71—73° (acid, m. p. 136—138°), being isolated after hydrolysis. Ethyl $\alpha\delta$ -dibromobutane- $\alpha\delta\delta$ -tetracarboxylate and ethyl disodioethanetetracarboxylate yield ethyl cyclobutane-1:1:2:2-tetracarboxylate and ethyl ethylene-tetracarboxylate. Ethyl $\alpha\delta$ -dibromobutane- $\alpha\delta\delta$ -tetracarboxylate and ethyl disodiobutane- $\alpha\delta\delta$ -tetracarboxylate yield ethyl cyclobutane-1:1:2:2-tetracarboxylate alone.

The mechanism of these reactions is discussed. An intramolecular reaction, where possible, will always be favoured in comparison with an intermolecular reaction. In this case the substances are of the type of bromomalonate esters, $\text{CRBr}(\text{CO}_2\text{Et})_2$, in which the bromine is "avid of electrons" and capable of substituting itself for hydrogen in suitably reactive molecules. The above reactions are considered to consist in rapid bromination of substituted sodiomalonate esters by substituted bromomalonate esters. There then follows, on the one hand, double decomposition of the normal type, and, on the other, intramolecular condensation.

Experiments were made to confirm these views. Ethyl $\alpha\gamma$ -dibromopropane- $\alpha\gamma\gamma$ -tetracarboxylate brominated boiling phenol, and the product, on hydrolysis, yielded *propane- $\alpha\gamma\gamma$ -tricarboxylic acid*, m. p. 125°, which lost carbon dioxide at 150—160°, yielding glutaric acid. Ethyl $\alpha\delta$ -dibromobutane- $\alpha\delta\delta$ -tetracarboxylate yielded similarly ethyl butane- $\alpha\delta\delta$ -tetracarboxylate, which gave adipic acid on

hydrolysis. Ethyl $\alpha\gamma$ -dibromopropane- $\alpha\gamma\gamma$ -tetracarboxylate in alcohol with β -naphthol and sodium ethoxide yielded a product in large amount from which *cyclopropane-1:1:2:2-tetracarboxylic acid*, m. p. 210—212° (effervescence), was obtained by hydrolysis.

The abnormal behaviour of ethyl $\alpha\epsilon$ -disodiopentane- $\alpha\gamma\gamma\epsilon\epsilon$ -hexacarboxylate previously noted (Bottomley and Perkin, J.C.S., 1900, 77, 298) again occurs in reaction with ethyl $\alpha\beta$ -dibromopropionate, when it yields ethyl cyclopentanepentacarboxylate (identified by conversion into *trans*-cyclopentane-1:2:4-tricarboxylic acid), and ethyl paramethylenemalonate. The first stage of this reaction is probably decomposition into ethyl paramethylenemalonate and ethyl disodiopropane- $\alpha\gamma\gamma$ -tetracarboxylate, and the latter then reacts with the ethyl $\alpha\beta$ -dibromopropionate.

R. K. CALLOW.

2:3-, 2:5-, 2:6-, and 3:5-Dibromophenylhydrazines, *p*-bromophenylmethylhydrazine and their derivatives with aldehydes and ketones. E. VOTOČEK and R. LUKEŠ (Chem. Listy, 1928, 22, 217—225).—The following 2:5-dibromophenylhydrazones were prepared: acetone, m. p. 73°, benzaldehyde, m. p. 79°, furfuraldehyde, m. p. 104°, arabinose, m. p. 170—175°, rhamnose, m. p. 184°, galactose, m. p. 207°, and the corresponding glucosazone, m. p. 228—229°. The following 3:5-dibromophenylhydrazones were prepared: acetone, m. p. 85—86°, benzaldehyde, m. p. 106—107°, furfuraldehyde, m. p. 116°, and dextrose, m. p. 172°. 2:3-Dibromophenylhydrazine, m. p. 112° (*benzylidene* derivative, m. p. 106°), and 2:6-dibromophenylhydrazine, m. p. 110° (*benzylidene* derivative, m. p. 51—52°; *furfurylidene* derivative, m. p. 62°), were prepared. *as*-*p*-Bromophenylmethylhydrazine, m. p. 33°, was prepared by bromination of phenylmethylhydrazine, and also, in order to establish the position of the bromine atom, from *p*-bromoaniline, by way of *p*-bromophenylmethylnitrosoamine, m. p. 74°; the corresponding hydrazone of benzaldehyde, m. p. 106—107°, and the osazone of *lævulose*, m. p. 153°, were prepared. The above bromohydrazones are in no way better for the identification of sugars than those commonly used.

R. TRUSZKOWSKI.

Behaviour of vanillin towards alkali sulphites and hydrogen sulphites. G. ROMEO and F. PIRRONÉ (Annali Chim. Appl., 1928, 18, 189—193).—Vanillin behaves abnormally towards sulphites and hydrogen sulphites, and when the authors' method for determining aldehydes is applied to it (B., 1925, 970), the standard sulphite solution undergoes, not a diminution, but an increase in acidity corresponding with one equivalent per mol. of vanillin. Probably the aldehyde group first reacts with formation of a sulphonate, the sodium atom then migrating from the sulphonate group to the phenolic hydroxyl with formation of a readily hydrolysable hydrosulphonic acid. Thus, with sodium hydrogen sulphite, the reactions would be: $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO} + \text{NaHSO}_3 \rightarrow$
 $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{SO}_3\text{Na} \rightarrow$
 $\text{ONa}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{SO}_3\text{H} \rightarrow$
 $\text{ONa}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO} + \text{H}_2\text{SO}_3$, and with sodium sulphite, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow$
 $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{SO}_3\text{Na} + \text{NaOH} \rightarrow$
 $\text{ONa}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO} + \text{NaHSO}_3 + \text{H}_2\text{O}.$

T. H. POPE.

Action of diazomethane on piperonal. E. MOSETTIG (Ber., 1928, 61, [B], 1391—1395).—Piperonal is converted by diazomethane in presence of methyl alcohol into a mixture of piperonylacetone (semicarbazone, m. p. 163—165°), acetyl piperone, m. p. 87—88.5° (semicarbazone, m. p. 239—240°), and, mainly, a pleasant-smelling liquid, $C_{10}H_{10}O_3$, b. p. 140—143°/9 mm., possibly α -3:4-methylene-dioxyphenylpropane α -oxide, which does not possess ketonic properties. If the reaction is effected in ethereal solution, the main product is acetyl piperone, whilst the substance $C_{10}H_{10}O_3$ is formed only in minimal amount.

H. WREN.

Three-carbon system. XVII. cyclohexylideneacetone and cyclohexylidenemethyl ethyl ketone. A. H. DICKINS, W. E. HUGH, and G. A. R. KON (J.C.S., 1928, 1630—1638).—The reaction of cyclohexylideneacetyl chloride with zinc ethyl iodide and decomposition of the product with ice and carbon dioxide yielded cyclohexylidenemethyl ethyl ketone (I), which was purified by distillation and conversion into the semicarbazone, m. p. 191° (cf. Kon and Narayanan, A., 1927, 878). The regenerated ketone had b. p. 112°/22 mm., d_4^{25} 0.93810, n_D^{25} 1.48945, $[R_L]_D$ 46.82. Occasionally a (possibly stereoisomeric) semicarbazone, m. p. 167°, yielding the same ketone, was produced. By the action of zinc ethyl iodide on Δ^1 -cyclohexenylacetyl chloride, Δ^1 -cyclohexenylmethyl ethyl ketone, (II), b. p. 107°/22 mm., d_4^{25} 0.93020, n_D^{25} 1.47320, $[R_L]_D$ 45.89, was prepared, being purified through its semicarbazone, m. p. 153° (Kon, A., 1926, 952). cyclohexylideneacetone (III), b. p. 89°/12.5 mm., d_4^{25} 0.94931, n_D^{25} 1.49128, $[R_L]_D$ 42.16 (semicarbazone, m. p. 180°), was prepared similarly to (I), using zinc methyl iodide. Δ^1 -cyclohexenylacetone (IV) (cf. Wallach, A., 1913, i, 182; Kon, J.C.S., 1921, 119, 816) was prepared from cyclohexenylacetyl chloride in the same way. The compounds (I) and (II) were previously obtained as an equilibrium mixture (Kon and Nutland, A., 1927, 153). The equilibria of this pair of isomerides and of (III) and (IV) were studied quantitatively by the method of Linstead and May (A., 1927, 1167). It was found that (I) and (III), although sensitive to mineral acids at the moment of formation, were scarcely affected by them when purified. Equilibration proceeded very slowly in the presence of small amounts of barium hydroxide, piperidine, or sulphuric acid. With sodium ethoxide in excess, equilibrium was established in 24 hrs. The equilibrium mixture of (I) and (II) contained 69% of (II), whilst that of (III) and (IV) contained 71% of (IV).

R. K. CALLOW.

Carbon rings. XI. Rings containing ten, eleven, twenty, and twenty-two carbon atoms, and formation of aliphatic together with cyclic ketones by decomposition of metal salts of polymethylenedicarboxylic acids. L. RUZICKA, M. STOLL, and H. SCHINZ (Helv. Chim. Acta, 1928, 11, 670—686; cf. this vol., 642).—The action of heat on yttrium nonane- α -dicarboxylate gives, in addition to cyclodecanone (A., 1926, 615), some cycloeicosane-1:11-dione (I), m. p. 49—51°, d_4^{25} 0.9232, n_D^{25} 1.4662 (dioxime, m. p. 147—148°), and methyl nonyl ketone (semicarbazone, m. p. 115°). When (I) is treated with

benzaldehyde in presence of sodium ethoxide, the resulting product heated with sodium hydrogen sulphate at 200°, ozonised, and then esterified with methyl alcohol, there is obtained dimethyl- λ -keto-octadecane- α -dicarboxylate, m. p. 59—60°. Reduction of the free acid by Clemmensen's method yields octadecane- α -dicarboxylic acid, m. p. 119—121°, whilst similar reduction of (I) affords cycloeicosanone, m. p. 58—59° (semicarbazone, m. p. 179—180°). Fractionation of the acidic hydrolysis products of Japan wax gives japanic acid (cf. Schaal, A., 1908, i, 3), now shown to be nonadecane- α -dicarboxylic acid, m. p. 111—113° (dimethyl ester, m. p. 56—57°). This acid is also obtained by electrolysis of a mixture of the sodium salts of methyl hydrogen tetradecane- α -dicarboxylate and Δ^1 -octenecarboxylic acid, and subsequent oxidation with ozone of the resulting Δ^1 -docosenecarboxylic acid. The thorium salt of japanic acid yields cycloeicosanone, which when oxidised with chromic anhydride and acetic acid yields a dicarboxylic acid, m. p. 102—104° (dimethyl ester, m. p. 51—53°), probably a mixture of octadecane- and heptadecane-dicarboxylic acids. Yttrium decane- α -dicarboxylate gives in addition to cycloundecanone, 1% of cyclodocosane-1:12-dione, m. p. 55—56°, d_4^{25} 0.9114, n_D^{25} 1.4633 (disemicarbazone, decomp. 228—230°; dioxime, m. p. 151—153°), and methyl decyl ketone (semicarbazone, m. p. 104—105°). Oxidation of the benzylidene derivative of the diketone yields after esterification dimethyl λ -ketoicosane- α -dicarboxylate, b. p. 240°/0.5 mm., m. p. 68—70°. Reduction of the free acid by Clemmensen's method gives eicosane- α -dicarboxylic acid, m. p. 120—122°.

During the preparation of cyclo-do-, tri-, penta-, hexa-, hepta-, and octa-decanones (*loc. cit.*), there are formed small quantities of methyl undecyl (semicarbazone, m. p. 115—116°), methyl dodecyl (semicarbazone, m. p. 115—117°), methyl tetradecyl, m. p. 38° (lit. m. p. 43°; semicarbazone, m. p. 117—118°), prepared by hydrolysis of ethyl tridecylacetate with barium hydroxide solution, methyl pentadecyl (semicarbazone, m. p. 116—118°), methyl hexadecyl (semicarbazone, m. p. 114—116°), and methyl heptadecyl (semicarbazone, m. p. 117—119°) ketones.

H. BURTON.

Carbon rings. XII. Preparation of methylated ketones containing fourteen, fifteen, and seventeen carbon atoms in the ring. L. RUZICKA, H. SCHINZ, and M. PFEIFFER (Helv. Chim. Acta, 1928, 11, 686—700).—The action of heat on the thorium or yttrium salts of tetradecane- β - and α -, β -methyl-dodecane- α -, pentadecane- α -, hexadecane- β -, β -methyltetradecane- α -, and β -dimethyltetradecane- α -dicarboxylic acids does not furnish more than traces of cyclic ketones. Small amounts of methyl methyltetradecyl ketone (semicarbazone, m. p. 122°) and methyl β -dimethyltetradecyl ketone (semicarbazone, m. p. 78—79°) were obtained from β -methyltetradecane- α - and β -dimethyltetradecane- α -dicarboxylic acids, respectively. Yttrium γ -methyltridecane- α -dicarboxylate furnishes 1-methylcyclotetradecan-4-one, b. p. 155°/12 mm., m. p. 28—29° (semicarbazone, m. p. 182—183°), together with a methyl methyltridecyl ketone, isolated as its semicarbazone, m. p. 118—119°. Methylation of cyclo-

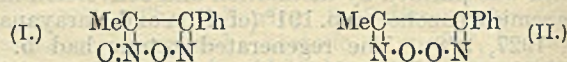
pentadecanone with sodamide and methyl iodide yields 2-methylcyclopentadecanone, b. p. 171—173°/12 mm., d_4^{16} 0.9213, n_D^{16} 1.4812 (semicarbazone, m. p. 149—150°). Magnesium methyl iodide converts cyclopentadecanone into 1-methylcyclopentadecan-1-ol (I), m. p. 85—86°, together with a compound, $C_{30}H_{56}O_2$ or $C_{30}H_{58}O_2$, m. p. 162°. Elimination of water from (I) by treatment with hot formic acid affords 1-methyl- Δ^1 -cyclopentadecene, b. p. 152—153°/12 mm., d_4^{21} 0.8697, n_D^{21} 1.4853, reduced by hydrogen in presence of platinum-black to methylcyclopentadecane, b. p. 147—148°/12 mm., d_4^{21} 0.8576, n_D^{21} 1.4735.

Thorium γ - and δ -methyltetradecane- α -dicarboxylates yield 1-methylcyclopentadecan-4-one, b. p. 125°/0.5 mm. (semicarbazone, m. p. 161—162°), and 1-methylcyclopentadecan-5-one, b. p. 125°/0.5 mm. (semicarbazone, m. p. 164°), respectively. From an optically active specimen of yttrium δ -methyltetradecane- α -dicarboxylate there was obtained *d*-1-methylcyclopentadecan-5-one, α_D in 30% alcohol +3.5°. Methylation of dihydrocivetone affords 2-methylcycloheptadecanone, b. p. 150°/0.5 mm. (semicarbazone, m. p. 142—143°). H. BURTON.

Conversion of a C_6 into a C_5 ring by molecular transposition: isomerisation of the oxides of phenylcyclohexene and 1-phenyl-4-methylcyclohexene. (MLLE.) J. LÉVY and J. SFIRAS (Compt. rend., 1928, 187, 45—47; cf. this vol., 410, 516).—When heated in presence of a trace of anhydrous zinc chloride 1-phenylcyclo- Δ^1 -hexene oxide affords 60% of 1-phenylcyclohexan-2-one (semicarbazone, m. p. 166°) and 9% of 1-phenylcyclopentane-1-aldehyde, b. p. 134°/15—16 mm. (semicarbazone, m. p. 196—5°), yielding on oxidation 1-phenylcyclopentane-1-carboxylic acid, m. p. 155—157° (amide, m. p. 108°). Similarly, 1-phenyl-4-methyl- Δ^2 -cyclohexene oxide, m. p. 36°, b. p. 140—141°/15 mm. (obtained by the action of perbenzoic acid on 1-phenyl-4-methyl- Δ^2 -cyclohexene), is converted into 1-phenyl-4-methylcyclohexan-2-one (yield 55%) (semicarbazone, m. p. 217°), oxidised by permanganate to 1-benzoyl-3-methylcyclopentane-5-carboxylic acid, m. p. 56° (semicarbazone, m. p. 214°), and into 2% of 1-phenyl-3-methylcyclopentane-1-aldehyde (semicarbazone, m. p. 172°). 1-Phenyl-3-methylcyclopentane-1-carboxylic acid has m. p. 124°. Rupture of the oxide ring takes place always on the same side, the isomerisation being determined by the migration of an adjacent hydrogen or carbon atom to saturate the carbon atom previously linked with oxygen. R. BRIGHTMAN.

Dioximes. L. G. PONZIO (Ber., 1928, 61, [B], 1316—1328, and Gazzetta, 1928, 58, 329—344).—A dioxime, m. p. 223°, isolated by the author must be added to the four isomeric dioximes of benzoyl *p*-methoxyphenyl ketone described by Meisenheimer, Lange, and Lamparter (A., 1925, i, 1073). It appears doubtful whether the α -form, m. p. 206—207°, is homogeneous, and the doubt extends also to the other compounds, so that the work cannot be regarded as an experimental verification of the Hantzsch-Werner theory. It is considered that this theory is not applicable to the dioximes of diketones, $CH_3\cdot CO\cdot CO\cdot Ar$, which have been obtained in only two forms. Thus β -phenylmethylglyoxime, m. p.

238—239° (partial decomp.), has a higher m. p. than the α -compound, yields a complex nickel salt insoluble in dilute acetic acid, and can be obtained by heating the α -variety. It is converted by dehydrogenation into two peroxides, $CH_3\cdot [C_2N_2O_2]\cdot Ar$, m. p. 96° and 62°, respectively; the former is reduced exclusively to the α -glyoxime, whereas the latter is converted entirely into the γ -glyoxime, which passes into the β -compound at the atmospheric temperature. The peroxides are not isomorphous and differ widely from one another in chemical behaviour. That of higher m. p. is irreversibly transformed when heated into that of lower m. p.; it reacts vigorously with phosphorus pentachloride giving phenylmethylfuroxan; with sodium ethoxide it affords an isomeric compound, $C_9H_8O_2N_2$, m. p. 178—179° (decomp.), soluble in bases. The glyoxime of lower m. p. does not react with phosphorus pentachloride or sodium ethoxide and cannot be transformed into the isomeric of higher m. p. The constitutions (I) and (II) are assigned to the peroxides of higher and lower

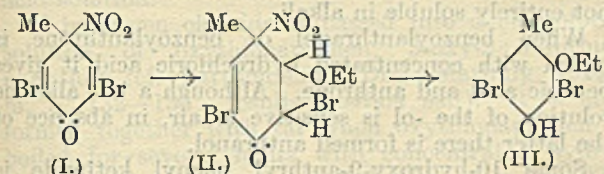


m. p., respectively. Since the β -glyoxime affords simultaneously the furoxan (I) and the peroxide (II) it must have both the *amphi*- and *syn*-configuration in the sense of the Hantzsch-Werner theory, whilst the α -glyoxime must have the *amphi*-configuration, since it yields exclusively the peroxide (II). These difficulties are avoided if one oximino-group is considered capable of behaving towards certain reagents in the nitron form. For the β -glyoxime the equilibrium $\text{MeC}(\text{NH}:\text{O})\cdot\text{CPh}:\text{N}\cdot\text{OH} \rightleftharpoons \text{MeC}(\text{N}\cdot\text{OH})\cdot\text{CPh}:\text{N}\cdot\text{OH}$ is assumed, whereas the α - and γ -glyoximes receive the constitutions $\text{MeC}(\text{NH}:\text{O})\cdot\text{CPh}:\text{N}\cdot\text{OH}$ and $\text{MeC}(\text{N}\cdot\text{OH})\cdot\text{CPh}:\text{N}\cdot\text{OH}$, respectively.

The following compounds are also described: β -anisylmethylglyoxime, m. p. 213—214° (partial decomp.); anisylmethylfuroxan, m. p. 99° (bromoderivative, m. p. 109—110°; nitro-compound, m. p. 88—89°); anisyl methyl peroxide, m. p. 78—79°; α -anisylmethylglyoxime, m. p. 125° (nickel salt; dibenzoyl derivative, m. p. 157—158°); bromoanisyl methyl peroxide, m. p. 115—116°; nitroanisyl methyl peroxide, m. p. 112°; β -*p*-bromophenylmethylglyoxime, m. p. 223—224° (partial decomp.), by the successive action of amyl nitrite and hydroxylamine on *p*-bromophenyl ethyl ketone; *p*-bromophenylmethylfuroxan, m. p. 108—109°; *p*-bromophenyl methyl peroxide, m. p. 88—89°. H. WREN.

Quinonitroles and quinamines. K. FRIES and G. OEHMKE (Annalen, 1928, 462, 1—24).—That quinonitroles are nitro-compounds and not, as suggested by von Auwers, the nitrous esters of the corresponding ψ -quinols is proved by the following experiments: When 3:5-dibromo-1:4-methylquinonitrole (I) is treated with alcoholic potassium hydroxide for 10 sec., the resulting solution then being acidified, there is produced 3:5-dibromo-1-nitro-2-ethoxy-4-keto- Δ^5 -tetrahydrotoluene (II), m. p. 145° (elimination of nitrous fumes), the constitution of which follows (1) from its non-reactivity towards reagents for hydroxyl groups, and (2) from its reduc-

tion by zinc dust and hydrochloric and acetic acids, to 3-bromo-*p*-cresol. It is converted by hydrogen bromide in acetic acid into bromonitro-*p*-cresol. Treatment of (I) for 2 days with alcoholic alkali, or of (II) with boiling 2*N*-sodium hydroxide, gives 3:5-dibromo-2-ethoxy-*p*-cresol (dibromocresorcinol ethyl ether) (III), m. p. 91° (acetyl derivative, m. p. 67°), which is converted by hydrogen bromide in acetic acid into 3:5-dibromocresorcinol (acetyl derivative, m. p. 67°), and is evidently formed from (I) by the annexed scheme :



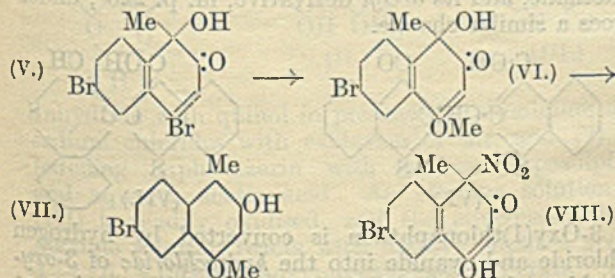
When (II) is allowed to remain in cold pyridine solution for 1 day, there are formed ethyl alcohol, 3-bromo-5-nitro-*p*-cresol, and 3:3:5-tribromo-1-nitro-2-ethoxy-4-keto- Δ^5 -tetrahydrotoluene (IV), m. p. 92°, reduced by zinc dust and hydrochloric acid to 3:5-dibromo-*p*-cresol, but not converted into a cresorcinol derivative by alkali, no doubt owing to its inability to undergo enolisation.

3:5-Dibromo-1-nitro-2-methoxy-4-keto- Δ^5 -tetrahydrotoluene has m. p. 166° (elimination of nitrous fumes); 3:3:5-tribromo-1-nitro-2-methoxy-4-keto- Δ^5 -tetrahydrotoluene has m. p. 105°; 3:5-dibromo-2-methoxy-*p*-cresol (dibromocresorcinol methyl ether) has m. p. 60° (acetyl derivative, m. p. 104°).

The above 3:5-dibromocresorcinol ethyl ether is transformed by dilute nitric acid or by sodium nitrite in acetic acid into 3-bromo-5-nitro-2-ethoxy-*p*-cresol, m. p. 73°, and by fuming nitric acid into 3:5-dibromo-2-ethoxy(?)1:4-methylquinonitrole, m. p. 75° (elimination of nitrous fumes), which with water or alcohol gives the above nitro-derivative, m. p. 73°.

An improved method is given for the preparation of the 3:5-dibromo-1:4-methyl- ψ -quinol, which is converted by alcoholic alkali into tarry products.

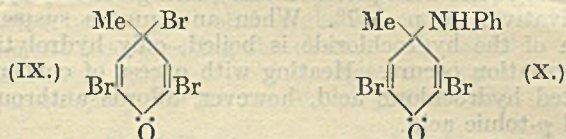
When 4:6-dibromo- $\alpha\beta$ -naphthamethyl- ψ -quinol (V) is treated with methyl-alcoholic sodium hydroxide there is formed 6-bromo-4-methoxy- $\alpha\beta$ -naphthamethyl- ψ -quinol (VI), m. p. 155° (acetyl derivative, m. p. 168°; (corresponding 4-ethoxy- ψ -quinol, m. p. 144°); the methoxy- and ethoxy- ψ -quinols are converted by warm aqueous alcoholic alkali into 6-bromo-4-hydroxy-



$\alpha\beta$ -naphthamethyl- ψ -quinol, m. p. 182° (diacetyl derivative, m. p. 147°), whilst reduction of the methoxy-

quinole with zinc dust in boiling glacial acetic acid produces 6-bromo-2-hydroxy-4-methoxy- α -methyl-naphthalene (VII), m. p. 143° (acetyl derivative, m. p. 125°). If the quinonitrole corresponding with (V) were the nitrous ester of (V), it should be converted by alcoholic alkali into (VI) and so on. Actually, however, it affords 6-bromo-4-hydroxy- $\alpha\beta$ -naphthamethylquinonitrole (VIII), m. p. 195° (decomp.), which is converted by boiling alcoholic potassium hydroxide or by boiling glacial acetic acid into an isomeride, m. p. 275° (decomp.).

When 1:3:5-tribromo-4-keto-1:4-dihydrotoluene (IX) (improved preparation from *p*-cresol described) is kept, or more rapidly when it is heated to its m. p. (105°), it passes into 3:5-dibromo-*p*-cresol ψ -bromide (3:5-dibromo-4-hydroxybenzyl bromide), whilst when it is treated with alcoholic aniline it gives 3:5-dibromo-1-anilino-4-keto-1:4-dihydrotoluene (X), reduced by zinc dust and acetic acid to 3:5-dibromo-*p*-cresol.



By similar processes, 3:5-dichloro-1-bromo-4-keto-1:4-dihydrotoluene is prepared from 3:5-dichloro-*p*-cresol. It has m. p. 106° and is convertible (1) into 3:5-dichloro-*p*-cresol ψ -bromide (3:5-dichloro-4-hydroxybenzyl bromide), m. p. 120°, (2) using zinc dust and hydrochloric and acetic acids, into 3:5-dichloro-*p*-cresol, and (3) into 3:5-dichloro-1-anilino-4-keto-1:4-dihydrotoluene, m. p. 148° (decomp.).

3:5-Dibromo-1-*o*-toluidino- and 3:5-dibromo-1-*p*-toluidino-4-keto-1:4-dihydrotoluene have m. p. 112° (decomp.) and 105° (decomp.), respectively.

When the quinamine (X) is treated with hydrochloric-acetic acid it is converted into 2:6-dibromo-4'-amino-4-methyldiphenyl ether, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{MeBr}_2$, m. p. 120° (acetyl derivative, m. p. 180°). The similarly obtained 2:6-dibromo-4'-amino-4:3'-dimethyldiphenyl ether, m. p. 122.5° (acetyl derivative, m. p. 211°), and 2:6-dichloro-4'-amino-4-methyldiphenyl ether, m. p. 99° (acetyl derivative, m. p. 187°), are described. The last-named acetyl compound results when the dichlorophenylquinamine is treated with acetic anhydride and sulphuric acid.

Treatment of 5-bromo-4-*m*-xylenol in glacial acetic acid with bromine in presence of sodium acetate gives the unstable 1:5-dibromo-4-keto- Δ^5 -dihydro-*m*-xylene, m. p. 63°, passing when heated at 100° into the ψ -bromide (3-bromo-4-hydroxy-5-methylbenzyl bromide), m. p. 104°, and converted by alcoholic aniline into 5-bromo-1-anilino-4-keto- Δ^5 -dihydro-*m*-xylene, m. p. 107° (blackening). The last with acetic and hydrochloric acids affords 6-bromo-4'-amino-2:4-dimethyldiphenyl ether, m. p. 81° (acetyl derivative, m. p. 163°).

Similarly are obtained 5-bromo-1-*o*-toluidino-4-keto- Δ^5 -dihydro-*m*-xylene, m. p. 103° (decomp.), and 6-bromo-4'-amino-2:4:3'-trimethyldiphenyl ether, m. p. 128° (acetyl derivative, m. p. 187°). E. E. TURNER.

Transformation products of anthranol and oxythionaphthen. F. KROLLPFEIFFER [with F. BRANSCH, F. THORN, and K. SCHNEIDER] (Annalen,

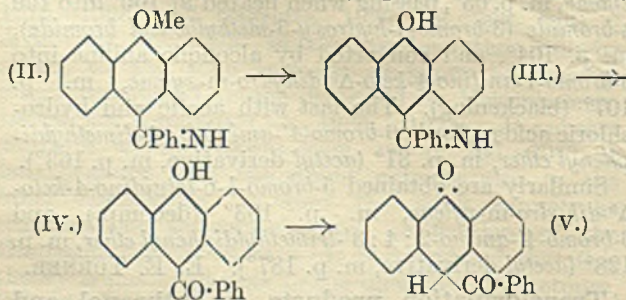
1928, 462, 46—72).—The ease of formation of ketimides of the general formula (I) by the method previously employed (A., 1924, i, 184) is affected considerably by the nature of substituents in the radical Ar. 10-Methoxy-9-anthryl phenyl ketimide forms an additive compound with benzonitrile and hydrogen chloride, viz., $C_{22}H_{17}ON.HCl.PhCN$, but not with aceto-, phenylaceto-, or *p*-toluo-nitrile. When the ketimide is heated with acetic anhydride it gives an *acetyl* derivative, m. p. 204—205°, hydrolysed by hydrochloric acid to anthrone and benzoic acid. The corresponding *benzoyl* derivative has m. p. 206—207°.

10-Methoxy-9-anthryl *p*-tolyl ketimide, m. p. 150°, is produced in poor yield from *p*-toluonitrile (*o*-toluonitrile fails to give a ketimide); it forms a *hydrochloride*, an additive compound with benzonitrile (although not with *p*-toluonitrile), and gives an *acetyl* derivative, m. p. 147°. When an aqueous suspension of the hydrochloride is boiled, only hydrolytic dissociation occurs. Heating with excess of concentrated hydrochloric acid, however, affords anthrone and *p*-toluic acid.

10-Methoxy-9-anthryl *m*-tolyl ketimide (*acetyl* derivative, m. p. 199—200°), m. p. 127°, is formed in poor yield from *m*-toluonitrile, whilst 10-methoxy-9-anthryl *benzyl* ketimide, m. p. 202—203°, is somewhat unstable and is readily converted by warm hydrochloric acid into anthrone and phenylacetic acid. 10-Methoxy-9-anthryl *p*-chlorophenyl ketimide, readily formed, has m. p. 147—148°, gives a *hydrochloride*, an additive compound with benzonitrile (although none with *p*-chlorobenzonitrile), and forms an *acetyl* derivative, m. p. 176—177°. *p*-Methoxybenzonitrile fails to give a ketimide, but, from propionitrile, 10-methoxy-9-anthryl *ethyl* ketimide (*acetyl* derivative, m. p. 201—202°) is obtained as *hydrochloride*.

Careful study of the hydrolysis of 10-methoxy-9-anthryl *p*-chlorophenyl ketimide shows that cold concentrated sulphuric acid effects hydrolysis of ketimide to ketone without simultaneous removal of the *p*-chlorophenyl group. Thus, whilst boiling a solution of the hydrochloride in acetic acid gives anthrone and *p*-chlorobenzoic acid, products formed in other, similar, ways, cold sulphuric acid gives *p*-chlorobenzoylanthrone, m. p. 206—208°, acidification of the alkaline solution of which produces *p*-chlorobenzoylanthranol.

When 10-methoxy-9-anthryl phenyl ketimide (II)



is treated with cold sulphuric acid, the *sulphate* of 10-hydroxy-9-anthryl phenyl ketimide (III) (*diacetyl*

derivative, m. p. 206—207°) is isolable if the product obtained by pouring on ice is at once collected, whilst if the latter is left in aqueous suspension for 2 days, benzoylanthranol (IV) results, together with some benzoylanthrone (V), m. p. 155—157°. When the last is melted, some benzoylanthranol is formed. Benzoylanthranol [*methyl ether*, m. p. 175—177° (decomp.); *acetyl* derivative, m. p. about 194° (impure)] has no definite m. p. It sinters at 125° and melts at 145° with slow heating; when heated rapidly it melts at about 140°, but the fused mass is not entirely soluble in alkali.

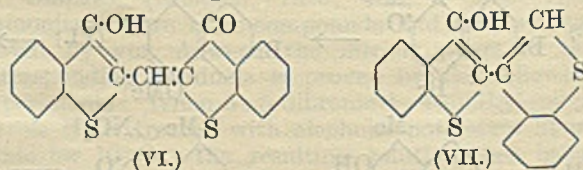
When benzoylanthranol or benzoylanthrone is boiled with concentrated hydrochloric acid it gives benzoic acid and anthrone. Although a hot alkaline solution of the -ol is sensitive to air, in absence of the latter there is formed anthranol.

Some 10-hydroxy-9-anthryl phenyl ketimide is formed during the preparation of the corresponding 10-methoxy-derivative, and a method for its isolation is given.

When anthranol methyl ether is treated with benzene, aluminium chloride, hydrogen cyanide, and hydrogen chloride, 10-methoxyanthracene-9-aldehyde, m. p. 165°, is formed. It is converted by hot concentrated hydrochloric acid into a mixture of anthrone, dianthrone, anthraquinone, and formic acid, whilst hydrochloric-acetic acid gives dianthrone after prolonged boiling, but a quantitative yield of anthranol after heating for 3 hrs. The aldehyde gives a *phenylhydrazone*, m. p. 138—139°, and an *oxime*, m. p. 142—143°. 10-Ethoxyanthracene-9-aldehyde, m. p. 93—94°, is formed similarly but in poorer yield.

Action of chloroform on a boiling alcoholic-alkaline solution of anthrone gives 9-(10'-hydroxy-9'-anthrylmethylene)anthrone, together with a substance, $C_{30}H_{18}O_2Cl_2$, m. p. 226—227°, for which two alternative formulae are proposed (containing the radical $\cdot CHCl_2$). The same substance is obtained when the methylene compound is heated with alkaline-alcoholic chloroform.

When a nitrobenzene solution of the methylene compound (*methyl ether*, m. p. 221—222°) is boiled, oxidation occurs, with formation of 9:9'-dianthronylidenemethane, m. p. 360°, reducible, if care is taken, to the substance from which it is prepared. The *acetyl* derivative of 9-(10'-hydroxy-9'-anthrylmethylene)anthrone is not oxidised in boiling nitrobenzene solution. Under similar conditions 3-oxy(1)thionaphthen-2-aldehydethioindogenide (VI) affords an oxidation product of type different from the above methane, and its *acetyl* derivative, m. p. 220°, undergoes a similar change.



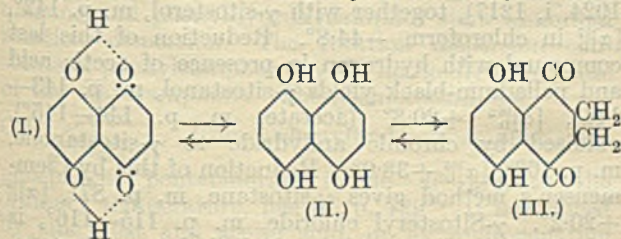
3-Oxy(1)thionaphthen is converted by hydrogen chloride and cyanide into the *hydrochloride* of 3-oxy(1)thionaphthen-2-aldimine, the free base passing at 135—155° into the above indogenide, and affording an *acetyl* derivative, m. p. 198°. When the aqueous

solution of the above hydrochloride is boiled, 3-oxy-(1)thionaphthen-2-aldehyde is formed (*methyl ether*, from 3-oxy(1)thionaphthen methyl ether, has m. p. 84—85°, b. p. 185°/14 mm., and gives a *phenylhydrazone*, m. p. 117—118°). When oxythionaphthen is heated with methyl iodide and alkali methoxide at 100°, the methyl ether is not formed, but, instead 3-methoxy(1)thionaphthen-2-aldehyde-2'-indogenide, m. p. 218—220°, also formed when (VI) is similarly methylated, and when 3-oxy(1)thionaphthen is condensed with its 2-aldehyde in alcoholic hydrochloric acid solution.

If hydrogen chloride is passed into a chloroform solution of oxythionaphthen, 3-oxy-2:3'-dithionaphthen (cf. Bartholomäus, Diss., Marburg, 1911), m. p. 132—133°, results (*sodium salt*). It is also formed together with tar when oxythionaphthen is boiled for several hours with concentrated hydrochloric acid, and forms a *methyl ether*, m. p. 96—97°.

When bromine is added to a carbon disulphide solution of oxythionaphthen, the 3-oxy(1)thionaphthenyl-2-ether of 3-oxy-2:3'-dithionaphthen (VIII), m. p. 198—199°, is formed, through the intermediate formation of 2-bromo-3-oxy(1)thionaphthen, not isolated. E. E. TURNER.

Constitution and mode of reaction of polynuclear polyhydroxyquinones. Naphthazarin and quinizarin. K. ZAHN and P. OCHWAT (Annalen, 1928, 462, 72—97).—Maleic anhydride condenses with quinol in presence of aluminium and sodium chlorides at 200—220° to give naphthazarin, a fact which definitely establishes this substance as 5:8-dihydroxy- α -naphthaquinone (I) (cf. Wheeler and Edwards, A., 1916, i, 392; Dimroth and Ruck, A., 1926, 297). When naphthazarin is reduced with zinc dust and dilute sulphuric acid in presence of ether, 1:4:5:8-tetrahydroxynaphthalene (II), m. p. 190°, is formed, and when this substance is boiled in alcoholic hydrochloric acid solution, air being excluded, it passes into the *keto*-form (III), viz., 5:8-dihydroxy-1:4-diketotetrahydronaphthalene, m. p. 153—154°, also obtained (1) by condensing succinic



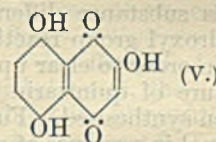
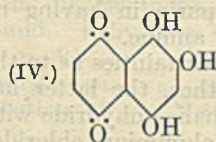
anhydride with quinol in presence of aluminium and sodium chlorides with exclusion of air, and (2) by reducing naphthazarin with sodium hyposulphite and aqueous acetic acid. An alkaline solution of (III) is readily oxidised, and the aqueous-alcoholic alkaline solution reacts with methyl sulphate giving 1:4:5:8-tetramethoxynaphthalene (Perkin and Weizmann, J.C.S., 1906, 89, 1659). The tetrahydroxynaphthalene described by Wheeler and

Edwards (*loc. cit.*) must be an isomeride or a more fully hydroxylated naphthalene.

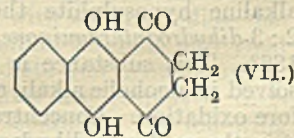
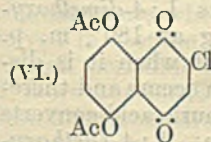
When the diketone is treated with acetic anhydride and a little concentrated sulphuric acid it gives 5:8-diacetoxy-1:4-diketotetrahydronaphthalene, readily converted into (III) by alkali. On the other hand, when naphthazarin diacetate is reduced, 1:4-dihydroxy-5:8-diacetoxynaphthalene is formed (cf. Wheeler and Edwards). Either acetyl compound or either dihydronaphthazarin passes into 1:4:5:8-tetra-acetoxynaphthalene when heated with acetic anhydride and sodium acetate.

Fusion of the diketone with phthalic anhydride and sodium and aluminium chlorides produces tetrahydroxynaphthacenequinone, m. p. above 300°, showing that di-enolisation precedes condensation.

When naphthazarin, for which formula (I) is suggested, is oxidised with nitric acid it gives oxalic acid, whilst in glacial acetic acid solution with lead tetra-acetate, 1:4:5:8-naphthadiquinone, decomp. 220°, results. The latter passes into naphthazarin when heated in alcohol or glacial acetic acid, reducing agents also effecting the change very rapidly. Concentrated sulphuric acid converts the diquinone into naphthopurpurin (IV) or (V), m. p. 160—162° (indef.),



also produced when naphthazarin is oxidised with manganese dioxide and sulphuric acid. Naphthopurpurin triacetate is formed by the action of acetic anhydride and sulphuric acid on the diquinone, which with hydrogen chloride in acetic acid gives chloronaphthazarin, m. p. 178—179°. Addition of chlorine in glacial acetic acid to naphthazarin diacetate, or acetylation of naphthazarin dichloride, affords diacetoxynaphthaquinone dichloride, m. p. 136—137°, decomposed by boiling alcohol to give chloronaphthazarin diacetate, m. p. 193—194°, which must be (VI) because it is also formed by acetylation



of the above chloronaphthazarin. When 1:4:5:8-naphthadiquinone is treated with chlorine in chloroform solution, the *dichloride*, decomp. 252—254°, is formed, and this substance is converted by potassium iodide or by sulphur dioxide into naphthazarin.

Fusion of 1:4-dihydroxynaphthalene with maleic anhydride and sodium and aluminium chlorides at 220° affords quinizarin, which is therefore 9:10-dihydroxy-1:4-anthraquinone. Reduction of quinizarin, followed by acetylation, produces 1:4-diacetoxy-2:3-dihydroanthraquinone, m. p. 215°, also obtained by reducing quinizarin with zinc dust and acetic acid. Excess of acetyl chloride and pyridine in the former process gives rise to 1:4:9:10-tetra-acetoxyanthracene, m. p. 240—242°. On the other hand, if dihydroquinizarin or the above diacetyl derivative is heated

(b. p.) with acetic anhydride and sodium acetate, the chief product is 1:4:9-triacetoxyanthracene, m. p. 210—211°.

Both chlorine atoms in 5:8-dichloroquinizarin are labile, so that when the latter substance is heated with aniline in presence of sodium acetate, 5:8-dianilino-1:4-dihydroxyanthraquinone, m. p. 258—260°, is formed. Reduction of dichloroquinizarin with tin and acetic-hydrochloric acid affords the dichlorodihydroquinizarin, reacting with aniline in presence of boric acid to give 5:8-dichloro-1:4-dianilinoanthraquinone, m. p. 234—235°. Reduction of this substance with stannous chloride in acetic acid affords dihydroquinizarin (VII).

Reduction of 2-methylquinizarin with tin and hydrochloric acid gives 2-methyldihydroquinizarin, m. p. 114—115°, converted by *p*-toluidine in presence of boric acid at 125°, followed by air oxidation, into 4-*p*-toluidino-1-hydroxy-2-methylantraquinone, m. p. 178°. Oxidation of 2-methylquinizarin with lead tetra-acetate gives 2-methyl-1:4:9:10-anthradiquinone, from which by the acetic anhydride-sulphuric acid method 2-methylpurpurin (acetyl derivative, m. p. 204—206°; triacetate, m. p. 207—208°) is obtained (cf. Eder and Manoukian, A., 1926, 407). This substance differs from purpurin in having no hydroxyl group reactive towards aniline.

In order to clear up existing uncertainties as to the nature of quinizarin dimethyl ether, the latter has been synthesised. Fusion of phthalic anhydride with quinol in presence of sodium and aluminium chlorides at 120—125° (higher temperatures give quinizarin) produces 2:5-dihydroxybenzophenone-2'-carboxylic acid, m. p. 189—190°. The dimethyl ether (m. p. 161—162°) of the latter, prepared using methyl sulphate and alkali, passes into quinizarin dimethyl ether, i.e., 1:4-dimethoxyanthraquinone, when dissolved in warm concentrated sulphuric acid. Alkylation of quinizarin is readily effected using the alkyl *p*-toluenesulphonate in trichlorobenzene solution in presence of sodium carbonate at 160—170°. The diethyl ether so obtained has m. p. 170—171°.

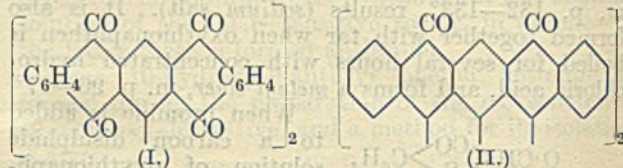
When quinizarin dimethyl ether is reduced with alkaline hyposulphite there results 1:4-dimethoxy-2:3-dihydroanthraquinone, sintering at 180°, m. p. 186°. This substance is stable, but when it is dissolved in alcoholic alkali, enolisation occurs and therefore oxidation. Concentrated sulphuric acid converts it in the cold into dihydroquinizarin. 1:4-Diethoxy-2:3-dihydroanthraquinone has m. p. 174—176°.

Acetic anhydride in presence of a little concentrated sulphuric acid converts dihydroquinizarin dimethyl and diethyl ethers, respectively, into 1:4-dimethoxy- (m. p. 225°) and 1:4-diethoxy-9:10-diacetoxyanthracene, m. p. 203—205°.

E. E. TURNER.

Dibenzoylxylenes and dinaphthanthradiquinones. IV. H. DE DIESBACH and T. JANZEN (Helv. Chim. Acta, 1928, 11, 724—730).—2-Amino-4:6-dibenzoyl-*m*-xylene, m. p. 188.5° (acetyl derivative, m. p. 190.5°), obtained by reducing the corresponding nitro-derivative (A., 1924, i, 1082) with iron powder and acetic acid, is converted by the Sandmeyer reaction into 2-chloro-4:6-dibenzoyl-*m*-xylene, m. p. 92.5° (2-bromo-derivative, m. p. 121—122°). Con-

secutive oxidation of this with nitric acid (*d* 1.15) at 170° in a sealed tube, and alkaline potassium permanganate affords 2-chloro-4:6-dibenzoylisophthalic acid, m. p. 155—157° (2-bromo-derivative, m. p. 206°), which when heated with concentrated sulphuric acid at 160—200° yields 6-chloro-5:7:12:14-dinaphthanthradiquinone, sublimes at 320° (6-bromo-derivative). When this chloro-compound is treated with copper powder in boiling nitrobenzene 2:3:2':3'-diphthalyl-1:1'-dianthraquinonyl (I), m. p. above 360°, is obtained, which is converted by the action of copper powder and concentrated sulphuric acid into the tetraketo-compound (II). This compound, which is a pyrene derivative, is reducible only with difficulty, and is therefore useless as a vat dye.



6-Amino- and 6-hydroxy-5:7:12:14-dinaphthanthradiquinone, sublimes at 300°, are described.

H. BURTON.

Dye intermediates [phenyl α -naphthyl ketone]. H. A. DRESCHER, J. THOMAS, & SCOTTISH DYES, LTD. —See B., 1928, 474.

Ketones of the anthracene series. I. G. FARBER and A. G. —See B., 1928, 516.

Plant sterols. K. BONSTEDT (Z. physiol. Chem., 1928, 176, 269—281).—When sitosterol, m. p. 137—138° (all m. p. are corr.), $[\alpha]_D^{25}$ in chloroform -33.9° , from soya-bean oil, is heated with finely-divided nickel (cf. Windaus, A., 1916, i, 813; 1927, 557), sitostanone, m. p. 156°, is produced. Prolonged treatment of a chloroform solution of sitostene with hydrogen chloride affords sitostene hydrochloride, m. p. 132—133°, which when heated with potassium acetate and alcohol gives ψ -sitostene, $C_{27}H_{46}$, m. p. 69°. Sitosterol hydrochloride has m. p. 155° (decomp.) and decomposes in warm chloroform solution. Fractional crystallisation of crude soya-bean sitosterol from alcohol gives a small amount of dihydro-sitosterol, m. p. 144°, $[\alpha]_D^{25} +28.0^\circ$ (cf. Anderson, A., 1924, i, 1217), together with γ -sitosterol, m. p. 142°, $[\alpha]_D^{25}$ in chloroform -44.8° . Reduction of this last compound with hydrogen in presence of acetic acid and palladium-black yields γ -sitostanol, m. p. 143—144°, $[\alpha]_D^{25} +20.8^\circ$ (acetate, m. p. 144—145°), oxidised by chromic anhydride to γ -sitostanone, m. p. 163°, $[\alpha]_D^{25} +38.0^\circ$. Reduction of this by Clemmensen's method gives γ -sitostane, m. p. 87°, $[\alpha]_D^{25} +20.2^\circ$. γ -Sitosteryl chloride, m. p. 115—116°, is reduced by sodium and amyl alcohol to γ -sitostene, m. p. 73°, $[\alpha]_D^{25} -59.3^\circ$.

The sterols of rape oil (Windaus and Welsch, A., 1909, i, 228) do not appear to contain any γ -sitosterol.

H. BURTON.

Constituents of *Phellodendron amurense*, Rupr. I. Y. YAMAMURA and J. TAKATA (J. Pharm. Soc. Japan, 1927, [550], 1035—1040).—One of the non-basic components of *Phellodendron* (a drug

widely used in Japan), which the authors name "obakunine," has the composition $C_{27}H_{33}O_7 \cdot 6H_2O$ or $C_{28}H_{35}O_7 \cdot 6H_2O$, m. p. 229—230° (semicarbazone, m. p. 224—225°; oxime, m. p. 275°). The mother-liquor of obakunine contains a phytosterol, $C_{26}H_{44}O \cdot H_2O$ or $C_{27}H_{46}O \cdot H_2O$, m. p. 142°, $[\alpha]_D^{20}$ -28.86° (Liebermann's colour reaction, positive; acetyl derivative, m. p. 135—137°), and some palmitic and linolenic acids. The drug contains about 1.6% of berberine as hydrochloride. Tetrahydroberberine, obtained from it by reduction with zinc dust, after being repeatedly crystallised from alcohol-chloroform, has m. p. 173° (lit. 167°).

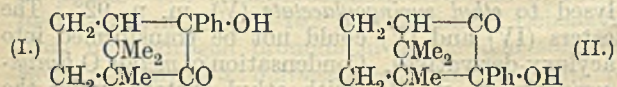
Higher-boiling constituents of essential oil of hops. A. C. CHAPMAN.—See B., 1928, 501.

Carene. M. LAGACHE (Bull. Inst. Pin, 1927, 255—256; Chem. Zentr., 1928, i, 904).—*Carene-nitroaniline*, $C_{10}H_{15}NO \cdot NH_2Ph$, obtained by heating the nitrosochloride with alcoholic aniline and precipitation with water, has m. p. 143—144°, $[\alpha]_{\text{yellow}}$ +60.50°, $[\alpha]_{\text{green}}$ +76.81° (in benzene); the corresponding *p*-toluidine compound has m. p. 148—149°, $[\alpha]_{\text{yellow}}$ +165.66°, $[\alpha]_{\text{green}}$ +203.31° (in benzene).

A. A. ELDRIDGE.

[Addition of chlorine and bromine to pinene.] O. ASCHAN (Ber., 1928, 61, [B], 1342—1343).—A reply to Kondakov (this vol., 526). H. WREN.

Phenylcamphor. H. RUPE [with A. WIRZ] (Verh. Naturforsch. Ges. Basel, 1927, 38, 164—187; Chem. Zentr., 1928, i, 907—908).—By the action of magnesium phenyl bromide on camphorquinone, only one keto-group is attacked, yielding *phenylhydroxycamphor* (I or II), m. p. 78—79°, b. p. 184—187°/10 mm., $[\alpha]_D^{20}$ +7.96° in benzene (methyl ether, b. p. 161—163°/10 mm.; ethyl ether, b. p. 165—166°/10 mm., d_4^{20} 1.0600, n_D^{20} 1.5284). The possibility of formulation as $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{OH} \\ \text{C} \cdot \text{OPh} \end{smallmatrix}$ or $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \text{CH} \cdot \text{OPh} \end{smallmatrix}$ is



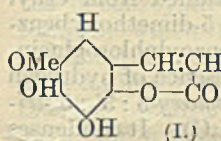
considered and rejected. The *cycloacetal* formulation for hydroxycamphor is not approved. Camphorquinone and phenylhydroxycamphor show abnormal rotation dispersion. The rotation dispersion constants of phenylcamphor deviate markedly from those of the alkylcamphors. Phenylchlorocamphor, $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \text{CClPh} \end{smallmatrix}$, from phenylhydroxycamphor and phosphorus pentachloride in 36—48 hrs. at the ordinary temperature, has m. p. 129°; it is reduced by zinc dust and acetic acid, or by hydrogenation in a mixture of alcohol, ethyl acetate, and water in presence of a nickel catalyst, to *phenylcamphor*, b. p. 172—174°/10 mm., m. p. 45—46°, $[\alpha]_D^{20}$ +184.42° or +180.45° in benzene. *Phenylborneol*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{OH} \\ \text{CHPh} \end{smallmatrix}$, obtained from phenylhydroxycamphor, sodium, and boiling alcohol, has m. p. 139—140°, $[\alpha]_D^{20}$ -76.19° in benzene (isomeride from petroleum, b. p. 179—182°/10 mm., d_4^{20} 1.0897, $[\alpha]_D^{20}$ +20.43°). Treatment

of this with formic acid or phosphoric acid affords *phenylbornylene*, $C_{18}H_{14} \begin{smallmatrix} \text{CH} \\ \text{CPh} \end{smallmatrix}$, b. p. 135—141°/11 mm., d_4^{20} 0.9767, n_D^{20} 1.54167, $[\alpha]_D^{20}$ +40.56°, or d_4^{20} 0.9865, n_D^{20} 1.54445, $[\alpha]_D^{20}$ +8.33°, respectively.

A. A. ELDRIDGE.

Essential oil from timber of rosewood (*Dysoxylon Fraserianum*). A. R. PENFOLD.—See B., 1928, 502.

Constitution of fraxetin. F. WESSELY and E. DEMMER (Ber., 1928, 61, [B], 1279—1284).—Fraxetin, m. p. 227—228° (slight decomp.) after darkening at 150°, is known to be the monomethyl ether of a trihydroxycoumarin. When treated with diazomethane it affords dimethylfraxetin, m. p. 103—104°, which is converted by successive treatment with sodium methoxide and methyl iodide into methyl tetramethoxycinnamate, transformed by hydrolysis followed by oxidation into 2:3:4:5-tetramethoxybenzoic acid, m. p. 87.5°. Synthesis of this acid is effected from 2:5-dimethoxy-3:4-methylenedioxybenzoic acid, which is transformed by resorcinol and concentrated sulphuric acid into 3:4-dihydroxy-2:5-dimethoxybenzoic acid, which, with diazomethane, yields the tetramethoxy-compound. Ethylation of fraxetin affords *diethylfraxetin*, m. p. 81—82°, degraded to 2:5-dimethoxy-3:4-dimethoxybenzoic acid, m. p. 83° (methyl ester), the constitution of which is established by its preparation from 3:4-dihydroxy-2:5-dimethoxybenzoic acid. The constitution (I) is therefore assigned to fraxetin, whereas fraxin contains the dextrose residue in place of one of the two hydroxyl hydrogen atoms. H. WREN.



Alkali periodide salts with organic neutral components. H. SCHMIDT (Ber., 1928, 61, [B], 1347—1353; cf. Löwenbein and Schmidt, A., 1927, 1072).—A solution of iodine and sodium iodide in acetone when concentrated in a vacuum yields the crystalline salt, $(\text{COMe}_2)_3\text{I}(\text{NaI})_3$. 3-Bromo-3-aryl-coumaranones when treated with sodium iodide dissolved in acetone deposit sodium bromide and yield sodium periodide salts of 2-keto-3-aryl coumaranyls; if more concentrated solutions are employed di-2-keto-3-aryl coumaranyls also separate. The following salts are described: $(\text{C}_{14}\text{H}_9\text{O}_2\text{I})_3(\text{NaI})_2$ from 3-bromo-3-phenylcoumaranone; $(\text{C}_{15}\text{H}_{11}\text{O}_2\text{I})_2(\text{NaI})_3$ from 3-bromo-3-phenyl-5-methylcoumaranone; $(\text{C}_{16}\text{H}_{13}\text{O}_3\text{I})(\text{NaI})_2$ from 3-bromo-3-*p*-anisyl-5-methylcoumaranone; $(\text{C}_{18}\text{H}_{11}\text{O}_2\text{I})(\text{NaI})_3$ and $(\text{C}_{18}\text{H}_{11}\text{O}_2\text{I})(\text{NaI})_2$ from 3-bromo-3-phenyl-4:5-benzocoumaranone; $(\text{C}_{19}\text{H}_{13}\text{O}_3\text{I})_2(\text{NaI})_3$ and $(\text{C}_{19}\text{H}_{13}\text{O}_3\text{I})(\text{NaI})_2$ from 3-bromo-3-*p*-anisyl-4:5-benzocoumaranone. The salts yield the di-2-keto-3-aryl coumaranyls when their solutions in benzene are titrated with aqueous thiosulphate or shaken with copper-bronze or molecular silver or mercury or when their solutions in acetone are boiled with zinc wool.

H. WREN.

Synthesis of pyrylium salts of anthocyanidin type. XV. Synthesis of cyanidin chloride by means of *O*-benzoylphloroglucinaldehyde. A.

ROBERTSON and R. ROBINSON (J.C.S., 1928, 1526—1532).—Condensation of ω :3:4-triacetoxyacetophenone and *O*-benzoylphloroglucinaldehyde in ethyl acetate-alcohol solution under the influence of hydrogen chloride yields 5-*O*-benzoylcyanidin chloride (+1.5H₂O). Hydrolysis by means of 8% cold aqueous-alcoholic sodium hydroxide involves, in addition, rupture of the pyrylium ring. Cyanidin chloride, identical with the natural product, is obtained on acidification of the solution. The constitution of cyanidin chloride is therefore fully established as 3:5:7:3':4'-pentahydroxyflavylium chloride (cf. Malkin and Nierenstein, this vol., 646).

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVI. Synthesis of pelargonidin chloride by means of *O*-benzoylphloroglucinaldehyde. A. ROBERTSON, R. ROBINSON, and J. SUGIURA (J.C.S., 1928, 1533—1537).—Condensation of *O*-benzoylphloroglucinaldehyde and ω -4-diacetoxyacetophenone in ethyl acetate solution in presence of hydrogen chloride yields 3:7:4'-trihydroxy-5-benzoyloxyflavylium chloride (5-*O*-benzoylpelargonidin chloride) (I) (+1.5H₂O). Debenzoylation gives pelargonidin chloride. The reactions of (I) resemble those of pelargonidin and pelargonin, thus confirming the view that pelargonidin is a pelargonidin 5- or 7-glucoside.

ω :3:5-Trimethoxyacetophenone, m. p. 42° (semicarbazone, m. p. 149—149.5°), obtained from ethyl α -dimethoxyacetoacetate and 3:5-dimethoxybenzoyl chloride, condenses with *O*-benzoylphloroglucinaldehyde in ethereal solution in presence of hydrogen chloride, giving 7-hydroxy-5-benzoyloxy-3:3':5'-trimethoxyflavylium chloride (II) (+2H₂O). It condenses with *O*-triacylphloroglucinaldehyde in presence of formic acid and hydrogen chloride, giving 5:7-dihydroxy-3:3':5'-trimethoxyflavylium chloride (III), (+0.5H₂O), alternatively obtained by hydrolysis of (II). The salt (III) decomposed on attempted demethylation by means of hydriodic acid in presence of phenol, although indications of the production of 3:5:7:3':5'-pentahydroxyflavylium chloride were obtained.

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVII. Synthesis of peonidin chloride by means of *O*-benzoylphloroglucinaldehyde. S. MURAKAMI and R. ROBINSON (J.C.S., 1928, 1537—1541; cf. A., 1926, 1043).—Condensation of *O*-benzoylphloroglucinaldehyde and ω :4-diacetoxy-3-methoxyacetophenone in ethyl acetate solution in presence of hydrogen chloride yields 5-*O*-benzoylpeonidin chloride (+0.5H₂O; +3H₂O). The alkali colour-reaction of this salt closely resembles that of peonin chloride. Debenzoylation yields peonidin chloride [+H₂O; +1.5H₂O (2 modifications)] identical in reactions with peonidin chloride of natural origin. The crystal habit and solubility relations could be equated, however, only after drastic purification of the anthocyanidin from peonin. A small trace of persistent impurity, probably malvidin, was still present in the natural product.

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVIII. Synthesis of malvidin chloride.

W. BRADLEY and R. ROBINSON (J.C.S., 1928, 1541—1569; cf. A., 1926, 1043).—When ethyl benzoylbenzoyloxyacetate, m. p. 61°, obtained by interaction of ethyl sodiobenzoyl acetate and benzoyl peroxide, is heated with water in a sealed tube at 200°, it yields ω -benzoyloxyacetophenone. Further degradation by means of boiling aqueous-alcoholic sulphuric acid gives only a poor yield of benzoylcarbinol. Interaction of the potassium derivative of ethyl 3:4:5-trimethoxybenzoylacetate (I) and benzoyl peroxide affords ethyl 3:4:5-trimethoxybenzoylbenzoyloxyacetate, m. p. 107°. Long-continued heating of this substance with water in a sealed tube at 200° gives ω -benzoyloxy-3:4:5-trimethoxyacetophenone, m. p. 98—100°, which cannot be condensed with *O*-benzoylphloroglucinaldehyde to a flavylium salt nor hydrolysed to trimethoxybenzoylcarbinol. Interaction of (I) with acetyl peroxide gives ethyl 3:4:5-trimethoxybenzoylacetate, m. p. 88°, which is converted by direct hydrolysis with hot dilute sulphuric acid into 3:4:5-trimethoxybenzoylcarbinol (II), m. p. 87—88° (the diphenylhydrazone of 3:4:5-trimethoxyphenylglyoxal has m. p. 137—138°). The ketone (II) condenses with *O*-benzoylphloroglucinaldehyde giving 3:7-dihydroxy-5-benzoyloxy-3':4':5'-trimethoxyflavylium chloride, converted by the successive action of cold aqueous sodium hydroxide and hydrochloric acid into delphinidin chloride 3':4':5'-trimethyl ether (III). Malvidin, contaminated with delphinidin or, more probably, delphinidin 3'-methyl ether, was obtained by hydrolysis of (III) with hydrogen bromide in acetic acid solution at 45—50°.

Condensation of *O*-acetylsyringoyl chloride, m. p. 126°, and ethyl sodioacetoacetate gives ethyl *O*-acetylsyringoylacetate (IV), m. p. 114°, which is hydrolysed to ethyl syringoylacetate (V), m. p. 92°. The esters (IV) and (V) could not be transformed into acyloxy-derivatives. Condensation of methyl *O*-benzoylsyringate, m. p. 71°, with ethyl acetate under the influence of sodium could not be effected. The acid chloride, m. p. 45°, of *O*-benzoylsyringic acid, m. p. 157° (amide, m. p. 152°), condenses with ethyl sodioacetoacetate, giving ethyl *O*-benzoylsyringoylacetate, m. p. 97—102°, which yields on hydrolysis ethyl *O*-benzoylsyringoylacetate (VI), m. p. 67° (copper derivative, m. p. 212°). Oxidation of (VI) with benzoyl peroxide gave a product converted by heating with water in a sealed tube at 160—170° into ω -benzoyloxy-4-benzoyloxy-3:5-dimethoxyacetophenone (VII), m. p. 105°, together with a small quantity of ω -hydroxy-4-benzoyloxy-3:5-dimethoxyacetophenone (VIII), m. p. 87—89°. Whilst the compound (VII) did not condense readily with *O*-benzoylphloroglucinaldehyde to form a flavylium salt, the compound (VIII) yielded a substance regarded as benzoylmalvidin chloride. Reaction of acetyl peroxide in ethereal solution with the potassium-derivative of ethyl benzoylsyringoylacetate gave a product yielding, on hydrolysis with dilute sulphuric acid, a crude benzoylcarbinol derivative together with a small quantity of a substance, m. p. 85—87°. Condensation of the benzoylcarbinol with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of hydrogen chloride gave a flavylium salt converted by debenzoylation and debenzoylation into a malvidin derivative

contaminated with salts and not containing a free hydroxyl group in position 3. Oxidation of ethyl benzylsyringoylacetate in acetic acid solution by lead tetraacetate gives *ethyl di(benzylsyringoyl)succinate* (?), m. p. 173—176°, alternatively prepared by the action of iodine on the potassium derivative of ethyl benzylsyringoylacetate. Interaction of diazomethane and benzylsyringoyl chloride in ethereal solution affords ω -*dialzo-4-benzoyloxy-3:5-dimethoxyacetophenone*, m. p. 122—123° (decomp.). The diazo-ketone decomposes in a vacuum, giving a substance, m. p. 58—59°. It is converted by the action of boiling dilute aqueous-alcoholic sulphuric acid into *O-benzylsyringoylcarbinol* (?), m. p. 85—86° (*diphenylhydrazone* of related phenylglyoxal derivative has m. p. 131° after sintering at 110°), and by warming with acetic acid into ω -*acetoxy-4-benzoyloxy-3:5-dimethoxyacetophenone* (IX), m. p. 60.5—61°. Condensation of *O*-benzoylphloroglucinaldehyde with (IX) in cold ethyl acetate solution under the influence of hydrogen chloride yields 5-benzoylmalvidin chloride (+2.5H₂O), the acetoxy- and benzoyloxy-groups being hydrolysed. The alkali colour-reaction of this 5-benzoylmalvidin chloride closely resembles that of malvin chloride. Debenzoylation by treatment with cold aqueous sodium hydroxide and subsequent acidification gives malvidin chloride (+H₂O), showing all the characteristic properties and reactions described by Willstätter and Miege (A., 1915, i, 287) and identical with a specimen obtained by hydrolysis of natural malvin chloride. When ethyl *O*-benzylsyringoylacetate is heated with water in a sealed tube at 178—180°, 4-benzoyloxy-3:5-dimethoxyacetophenone (X), m. p. 60—61° [*semi-carbazone*, m. p. 166°; 2:4-dinitrophenylhydrazone, m. p. 192—193°; *isonitroso*-derivative, m. p. 107—108° (*oxime*, m. p. 141—142°)], is obtained. Debenzoylation by hydrogen bromide in acetic acid solution yields 4-hydroxy-3:5-dimethoxyacetophenone, m. p. 117°. Attempts to prepare this substance by condensation of pyrogallol 1:3-dimethyl ether and acetyl chloride in carbon disulphide in presence of anhydrous ferric chloride resulted in formation of 3-acetoxy-2:4-dimethoxyacetophenone. Condensation of (X) with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of dry hydrogen chloride gives a mixture of the anticipated flavylum salt with a debenzoylated derivative. On complete debenzoylation and debenzoylation 5:7:4'-*trihydroxy-3':5'-dimethoxyflavylum chloride* (+H₂O), m. p. 280°, is obtained. *O*-Acetylsyringoyl chloride reacts with ethyl sodio- α -dimethoxyacetacetate, giving a product which on hydrolysis affords 4-hydroxy- ω :3:5-trimethoxyacetophenone (XI), m. p. 90°. Condensation of (XI) with *O*-benzoylphloroglucinaldehyde and hydrogen chloride gives 7:4'-*dihydroxy-5-benzoyloxy-3:3':5'-trimethoxyflavylum chloride*, converted by debenzoylation into 5:7:4'-*trihydroxy-3:3':5'-trimethoxyflavylum chloride* (+0.5H₂O) (*malvidin chloride 3-methyl ether*). This substance gives alkali colour-reactions divergent from those of malvin, malvidin, and 5-benzoylmalvidin. It is concluded that a free hydroxyl group not only in position 4', but also in position 3 is essential for the exhibition of a pure greenish-blue alkali colour-reaction in the malvidin series and that malvin is therefore a malvidin

5- or 7-diglucoside. The experiments of Karrer (A., 1927, 1197), who considers it to be malvidin 3-diglucoside, are, however, consistent with the hypothesis that malvin may be a 3- or 5-diglucoside. The 7-diglucoside configuration is thus excluded and malvin should be the 5-diglucoside of malvidin.

M. CLARK.

Synthesis of anthocyanins. V. Synthesis of 3- β -glucosidylpelargonidin chloride, believed to be identical with callistephin chloride. A. ROBERTSON and R. ROBINSON (J.C.S., 1928, 1460—1472).— ω -Chloro-4-hydroxyacetophenone is converted into ω -acetoxy-4-hydroxyacetophenone, m. p. 133° (lit. 127°), and then by means of aqueous sodium hydroxide into the sodium salt of ω -4-dihydroxyacetophenone (I) (4-carbomethoxy-derivative, m. p. 84°; 4-benzoyl derivative, m. p. 140—141°; ω :4-di-benzoyl derivative, m. p. 180—182°). Partial acetylation of (I) yields ω -hydroxy-4-acetoxyacetophenone, m. p. 95—96°, which condenses with *O*-tetra-acetyl- α -glucosidyl bromide in presence of silver carbonate in benzene solution at 35°, giving ω -*O*-tetra-acetyl- β -glucosidoxy-4-acetoxyacetophenone (II), m. p. 132°. Condensation of *O*-benzoylphloroglucinaldehyde with (II) in a mixture of ether and chloroform under the influence of dry hydrogen chloride yields 3-*O*-tetra-acetyl- β -glucosidoxy-7-hydroxy-5-benzoyloxy-4'-acetoxyflavylum chloride (III). Hydrolysis of (III) with 8% cold aqueous sodium hydroxide gives a solution of the debenzoylated and deacetylated glucoside in a form in which the pyran ring is probably open. Acidification regenerates the pyrylium salt, giving, after a difficult purification, 3- β -glucosidylpelargonidin chloride (+2H₂O) (*picrate*). This substance, which gave, on hydrolysis with 15% hydrochloric acid, pelargonidin chloride, was identical in properties with naturally-occurring callistephin chloride (A., 1917, i, 44). The distribution number between amyl alcohol and 0.5% hydrochloric acid is 32.

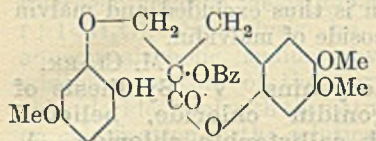
ω -*O*-Tetra-acetyl- β -glucosidoxy-4-benzoyloxyacetophenone, m. p. 147°, fails to condense with *O*-benzoylphloroglucinaldehyde to give a derivative of callistephin. ω -*O*-Tetra-acetyl- β -glucosidoxy-4-methoxyacetophenone has m. p. 133°.

Recognition of the 3-glucosidyl structure of callistephin and consideration of its properties and those of pelargonidin and pelargonin leads to the conclusion that the two last-named compounds are 5- or 7-saccharides; Karrer's experiments (A., 1927, 1197) are consistent only with the hypothesis that these anthocyanins are 3- or 5-saccharides. The 5-saccharide configuration is thus most probable.

M. CLARK.

Synthesis of brazilin and hæmatoxylin and their derivatives. III. W. H. PERKIN, jun., J. N. RAY, and R. ROBINSON (J.C.S., 1928, 1504—1513).—Reduction of trimethylbrazilone by phenylhydrazine in acetic acid solution yields deoxytrimethylbrazilone (I), together with a by-product, C₂₅H₂₂O₄N₂, m. p. 245°, described by Herzig and Pollak (A., 1905, i, 605) as the main product of this reaction. Possible constitutions for the by-product are suggested. Attempts to add the elements of water or of an acid, HX, to (I) were unsuccessful owing to the ease with which the substance under-

goes oxidation or conversion, in presence of acids, into the *isobrazilein* salt. Oxidation of (I) with perbenzoic acid in chloroform solution, under the conditions described, gives a substance, $C_{26}H_{24}O_9$, m. p. 152° , to which the annexed formula is ascribed, by analogy with the products derived from brazilein derivatives by oxidation with hydrogen peroxide.



Deoxytrimethylbrazilone yields a deep crimson *dibromide* (which gives up bromine to form *isobrazilein* hydrobromide trimethyl ether), and a *perbromide*, $C_{19}H_{18}O_4Br_6$. Reduction of (I) with hydrogen and a palladium catalyst yields a *dehydro-derivative*, m. p. 109° , converted into trimethylbrazilone (II) on oxidation with chromic acid in acetic acid solution. Reduction of (II) by aluminium amalgam yields a compound, $C_{19}H_{20}O_6 \cdot 0.5H_2O$ (?), m. p. 129° (decomp.), converted by the action of acetic anhydride into a derivative, m. p. 116° . Reduction of (II) by zinc dust in alcoholic acetic acid solution yields an intramolecular *pinacol*, $C_{19}H_{20}O_6$, m. p. $167-168^\circ$, resembling in its behaviour tetramethyldihydrobrazileinol. The pinacol yields a *formate*, *anhydro-sulphate*, and *anhydro-hydrochloride*. *O-Triacetyl-brazilone* ($+0.5H_2O$) has m. p. 187° (decomp.). *O-Tribenzoylbrazilone* has m. p. 205° (decomp.).

The nature of deoxytrimethylbrazilone dibromide and of the brazilein salts is discussed and a scheme for the synthesis of brazilein is indicated. M. CLARK.

4-Keto-2:3-thionaphthen-5:6-dihydro- γ -pyran. F. KROLLPFEIFFER and K. SCHNEIDER (Ber., 1928, 61, [B], 1284-1291).— β -3-Hydroxythionaphthenylpropionic acid,

$S \begin{smallmatrix} C_6H_4 \\ \diagup \quad \diagdown \\ CH \end{smallmatrix} \cdot C \cdot O \cdot CH_2 \cdot CH_2 \cdot CO_2H$, m. p. $164-165^\circ$, is prepared by the action of β -chloropropionic acid on 3-hydroxythionaphthen in presence of potassium hydroxide. Ring closure does not occur when it is distilled in a vacuum over phosphoric oxide or treated with concentrated sulphuric acid. It is converted through the chloride by means of aluminium chloride into 4-keto-2:3-thionaphthen-5:6-dihydro- γ -pyran, $C_6H_4 \cdot C \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ CO \cdot CH_2 \end{smallmatrix}$, m. p. $144-145^\circ$ (semicarbazone),

converted by warm alkali hydroxide into 2- β -hydroxypropionyl-3-hydroxythionaphthen, m. p. $129-130^\circ$ (phenylcarbamate, m. p. $148-150^\circ$), obtained also from 2- β -chloropropionyl-3-hydroxythionaphthen and sodium hydroxide. The following compounds are obtained by treating the methyl ether of 3-hydroxythionaphthen with the requisite acid chloride and aluminium chloride in presence of carbon disulphide: 2-acetyl-3-hydroxythionaphthen, m. p. 82° ; 2-propionyl-3-hydroxythionaphthen, b. p. $183^\circ/15$ mm., m. p. $73-74^\circ$ (semicarbazone, m. p. $188-189^\circ$); 2- β -chloropropionyl-3-hydroxythionaphthen, m. p. $121-122^\circ$, reduced by zinc dust and acetic acid to 2-propionyl-3-hydroxythionaphthen and converted by sodium carbonate into 4-keto-2:3-thionaphthen-5:6-dihydro- γ -pyran; 2-benzoyl-3-hydroxythionaphthen, m. p. $118-119^\circ$ (phenylhydrazone, m. p. $167-168^\circ$).

4-Keto-2:3-thionaphthen-5:6-dihydro- γ -pyran is not affected by bromine in carbon disulphide, but is transformed by free bromine into the *monobromo-derivative*, $C_{11}H_7O_2BrS$, m. p. $189-190^\circ$, which is not affected by boiling dimethylaniline, but is converted by 2*N*-sodium hydroxide into the compound $C_{11}H_9O_3BrS$, m. p. $135-136^\circ$. 2-Acetyl-4-methylthioltoluene is converted by bromine in carbon disulphide into the ω -bromoacetyl derivative, m. p. $77-78^\circ$ (in glacial acetic acid a compound, m. p. $226-227^\circ$, is produced), which in boiling glacial acetic acid affords a mixture of 5:5'-dimethylindigotin and 3-hydroxy-5-methylthionaphthen; the latter compound is also obtained when the bromo-substance is distilled with steam or heated above its m. p. or, similarly, from the corresponding ω -iodo-compound, m. p. $86-87^\circ$ (from the bromo-derivative and potassium iodide in acetone). 2-Propionyl-4-methylthioltoluene, b. p. $176-177^\circ/10$ mm., m. p. $42-43^\circ$, and the corresponding α -bromo-compound, m. p. 98° , are described. The latter compound loses methyl bromide when distilled with steam, yielding products, m. p. 199° and b. p. $165^\circ/10$ mm., m. p. $126-127^\circ$. 2-Bromoacetyl-4-methoxytoluene has m. p. $74-75^\circ$.

H. WREN.

[Derivatives of] diphenylene sulphide. C. COURTOT, L. NICOLAS, and T. H. LIANG (Compt. rend., 1928, 186, 1624-1626).—Chlorodiphenylene sulphide, m. p. $113-114^\circ$, is obtained from the corresponding amino-derivative (A., 1926, 605) by the Sandmeyer reaction, or by the action of cold thionyl chloride on nitrodiphenylene sulphide, m. p. 184° (loc. cit.). Bromodiphenylene sulphide, m. p. $125-126^\circ$, is prepared similarly, and also by direct bromination of diphenylene sulphide in chloroform solution. Iododiphenylene sulphide, m. p. $87-88^\circ$, is obtained by the Sandmeyer reaction. Dichloro-, m. p. $205-206^\circ$, dibromo-, m. p. 229° , and di-iodo-diphenylene sulphides, m. p. $219-220^\circ$, have been prepared from the corresponding diamino-derivative (A., 1926, 620). The same dibromo-derivative results when diphenylene sulphide is brominated. The above mono- and dibromo-compounds undergo the Grignard reaction, and monocarboxy-, m. p. 255° , and dicarboxy-, m. p. 320° , derivatives of diphenylene sulphide have been prepared. Nitration of bromodiphenylene sulphide affords a bromonitro-derivative, m. p. $264-265^\circ$, together with bromodiphenylene sulphinone, m. p. $171-172^\circ$. Reduction of the nitro-derivative gives bromoaminodiphenylene sulphide, m. p. $150-151^\circ$, from which the above dibromo-compound is obtained. The orientation of the bromonitro-derivative is therefore the same as that of the diamino-compound.

The ultra-violet absorption spectra of the above derivatives have been examined. Introduction of one halogen atom into the diphenylene sulphide molecule induces bathochromic and hyperchromic effects, which are least marked for iodine. A second halogen atom causes an increase in the bathochromic effect, the di-iodo-derivative being the most powerful, although not so pronounced as hydroxy-, amino-, or nitro-derivatives.

H. BURTON.

Organic compounds of sulphur. IX. Preparation of aromatic thioketones by the action

of thioacetic acid on keto-chlorides. Action of copper bronze on thiobenzophenone and its derivatives. A. SCHÖNBERG, O. SCHÜTZ, and S. NICKEL [with H. KRÜLL, W. MARSCHNER, and F. KAPLAN] (Ber., 1928, **61**, [B], 1375—1385; cf. this vol., 72).—A general method for the preparation of aromatic thioketones consists in the treatment of the corresponding keto-chlorides with thioacetic acid:

$\text{CAr}_2\text{Cl}_2 \xrightarrow{\text{AcSH}} \text{CAr}_2\text{Cl}\cdot\text{SH} \rightarrow \text{CAr}_2\cdot\text{S}$. Thiobenzophenone, b. p. 126—129°/0.05 mm., m. p. 51°, forms blue needles which are converted by exposure to air into a colourless, crystalline compound (decomp. above 100°) containing sulphur. 4:4'-Diphenylthiobenzophenone has m. p. 228—229°. 4-Methoxy-4'-ethoxybenzophenone, m. p. 112°, prepared from anisyl chloride and phenetole in the presence of aluminium chloride and carbon disulphide, is transformed by the successive action of oxalyl chloride and thioacetic acid into 4-methoxy-4'-ethoxythiobenzophenone, m. p. 94—96°. 2:2'-Dimethoxythiobenzophenone, m. p. 121°, and 4:4'-dimethoxythiobenzophenone, m. p. 114—115°, are described. The action of oxalyl chloride and thioacetic acid on xanthone affords xanthione, $\text{C}_{13}\text{H}_8\text{OS}$, m. p. 156°, converted by repetition of the treatment into thioxanthione, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CS} \\ \text{S} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, m. p. 168°. N-Phenylthioacridone, m. p. 227—228°, is prepared by the action of phosphorus pentasulphide on N-phenylacridone in boiling benzene.

Treatment of thiobenzophenone with copper bronze in boiling xylene in an atmosphere of nitrogen yields tetraphenylethylene. Tetra-anisylethylene, m. p. 183°, tetraphenylethylene, and tetra-4-ethoxy-m-tolylethylene are similarly prepared. Xanthione and thioxanthione afford dixanthylene and dithioxanthylene, m. p. not below 340°, respectively, whereas N-phenylthioacridone remains unchanged. H. WREN.

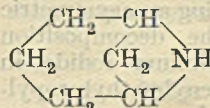
Action of aromatic Grignard reagent on methylsuccinimide. Synthesis of 2:5-diphenyl-1-methylpyrrole. R. LUKES and V. PRELOG (Chem. Listy, 1928, **22**, 244—251).—N-Methylsuccinimide reacts with magnesium phenyl bromide to yield 2-hydroxy-2-phenyl-1-methylpyrrolid-2-one, m. p. 139—141° (phenylhydrazone, m. p. 186°), and 2:5-diphenyl-1-methylpyrrole, m. p. 204°, b. p. 225—235°/12 mm. Where the Grignard reagent is not present in excess and the time of reaction is short, the former product predominates; otherwise the latter is the main product. The former substance on acid hydrolysis yields methylamine and β -benzoylpropionic acid, and on distillation under reduced pressure gives water and 5-phenyl-1-methylpyrrolone, m. p. 59°, b. p. 150—165°/9 mm. R. TRUSZKOWSKI.

The dicyclic 2:6-methylenepiperidine. J. VON BRAUN, W. HAENSEL, and F. ZOBEL (Annalen, 1928, **462**, 283—300).—In continuation of previous work (A., 1927, 266) an attempt has been made to prepare and investigate β -3-chlorocyclohexylethylmethylamine.

Resorcinol monoisoamyl ether, b. p. 165°/12 mm. (benzoate, m. p. 31—32°), from resorcinol, sodium ethoxide, and isoamyl bromide in alcoholic solution, is reduced by Sabatier's method to 3-hydroxycyclo-

hexyl isoamyl ether, b. p. 140°/16 mm. Oxidation of the latter substance gives 3-isoamylloxycyclohexanone, m. p. 128—130°/16 mm., d_4^{25} 0.9421, n_D^{25} 1.4518 (semicarbazone, m. p. 146°; oxime, b. p. 162°/12 mm.), readily converted by alkali into a ketone, $\text{C}_6\text{H}_8\text{O}$, b. p. 170—172°. The cyclohexanone reacts with a mixture of magnesium and ethyl bromoacetate in ether to give ethyl β -hydroxy- β -3-isoamylloxycyclohexylpropionate, b. p. 175°/12 mm. (?), which, when heated with potassium hydrogen sulphate at 150°, is converted into ethyl 3-isoamylloxycyclohexenylacetate, b. p. about 170°/12 mm. (?), d_4^{25} 0.9740, n_D^{25} 1.4670. Reduction of this ester with sodium and alcohol produces the corresponding acid (b. p. 190°/11 mm.), together with β -3-isoamylloxycyclohexenylethyl alcohol, b. p. 162°/11 mm., d_4^{25} 0.951, n_D^{25} 1.474. Reduction of the same ester with platinum or palladium in methyl alcohol produces 3-ethylcyclohexyl isoamyl ether, b. p. 110—120°/12 mm., together with β -3-isoamylloxycyclohexylethyl alcohol, b. p. 160°/12 mm., d_4^{25} 0.941, n_D^{25} 1.468 (7 g. from 500 g. of resorcinol). Treatment of the latter alcohol with phosphorus pentabromide in chloroform solution gives β -3-isoamylloxycyclohexylethyl bromide, b. p. 155°/16 mm., which is converted by methylamine in benzene solution at 100° into β -3-isoamylloxycyclohexylethylmethylamine, b. p. 140°/14 mm., and the latter, with concentrated hydrochloric acid at 125°, affords the hydrochloride and thence the chloroplatinate of β -3-chlorocyclohexylethylmethylamine, m. p. 171—173° (previous sintering), obtained only in minute quantities.

Sodium and alcohol reduction of 3-isoamylloxycyclohexanone oxime (above) gives 3-isoamylloxycyclohexylamine, b. p. 120°/13 mm., d_4^{25} 0.898 (hydrochloride, m. p. 134—136°; chloroplatinate, decomp. 240—243°; acetyl derivative, b. p. 190—192°/12 mm.; benzoyl derivative, m. p. 61—64°). When the base is heated with fuming hydrobromic acid at 100° it is converted into 3-bromocyclohexylamine, hydrobromide, m. p. 206—208° (corresponding picrate, m. p. 175—177°). Cold alkali, or warm alkali for only a short time, liberates the free base, but prolonged action of warm alkali gives a mixture of the following substances: (1) tetrahydroaniline, giving a p-toluenesulphonyl derivative, m. p. 75°; (2) 2:6-methylenepiperidine (annexed formula) (hydrochloride, m. p. 258°; picrate, m. p. 158—162°; N-p-toluenesulphonyl derivative, m. p. 123°), reduced by hydrogen and palladised animal



charcoal to cyclohexylamine; (3) N-cyclohexenyl-1:3-diaminocyclohexane, $\text{C}_6\text{H}_9\cdot\text{NH}\cdot\text{C}_6\text{H}_9\cdot\text{NH}_2$, b. p. 112—115°/14 mm. (dibenzoyl derivative, m. p. 188—189°), giving when exhaustively methylated (one stage) a salt from which a chloroplatinate, $\text{C}_{17}\text{H}_{33}\text{N}_2\text{Cl}_6\text{Pt}$, m. p. 185—186°, is isolable; and (4) a base regarded, on account of its b. p. (140—145°/14 mm.), as $(\text{C}_6\text{H}_{11}\text{N})_3$. In the actual identification of (1) and (2) (mixed together after preliminary separation of the whole mixture by distillation), exhaustive methylation was carried out. This gave two methiodides: (1) that, $\text{C}_9\text{H}_{18}\text{NI}$, m. p. 241—242°, derived from tetrahydroaniline, and (2) that, $\text{C}_8\text{H}_{16}\text{NI}$, m. p. 206—208°, derived from methylenepiperidine.

When the above *isoamyloxycyclohexanone* is treated with phenylhydrazine etc. in the course of a dihydrocarbazole synthesis, amyl alcohol is eliminated. Such removal is much less ready in the case of 2-*isoamyloxycyclohexanone*, b. p. 116°/12 mm., d_4^{20} 0.9377 (*semicarbazone*, m. p. 166°; *oxime*, b. p. 155°/14 mm.), which may be obtained by oxidising *hexahydropyrocatechol monoisoamyl ether* (2-*hydroxycyclohexyl isoamyl ether*), b. p. 122°/12 mm. E. E. TURNER.

Asymmetric nitrogen atom. LV. True autoracemisation with optically active ammonium salts. E. WEDEKIND and G. L. MAISER (Ber., 1929, 61, [B], 1364—1375; cf. this vol., 74).—1-Methyl-1-allyltetrahydroquinolinium iodide is resolved into its optical components by treatment with silver *d*-bromocamphorsulphonate in a mixture of acetone and ethyl acetate, removal of silver iodide, and concentration of the filtrate. The highest observed molecular rotations for the cation are +202° and -157°. Conversion into the active iodides by the action of potassium iodide in water or sodium iodide in acetone on the camphorsulphonates requires great caution to avoid racemisation. The highest observed values for $[M]_D$ for the active iodides are +28° and -27°, these figures being notably lower than those calculated. Water and methyl and ethyl alcohols cause a relatively rapid diminution of activity, whereas acetone and chloroform are without action. The effect of water accounts for the difference between the observed and calculated values for the optical activity of the iodides. In water at 20° the reaction coefficient for a unimolecular change is found to be $k=0.00543$, whereas in alcoholic solution $k=0.00643$. In chloroform at 25° $k=0.00131$ to 0.00198, whereas optical constancy is observed in solutions in acetone. In water or alcohol the rate of reaction remains constant throughout the change, whereas in chloroform the values of k increase progressively. This latter phenomenon is characteristic of inactivation due to the decomposition of the molecule. In water and alcohol, on the other hand, the electrical conductivity remains unchanged throughout the reaction and hence inactivation is a truly stereochemical transformation such as was observed previously with compounds containing an asymmetric carbon atom. The course of the decomposition of 1-methyl-1-allyltetrahydroquinolinium iodide in chloroform resembles that of phenylmethylpropyl-allylammonium iodide, so that ring formation appears to have no influence on this property. The absence of decomposition in alcoholic solution is further established by the almost quantitative recovery of the iodide by precipitation with ether after such period as would suffice for complete racemisation and by the observation that the temperature coefficient in the interval of 10° (20—30°) is 2.06, whereas for a decomposing salt the value is 3.6—4.1. True autoracemisation is observed only with salts containing ionisable halogen attached to nitrogen. Aqueous solution of 1-methyl-1-allyltetrahydroquinolinium bromocamphorsulphonate are optically stable after addition of alkali nitrate or sulphate, whereas the activity falls after addition of potassium chloride, bromide, or iodide.

1-Methyl-1-ethyltetrahydroquinolinium iodide, m. p. 174°, and 1-ethyl-1-allyltetrahydroquinolinium iodide (two forms, decomp. 136° and 118°) are incidentally described. H. WREN.

Stereoisomerism of 8-hydroxydecahydroquinoline and its derivatives. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 161—171).—The hydrogenation of 8-hydroxyquinoline in acetic acid at 40—45° in presence of platinum-black yielded decahydroquinoline (10%), b. p. 89—93°/20 mm., and two isomeric 8-hydroxydecahydroquinolines, b. p. 136—146°/20 mm., (A), m. p. 111—112° (50—60%), obtained by recrystallisation from light petroleum, and (B), m. p. 92—93° (30—40%), separated by recrystallisation of its *hydrobromide*, m. p. 251°. A third isomeride (C), m. p. 101—102°, was obtained from (A) or (B) by heating the sodium derivatives. (A) yielded a *hydrochloride*, m. p. 201—202°, *hydrobromide*, m. p. 202—203°, *chloroaurate*, m. p. 191—192°, O-benzoyl derivative, m. p. 89—91° (+H₂O) and 130—131° (anhydrous) [*hydrochloride*, m. p. 255—256° (decomp.)], NO-dibenzoyl derivative, m. p. 81—83° (by the action of benzoyl chloride in pyridine), and *d*-bromocamphorsulphonate, m. p. 189—192°. (B) yielded a *hydrochloride*, m. p. 247—248°, *chloroaurate*, m. p. 188—189°, and O-benzoyl derivative, m. p. 93—95° (+H₂O) and 135—136° (anhydrous) [*hydrochloride*, m. p. 251° (decomp.)]. (C) yielded a *hydrochloride*, m. p. 245—246°, *chloroaurate*, m. p. 152—153°, O-benzoyl derivative (anhydrous), m. p. 99—100°, and NO-dibenzoyl derivative, m. p. 92—93°, stable to permanganate. Heating the *hydrochloride* of (C) with formaldehyde yielded the *N*-methyl derivative, b. p. 125—126°/8 mm. [double salts not crystallisable with exception of the *picrate*, m. p. 123—124°, and *methiodide*, m. p. 285—286° (decomp.)], from which was obtained the O-benzoyl-*N*-methyl derivative, m. p. 91—92° (*chloroplatinate*, m. p. 231°; *picrate*, m. p. 193—195°). The hydroxyl group in (C) was not methylated by methyl sulphate and alkali, only the above *N*-methyl methiodide being isolated after treatment with potassium iodide. This methiodide gave on decomposition a small quantity of a *base*, isolated as the *picrate*, C₁₇H₂₄O₇N₄, m. p. 173—174°. d-8-Hydroxydecahydroquinoline (C) *d*-bromocamphorsulphonate, m. p. 294—295°, $[\alpha]_D^{25} +84.9^\circ$, separated from water, and yielded the *d*-base, $[\alpha]_D^{25} +47.6^\circ$ (*hydrobromide*, m. p. 213—214°, $[\alpha]_D^{25} +29.6^\circ$). The salt of the *l*-base (from the mother-liquors), m. p. 262—263°, $[\alpha]_D^{25} +41.8^\circ$, yielded the *l*-base, $[\alpha]_D^{25} -53.1^\circ$ (*hydrobromide*, m. p. 211—213°, $[\alpha]_D^{25} -31.6^\circ$).

Hydrogenation of quinoline in presence of platinum-black (cf. Hückel and Stepf, A., 1927, 572) yielded decahydroquinoline, m. p. 48—48.5° [*hydrobromide*, m. p. 277—279°; *chloroaurate*, m. p. 124—125°; *chloroplatinate*, m. p. 228° (decomp.)]; benzoyl derivative, m. p. 53—54° (yielding on oxidation β-2-benzamidocyclohexylpropionic acid, m. p. 199—200°), and a liquid isomeride, b. p. 205—206° and 89—91°/19—21 mm., d_4^{20} 0.9426, n_D^{20} 1.4926 [*hydrobromide*, m. p. 232°; *hydrochloride*, m. p. 223—224°; *chloroaurate*, m. p. 157—158°; *picrate*, m. p. 135—136°; *benzoyl derivative*, m. p. 96—97° (yielding on oxidation β-2-benz-

amidocyclohexylpropionic acid, m. p. 156—157°]. The liquid isomeride was also obtained in 10% yield on reduction by Sabatier's method (A., 1914, i, 323).

R. K. CALLOW.

Reactions of bromo-derivatives of 2-amino-pyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (Ber., 1928, 61, [B], 1236—1244; cf. following abstract).—The interaction of methyl iodide with 3:5-dibromo-2-aminopyridine resembles that with 2-aminopyridine, yielding mainly 3:5-dibromo-1-methyl-2-pyridoneimide, m. p. 99—100° [hydriodide (+0.5H₂O), m. p. 218—219° (decomp.) after darkening at 200°], with a small proportion of 3:5-dibromo-2-methylaminopyridine, m. p. 56.5—57°. The constitution of the latter compound follows from its formation by the action of methyl sulphate on the sodium derivative of 3:5-dibromo-2-aminopyridine and by the direct bromination of 2-methylaminopyridine, whereby 5-bromo-2-methylaminopyridine, m. p. 70—71°, is isolated as an intermediate product. With nitrous acid it gives the corresponding nitroso-derivative, m. p. 56—57°, whereas 3:5-dibromo-1-methyl-2-pyridoneimide gives 3:5-dibromo-1-methyl-2-pyridone. Dibromomethylaminopyridine with sulphuric and nitric acids yields 3:5-dibromo-2-nitromethylaminopyridine, m. p. 100—101°. Under similar conditions, 3:5-dibromo-2-aminopyridine affords a mixture of 3:5-dibromo-2-nitroaminopyridine, m. p. 123° (decomp.) after darkening at 121°, and 3-bromo-5-nitro-2-aminopyridine, m. p. 216—217°. Methylation of 3:5-dibromo-2-nitroaminopyridine with methyl sulphate affords 3:5-dibromo-2-methylnitroaminopyridine, m. p. 100—101°, and 3:5-dibromo-1-methyl-2-pyridonenitroimide, m. p. 186—187°. The latter compound is also obtained by the nitration of 3:5-dibromo-1-methyl-2-pyridoneimide; it is transformed by boiling water into 3:5-dibromo-1-methyl-2-pyridone, m. p. 182°. Nitrous acid converts the dibromomethylpyridoneimide into 3:5-dibromo-1-methyl-2-pyridone. The action of concentrated sulphuric acid on 3:5-dibromo-2-nitroaminopyridine and 3:5-dibromo-2-methylnitroaminopyridine affords 3:5-dibromo-2-hydroxyaminopyridine, m. p. 208°, and 3:5-dibromo-2-methylnitrosoaminopyridine, m. p. 56—57°. Replacement of bromine by the nitro-group or wandering of the methyl radical does not occur with 3:5-dibromo-1-methyl-2-pyridonenitroimide under similar conditions.

H. WREN.

Nitro-derivatives of methylated forms of 2-aminopyridine. II. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (Ber., 1928, 61, [B], 1233—1235; cf. A., 1925, i, 1328).—Repetition and extension of previous work on the methylation of nitroaminopyridines shows that the methyl group wanders from the ring nitrogen atom of the pyridine nucleus to the amino-group. The presence of nitro-groups in one of the 3 or 5 positions impedes the addition of methyl iodide to the ring nitrogen atom; if a methyl group is already attached to this atom, the union is loosened.

5-Nitro-2-aminopyridine is converted by methyl iodide at 120° almost quantitatively into 5-nitro-2-methylaminopyridine, m. p. 181° (regarded previously as 5-nitro-1-methylpyridoneimide). 3-Nitro-2-amino-

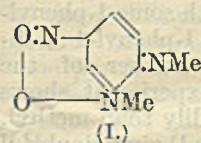
pyridine is transformed similarly into 3-nitro-2-methylaminopyridine, m. p. 63—64°, b. p. 262—262.5°/740 mm. 1-Methyl-2-pyridonenitroimide is isomerised by cold, concentrated sulphuric acid to a mixture of the nitromethylaminopyridines described above. 2-Methylaminopyridine is converted by a mixture of concentrated sulphuric acid and nitric acid (d 1.5) into 2-nitromethylaminopyridine, C₅H₄N·NMe·NO₂, m. p. 30—31°, which is converted by concentrated sulphuric acid into 2-nitrosomethylaminopyridine, m. p. 111—112°, 5-nitro-2-methylaminopyridine, m. p. 181°, and 3-nitro-2-methylaminopyridine, m. p. 63—64°. Boiling, dilute alkali hydroxide converts 5-nitro-2-methylaminopyridine into 5-nitro-2-hydroxypyridine, m. p. 190—191°, and methylamine, a similar change occurring with the isomeride. More concentrated alkali hydroxide decomposes the methylamino-compounds completely, whereas 5-nitro-2-aminopyridine is smoothly transformed into 5-nitro-2-hydroxypyridine and ammonia under these conditions. The preparation of 5-nitro-2-nitrosomethylaminopyridine, m. p. 112—113°, and 3-nitro-2-nitrosomethylaminopyridine, m. p. 102—103°, is recorded. 3-Bromo-5-nitro-2-methylaminopyridine, m. p. 163—164°, and 5-bromo-3-nitro-2-methylaminopyridine, m. p. 149—150°, are described. 3-Nitro-2-methylaminopyridine is converted by concentrated sulphuric acid and nitric acid (d 1.5) into 3-nitro-2-methylnitroaminopyridine, m. p. 89°. Methylation of 5-nitro-2-nitroaminopyridine with methyl sulphate affords 5-nitro-2-nitroaminomethylpyridine, m. p. 59—60°, and 5-nitro-1-methyl-2-pyridonenitroimide. The following isomerisations of methyl derivatives of nitroaminopyridines by sulphuric acid are recorded: 3-nitro-2-nitromethylaminopyridine to 3:5-dinitro-2-methylaminopyridine, m. p. 147—148°, also obtained (in addition to other compounds) from 5-nitro-2-nitroaminomethylpyridine; 5-nitro-1-methyl-2-pyridonenitroimide chiefly to 3:5-dinitro-2-methylaminopyridine or 5-nitro-2-methylaminopyridine, mainly according to temperature. 3-Nitro-2-nitroaminopyridine is isomerised to dinitro-2-amino-pyridine.

5-Nitro-2-methylaminopyridine is converted by methyl iodide at 125° into a mixture of 5-nitro-2-methylaminopyridonium iodide, m. p. 225° (decomp.), and 5-nitro-2-dimethylaminopyridine, m. p. 152—153°. The methyl iodide is converted by ammonia into the compound (I), m. p. 149.5—150.5°, obtained also by nitration of 1-methyl-2-pyridonemethyl-imide; it is transformed by boiling water into 5-nitro-1-methyl-2-pyridone, m. p. 171—172°, 5-nitro-2-methylaminopyridine, m. p. 181°, methyl alcohol, and methylamine.

5-Nitro-2-dimethylaminopyridine is transformed by boiling 5% sodium hydroxide into 5-nitro-2-hydroxypyridine and dimethylamine. Acetic anhydride at 100° converts 5-nitro-2-methylaminopyridine into its acetyl derivative, m. p. 99°; 3-nitro-2-methylaminopyridine is unchanged under these conditions.

H. WREN.

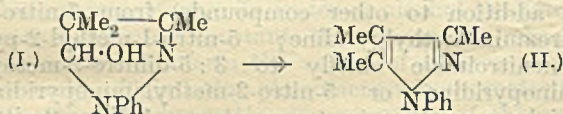
Molecular compounds in the veronal series. P. PFEIFFER and R. SEYDEL (Z. physiol. Chem., 1928,



176, 1—16).—Veronal but not dimethylveronal forms additive compounds with pyramidone, antipyrine, and sarcosine anhydride (cf. Pfeiffer and Angern, A., 1926, 739); monosubstituted veronals, *N*-methylveronal, and *N*-phenylveronal form no true chemical compounds of this type, as determined by the mixed m.-p. curve method. Substitution of the two ethyl groups of veronal by hydrogen (barbituric acid) or one only by phenyl (luminal) does not destroy the power to form additive compounds. Luminal gives molecular compounds with antipyrine, with pyramidone, m. p. 132°, and with sarcosine anhydride (mol. ratio 2 : 1), m. p. 127°; barbituric acid forms compounds with antipyrine and with sarcosine anhydride, but these compounds have not been isolated. *N*-Methylbarbituric acid, like methylveronal, does not give additive compounds. Veramone solutions precipitated with ammonium sulphate yield precipitates which contain veronal and pyramidone in the mol. ratio 1 : 1, and not 1 : 2 as suggested by Mareeuw (Pharm. Weekblad, 1927, 30, 753).

A. WORMALL.

Ease of wandering and strength of attachment of organic radicals in transformations of alkylated hydroxypyrazolines. K. VON AUWERS and F. DERSCH (Annalen, 1928, 462, 104—134).—As stated by Knorr and Jochheim (A., 1903, i, 528), 5-hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline (I) is converted by concentrated sulphuric acid into 1-phenyl-3 : 4 : 5-trimethylpyrazole (II). This type of change has now been extensively studied in order to obtain further evidence as to the strengths of attachment, i.e., valency requirements, of different radicals. Some striking dissimilarities are discovered. The 4 : 4-diethylpyrazoline changes like (I), but does so much more readily, whilst the 4 : 4-dipropyl deriv-



ative eliminates propyl alcohol and not water, giving 1-phenyl-3-methyl-4-propylpyrazole. (The diallyl member gave tars, whilst the dibenzyl and diphenyl compounds could not be prepared.) The 4-methyl-4-ethyl compound gives mainly 1-phenyl-3 : 4-dimethyl-5-ethylpyrazole, together with some 1-phenyl-3 : 5-dimethyl-4-ethylpyrazole or 1-phenyl-4 : 5-dimethyl-3-ethylpyrazole. Although neither of the latter can be isolated pure, the experiment shows that ethyl migrates much more readily than methyl. The 4-ethyl-4-*n*-propyl compound (as I) gives doubtful results when treated with sulphuric acid, but an examination of the less complex case of 5-hydroxy-1-phenyl-3 : 4-diethyl-4-*n*-propylpyrazoline shows that the propyl group retains its position, whilst the ethyl group wanders. 5-Hydroxy-1-phenyl-3 : 4-dimethyl-4-*n*-propylpyrazoline is converted by sulphuric acid into 1-phenyl-3 : 4-dimethylpyrazole, with total elimination of propyl, and a similar result is obtained with the corresponding pyrazolines containing isopropyl, *n*-butyl, allyl, and benzyl radicals together with methyl in position 4. In every case 1-phenyl-3 : 4-dimethylpyrazole is formed, although the precise proportions of other products are difficult to establish.

The work enables certain definite conclusions to be reached. Measurement of the speed of disappearance of the different pyrazolines shows firstly that the nature of the substituent in position 3 is of no great consequence. Secondly, assuming in the cases in which water alone is eliminated that the intermediate at once changes to a pyrazole, it is clear that elimination of water is aided by substitution of methyl (in position 4) once or twice by ethyl. This again shows the smaller valency requirement of ethyl as against methyl. The loosely-attached allyl group confers a very high transformation rate on the pyrazolines studied, as would be anticipated, yet the benzyl group unexpectedly produces the converse effect. Other anomalies are that the 4 : 4-methylpropyl- and -dipropyl-pyrazoline derivatives undergo rapid conversion, whilst the intermediate ethylpropyl compound is particularly slow in changing. The results do show, however, that a methyl group is most firmly held, and that *n*-butyl, allyl, and benzyl groups are loosely held. Intermediately come ethyl, *n*-propyl, and isopropyl. Further, it is by no means certain that a radical (e.g., phenyl) possessing large valency requirements is necessarily firmly held.

The pyrazolines required are prepared by reducing the appropriate pyrazolones using sodium and boiling amyl alcohol. The pyrazolones are obtained by converting a β -ketonic ester into the phenylhydrazone (at 100°), and then heating the latter, as a rule, at 180° until a test portion heated with acid no longer gives phenylhydrazine.

1-Phenyl-3-methyl-4-propyl-5-pyrazolone, from ethyl *n*-propylacetoacetate, has m. p. 101—102°; the isopropyl analogue has m. p. 116—117° and b. p. 186—190°/15 mm.; the *n*-butyl analogue has m. p. 93.5—94.5° and b. p. 210°/16 mm. 1-Phenyl-3 : 4 : 4-trimethyl-5-pyrazolone has b. p. 300—303°/750 mm. and 158—160°/12 mm. 1-Phenyl-3 : 4-dimethyl-4-ethyl-5-pyrazolone, from ethyl methylethylacetoacetate, has m. p. 25.5—27.5°, b. p. 301°/760 mm. and 163—165°/12 mm. The 4-*n*-propyl analogue has b. p. 185—189°/13 mm.; the isopropyl analogue (intermediate phenylhydrazone has m. p. 111—113°) has m. p. 66—75° (indef.); the 4-*n*-butyl analogue has b. p. 205°/20 mm., d_4^{20} 1.039, and n_D^{20} 1.54023; the 4-allyl analogue has b. p. 189°/12 mm., d_4^{20} 1.0684, and n_D^{20} 1.55564; the 4-benzyl analogue has m. p. 81—82°. 1-Phenyl-3-methyl-4 : 4-diethyl-5-pyrazolone has m. p. 51—52°, b. p. 170°/11 mm., 1-phenyl-3-methyl-4-ethyl-4-*n*-propyl-5-pyrazolone, b. p. 181°/12 mm., 1-phenyl-3-methyl-4 : 4-di-*n*-propyl-5-pyrazolone, b. p. 184°/12 mm., and 1-phenyl-3-methyl-4 : 4-diallyl-5-pyrazolone, b. p. 192°/11 mm. Ethyl propiopropionate, from ethyl propioacetate and methyl iodide etc., has b. p. 199° or 83°/15 mm., and is convertible into ethyl α -dimethylpropioacetate, b. p. 83°/15 mm., from which 1-phenyl-3-ethyl-4 : 4-dimethyl-5-pyrazolone, b. p. 310° or 177°/11 mm., is obtained. 1-Phenyl-3 : 4-diethyl-4-*n*-propyl-5-pyrazolone, b. p. 203—208°/30 mm., d_4^{20} 1.035, n_D^{20} 1.54634, is obtained from ethyl α -ethyl- α -*n*-propylpropioacetate, b. p. 138—142°/40 mm., synthesised from ethyl α -*n*-propylpropioacetate, b. p. 127°/30 mm. 1-Phenyl-4 : 4-dimethyl-3-*n*-propyl-5-pyrazolone, b. p. 305°/30 mm., is obtained from ethyl α -dimethyl-*n*-butyroacetate, b. p. 99—104°/15

mm., itself obtained from ethyl α -methyl-*n*-butyrate, which has b. p. 115—121°/38 mm.

Whilst ethyl dibenzylacetoacetate may be converted into the *hydrazone*, m. p. 112—113° (cf. Giua, A., 1916, i, 608), the latter does not pass normally into the expected 1-phenyl-4:4-dibenzyl-3-methyl-5-pyrazolone, which, however, may be the *product*, m. p. 139—140°, of the action of benzyl chloride on 1-phenyl-4-benzyl-3-methyl-5-pyrazolone in alcoholic sodium ethoxide solution.

The following 5-hydroxy-1-phenyl-3:4-dimethyl-4-alkyl-pyrazolines are described: 4-ethyl-, m. p. 97—98°; 4-*n*-propyl-, m. p. 98°; 4-*n*-butyl-, m. p. 104.5—106°; 4-allyl-, m. p. 95.5—97.5°; and 4-benzyl-, m. p. 121°.

5-Hydroxy-1-phenyl-3-methyl-4:4-diethylpyrazoline has m. p. 94—95°; 5-hydroxy-1-phenyl-3-methyl-4:4-di-*n*-propylpyrazoline, m. p. 87—89.5°; 5-hydroxy-1-phenyl-4:4-dimethyl-3-ethylpyrazoline, m. p. 78.5—79.5°; and 5-hydroxy-1-phenyl-4:4-dimethyl-3-*n*-propylpyrazoline, m. p. 85—86°.

The following pyrazoles, prepared largely as reference compounds, were made either from $\alpha\gamma$ -diketones and phenylhydrazine or from the corresponding pyrazolones and phosphorus tribromide and yellow phosphorus at 200°. 1-Phenyl-3-methyl-4-*n*-propylpyrazole has b. p. 155—164°/15 mm. [*picrate*, m. p. 111—112.5°; *mercuric chloride additive* compound, m. p. 180° (indef.); *hydrochloride*, m. p. 84—91°; *hydrobromide*]. 1-Phenyl-3-methyl-4-isopropylpyrazole has b. p. 160—165°/15 mm. (*picrate*, m. p. 100.5—101.5°; *hydrobromide*, m. p. 144°). 1-Phenyl-3-methyl-4-*n*-butylpyrazole, b. p. 170°/16 mm., forms a *picrate*, m. p. 90—93°. 1-Phenyl-3:4-dimethyl-5-ethylpyrazole has b. p. 283° or 150°/12 mm. (not 150°/75 mm. as lit.) (*picrate* formation suggests presence of the other possible isomeride, since two *picrates*, m. p. 112° and 87—94°, result) (*mercuric chloride* compound, m. p. 108—110°). 1-Phenyl-3:5-dimethyl-4-ethylpyrazole has m. p. 79—80°, b. p. 159°/15 mm. (*picrate*, m. p. 114.5—115°; *mercuric chloride* compound, m. p. 135—139°). 1-Phenyl-3-methyl-4:5-diethylpyrazole, b. p. 170°/17 mm., gives a *picrate*, m. p. 89.5—90.5°, and a *mercuric chloride* compound, m. p. 142.5—143.5°. 1-Phenyl-3-methyl-4-ethyl-5-*n*-propylpyrazole, b. p. 175°/12 mm., forms two interconvertible *picrates*, m. p. 53—65° and 84—85°, and a *mercuric chloride* compound, m. p. 126—127°. 1-Phenyl-3:5-dimethyl-4-*n*-propylpyrazole has b. p. 166°/11 mm. (*picrate*, m. p. 99—100°; *mercuric chloride* compound, m. p. 127.5—128.5°). 1-Phenyl-3:4-dimethyl-5-*n*-propylpyrazole has b. p. 190—192°/33 mm. and 160°/11 mm. (*picrate*, m. p. 75—76°; *mercuric chloride* compound, m. p. 102—104°). 1-Phenyl-3-methyl-5-ethyl-4-*n*-propylpyrazole, b. p. 172°/12 mm., forms a *picrate*, m. p. 85—87°, and a *mercuric chloride* compound, m. p. 136—137°. 1-Phenyl-3:5-dimethyl-4-isopropylpyrazole has m. p. 36—37°, b. p. 194°/40 mm., d_4^{20} 1.024, and n_D^{20} 1.55810 (*picrate*, m. p. 92.5—93.5°; *mercuric chloride* compound, m. p. 128—130°). 1-Phenyl-3:5-dimethyl-4-*n*-butylpyrazole has b. p. 180—184°/14 mm., 1-phenyl-3:5-dimethyl-4-allylpyrazole, b. p. 205°/40 mm., d_4^{20} 1.028, and n_D^{20} 1.56932 (*picrate*, m. p. 87—89.5°). $\alpha\alpha$ -Dipropionylbutane, b. p. 100°/15 mm. (*copper salt*,

m. p. 160—161°), is converted by phenylhydrazine into 1-phenyl-3:5-diethyl-4-*n*-propylpyrazole, b. p. 180—185°, d_4^{20} 0.996, n_D^{20} 1.54474 (*picrate*, m. p. 103.5—105.5°; *mercuric chloride* compound, m. p. 102—105°).

The conversions of pyrazolines into pyrazoles are in general effected by means of concentrated sulphuric acid at 100°. The following data are recorded: The 3:4:4-trimethylpyrazoline is completely transformed in 1 hr. into 1-phenyl-3:4:5-trimethylpyrazole, the *mercuric chloride* compound of which has m. p. 167.5° (not 131—132° as Jochheim, Diss., Jena, 1896). The 3-methyl-4:4-diethylpyrazoline takes 2—5 min. for transformation into 1-phenyl-3-methyl-4:5-diethylpyrazole, b. p. 284° or 141°/15 mm. The 3-methyl-4:4-di-*n*-propylpyrazoline rapidly affords a mixture of mono- and di-propylpyrazoles. The 3:4-dimethyl-4-ethyl compound (2 min.) gives 1-phenyl-3:4-dimethyl-5-ethylpyrazole, b. p. 154°/15 mm., from which the *picrate*, m. p. 112°, is obtained (see above). The 4:4-dimethyl-3-ethylpyrazoline ($\frac{1}{2}$ —1 hr.) affords 1-phenyl-4:5-dimethyl-3-ethylpyrazole, b. p. 282° or 156°/12 mm. (*picrate*, m. p. 110—111°; *mercuric chloride* compound, m. p. 130—130.5°). The 3-methyl-4-ethyl-4-propylpyrazoline (1½ hrs.) affords some 1-phenyl-3-methyl-4-ethylpyrazole (*mercuric chloride* compound, m. p. 123—125°), but mainly a *phenylmethylethylpropylpyrazole*, b. p. 295—297° or 173—175°/17 mm., which forms a *mercuric chloride* compound, m. p. 132—133°, and may or may not be identical with the above 1-phenyl-3-methyl-5-ethyl-4-propylpyrazole. The 3:4-diethyl-4-propylpyrazoline gives 1-phenyl-3:5-diethyl-4-propylpyrazole, b. p. 175—180°/16 mm. or 170—175°/10 mm. The 4:4-dimethyl-3-*n*-propylpyrazoline readily passes into 1-phenyl-4:5-dimethyl-3-propylpyrazole, b. p. 180—185°/35 mm., d_4^{20} 1.014, n_D^{20} 1.55435 (*picrate*, m. p. 72—74°; *mercuric chloride* compound, m. p. 110—111°). The 3:4-dimethyl-4-propylpyrazoline gives a mixture of products, containing 1-phenyl-3:4-dimethylpyrazole.

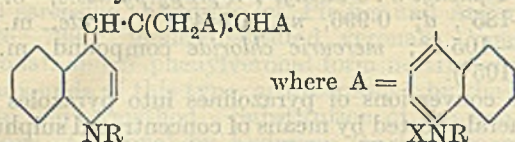
E. E. TURNER.

Preparation of 2:2'-dipyridyl. J. P. WIBAUT and J. OVERHOFF (Rec. trav. chim., 1928, 47, 761—763).—2:2'-Dipyridyl, m. p. 70.1°, b. p. 273—275° (*picrate*, m. p. 157—158.5°), is obtained in 60% of the theoretical yield by boiling a solution of 2-bromopyridine in *cymene* with copper powder for 1½ hrs. Some pyridine is also formed. With 2-iodopyridine the yield of 2:2'-dipyridyl is only 20%; 2-chloropyridine does not react.

R. BRIGHTMAN.

Neocyanine. F. M. HAMER (J.C.S., 1928, 1472—1478).—The formation of neocyanine (B., 1927, 566) as a by-product in the preparation of 1:1'-diethyl-4:4'-carbocyanine iodide by the action of ethyl orthoformate on lepidine ethiodide in presence of pyridine (this vol., 76) has been described. This method is now applied to the preparation of *neocyanine ethiodide*, m. p. about 284° (decomp.), *ethobromide*, m. p. about 291° (decomp.), and *methobromide*, m. p. about 288° (decomp.); the best yield of neocyanine obtained was 41% of theory. By increasing the amount of pyridine, the yield of the 4:4'-carbocyanine is increased at the expense of that of the

neocyanine. It is suggested that neocyanine is represented by the formula



This hypothesis is based on analytical evidence, a consideration of the method of formation and of the properties of the neocyanines, and on analogy.

M. CLARK.

Porphyrin syntheses. XVII. Syntheses of opso- and hæmo-pyrrolicarboxylic acids. Synthesis of coproporphyrin. II. H. FISCHER and W. LAMATSCH (Annalen, 1928, 462, 240—250).—The methods (A., 1926, 1261) by which opso-pyrrolicarboxylic acid (4-methylpyrrole-3-propionic acid) was obtained are unsuitable for preparative purposes and other methods have been sought. Reduction of bis-(5-carbethoxy-4-methyl-3- β -carboxyethylpyrrol)-methane with hydriodic and acetic acids gives a 40—48% yield of opso-pyrrolicarboxylic acid, but, in addition, 80—84% of the theoretical yield of cryptopyrrolicarboxylic acid, so that this method is also unsuitable.

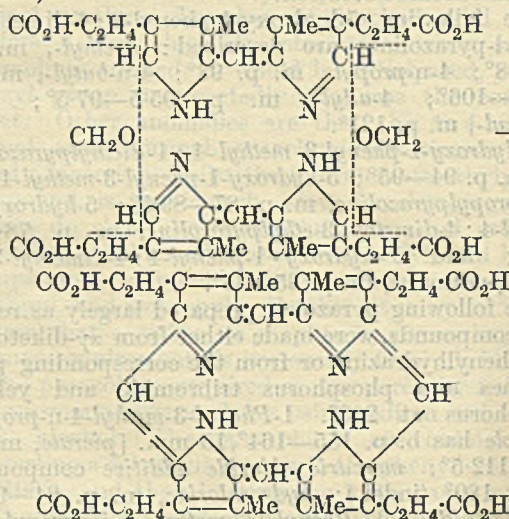
The readily obtained 5-carbethoxy-2:4-dimethylpyrrole-3-aldehyde is convertible without difficulty into the -3-acrylic and thence into the -3-propionic acid, viz., 5-carbethoxycryptopyrrolicarboxylic acid. The bromination of the latter is now under investigation; the resulting bromo-compound (readily characterised by heating it with alcohol, which converts it into 5-carbethoxy-4-methyl-2-ethoxymethylpyrrole-5-propionic acid, m. p. 152°) reacts with 3 mols. of sulphuryl chloride (cf. this vol., 776) in cold ethereal solution to give 5-carbethoxy-4-methyl-3- β -carboxyethylpyrrole-2-carboxylic acid, m. p. 243°, hydrolysed by alkali to 4-methyl-3- β -carboxyethylpyrrole-2:5-dicarboxylic acid, m. p. 220° [or (?) 224—226°]. The latter, when heated in a vacuum at 220°, passes into opso-pyrrolicarboxylic acid, which is, however, better prepared by heating the carbethoxy-acid, m. p. 243°, with alkali at 175—180°, under pressure. Opso-pyrrolicarboxylic acid resists all attempts at esterification, and when treated with sodium nitrite gives, not the oxime of cryptopyrrolicarboxylic acid, but a 50% yield of hæmatic acid.

When heated with formic and hydrobromic acids, opso-pyrrolicarboxylic acid is converted into (3-methyl-4- β -carboxyethylpyrrol)-(3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. 194—195° (decomp.), which, with glacial acetic and hydriodic acids at 100°, undergoes scission into opso- and hæmo-pyrrolicarboxylic acids. Opso-pyrrolicarboxylic acid, when dissolved in chloroform and ether, reacts with hydrogen cyanide and chloride to give the expected imine (not isolated), which, when reduced by the Kishner-Wolff method at 160°, gives a good yield of hæmopyrrolicarboxylic acid.

Bromination of the last-named methene (hydrobromide?) affords (5-bromo-3-methyl-4- β -carboxyethylpyrrol)-(5-bromo-3-methyl-4- β -carboxyethylpyrrolenyl)-methene hydrobromide, which, when heated with cryptopyrrolicarboxylic acid and succinic acid at

180°, is converted into the tetramethyl ester, m. p. 288°, of coproporphyrin II.

When opso-pyrrolicarboxylic acid methene hydrobromide is heated at 120° with formic and hydrobromic acids, only traces of porphyrin are produced, but the ester, m. p. 288°, results when the methene hydrobromide is heated with formaldehyde and hydrobromic acid at 120—125°, the constitution of coproporphyrin II thus being definitely established (annexed scheme):



Opso-pyrrolicarboxylic acid 2-aldehyde, when heated with hydrobromic acid or with formic and hydrochloric acids, gives a methene identical with that obtained from opso-pyrrolicarboxylic acid (when the methene so formed is heated with hydrobromic acid and formaldehyde, coproporphyrin II is formed and may be identified as the tetramethyl ester).

E. E. TURNER.

Hæmin syntheses. I. H. FISCHER and K. ZEILE (Annalen, 1928, 462, 210—230).—Addition of bromine (vapour) in light petroleum solution to ethyl 2:4-dimethyl-3-vinylpyrrole-5-carboxylate produces ethyl 2:4-dimethyl-3- $\alpha\beta$ -dibromoethylpyrrole-5-carboxylate, m. p. 133°, whilst use of 3 mols. of bromine in glacial acetic acid gives ethyl 3-bromo-2:4-dimethylpyrrole-5-carboxylate, identical with the product of brominating ethyl 2:4-dimethylpyrrole-5-carboxylate. When a carbon disulphide or light petroleum solution of the vinylpyrrole is treated with hydrogen chloride, ethyl 2:4-dimethyl-3- α -chloroethylpyrrole-5-carboxylate, m. p. 95°, is formed, and this reacts with methyl-alcoholic potassium methoxide to give ethyl 2:4-dimethyl-3- α -methoxyethylpyrrole-5-carboxylate, m. p. 115°, also produced when the vinylpyrrole is treated with methyl-alcoholic hydrogen chloride, followed by basification. On the other hand, when the vinylpyrrole is heated with methyl-alcoholic sulphuric acid, it is apparently converted into methyl 2:4-dimethyl-3-vinylpyrrole-5-carboxylate, m. p. 123°.

Oxidation of the methoxyethyl derivative with chromic anhydride in acetic acid gives a mixture of ethyl 2:4-dimethyl-3-vinylpyrrole-5-carboxylate and 5-carbethoxy-2:4-dimethylpyrrole-3-carboxylic acid, the latter being formed by the similar oxidation of the vinyl derivative. Bromine converts ethyl 2:4-

dimethyl-3- α -methoxyethylpyrrole-5-carboxylate into ethyl 3-bromo-2:4-dimethylpyrrole-5-carboxylate.

When ethyl 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate is treated with magnesium methyl iodide, there is formed ethyl 2:4-dimethyl-3- α -hydroxyethylpyrrole-5-carboxylate, m. p. 100.5°, converted by phosphorus pentachloride in carbon disulphide into a chloro-compound which with potassium methoxide affords a methoxy-derivative identical with that (m. p. 115°) described above, the constitution of which is thus established.

If ethyl 2:4-dimethyl-3- α -hydroxyethylpyrrole-5-carboxylate is heated in a vacuum at 150°, there is formed a dimeride, m. p. 187°, also produced by boiling a light petroleum solution of ethyl 2:4-dimethyl-3- α -chloroethylpyrrole-5-carboxylate.

A well-defined potassium salt of ethyl 2:4-dimethyl-3- β -nitrovinylpyrrole-5-carboxylate is obtained by treating the latter with methyl-alcoholic potassium methoxide. The nitrovinyl ester brominates abnormally in acetic acid solution, the monobromo-derivative (m. p. 177°) formed not containing a 2-bromomethyl group, since instead of being converted by boiling water into a methene, it gives ethyl 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate. Similarly, 2:4-dimethylpyrrole-3-aldehyde is readily brominated, but apparently to give 5-bromo-2:4-dimethylpyrrole-3-aldehyde, m. p. 149° (decomp.). A methene of the type desired is, however, obtained as follows: 2:4-dimethylpyrrole-3-aldehyde is converted by formaldehyde in boiling aqueous alcoholic solution into bis-(3-aldehydo-2:4-dimethylpyrrol)methane, m. p. 286° (condensation product with aniline, C₂₁H₂₁N₃, has m. p. 165°; condensation product with Wurster's base, C₂₃H₂₆N₄, has m. p. 145°), which passes into the corresponding methene hydrobromide when treated with bromine in acetic acid (methene base sinters at 207°, decomp. 255–260°).

2:4-Dimethylpyrrole-3-aldehyde condenses with nitromethane in alcoholic solution, in presence of a little methylamine hydrochloride and sodium carbonate, to give 2:4-dimethyl-3- β -nitrovinylpyrrole, m. p. 149°, converted by hot formaldehyde solution into bis-(2:4-dimethyl-3- β -nitrovinylpyrrol)methane. 2:4-Dimethylpyrrole-3-aldehyde and malononitrile condense in presence of alcoholic methylamine (as above) giving 2:4-dimethyl-3- $\beta\beta$ -dicyanovinylpyrrole, m. p. 148° (the similarly prepared 2:4-dimethyl-5- $\beta\beta$ -dicyanovinylpyrrole has the same m. p.), which is converted by formaldehyde into bis-(2:4-dimethyl-3- $\beta\beta$ -dicyanovinylpyrrol)methane. The latter, when boiled with alkali, gives bis-(3-aldehydo-2:4-dimethylpyrrol)methane, as does the last-named nitrovinylmethane.

2:4-Dimethyl-3- $\beta\beta$ -dicyanovinylpyrrole is converted by hydrogen cyanide in chloroform and ether in presence of hydrogen chloride into the imino hydrochloride, which with ice-water passes into 2:4-dimethyl-3- $\beta\beta$ -dicyanovinylpyrrole-5-aldehyde, m. p. 207°, and this when heated with alkali gives 2:4-dimethylpyrrole-3:5-dialdehyde, m. p. 165° (Waseneger, Diss., Techn. Hochsch., München, 1927).

Ethyl 2:4-dimethylpyrrole-5-carboxylate is converted by β -chloropropionyl chloride and aluminium chloride in carbon disulphide solution into ethyl

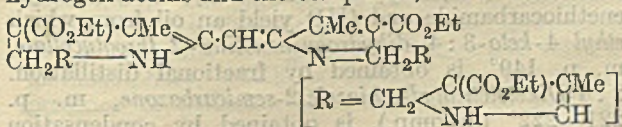
3- β -chloropropionyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 138°, reacting with dimethylamine to give ethyl 3- β -dimethylaminopropionyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 78° (sintering) (hydrochloride, m. p. 184°). The similarly prepared ethyl 3-dimethylaminoacetyl-2:4-dimethylpyrrole-5-carboxylate has m. p. 87–88° (hydrochloride, m. p. 214°). 3-Hydroxyacetyl-2:4-dimethylpyrrole-5-carboxylic acid, m. p. 231°, is formed when ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate is heated with alkali, and, when heated at 210–230°, passes into 3-hydroxyacetylpyrrole-2:4-dimethylpyrrole, m. p. 143°. The last with formaldehyde affords bis-(3-hydroxyacetyl-2:4-dimethylpyrrol)methane, m. p. 252° (previously sintering).

3-Methoxyacetyl-2:4-dimethylpyrrole-5-carboxylic acid at 170° gives 3-methoxyacetyl-2:4-dimethylpyrrole, m. p. 127°. Ethyl 3-ethoxyacetyl-2:4-dimethylpyrrole-5-carboxylate has m. p. 113–114°.

E. E. TURNER.

Determination of active hydrogen in hæmin, in certain of its derivatives, and in pyrroles. III. H. FISCHER and P. ROTHMUND (Ber., 1928, 61, [B], 1268–1276; cf. A., 1926, 630; 1927, 1099).—In consequence of the very varying results obtained by the application of Zerevitinov's method to hæmins and pyrroles, the reaction itself has been subjected to critical examination. Zerevitinov's postulate that experiments are valid only when the blank value zero is obtained can be fulfilled by suitable treatment of pyridine, but very slight exposure of the solvent to moist air frequently suffices to destroy this ideal condition so that it is not practicable to fulfil this desideratum invariably. Further, comparable data are obtained only when analyses are completed within approximately equal times and the minimum gas evolution is adopted for calculation, thus introducing a somewhat arbitrary factor. It is essential that the compound under investigation should be completely dissolved throughout the whole reaction. Under these conditions, bis-2-carbethoxy-2:4-dimethylpyrrolmethene gives 1–1.5 active hydrogen atoms, whereas for its hydrobromide the value 2.6–2.97 is obtained (about 1 atom more than required by theory). High results are obtained with (2-bromo-3-carbethoxy-4-methylpyrrol)-(3'-carbethoxy-2':4'-dimethylpyrrol)methene, whereas almost identical values are obtained with the aldazine of 5-aldehydo-2:4-dicarbethoxy-3-methylpyrrole and its copper derivative.

It appears therefore that the methene as well as the imino-group of pyrroles is active toward the Grignard reagent. The Zerevitinov method is thus not applicable to the hæmins and porphyrins which contain four methene groups of which the behaviour cannot be predicted. Confirmation of this view is found in the observation that (4-hydroxy-3-carbethoxy-2-methylpyrrol)-(3'-carbethoxy-2':4'-dimethylpyrrolenyl)methane gives only two active hydrogen atoms and the compound,



contains only 2.6. Determination of active hydrogen in a series of hæmins and porphyrins with exclusion of all possible errors fails to give concordant results. With hæmin the variation is between two and three at the atmospheric temperature. Hæmin dimethyl ester and the iron salt of tetramethylhæmatoporphyrin contain exactly one active hydrogen atom. As a mean, hæmin has three active hydrogen atoms, but certain data must be disregarded without apparent reason. Uro- and isouro-porphyrin esters, octaethylporphyrin, and acetonepyrrole give varying results from which definite conclusions cannot be reached. With xanthoporphinogens paradoxical values are obtained. Contrary to the literature, azobenzene does not contain active hydrogen.

It is concluded that unavoidable catalysts greatly influence the evolution of gas during the Zerevitinov reaction and that this effect is also produced by complex pyrrole derivatives. H. WREN.

Thiazole derivatives. II. H. W. STEPHEN and F. J. WILSON (J.C.S., 1928, 1415—1422; cf. A., 1926, 1262).—Diacetophenonethiocarbohydrazone reacts in alcoholic solution in presence of sodium ethoxide with ethyl α -bromopropionate (I), ethyl α -bromo-n-butyrate (II) and ethyl phenylbromoacetate, yielding 3-phenylmethylmethylenamino-2:4-diketo-5-methyl (ethyl or phenyl)tetrahydrothiazole-2-phenylmethylmethylenehydrazone, m. p. 150°, 110°, and 165°. Thiocarbohydrazide and ethyl chloroacetate (III) yield 3-amino-2:4-diketo-5-tetrahydrothiazole-2-hydrazone (?), m. p. 119—120°. 3-Amino-2:4-diketo-5-methyltetrahydrothiazole-2-hydrazone, m. p. 100—101° (dibenzylidene derivative, m. p. 114°), and 3-amino-2:4-diketo-5-ethyltetrahydrothiazole-2-hydrazone (?), m. p. 92—93° (dibenzylidene derivative, m. p. 106°), were prepared similarly from (I) and (II), respectively. *o*-Phenyleneithiocarbamide with sodium ethoxide and (I) or (II) yields respectively ethyl benziminazolyl-2- α -thiolpropionate (IV), m. p. 100° (dimorphous), and ethyl benziminazolyl-2- α -thiol-n-butyrate (V), m. p. 108—109° (dimorphous). Hydrolysis of (V) with hydrochloric acid affords benziminazolyl-2- α -thiol-n-butyric acid, m. p. 176° (decomp.). When (IV) is heated in dry benzene solution with sodium and the solid thereby deposited is treated in alcoholic solution with concentrated aqueous hydrochloric acid, no compound of dicyclic structure can be isolated, but benziminazolyl-2- α -thiolpropionic acid, m. p. 179° (decomp.), is formed. When dry gaseous hydrogen chloride is substituted for aqueous hydrochloric acid in the above procedure, a compound, m. p. 118—119°, is produced. When (V) undergoes similar treatment, a compound, m. p. 120°, results. Benziminazole-2-thioglycollic acid, m. p. 215°, is obtained by heating together *o*-phenyleneithiocarbamide and aqueous chloroacetic acid. Ethyl 1:4:5:6-tetrahydropyrimidine-2-thioglycollate, m. p. 256° (decomp. from 200°), is prepared by heating trimethylenethiocarbamide and (III) in pyridine solution, whilst benzoylenethiocarbamide and (III) yield an oil from which ethyl 4-keto-3:4-dihydroquinazoline-2-thioglycollate, m. p. 149°, is obtained by fractional distillation. 2:4-Diketotetrahydrothiazole-2-semicarbazone, m. p. 221—222° (decomp.), is obtained by condensation

of hydrazothiodicarbonyl with chloroacetic acid, and yields 2:4-diketotetrahydrothiazole and semicarbazide on hydrolysis with hydrochloric acid. Hydrazodithiodicarbonyl and (III) in alcoholic sodium ethoxide solution yield a substance regarded as 2:4-diketotetrahydrothiazole-2-ketazine, since it is hydrolysed by hydrochloric acid to 2:4-diketotetrahydrothiazole and hydrazine. This substance was previously regarded by Frerichs and Höller (A., 1913, i, 909) as 3:3-bis- ψ -thiohydantoin. Acetophenone-8-phenylthiosemicarbazone has m. p. 195°. M. CLARK.

Aminothiophenol [benzthiazole] derivatives. J. POLLAK, E. RIESZ, and Z. KAHANE (Monatsh., 1928, 49, 213—228).—4:4'-Dichloro-2:2'-dinitrodiphenyl disulphide (Blanksma, A., 1901, i, 461) on treatment with an alkaline sodium sulphide solution yields the sodium salt of chloronitrothiophenol, which without being isolated is treated with chloroacetic acid; on acidification, 4-chloro-2-nitrophenylthioglycollic acid, m. p. 209—210°, separates. This when treated with concentrated sulphuric acid at 100° yields 5:5'-dichloro-7:7'-dinitrobisthionaphthen-indigo; it is oxidised by peracetic acid to 4-chloro-2-nitrophenylsulphonacetic acid, m. p. 158°, and reduced by zinc and acetic acid to 6-chlorobenzo-3-ketodihydro-1:4-thiazine, $C_6H_3Cl \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{S}-\text{CH}_2 \end{smallmatrix}$, m. p. 204°.

Dichlorodinitrodiphenyl disulphide is reduced by zinc and acetic acid to a product which, filtered from zinc and zinc mercaptide and recrystallised from hydrochloric acid, is 4-chloro-2-aminothiophenol hydrochloride, m. p. 207°. This when heated with nitrous acid yields 5-chlorobenzthiadiazole.

$C_6H_3Cl \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{N}$, m. p. 107° (cf. Beilstein and Kurbatow, A., 1879, 231). When the chloroaminothiophenol in alcoholic solution is treated with picryl chloride, a picryl derivative, $C_{12}H_7O_6N_4ClS$, is obtained, decomp. on heating; when, however, a solution of the hydrochloride in alcohol is treated with picryl chloride and sodium acetate, and the mixture is heated, the product is 6-chloro-2:4-dinitrophenanthiazine (cf. Kehrman, A., 1900, i, 62), m. p. 280° (charring). When the reduction of the dichlorodinitrodiphenyl disulphide is effected by zinc in a mixture of acetic acid, acetic anhydride, and sodium acetate, the product is 4-chloro-1-methylbenzthiazole, $C_6H_3Cl \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{CMe}$.

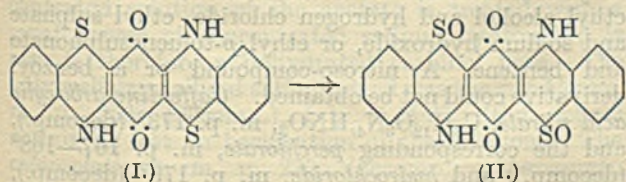
The reagent chloronitrophenylsulphur chloride condenses with dichlorodiaminodiphenyl disulphide in ether to give the hydrochloride, m. p. 182°, of a base, 4'-chloro-2'-nitrophenylthiol-2:2'-diamino-4:4'-dichlorodiphenyl disulphide, m. p. 164—165°, which further condenses in benzene with the reagent, to give bis-[4-chloro-2-(*p*-chloro-*o*-nitrophenylthiolamino)-phenyl] disulphide, $(NO_2 \cdot C_6H_3Cl \cdot S \cdot NH \cdot C_6H_3Cl \cdot S)_2$, m. p. 159°. No reaction is observed between chloroaminothiophenol and the reagent. *p*-Aminothiophenol in ether condenses with the reagent to give the hydrochloride, m. p. 205°, of the base 4'-chloro-2'-nitro-4-aminodiphenyl disulphide, m. p. 130—131°; the latter condenses with a further quantity of the reagent to give chloronitroaminodiphenyl disulphide

hydrochloride and 4-chloro-2-nitro-4'-(*p*-chloro-*o*-nitro-phenylthiolamino)diphenyl disulphide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{S}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{S} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NO}_2$, m. p. 187°. It is suggested that the failure of *p*-chloro-*o*-aminothiophenol to react with the reagent is due to its existence as an internal salt, thus: $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{NH}_2 \\ \text{S} \end{smallmatrix}$.

When anilinetrisulphonyl chloride (Lustig and Katscher, A., 1927, 867) is reduced in acetone by zinc and hydrochloric acid, and filtered immediately a cloudiness or precipitate appears, dilution with water followed by ether extraction gives the unstable 2:4:6-trithiolaniline. This with picryl chloride yields a tripicryl derivative, which on treatment with alcoholic potassium hydroxide gives 2:4-dinitro-7:9-di(picrylthiol)phenthiazine, soluble in nitrobenzene only. Reduction of anilinetrisulphonyl chloride by zinc, acetic acid and anhydride, and sodium acetate yields in the ethereal extract 3:5-di(acetylthiol)-1-methylbenzthiazole, m. p. 127°, and in the residue a product extracted by hydrochloric acid, and also obtained by the action of alcohol and hydrochloric acid on the above product, viz., 3:5-dithiol-1-methylbenzthiazole, m. p. 180–181°. This and the corresponding disulphide obtained by oxidation are only faintly yellow, and are not dyes, for the production of which a second fused benzene ring or series of rings is required.

E. W. WIGNALL.

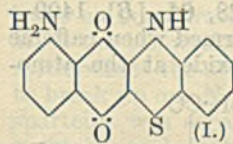
Dibenzodithiazinoquinone, a class of vat dyes. II. Reaction between nitric acid and dibenzodithiazinequinone. R. SHIBATA (J. Soc. Chem. Ind. Japan, 1928, 31, 73–75).—When dibenzodithiazinequinone was treated with a cold mixture of fuming nitric acid and glacial acetic acid, a substance was obtained which resembles orange-II in colour, is soluble in dilute alkali, and forms crystalline compounds with alkali hydroxides which are soluble in water. From the hyposulphite vat containing sodium hydroxide, it gives the same shade on fibres as dibenzodithiazinoquinone (I). Analysis shows that the action of the mixed acid is one of oxidation, not of nitration, resulting in the formation of the corresponding sulfoxide (II).



Y. TOMODA.

lin-Benzo-*p*-thiazinoquinones. K. FRIES, W. PENSE, and O. PEETERS (Ber., 1928, 61, [B], 1395–1402; cf. A., 1922, i, 577; 1924, i, 525).—2:5-Dianilino-3:6-dimethylthiol-*p*-benzoquinone, m. p. 260°, is unexpectedly converted by hydrogen peroxide in glacial acetic acid into 2:5-dianilino-*p*-benzoquinone. Dibenzothiazinoquinone (formula I, preceding abstract), which does not melt below 360°, is obtained by treating dichlorodianilino-*p*-benzoquinone with sodium disulphide in boiling alcohol. With alkali hydroxide and sodium hyposulphite it gives a golden-yellow vat from which

cotton is dyed feebly, wool readily. The diacetyl compound is described. The quinone is reduced to the corresponding quinol, m. p. above 360° (tetraacetyl derivative, m. p. 305°). Oxidation of the dye with hydrogen peroxide in concentrated sulphuric acid affords the disulphone, $\text{C}_{18}\text{H}_{10}\text{O}_6\text{N}_2\text{S}_2$, m. p. above 360°. Chloranil and *p*-anisidine yield 2:5-dichloro-3:6-di-*p*'-methoxyanilino-*p*-benzoquinone, m. p. 291°, transformed into dimethoxybenzothiazinoquinone, m. p. above 300°. 2:2:3:3:4-Pentachloro-5-nitro-1-keto-1:2:3:4-tetrahydronaphthalene, m. p. 159° (decomp.), is obtained by prolonged treatment of a solution of 5-nitro- α -naphthylamine in hydrochloric and acetic acids with chlorine. It is converted by treatment with aqueous sodium hydrogen sulphite into 2:3:4-trichloro-5-nitro- α -naphthol, m. p. 208° (acetate, m. p. 150°), which is transformed by nitric acid in glacial acetic acid into 2:3:4-trichloro-4:5-dinitro-1-keto-1:4-dihydronaphthalene, m. p. 85° (decomp.). When warmed with concentrated sulphuric acid the ketone is converted into 2:3-dichloro-5-nitro-1:4-naphthaquinone, m. p. 176°. The latter compound is also obtained by the nitration of 2:3-dichloro-1:4-naphthaquinone. 3-Chloro-5(8)-nitro-2-anilidonaphthaquinone, m. p. 273°, and sodium sulphide in aqueous alcohol afford 5(8)-amino-2-anilino-3-thiol-1:4-naphthaquinone, which is further converted into 9-amino-*lin*-benzo-naphtho-*p*-thiazinoquinone (I), m. p. 300° (monoacetyl derivative, m. p. 300°).



m. p. 300°).

2:3-Dichloro-5-nitro-1:4-naphthaquinone is reduced by stannous chloride and hydrochloric acid in glacial acetic acid to 2:3-dichloro-5-amino-1:4-dihydroxynaphthalene hydrochloride, oxidised by ferric chloride to 2:3-dichloro-5-amino-1:4-naphthaquinone, m. p. 220°. 3-Chloro-5(8)-amino-2-anilino-1:4-naphthaquinone has m. p. 210°.

H. WREN.

Stereochemistry of the saturated tervalent nitrogen atom. VIII. Methylisopelletierine. J. MEISENHEIMER and E. MAHLER (Annalen, 1928, 462, 301–316).—Methylconhydrinone and methylisopelletierine, regarded by Hess and Grau as stereoisomerides (A., 1925, i, 425), are shown to be structural isomerides. The former substance is, as these authors suppose, α -2-*N*-methylpiperidylpropan- α -one [2-propionyl-1-methylpiperidine], but methylisopelletierine is now shown to be α -2-*N*-methylpiperidylpropan- β -one [2-acetonyl-1-methylpiperidine].

If Hess and Grau's contention were correct, the supposed stereoisomerides should give one and the same methiodide, but two distinct methiodides are obtained. Further, methylisopelletierine and methylconhydrinone differ greatly in their reactions as ketones. The former is readily reduced to an alcohol, the latter is not, and so on.

Hess' supposed α -2-*N*-methylpiperidylpropan- β -one is shown to be a mixture (cf. A., 1917, i, 350, 352; 1918, i, 34). The pure ketone has been synthesised as follows: 2- β -hydroxy-*n*-propylpyridine (preparative details for this are given) is converted into the methosulphate, which is reduced catalytically in presence of platinum-platinum oxide to 1-methyl-

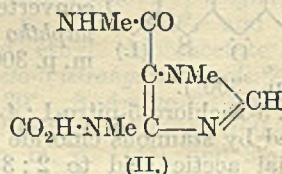
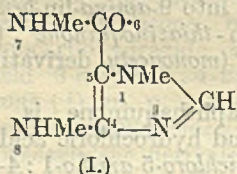
2- β -hydroxy-*n*-propylpiperidine, b. p. 110—120°/22 mm. Oxidation of the latter with chromic anhydride in glacial acetic acid at the b. p. gives methylisopelletierine, identified by conversion into the picrate, hydrochloride, hydrobromide, chloraurate, methiodide, semicarbazone, and semicarbazone hydrochloride.

Catalytic reduction of 2- β -hydroxy-*n*-propylpyridine affords 2- β -hydroxy-*n*-propylpiperidine, m. p. 69—70° (the low m. p. 45—47° given by Ladenburg is accounted for by the hygroscopic nature of the substance). Oxidation of the latter with chromic anhydride in acetic acid produces isopelletierine [α -2-piperidylpropan- β -one], the picrate of which melts at 147—148°, not at 113—115° as stated by Hess and Eichel (A., 1918, i, 34).

Methylation of 2- β -hydroxy-*n*-propylpiperidine by Hess' method (A., 1916, i, 67; 1917, i, 351) gives 1-methyl-2- β -hydroxy-*n*-propylpiperidine, identical with the above product. Its picrate melts at 145°, not at 136—137° as stated by Hess, whose product was evidently a mixture; the semicarbazone hydrochloride has decomp. 210°, not 183° (Hess).

E. E. TURNER.

Caffeidine and caffeidinecarboxylic acid. H. BILTZ and H. RAKETT (Ber., 1928, 61, [B], 1409—1422).—Caffeidine (I) is readily formed when caffeine is shaken with 2*N*-sodium hydroxide at the atmo-



spheric temperature and is separated from the resulting solution as the *nitrate*, m. p. 215° (decomp.). The filtrate from the salt is treated with sodium acetate and copper acetate, whereby copper caffeidinecarboxylate is precipitated. Caffeidine, m. p. 93°, is isolated from the nitrate by dissolution in sodium carbonate and extraction with chloroform. When moist, it is very sensitive to air, but can be preserved unchanged when dry if protected from light. It behaves as a monoacid base; the *perchlorate*, $\text{C}_7\text{H}_{12}\text{ON}_4\cdot\text{HClO}_4$, m. p. 220—221° (decomp.), *hydrochloride*, m. p. 215° (decomp.), and the *vanadylmalonate*, $(\text{C}_7\text{H}_{12}\text{ON}_4)_2\cdot\text{H}_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, are described. With silver nitrate and a little ammonia it affords *silver dicaffeidine nitrate*, $\text{Ag}(\text{C}_7\text{H}_{12}\text{ON}_4)_2\cdot\text{NO}_3$. The basic nature of caffeidine appears to be due to the nitrogen atom 3; the methylamino-residue attached to carbon atom 4 appears incapable of adding acid, probably owing to the immediate presence of the double linking. *Benzoylcaffeidine* has m. p. 174°. The action of nitrous acid gives *nitrosocaffeidine*, m. p. 155° (decomp.), in which the imino-group 8 suffers change, the methylamino-residue 7 remaining unaffected, since *allocaffuric acid* and *caffeidinecarboxylic acid* do not react with nitrous acid. Methyl sulphate and potassium hydroxide transform caffeidine into *methylcaffeidine*, m. p. 86° (*perchlorate*, m. p. 173°), whereas it is not affected by diazomethane. 1:3-Dimethylparabanic acid is readily formed by oxidation of caffeidine, probably according

to the scheme: $(\text{I}) \rightarrow \text{NHMe}\cdot\text{CO}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}\cdot\text{NMe} > \text{CO}$. The double linking between carbon atoms 4 and 5 is readily established by the action of methyl alcohol and chlorine, whereby the *dimethyl ether of caffeidine-4:5-glycol*, m. p. 164° (*hydrochloride*), is produced. The action of chlorine water on caffeidine affords the *monohydrated hydrochloride* of the base, $\text{CO} < \text{NMe} \begin{array}{c} \text{CH}\cdot\text{OH} \\ | \\ \text{NH}\cdot(\text{NHMe})\text{C}\cdot\text{OH} \end{array}$, m. p. 112°, from which the free base, m. p. 163° (decomp.), is derived by means of potassium cyanate.

Caffeidine is readily converted into caffeine by treatment with ethyl chloroformate or potassium cyanate. Carbamide and caffeidine when treated with hydrogen chloride afford *caffeidine-8-carboxylamide*, m. p. 244—245°, which is transformed by boiling, dilute mineral acids into theobromine and methylamine, thus establishing the constitution of the amide; analogous reactions could not be effected with thiocarbamide or guanidine. With thiocarbonyl chloride caffeidine affords *2-thiocaffeine*, m. p. 205° after softening at 203° [*perchlorate*, m. p. 239—240° (decomp.)], which is readily chlorinated in chloroform to *8-chloro-2-thiocaffeine*, m. p. 186—187°. Treatment of the latter compound with sodium methoxide affords *8-methoxy-2-thiocaffeine*, m. p. 174°, from which *2-thiotetramethyluric acid*, m. p. 297—298°, and *2-thio-1:3:7-trimethyluric acid*, m. p. 343° (apparent decomp.), are derived by the action of methyl alcohol at 200° and warm dilute hydrochloric acid, respectively. 8-Chloro-2-thiocaffeine and potassium hydrogen sulphide afford *2:8-dithio-1:3:7-trimethyluric acid*, $\text{C}_8\text{H}_{10}\text{ON}_4\text{S}_2$, m. p. 285° (decomp.) (*monosodium* and *monopotassium* salts). Treatment of the dithioacid with alkali hydroxide and the requisite alkyl sulphate or bromide yields the *methyl*, m. p. 183°, *ethyl*, m. p. 156°, and *allyl*, m. p. 98°, *ethers* of 2-thio-8-thiolcaffeine.

Caffeidinecarboxylic acid, m. p. 159° (decomp.), with acetic acid of crystallisation, m. p. 127—129°, is obtained from the copper salt (see above). An ester could not be obtained by treating the copper salt with ethyl iodide at 105—110° or from the free acid by ethyl alcohol and hydrogen chloride, ethyl sulphate and sodium hydroxide, or ethyl *p*-toluenesulphonate and benzene. A nitroso-compound or a benzoyl derivative could not be obtained. *Caffeidinecarboxylic acid nitrate*, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_4\cdot\text{HNO}_3$, m. p. 173° (decomp.), and the corresponding *perchlorate*, m. p. 167—168° (decomp.), and *hydrochloride*, m. p. 179° (decomp.), are described.

H. WREN.

Sparteine. I. K. WINTERFELD (Arch. Pharm., 1928, 266, 299—325).—Sparteine is not readily attacked by many reagents: it is recovered unchanged after being treated with ethyl chloroformate, or hydrogen iodide in glacial acetic acid at the b. p. or even at 180°. When oxidised it tends to break down completely, but Gadamer's reagent, viz. mercuric acetate in dilute acetic acid, is now found to effect a stepwise dehydrogenation. In the cold two hydrogen atoms are removed and, when the three acetatomercuric groups introduced are eliminated, there remains in the solution the acetate of *dehydrosparteine*,

$C_{15}H_{24}N_2$. Dehydrosparteine is isomeric with Willstätter's spartyrine (A., 1905, i, 544), but differs completely from the dehydro-compound of Wolfenstein and Reitmann (A., 1927, 887). It is a viscous oil, unsaturated and unstable when exposed to air. It has $[\alpha]_D -142.10^\circ$ (in chloroform) and so presumably a double linking has been formed in proximity to an asymmetric carbon atom. It is not displaced from its salts except by alkali hydroxide and so appears to be the anhydride of the carbinol form of a quaternary ammonium base. Moureu and Valeur's formula for sparteine (A., 1913, i, 89) allows of various possibilities, but, as will be seen, the main result of the present work is to throw doubt on the validity of this formula. Dehydrosparteine chloroplatinate, m. p. 255° (decomp.), chloroaurate, m. p. $155-158^\circ$, and mercuric chloride double salt, m. p. $256-257^\circ$ (decomp.), are described. When the base is reduced with zinc and hydrochloric acid sparteine is apparently not regenerated, for the product has $[\alpha]_D$ about -18.5° and yields an amorphous chloroaurate, m. p. $166-167^\circ$. Dehydrosparteine is oxidised by potassium permanganate in cold acetone solution, the equivalent of five oxygen atoms being consumed. The acid so obtained is a syrup which is converted with difficulty into the methyl or ethyl ester. The methyl ester, $C_{15}H_{26}O_2N_2$, yielded once a solid chloroplatinate, m. p. $256-257^\circ$ (decomp.), but other solid derivatives were not obtained. Efforts to prepare a chloride or an amide, or to reduce the ethyl ester to the corresponding alcohol were likewise fruitless, and on distillation the esters decomposed completely. The methyl ester yields an oily monoacetyl and an oily mononitroso-derivative, so that it is evident that in the oxidation one nitrogen atom has become secondary in function. A hydrazide (benzylidene derivative, m. p. 207°) is also obtained; this yields a nitrosoazide which is normally converted by way of the nitrosourethane into the amine (picrate, m. p. 187°), but all these derivatives are either gummy or viscous oils. When the oxidation of sparteine with mercuric acetate is carried out in hot solution, four hydrogen atoms are lost. The product, didehydrosparteine, $C_{15}H_{22}N_2$, is extracted only by using an ether-chloroform mixture, when a concentrated solution of the acetate is treated with a great excess of concentrated sodium hydroxide; it also is therefore a dehydrated carbinol base. The only well-crystallised salt obtained was the perchlorate, m. p. 256° (decomp.), $[\alpha]_D +44.87^\circ$ (the optical activity is lost on basification of the solution). The chloroplatinate, m. p. 273° (decomp.), chloroaurate, m. p. 147° (decomp.), picrate, m. p. 178° (decomp.), and mercuric chloride double salt, m. p. $196-198^\circ$ (decomp.), are also described. This stepwise oxidation of sparteine is evidence that there are two independent nitrogen ring systems in the compound, but suggests that they are either not, as Moureu and Valeur's formula (*loc. cit.*) would indicate, symmetrically arranged about a central carbon atom or not built on a similar plan. Didehydrosparteine is oxidised by potassium permanganate in cold dilute sodium carbonate solution, the equivalent of ten oxygen atoms being consumed, to a dibasic acid, the methyl ester, $C_{15}H_{26}O_4N_2$, and ethyl ester, $C_{17}H_{30}O_4N_2$, of which are syrups. The methyl ester yields diacetyl,

and dinitroso-derivatives, and so it is proved that both nitrogen atoms are now secondary in function. The acetyl derivative of the ester was reduced by Karrer's modification of Bouveault and Blanc's method to the corresponding amino-alcohol, which was obtained in passable yield; it was converted directly by treatment first with phosphorus pentachloride in chloroform solution, and then with amalgamated zinc and hydrochloric acid into a base, $C_{13}H_{24}N_2$ (?), the chloroaurate of which had m. p. 145° (decomp.). The methyl ester gave a dihydrazide, a resinous mass [benzylidene derivative, m. p. 175° (decomp.)], which was successively converted into an oily dinitrosodiazide, a syrupy dinitrosourethane, and so into a diamino-compound, which, as was to be expected from its possessing two primary and two secondary amino-groups, yielded a tetrabenzoyl derivative; this was an oil, but gave a crystalline chloroaurate, m. p. 98° (decomp.).

[With W. IPSEN.]—A preliminary account is given of attempts to carry out the Hofmann exhaustive methylation, which was the main theme of Moureu and Valeur's work (*loc. cit.*), with particular attention to the following points: (i) the products of each destructive distillation to be hydrogenated so as to leave no unsaturated linkings; (ii) after each methylation the isomerides to be separated; (iii) in forming methiodides the action to be if possible stepwise, *i.e.*, to break up one N-ring at once. The α -methiodide of sparteine was separated and converted into methylsparteine as described by Moureu and Valeur. It was not found possible to hydrogenate this directly by catalytic methods. The substance is a mixture of α - and β -methylsparteines, and the α -compound was separated in a pure condition as the sparingly soluble monohydriodide. It was then successfully hydrogenated, in glacial acetic acid solution and using platinum oxide as catalyst, to dihydro- α -methylsparteine, which is converted, with difficulty, into a dimethiodide, m. p. 125° . The formation of this dimethiodide rendered it impossible to carry out proposal (iii).

W. A. SILVESTER.

Solutions of quinine in ethylurethane. M. GIORDANI (Annali Chim. Appl., 1928, 18, 239—244).—When heated at 100° or exposed to ultra-violet rays in presence of various substances, solutions of quinine undergo transformation into the toxic isomeride, quinotoxin. Among the accelerators of this change are urethane and glycerol, which are largely used in the preparation of doses for endomuscular or endovenous injection. Alcohol, chloroform, and hydrochloric acid are inactive in this respect. The abnormal effects sometimes observed when quinine is administered orally may arise from the ingestion of foods, such as milk, fruit, etc., giving rise to the formation of malic, citric, or lactic acid, which may effect partial conversion of the quinine into quinotoxin.

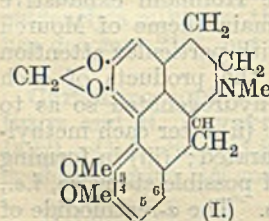
T. H. POPE.

Double salts of alkaloids with zinc iodide. R. DANET (J. Pharm. Chim., 1928, 7, [viii], 548—550).—Crystalline compounds of quinine and codeine, containing 1 mol. of zinc iodide to 1 mol. of quinine dihydriodide and 2 mols. of codeine hydriodide, respectively, are obtained by mixing warm solutions

of the appropriate salts acidified with hydriodic acid, and cooling slowly.

B. FULLMAN.

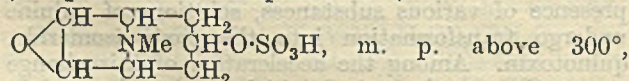
Alkaloid of *Corydalis cava*. XII. Synthesis of *d*-bulbocapnine methyl ether. E. SPÄTH and O. HROMATKA (Ber., 1928, 61, [B], 1334—1342; cf. Gadamer, A., 1911, i, 1012; Späth and others, this vol., 432). — *Nitrohomoveratroylhomopiperonylamide*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{NO}_2$, m. p. 158°, is obtained in 94.6% yield by the action of *nitrohomoveratroyl chloride*, m. p. 54—56°, on homopiperonylamine in benzene, sodium hydroxide being added to complete the reaction. It is transformed by the relatively prolonged action of phosphoric oxide on small quantities of the material into 6:7-methylene-dioxy-1:2'-nitro-3':4'-dimethoxybenzyl-3:4-dihydroisoquinoline, m. p. 167.5—168° [hydrochloride, decomp. 217—218°; methiodide, m. p. 192—193° (decomp.)]. The methiodide is converted into the more freely soluble *methochloride*, which is reduced by tin and hydrochloric acid in alcoholic solution to the non-



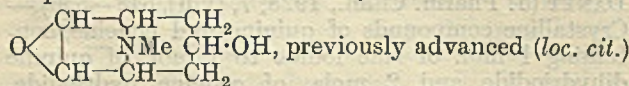
crystalline amino-derivative. Diazotisation of the latter followed by treatment with copper powder and reduction with zinc dust and concentrated hydrochloric acid affords bulbocapnine methyl ether (I), with bases of the type of dilaudanosi-

phenolic bases, and other impurities. Purification of bulbocapnine methyl ether is exceptionally difficult and is largely effected by distillation in a high vacuum, whereby a fraction of b. p. 170—190°/0.0005 mm. is obtained closely analogous to the methyl ether of natural bulbocapnine. A small portion, soluble in light petroleum, is undoubtedly *dl*-bulbocapnine methyl ether. Resolution of the crude product with *l*-tartaric acid yields *d*-bulbocapnine methyl ether, identical with the natural product. H. WREN.

Constitution of ψ -scopine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1928, [iv], 43, 590—603).—Mainly an account of work already published (this vol., 310). In the conditions described by Gadamer (A., 1921, i, 588) chlorosulphonation of ψ -scopine affords a sulphuric ester,



regenerating ψ -scopine on hydrolysis. ψ -Scopine is unattacked by sodium in xylene, whereas scopine is partly converted into a sparingly soluble sodium compound which readily dissociates. These results, the formation of *nor*- ψ -scopine by alkaline oxidation with barium permanganate, the formation of the same degradation products in approximately the same yield with chromic and sulphuric acid as are afforded by scopinium salts, and the difference in properties between the phenylurethanes of ψ -scopine and scopine confirm the structure,



for ψ -scopine, the ψ -scopine and scopine derivatives

differing structurally, not being simply *cis-trans*-isomerides.

R. BRIGHTMAN.

Organic derivatives of silicon. XXXVI. Highly complex condensation products of diphenyl- and di-*p*-tolyl-silicanediol. Fission of the Si-Ph linking. F. S. KIPPING and A. G. MURRAY (J.C.S., 1928, 1427—1431).—Three open-chain and two closed-chain condensation products formed from 2, 3, or 4 mols. of diphenylsilicanediol have been described (J.C.S., 1912, 101, 2108; J.C.S., 1914, 105, 484) and also 2 (or 3) closely related derivatives of di-*p*-tolylsilicanediol (J.C.S., 1923, 123, 2833). By the action of alkalis at 100°, each of these diols is converted into a mixture of much more complex condensation products, which with the aid of boiling benzene can be separated into an insoluble (A) and a soluble portion (B); all these four substances seem to be amorphous and melt indefinitely or decompose at high temperatures. The mol. wts. of the two (B) compounds determined in camphor indicate molecules of the order of $(\text{SiR}_2\text{O})_{20}$, but it has not been possible to decide whether any of the four products is an open- or a closed-chain compound; if of the former type the silicanediols may be compared with methylene glycol in their capacity for forming a whole series of anhydro-derivatives; if of the latter type, it would seem that compounds containing closed chains of 20 or more $-\text{SiR}_2\text{O}-$ groups are formed even more readily than the $\text{C}_{10}-\text{C}_{16}$ cyclic ketones investigated by Ruzicka.

Diphenylsilicanediol is very slowly decomposed by 20% sodium hydroxide solution at 95—100° with formation of benzene and sodium silicate.

M. CLARK.

Organic derivatives of silicon. XXXVII. Production of tetrabenzylsilicane, tribenzylsilicyl oxide, and other products by the action of sodium on dibenzylsilicon dichloride. A. R. STEELE and F. S. KIPPING (J.C.S., 1928, 1431—1439).—Complex changes occur when dibenzylsilicon dichloride is heated with sodium (or potassium) in toluene solution in absence of oxygen, and no silico-hydrocarbon corresponding with one or other of the four compounds $(\text{SiPh}_2)_n$ produced from diphenylsilicon dichloride (this vol., 79) has been obtained. The soluble product contains a very small proportion of tribenzylsilicyl oxide and about 15% of tetrabenzylsilicane, the rest consisting of a resinous substance which seems to be an oxide $[\text{Si}(\text{CH}_2\text{Ph})_2]_4\text{O}$; some insoluble material which contains less than one benzyl group to each silicon atom is also formed. The apparent migration of benzyl groups from silicon to silicon seems to be due to the fission of the $\text{Si}-\text{CH}_2\text{Ph}$ binding by the alkali metal with formation of sodium benzyl, which then reacts with the unchanged dichloride; there is ample evidence that organic sodium compounds are produced at some stage of the interaction although their nature is unknown. The fact that the main product is an oxide (as proved by determinations of its hydrogen value), in spite of all precautions having been taken to exclude oxygen and moisture, is ascribed to the presence of a very small proportion of oxides in the alkali metals. The properties of this oxide rendered its investigation a matter of considerable difficulty and no crystalline

derivative, except dibenzylsilicanediol, has been obtained from it. During its examination, it was found that certain benzyl derivatives of silicon are readily attacked by alkalis, with fission of the carbon-silicon binding; dibenzylsilicol, for example, is decomposed into toluene and silica or benzyl-siliconic acid at temperatures below 100°.

M. CLARK.

Behaviour of polypeptides and their derivatives towards alkalis and acids. VI. Experiments with polypeptides substituted in the amino-group. E. ABDERHALDEN and P. MÖLLER (Z. physiol. Chem., 1928, 174, 196—213).—The previous findings (cf. this vol., 81), that the velocity of hydrolysis of polypeptides by dilute alkalis is influenced by substitution in the free amino-group and that the benzoyl group accelerates whilst the β -naphthalenesulphonyl group retards this hydrolysis, have been confirmed with other di- and tri-peptides. Thus benzoyl-*dl*-leucylglycine is hydrolysed by *N*-sodium hydroxide at 38° more quickly than *dl*-leucylglycine, whilst the β -naphthalenesulphonyl derivative undergoes no significant hydrolysis. Similar results have been obtained with *dl*-leucyl-*dl*-leucine (with 3*N*-sodium hydroxide at 100°), glycyl-*dl*-leucylglycine and glycyl-*dl*-leucyl-*dl*-leucine and their derivatives. With glycyl-*dl*-leucyl-*dl*-leucine, cleavage of the glycine occurs first with the formation of leucyl-leucine, which is hydrolysed very slowly. The following groups have an accelerating influence similar to that of benzoyl, whereas the oleoyl group retards: propionyl, butyryl, and isovaleryl. The following compounds have been prepared: *chloroacetyl-dl-leucylglycine*, m. p. 145°, *glycyl-dl-leucylglycine*, decomp. at 232°, *chloroacetyl-dl-leucyl-dl-leucine*, m. p. 138° (sinters at 136°), *glycyl-dl-leucyl-dl-leucine*, decomp. at 227°, *benzoyl-dl-leucyl-dl-leucine*, m. p. 185° (sinters at 183°), *benzoylglycyl-dl-leucylglycine*, m. p. 177°, *benzoylglycyl-dl-leucyl-dl-leucine*, m. p. 117—118°, *p*-nitro-*benzoyl-dl-leucylglycine*, m. p. 184°, β -*naphthalenesulphonyl-dl-leucyl-dl-leucine*, m. p. 158° (sinters at 156°), β -*naphthalenesulphonylglycyl-dl-leucylglycine*, m. p. 158°, β -*naphthalenesulphonylglycyl-dl-leucyl-dl-leucine*, m. p. 140°, *propionyl-dl-leucylglycine*, m. p. 140°, *butyryl-dl-leucylglycine*, m. p. 150°, *isovaleryl-dl-leucylglycine*, m. p. 180—181°, *benzenesulphonyl-dl-leucylglycine*, an oil, and *oleoyl-dl-leucylglycine*, m. p. 129°.

A. WORMALL.

Chromoproteins. Acid-combining properties of globin. N. ISHIYAMA (Z. physiol. Chem., 1928, 176, 294—300).—When a solution of globin in a large excess of 0.1*N*-hydrochloric acid is treated with alcohol and ether, a *hydrochloride* is precipitated.

Similarly salts containing phosphoric acid, eosin, and taurine, have been obtained. Maximum combination occurs with strong inorganic acids.

H. BURTON.

Preparation of electrolyte-free gelatin. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1928, 11, 477—479).—Powdered gelatin is treated with acetic acid (*M*/128) to remove cations, and then with dilute sodium hydroxide solution to remove anions. The gelatin is brought back to its isoelectric point with dilute acetic acid and washed well to remove electrolyte.

W. O. KERMAK.

Determination of organic carbon in soil and in pure organic compounds by means of permanganic anhydride. L. U. DE NARDO (Giorn. Chim. Ind. Appl., 1928, 10, 253—255).—Durand's method (A., 1924, ii, 500, 546) may be modified to make it of general applicability. With a soil, 0.2—4 g. of the powdered sample and 5 c.c. of 30% sulphuric acid solution are introduced into a carbon dioxide flask which, if the soil is calcareous, is heated for a few moments and freed from the liberated carbon dioxide by a current of air and then cooled. The flask is fitted with means for introducing reagent, and connected with suitable absorption vessels etc. Permanganic anhydride (prepared by dissolving 1 g. of potassium permanganate in 10 c.c. of cold, concentrated sulphuric acid) is drawn gradually into the flask, the reaction with the soil occupying only a few seconds. The flask is then heated to boiling in 5 min. and the heating discontinued, a stream of air being drawn through the apparatus for 10—15 min., and the absorption apparatus detached, cooled, and weighed.

With a pure organic compound, 0.1—0.2 g. is added to or, better, dissolved in 5 c.c. of sulphuric acid, 10 c.c. of the permanganic anhydride are added, and the heating is carried out carefully, the liquid being finally kept boiling for 2—3 min. The subsequent procedure is as with soil. The whole operation occupies 20—30 min.

With pure compounds, the results obtained are practically of theoretical accuracy, and with soils, values virtually identical with those given by ordinary elementary analysis are found.

T. H. POPE.

Elementary organic analysis. A. WAHL and J. P. SISLEY (Compt. rend., 1928, 186, 1555—1558).—The rapidity of the combustion method of Heslinga (A., 1925, ii, 65) is due to the small amounts of material used and not to the replacement of the copper oxide by manganese dioxide. Operating with 0.08—0.1 g. of the substance and a shortened tube (55—60 cm.) of the usual construction, accurate determinations may be made in $\frac{1}{2}$ —1 hr.

G. A. C. GOUGH.

Biochemistry.

Determination of the respiratory elimination of acetone in man. R. COQUOIN (Compt. rend., 1928, 186, 1581—1582).—Acetone is eliminated by respiration after oral administration in approximately constant amounts during the first period and then in smaller amounts. The acetone in the breath is absorbed by passage through an aqueous solution of

sodium sulphite and hydrogen sulphite, liberated by distillation with sodium hydroxide, and collected in water. The distillate is basified with sodium hydroxide and a known excess of iodine added. The amount of acetone present is determined by titration of the excess iodine with sodium thiosulphate.

G. A. C. GOUGH.

Minimum oxygen pressure necessary for life. BEHAGUE, GARSAX, and C. RICHET, jun. (Compt. rend., 1928, **186**, 1573—1575).—The minimum partial pressure of oxygen necessary for life in a non-toxic gas mixture (critical physiological oxygen pressure) is found to be lower in mixtures containing a smaller proportion of oxygen. It is concluded that the absolute pressure of the oxygen is not the only factor affecting respiration and that consequently, in aviation, life should become impossible at lower altitudes than those indicated by the theory of Bert. G. A. C. GOUGH.

Respiration of nerve in oxygen and in nitrogen. R. W. GERARD (Amer. J. Physiol., 1927, **82**, 381—404).—The oxygen consumption of the resting frog's sciatic nerve, the oxygen consumption and carbon dioxide production of the stimulated nerve and of the nerve after being kept in nitrogen have been determined manometrically. The resting oxygen consumption after the first hour is constant for 20 hrs. Small amounts of dextrose and sodium lactate are without effect. Potassium cyanide diminishes but does not abolish the oxygen consumption even in 0.01*M*-concentration. The temperature coefficient is 2.2 between 15° and 25°. The respiratory quotient is 0.77. The quantitative and time relations between the character of the stimulus and the extra metabolism of the stimulated nerve are reported and good agreement is found between the extra oxygen consumption and the extra heat produced. The temperature coefficient of extra oxygen consumption is 2.1 and the respiratory quotient of excess metabolism is 0.97. The question of the rate of diffusion of oxygen into isolated nerves is considered mathematically. A nerve kept in nitrogen develops an "oxygen debt." It is considered that nerve does not rely on a lactic acid mechanism as a source of anaërobie energy for activity, but that some oxidising reserve is present. R. K. CANNAN.

Union of carbon dioxide and hæmoglobin. B. GROÁK (Biochem. Z., 1928, **196**, 478—487).—The results of Straub and Meier (A., 1918, ii, 467; 1919, i, 53; 1920, i, 200) are critically discussed and their conclusions are tested. Hæmoglobin unites with carbon dioxide both as an acid and in virtue of the ampholytic character of hæmoglobin, the union being therefore affected by the presence of neutral salts. P. W. CLUTTERBUCK.

Determination of hæmoglobin by means of the silver iodide photogalvanic cell. K. UCHIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 173—184).—The coincidence of the principal absorption bands of hæmoglobin with the region of maximum sensitivity of the silver iodide photogalvanic cell has been utilised for the determination of hæmoglobin in blood, the amount of absorption as measured by the silver iodide cell being made an index for the concentration of hæmoglobin in the absorbing layer. E. A. LUNT.

Oxidation of sodium lactate by red blood cells. G. B. RAY (Amer. J. Physiol., 1927, **82**, 405—414).—The consumption of oxygen and production of carbon dioxide have been demonstrated in suspensions of blood cells in isotonic buffered solutions of sodium

lactate. In the absence of oxygen the product is acetaldehyde. In the presence of oxygen methæmoglobin is formed. R. K. CANNAN.

Effect of carbon monoxide and oxygen at high pressure on the oxidation of guaiacum by animal tissue. A. L. MEYER (Amer. J. Physiol., 1927, **82**, 370—375).—The ability of blood to oxidise guaiacum in the presence of hydrogen peroxide depends on the ratio of peroxide to blood. In the presence of carbon monoxide, the proportion of hydrogen peroxide required is increased. Carbon dioxide, on the other hand, does not inhibit the peroxidase reaction of muscle tissue. Brain tissue that has been exposed to oxygen under pressure gives a weaker test than does untreated brain tissue. R. K. CANNAN.

Fall of osmotic pressure and of hydrogen-ion concentration in the arterial blood and the blood of the portal and hepatic veins. C. HÄBLER and K. WEBER (Biochem. Z., 1928, **195**, 364—375).—The osmotic pressure of arterial blood and blood of the hepatic and portal veins is determined cryoscopically before and after removal of carbon dioxide. In fasting animals, when the tension of carbon dioxide is not taken into account, the osmotic pressure of the blood of the portal vein is not higher than that of the arterial vein and that of the hepatic vein is only slightly higher, whilst if the tension of carbon dioxide is taken into consideration, the osmotic pressure of the blood of the portal vein is definitely higher than that of the arterial, but that of the blood of the hepatic vein is not higher than that of the portal vein blood. A method is described for obtaining the "actual" reaction of blood, the blood of the portal vein being found usually to be more acid than the arterial, and of the hepatic vein, more alkaline than that of the portal vein. P. W. CLUTTERBUCK.

Regulation of the hydrogen-ion concentration of blood. IV. Chemical properties of quinone, quinol, and quinhydrone and their relation to the reduction and oxidation systems of blood. V. Influence of salts, acids, and bases and of temperature on the course of the potential of quinone, quinol, and quinhydrone. VI. Thermodynamic action of different standard solutions on the quinhydrone electrode. VII. Relationship of buffering to the chemical reactions of quinone, quinol, and quinhydrone. Buffer regulation of the chemical reactions of blood and tissue fluids. VIII. Influence of temperature on the development of potential by serum, plasma, blood, blood-corpuscule suspensions, and hæmoglobin solutions during the use of the quinhydrone electrode. S. K. LEE (Biochem. Z., 1928, **195**, 248—273, 274—300, 301—308, 309—335, 336—363; cf. A., 1927, 786).—IV. The course of the potential during dissolution of quinone, quinol, and quinhydrone is irregular, rising, during thorough stirring, for the first 5—10 min. and then gradually falling. A saturated solution of quinone shows a smaller, of quinol a larger, and of quinhydrone an intermediate *P.D.* The potential, in an oxidation-reduction system, is directly proportional to the reduction and inversely to the oxidation of quinhydrone. Reduction and oxidation of quinhydrone change not

only the hydrogen-ion concentration, but also the number of charges absorbed in these reactions. The reactions between quinone and quinol and between oxy- and met-haemoglobin are theoretically discussed and relationships deduced between concentration of hydrogen ions and of other materials and between the reaction velocity coefficients. Quinone, quinol, and quinhydrone can convert oxyhaemoglobin and possibly reduced haemoglobin into methaemoglobin, the reduction with quinone and quinhydrone being very rapid.

V. The potential developed during dissolution of quinone, quinol, and quinhydrone is increased by rise in temperature, but is not doubled by a rise of 10° . The course of the potential is not affected by dilute, but is inhibited by saturated, salt solutions and also by strongly acid or alkaline solutions, but is increased in neutral and faintly alkaline dilute solution. Oxidation of quinol takes place very rapidly and the rate is greatly influenced by temperature.

VI. The quinhydrone *P.D.* for the three standard solutions most frequently used in the electrode, viz., standard acetate, Veibel's, and electrode solution, after thorough stirring for 30–60 sec., shows no real variation. The potential of these three solutions is lowered by rise of temperature, the change of potential being almost a linear function of change of temperature. By change of temperature of the opposed positive and negative electrodes, it can be shown that the *P.D.* of standard acetate and electrode fluids is almost a linear function of temperature, whereas the curve for Veibel's solution and standard electrode fluid shows considerable deviation. For the determination of p_H by the quinhydrone electrode, absolute equality of temperature of the two electrodes is essential.

VII. The relationships between change of potential and displacement of hydrogen-ion concentration, between potential changes and buffering, between the oxidation-reduction system of quinhydrone and haemoglobin, and between reaction velocity and buffering are formulated, discussed theoretically, and experimentally investigated. Buffering, apart from regulating acid-base equilibrium, appears also to inhibit many chemical reactions such as reduction and oxidation of quinhydrone and the reductions and oxidations of blood and tissue fluids. An investigation of the influence of temperature on the chemical reactions between different buffer mixtures and saturated quinhydrone shows that a rise of 10° does not double the reaction velocity.

VIII. The reaction velocity or rate of fall of potential of dilute (1 in 4) blood or serum is about doubled for each rise of 10° from 10° to 40° . For whole blood, the rate of change of potential does not run parallel with temperature. The thermodynamic relationship between oxy- or met-haemoglobin, total buffering, and quinhydrone is theoretically discussed. The determination of the initial potential of serum, plasma, diluted blood, and haemoglobin solutions is best carried out at lower temperatures when the velocity is much smaller. The chief disadvantage of the quinhydrone electrode for the determination of the p_H of blood lies in the reduction processes between quinhydrone and the hydrogen ions or the haemoglobin.

The reduction process with quinhydrone and oxy-haemoglobin is more sensitive to change of temperature and occurs more quickly than the oxidation process.

P. W. CLUTTERBUCK.

Colorimetric determination of p_H of urine and of blood. V. C. MYERS and E. MUNTWYLER (J. Biol. Chem., 1928, 78, 225–242, 243–255).—The p_H of urine diluted 1:5 with 0.9% sodium chloride and kept under oil during the experiment, is determined colorimetrically by the use of the appropriate indicator of the phthalein series and a bicolorimeter; subtraction of 0.2 from the figure so observed at 25° gives the true (electrometric) p_H of the undiluted urine at 38° . The salt errors of the various indicators employed have been investigated. Application of the bicolorimeter to the method of Cullen (A., 1922, ii, 672) for the determination of the p_H of blood-plasma gives good results, the observed value at 25° being, for human blood, 0.22 p_H greater than the true value at 38° ; the difference between the observed and the true value is chiefly due to the difference of temperature.

C. R. HARRINGTON.

Determination of catalase in blood. P. I. GOLTZOV and V. D. JANKOVSKI (Russ. J. Physiol., 1928, 11, 33–42).—The method of Bach and Zubkova (A., 1922, i, 392) is not suitable for the determination of catalase in blood, but satisfactory results are obtained if the amount of hydrogen peroxide used is doubled. If the blood solution has been kept at the ordinary temperature for some time before extracting the catalase it is necessary to add traces of ethyl alcohol (1:5000) in order to reactivate the catalase.

W. O. KERMACK.

Fate of acetylcholine in blood. I and II. O. GALEHR and F. PLATTNER (Pflüger's Archiv, 1927, 218, 488–505, 506–513; Chem. Zentr., 1928, i, 1056).—"Vagus substance" and acetylcholine are apparently identical. Acetylcholine is deacetylated very rapidly by human blood, the reaction being complete in 24 sec. at 20° , or 15 sec. at 40° ; the effect appears to be due to the albumin fraction, and not the globulin fraction, and is less rapid with animal blood than with human blood.

A. A. ELDRIDGE.

Adsorption of phenol-red by the blood of animals. L. BRAUN (Pflüger's Archiv, 1927, 218, 523–527; Chem. Zentr., 1928, i, 1054).—Differences in the absorption of phenol-red by blood and sera do not support the supposed connexion between adsorptive power and fission of acetylcholine.

A. A. ELDRIDGE.

Adsorption of quinine by blood cells. O. S. GIBBS (J. Pharm. Exp. Ther., 1928, 33, 185–190; cf. Acton and King, A., 1921, i, 474).—In the method of Ramsden and Lipkin (Brit. Med. J., 1918, i, 580) for determining quinine in small amounts of blood ten separate extractions of 10 c.c. were substituted for the repeated process. By extracting for several minutes with 0.6% acid, followed by saturation of the extract with solid ammonium sulphate in known amounts, crystallisation during filtration was avoided. The importance of adsorption errors is emphasised. The results of Acton and King were confirmed. It was found that under the conditions of experiment (defibrinated rabbit's blood was used) about 75% of

the quinine added to blood can be recovered and that the quinine is distributed approximately equally between cells and serum. W. MCCARTNEY.

Bilirubin content of blood following injections of chlorophyll. J. L. BOLLMAN, C. SHEARD, and F. C. MANN (*Amer. J. Physiol.*, 1927, 82, 239—240).—No increase occurred in the rate of bilirubin formation in dogs following intravenous injection of chlorophyll. R. K. CANNAN.

Detection of menstrual blood. II. Menotoxin and yeast fermentation. K. BÖHMER (*Deut. Z. ges. gerichtl. Med.*, 1927, 10, 448—456; *Chem. Zentr.*, 1928, i, 1055).—Dried menstrual blood of the first and second days in 6–6–10% solution arrests the fermentation of dextrose; inhibition by blood of the umbilical cord or of cadavers is less marked. Inhibition is particularly marked with premenstrual and menstrual saliva. Umbilical cord blood-serum appears to contain an inhibitive agent which is paralysed by the blood-corpuscles. A. A. ELDRIDGE.

Properties of serum-proteins. M. PIETTRE (*Compt. rend.*, 1928, 186, 1657—1659).—When serum-globulin is precipitated by hydrochloric acid the protein is halogen-free. Determinations of the p_H values of 0.01*M*-hydrochloric acid and sodium hydroxide solutions, and of similar solutions to which various amounts of globulin have been added, show that there is no appreciable difference in the two sets of values, even after 72 hrs. Similarly, serum-albumin in 0.01—0.001*N*-hydrochloric acid gives only small variations in the p_H values. The amino- and ammoniacal nitrogen in serum-albumin and globulin is small, and it is concluded that the nitrogen in these proteins is combined in peptide form. H. BURTON.

Micro-determination of the residual nitrogen of blood by means of sodium hypobromite. R. IWATSURU (*Biochem. Z.*, 1928, 195, 442—448).—The tungstate blood filtrate is ashed and the nitrogen determined by treating with standard hypobromite and determining the iodine liberated on adding potassium iodide and acid. The error of the method when the values were compared with a Kjeldahl determination was, for the residual nitrogen of human serum —3%, of guinea-pig's blood —1.8%, for total nitrogen of human urine —1.1%, for total nitrogen of human blood 0, for uric acid —0.1%, for carbamide +3.2%, and for glycine —0.2%. P. W. CLUTTERBUCK.

Determination of sugar in blood. J. P. BOSE (*Indian Med. Gaz.*, 1928, 63, 72—76).—After removal of the protein with sodium tungstate and sulphuric acid, the filtrate and a standard dextrose solution are both warmed with alkaline copper solution, treated with phosphomolybdic acid, and the colours adjusted by dilution. CHEMICAL ABSTRACTS.

Distribution of sugar in normal human blood. M. SOMOGYI (*J. Biol. Chem.*, 1928, 78, 117—127).—The ratio corpuscle-sugar:serum-sugar in normal human blood is, on the average, 1.1 for apparent sugar (*i.e.*, total reducing substances), but 0.77 for true (*i.e.*, yeast-fermentable) sugar. C. R. HARINGTON.

Distribution of sugar between blood corpuscles and plasma in various species, in normal human beings, and in diabetics. R. E. SHOPE (*J. Biol. Chem.*, 1928, 78, 107—110, 111—115).—Figures are given for the distribution of sugar in the blood of various animals. In normal human beings and in diabetic patients with and without insulin treatment, approximately 50% of the total blood-sugar is contained in the corpuscles. There must therefore be free interchange of sugar between corpuscles and plasma. C. R. HARINGTON.

Relation between blood-sugar and coagulation time. A. PAROS and F. SVEC (*Pflüger's Archiv*, 1927, 218, 209—215; *Chem. Zentr.*, 1928, i, 1057).—The rapidity of coagulation runs parallel with the blood-sugar content for rabbit's blood. A. A. ELDRIDGE.

Blood-sugar. IX. Effect of the Hofmeister series on glycolysis in blood. H. K. BARRENSCHEEN and K. HÜBNER (*Biochem. Z.*, 1928, 196, 488—494).—Addition of sulphate to suspensions of red blood-corpuscles accelerates glycolysis in the same way as do phosphate ions. The other anions and cations of the series are without effect. P. W. CLUTTERBUCK.

Hydrolysis of blood-plasma and sugar combined with protein. H. BIERRY (*Compt. rend. Soc. Biol.*, 1927, 97, 1456—1458; *Chem. Zentr.*, 1928, i, 936).—Hydrolysis of horse's blood-plasma with dilute sulphuric acid in an autoclave at 130° for 30 min. increases the reduction value (as dextrose) from 0.5 to 2.1 g. per litre. Values for dog's and rabbit's blood are 1.15, 2.20, and 1.20, 2.50, respectively. A. A. ELDRIDGE.

Calcium, inorganic phosphorus, and alkaline reserve of the blood of horses which have undergone various endurance tests. N. A. FEDOROV (*J. med.-biol.*, 1928, 4, 84—92).—The blood-calcium of horses during fatigue (after trotting, galloping, or doing hard work) is subnormal but independent of the alkaline reserve. The variations in calcium and phosphorus show an inverse relationship. W. O. KERMACK.

Equalisation of the chloride concentration between blood-corpuscles and sodium chloride solutions and its relation to "osmotic resistance." E. SKUJIN (*Pflüger's Archiv*, 1927, 218, 343—353; *Chem. Zentr.*, 1928, i, 1057).—Equalisation of the chloride concentration of sodium chloride solution and of erythrocytes suspended therein is not reached in 24 hrs.; the deviation is maximal for 0.60% sodium chloride solution, and is diminished by treatment with carbon dioxide, keeping the blood-corpuscles, or by narcosis. A. A. ELDRIDGE.

Potassium content of the blood of normal men. Kramer-Tisdall method for the determination of potassium. H. TÖMASSON (*Biochem. Z.*, 1928, 195, 475—485).—Kramer and Tisdall's method (*A.*, 1921, ii, 412) for the determination of potassium was tested with a pure solution of potassium chloride, a mixture of potassium and sodium chlorides, a mixture of potassium chloride and ammonia, and also with sera with and without added potassium chloride. Trustworthy results were obtained with potassium

chloride and with the mixture of potassium and sodium chlorides, but the presence of large amounts of ammonia made the method unusable. Determinations of potassium added to serum gave low results. The small amount of ammonia in serum causes slightly high results, but the method is usable with care. In 13 normal persons, the mean potassium content of 100 c.c. of serum was 20.30 mg., the lowest value being 17.7 and the highest 22.1 mg.-%. At the beginning of menstruation an increase in serum-potassium was found. Excessive bodily work does not change the serum-potassium value. P. W. CLUTTERBUCK.

Iron, copper, and manganese content of blood-serum. E. ABDERHALDEN and P. MÖLLER (*Z. physiol. Chem.*, 1928, **176**, 95—100).—The differences between the total iron present in horse blood-serum and that present as hæmoglobin are so small that it is doubtful if non-hæmoglobin iron is present in the serum. The amount of copper present in horse serum is of the same order as that found by Warburg for human serum (cf. A., 1927, 985; Warburg and Krebs, this vol., 192), whilst the serum contains 1.15 mg. of manganese per litre. Only very small amounts of the copper and iron of serum are dialysable and it appears probable that both elements are present in organic combination, although the non-dialysability may be due to adsorption on the proteins.

A. WORMALL.

Action of arsenic and related elements. VII. Arsine hæmolysis and effect of colloidal arsenic. R. LABES (*Arch. exp. Path. Pharm.*, 1928, **131**, 322—334).—An arsenic sol, free from protective colloid, the preparation and properties of which are described, is able to effect hæmolysis of red blood-cells in Ringer solution, but this action is inhibited if small quantities of serum are present or if the arsenic sol has been heated or kept for some time. The effects of various other factors, e.g., hydrogen-ion concentration, certain inorganic salts, and the concentration of the red blood-cells, have also been investigated. It is considered probable that hæmolysis by arsine (cf. this vol., 317) is dependent on its oxidisability to arsenic.

W. O. KERMACK.

Inhibitory effect of sugars on hæmolysis by sodium taurocholate. E. PONDER and J. F. YEAGER (*Biochem. J.*, 1928, **22**, 703—710).—The inhibitory action of sucrose, dextrose, and lactose on sodium taurocholate hæmolysis was studied quantitatively. The inhibition is due to a double effect of the added sugar. One effect increases the resistance of the cells, the other depresses the activity of the lysin. The activity of the lysin is most depressed in those concentrations in which it is commonly found to be most unstable.

S. S. ZILVA.

Imitation of organic forms by means of albumin. L. A. HERRERA (*Atti R. Accad. Lincei*, 1928, [vi], **7**, 544—547).—Descriptions and illustrations are given of the forms produced by egg-albumin with hydrochloric and sulphuric acids.

Permeability of surviving animal membranes. R. AMMON (*Biochem. Z.*, 1928, **196**, 441—464).—The diffusion constants to dextrose of a variety of surviving and dead mouse, frog, and guinea-pig membranes are determined and compared with the

diffusion of dextrose in water. The individual membranes differ considerably in their permeability and the diffusion constants are very small compared with the diffusion constant in water. The permeability of the dead membranes is 3—5.5 times that of the surviving. Apparent changes in permeability due to insulin are more probably explained in terms of increased oxidation of sugar in its presence.

P. W. CLUTTERBUCK.

Calcium content of bone cartilage. A. POLICARD (*Compt. rend.*, 1928, **186**, 1380—1382).—Descriptions are given of the ash obtained by micro-incineration of the various layers of cartilage during the ossification of certain regions of the tibia. The probable sequence of the modifications which take place is discussed.

E. A. LUNT.

Quantitative analysis of skin. I and II. Sugar content of normal skin. E. URBACH and P. FANTL (*Biochem. Z.*, 1928, **196**, 471—473, 474—477).—The sugar of normal rabbit's skin, carefully separated from subcutaneous fat, was determined by the Hagedorn-Jensen method and varied in a large number of determinations from 89 to 144 mg. per 100 g. of tissue, the blood-sugar by the same method varying from 89 to 125 mg.-%.

P. W. CLUTTERBUCK.

Acid covering of the skin. H. SCHADE and A. MARCHIONINI (*Klin. Woch.*, 1928, **7**, 12—14; *Chem. Zentr.*, 1928, i, 1061).—Electrometric observations on the thin film of acid left by evaporation on the skin were made.

A. A. ELDRIDGE.

Iodine compounds in fish products. G. LUNDE and K. CLOSS (*Tidsskr. Kjem. Berg.*, 1928, **8**, 33—34).—Sea fishes contain a relatively large amount of iodine (3.2—4.2 mg. per kg.) and most of this remains in the dried and salted product. A portion of the total iodine can be extracted by shaking an acidified aqueous extract of the fish with chloroform (lipoid iodine) and a little is present in the form of protein substances (protein iodine), but the greater portion is in the form of unknown organic iodine compounds, insoluble in water. Deep-sea fishes contain more iodine than those living near the surface: dried haddock contains six times as much iodine as coalfish, and twenty times as much as herring. In the deep-sea prawn the iodine appears to be mainly concentrated in the skin and internal organs, the muscles being relatively poor in this constituent.

H. F. HARWOOD.

Pepsin content of gastric juice. F. DELHOUCNE (*Deut. Arch. klin. Med.*, 1927, **157**, 299—308; *Chem. Zentr.*, 1928, i, 948—949).—The pepsin concentration varies during a period of secretion between fairly wide limits. Histamine stimulates the secretion of pepsin. The clinical significance of determinations in pathological conditions is considered.

A. A. ELDRIDGE.

Clinical significance of cholesterol in bile and blood-serum. IV. Experimental alteration of cholesterol concentration and p_H in fistula bile. R. STERN (*Arch. exp. Path. Pharm.*, 1928, **131**, 221—232).—Cholesterol in the bile of a dog is not necessarily increased when the blood-cholesterol is increased, e.g., after the intravenous administration of cholesterol. It was not possible experimentally

to decrease the p_H of bile sufficiently to account for the coagulation of cholesterol which results in the formation of gallstones (cf. A., 1927, 1025).

W. O. KERMACK.

Lange's ring-test for acetone in urine. GABRIELSEN (Pharm. Ztg., 1928, 73, 792).—The Kraft-Kissingen modification is described.

E. H. SHARPLES.

Excretion of fat in the urine after cutaneous absorption. H. MOSER and A. WERNLI (Pharm. Zentr., 1928, 69, 401—405).—The influence of cutaneous absorption of fat on the fat content of the urine has been examined. Moderate quantities of fat applied to the skin cause increased fat content of the urines. Cutaneous absorption leads to no allergic phenomena as is the case with protein absorption. The relationship between the quantities of fat injected and fat excreted is discussed graphically. Ingestion of large quantities of fat in some cases could not be detected in the urine and in others only a very small quantity could be detected.

E. H. SHARPLES.

Colorimetric micro-determination of phosphate [in urine]. K. HINSBERG and K. LANG (Biochem. Z., 1928, 196, 465—470).—A method is described for the determination of phosphate in 0.2 c.c. of urine, the error of which is less than 1%. The urine is diluted, the phosphate precipitated with a standard solution of uranium acetate, and the excess of uranium in the filtrate determined colorimetrically with ferrocyanide.

P. W. CLUTTERBUCK.

Amino-acid determination in urine by Folin's colorimetric method. E. SCHMITZ and H. SCHOLTYSEK (Z. physiol. Chem., 1928, 176, 89—94).—Technical permute may be used instead of Folin's purified permute for the removal of ammonia from urine prior to the determination of amino-nitrogen by Folin's β -naphthaquinonesulphonic acid method (A., 1922, ii, 540) when the phenolphthalein modification used for the determination with blood is introduced.

A. WORMALL.

Determination of dextrose in normal urine. R. H. HAMILTON, jun. (J. Biol. Chem., 1928, 78, 63—65).—Successive extraction of Lloyd's reagent with hydrochloric and nitric acids yields a product which can be successfully employed in the method of Folin (A., 1926, 648) without necessitating the use of permute.

C. R. HARINGTON.

Reducing power of urine. AUFRECHT (Pharm. Ztg., 1928, 73, 729; cf. this vol., 542, 789).—The reducing properties of urine are not due to the presence of indican, which can act as a reducing agent only after hydrolysis with mineral acid. The strongest reducing activity of urine (sugar- and protein-free) is due to purine substances, especially uric acid and urates, uric acid alone being responsible for about one third of the reducing power. Smaller importance is attached to creatinine, which reduces metallic oxides only after long boiling. The fermentation test for the presence of sugar in urine is advisable in doubtful cases.

E. H. SHARPLES.

Indican in urine investigations. G. MAUE (Pharm. Ztg., 1928, 73, 791—792).—Glycuronic acid,

which, according to Schlecht, is in combination with indican in the urine, and reduces Fehling's and Nylander's solutions when it is liberated by hydrolysis, occurs also in the urine combined with certain products such as phenol, terpenes and their derivatives, and pyrazolone derivatives when these compounds are administered medicinally. Indican in urine is not present as plant indican, as stated by Aufrecht (see preceding abstract), but as potassium indoxylsulphonate, and the simplest representation of the formation of indigotin is by oxidation of the free indoxylsulphonic acid, with liberation of sulphuric acid.

E. H. SHARPLES.

Reducing power of urine. C. OTTO (Pharm. Ztg., 1928, 73, 792).—In reply to Aufrecht (cf. preceding abstracts), uric acid and its salts reduce Fehling's but not Nylander's solution.

E. H. SHARPLES.

Ammonia in sweat. G. A. TALBERT, R. FINKLE, and D. KATSUKI (Amer. J. Physiol., 1927, 82, 639—643).—The ammonia-nitrogen in the sweat varied between 0.05 and 0.35 mg. per c.c. (73 determinations). An increase of ammonia in the urine as a result of sweating is indicated.

R. K. CANNAN.

Amino-acids in sweat. C. O. HAUGEN and G. A. TALBERT (Amer. J. Physiol., 1928, 85, 224—228).—The amino-acid nitrogen of the sweat varied from 1.57 to 4.76 mg. per 100 c.c. in 23 subjects. No relationship was evident between the amino-acid nitrogen of the blood, urine, and sweat.

R. K. CANNAN.

Blood as a physico-chemical system. VII. Composition and respiratory exchanges of human blood during recovery from pernicious anaemia. D. B. DILL, A. V. BOCK, C. VAN CAULAERT, A. FÖLLING, L. M. HURXTHAL, and L. J. HENDERSON (J. Biol. Chem., 1928, 78, 191—214).—Nomographic representations are given of the condition of the blood of a patient suffering from severe pernicious anaemia and of the blood of the same patient after recovery under treatment with liver.

C. R. HARINGTON.

Ultra-violet chemiluminescence of cells in relation to the problem of carcinoma. A. and L. GURWITSCH (Biochem. Z., 1928, 196, 257—275).—Rays of short wave-length ("primary" radiation) emanate from many growing plant and animal cells and may be detected by the increase in the number of mitoses which they cause in tissues exposed to them. The immediate effect of this mitogenetic induction is the breakdown of a carbohydrate substance stored in the cell, thus providing energy for cell division. If this reaction proceeds far enough the cell reacts by mitosis, but if it does not, the energy liberated is radiated as a "secondary" radiation. Transplantable adenocarcinoma of mouse, transplantable carcinoma of rat, and a very malignant melanosarcoma of man all showed a mitogenetic induction power which was primary, i.e., it appeared without irradiation with ultra-violet light.

P. W. CLUTTERBUCK.

A. Phosphate excretion by surviving tumour sections. B. Action of potassium cyanide on phosphate excretion of surviving tumour section.

C. Action of narcotics on the phosphate excretion of surviving tumour sections. D. Further researches on surviving tumour sections. H. LANGE and N. HENNING (*Arch. exp. Path. Pharm.*, 1928, 131, 70—74, 75—79, 115—118, 119—126).—A. Thin sections of rat's sarcoma, suspended immediately after excision in dextrose-Ringer solution saturated with oxygen, produce phosphoric acid at first comparatively rapidly, then less quickly, and after a short time at a constant rate.

B. If during this last period the section is treated with potassium cyanide a marked increase occurs in the rate of excretion of phosphoric acid, which returns to normal again after the cyanide has been removed, provided that the concentration of cyanide is sufficiently low and its period of action not too prolonged.

C. The increase in the phosphate excretion of surviving tumour sections which occurs when they are treated with potassium cyanide (see above) is also observed when they are treated with other narcotics, *e.g.*, phenylurethane.

D. The influence of various factors (*e.g.*, keeping) on the phosphate excretion of tumour sections and on the effect of the application of phenylurethane is described.

W. O. KERMACK.

Effect of insulin on nitrogen metabolism in diabetes. LABBÉ, F. NEPVEUX, and HIERNAUX (*Compt. rend.*, 1928, 186, 1384—1386).—The effect of insulin on the decreased capacity for nitrogen retention occurring in severe diabetes has been studied in 15 cases; the effect varies from zero to complete restoration to normality. In the majority of cases the ratio amino-nitrogen/total-nitrogen in the serum was restored to normal by insulin administration.

E. A. LUNT.

Variations of the different forms of phosphorus under the influence of diabetes and hypoglycaemic agents. G. FLORENCE, J. ENSELME, and T. ZOLA (*Bull. Soc. Chim. biol.*, 1928, 10, 675—683).—In the blood-plasma of diabetics, the inorganic phosphorus is diminished, whilst the esterified phosphorus is increased about seven times and the other organic phosphorus is doubled. Injection of insulin or synthalin tends to the adjustment of the values to the normal. In the muscle, the amounts of inorganic and organic phosphorus are respectively reduced and increased, whilst the lipid-phosphorus values remain unchanged.

G. A. C. GOUGH.

Blood and cerebrospinal fluid in epilepsy. M. OSANTO, J. A. KILLIAN, T. GARCIA, and M. R. MATTICE (*Brain*, 1927, 50, 581—600).—In epilepsy the following results were obtained: blood serum-calcium 9.5—12.1 (average 10.94) mg. per 100 c.c.; inorganic phosphorus 2.7—4.5 (3.51); blood total phenols (1.8 mg.); cerebrospinal fluid, calcium 5.0—6.3 (5.68), inorganic phosphorus 1.2—1.9 (1.59), total phenols (0.69). The blood-cholesterol was usually 0.125—0.171 (average 0.140) %; the cerebrospinal fluid contained only traces. Most of the cerebrospinal fluid protein values were above 50 mg. per 100 c.c. The blood-sugar is normal, but the dextrose content of both blood and fluid rises after seizures. The cerebrospinal fluid sugar value was about 74% of the

blood-sugar value. The p_H of the blood and fluid was normal.

CHEMICAL ABSTRACTS.

Nitrogen content of the bile in diagnosis. A. J. BOEKELMAN (*Klin. Woch.*, 1928, 7, 65—67; *Chem. Zentr.*, 1928, i, 1075).—The gall-bladder bile contains less than 200 mg.-% N; the nitrogen content in disease of the gall bladder is recorded.

A. A. ELDRIDGE.

Insulin sensitiveness of man. K. CSÉPAI and Z. ERNST (*Wien. klin. Woch.*, 1928, 41, 25—26; *Chem. Zentr.*, 1928, i, 1055).—In exophthalmic goitre and hyperthyreosis sensitiveness to insulin is markedly increased in man, the minimal blood-sugar value being reached in 1 hr. or more instead of 39 min., and the normal value being still not reached after 2 hrs.

A. A. ELDRIDGE.

Elimination of amino-acids in hepatic disease. E. DERRA (*Z. ges. exp. Med.*, 1927, 57, 657—671; *Chem. Zentr.*, 1928, i, 1060—1061).—The urinary amino-acid is increased in fever, but scarcely in pernicious anaemia; in hepatic disease it is variable.

A. A. ELDRIDGE.

Carbohydrate metabolism in hyperthyroidism. H. J. JOHN (*Endocrinology*, 1927, 11, 497—581).—There is no typical dextrose tolerance curve for hyperthyroidism. The association of diabetes with hyperthyroidism is discussed. Depletion of glycogen is due to a toxic condition or to rapid consumption of the available carbohydrate on account of the high basal metabolism.

CHEMICAL ABSTRACTS.

Rickets in rats. IV. Effect of varying acid-base content of diet. A. T. SHOHL, H. B. BENNETT, and K. L. WEED (*J. Biol. Chem.*, 1928, 78, 181—190).—Rickets was produced in rats by means of a diet deficient in vitamin-D and with a Ca : P ratio of 0.45; phosphate was added to the diet to bring the Ca : P ratio to 0.95, but with different amounts of base or acid, so that the final diets varied in reaction. Cure of the rickets ensued in all cases; the best retention of calcium and phosphorus and ash-deposition in the bones occurred in rats on the neutral diets, and the poorest in those on acid diets; the animals on neutral diets, however, and sometimes those on alkaline diets, showed symptoms of tetany.

C. R. HARRINGTON.

Mode of action of irradiated ergosterol in rickets. A. HOTTINGER (*Naturwiss.*, 1928, 16, 484—491).—An account is given of clinical experience with irradiated ergosterol. The D-factor appears to render innocuous some material which can hinder the assimilation of calcium. This substance may possibly be an enzyme capable of decomposing calcium glycerol- and hexose-phosphates.

R. A. MORTON.

Hypoglycaemia in scleroderma. W. T. LONGCOPE (*J. Amer. Med. Assoc.*, 1928, 90, 1—7).

Rôle of fat in the human organism (during starvation and in tuberculosis). W. H. STEFKO (*Biochem. Z.*, 1928, 195, 396—402).—During starvation the Hübl iodine value of tissue fat decreases and approximates to that of the peripheral fat. The decrease of fat in the organism, especially of oleic acid (as measured by iodine value), may be regarded as indicating a decrease of resistance to tuberculosis.

P. W. CLUTTERBUCK.

Hydrogen sulphide in blood in uræmia; hydrogen sulphide-decomposing power of blood and other body fluids. E. BECHER (Munch. med. Woch., 1927, 74, 1950—1951; Chem. Zentr., 1928, i, 1056).—In severe renal insufficiency and true uræmia hydrogen sulphide could not be detected in the blood; that obtained on acidification and distillation probably arose from thiocyno-compounds. All body fluids can oxidise hydrogen sulphide to thiosulphuric acid. The disappearance of hydrogen sulphide added to blood does not depend on the formation of sulph-hæmoglobin. A. A. ELDRIDGE.

Metabolism of stationary and growing tissues. O. ROSENTHAL and A. LASNITZKI (Biochem. Z., 1928, 196, 340—425).—The metabolism of resting and growing tissues of warm-blooded animals is investigated *in vitro*. Since the morphological character of tissues of mesenchymatous origin (connective tissue, smooth muscle, lymphadenoid tissue) changes greatly during growth, it is not possible strictly from measurements of metabolism to reach conclusions on the changes of cellular metabolism, but it is possible to say that the anaërobic fermentation of the whole tissue attains its highest value with the strongest growth. On the other hand, the fermentative power of three human sarcomata was smaller than that of the Jensen rat sarcoma. Of the stationary epithelial tissues, mucous membrane has a greater fermentative power than epithelial glands. The rather small fermentative power of liver and kidney in the stationary condition is considerably increased in foetal and post-foetal growth. Fermentative power progressively decreases with development, but respiration increases. Pathologically growing epithelial tissue possesses considerable fermentative power. In normally growing thyroid gland tissue and with greater colloid content, fermentation appeared to be greater than in the stationary condition. The excess fermentation $U = Q_M^3 - 2Q_0$, is positive in abnormally growing tissue except in human sarcoma, but in most normal tissues its mean value is negative. The Warburg quotient Q_M^3/Q_0 , for stationary and normally growing tissue is ≤ 0.3 , for regulated pathological growth 0.5—1.3 and for unregulated pathological growth > 2 . For human sarcoma the coefficient is, however, about 1. In a number of experiments the metabolism was measured both in Ringer's solution and in serum. The small aërobic fermentation of the mucous membrane of the rabbit's large intestine, always obtained in Ringer's solution, disappears in its own serum (active or inactivated), but inactivated foreign serum had no effect. The aërobic fermentation of liver tissue of foetal and grown rats and of rat tumours does not change in horse serum. On the other hand, the respiration of rat's kidney in inactivated horse serum is about 50% and of smooth muscle of rabbit's large intestine 50—100% greater than in Ringer's solution. P. W. CLUTTERBUCK.

Physico-chemical phenomena during regeneration. I. Determination of the hydrogen-ion concentration of the regenerating extremities of the axolotl. N. OKUNEFF (Biochem. Z., 1928, 195, 421—427).—On the first day after amputation, the p_H of the extremity of the axolotl decreases

from 7.178 to 6.818, during the second and third days it increases to 6.963—6.980, but does not attain normal, on the fifth and sixth days it shows a fresh decrease to 6.638, and finally the p_H gradually rises to normal by about the fifteenth day. The meaning of these changes is discussed. P. W. CLUTTERBUCK.

Physical chemistry of resorption. I. P. J. JURISIC (Biochem. Z., 1928, 196, 223—245).—An examination of the phenomena associated with the Reid experiment (movement of liquid through frog skin etc. in a direction contrary to the laws of osmotic pressure). Experiments are recorded with frog skin and also with artificial membranes of gelatinised collodion; on the basis of the latter a tentative explanation of the phenomenon is advanced.

J. H. BIRKINSHAW.

Carbon dioxide dissociation curve of nerve and muscle. W. O. FENN (Amer. J. Physiol., 1928, 85, 207—223).—Variations in the carbon dioxide-combining capacity of nerves and muscles have been measured in fatigue, death, rigor, and anoxæmia. From the data, inferences are drawn concerning the p_H inside the tissues in different conditions. The carbon dioxide-combining capacity is less in winter than in summer frogs and is only one third to one half that of blood. About half the lactic acid formed in muscle is neutralised by liberation and escape of carbon dioxide. The rate at which carbon dioxide diffuses into nerves agrees with that predicted from Fick's law of diffusion. The diffusion coefficient is 7.1×10^{-5} cm.²/min. in nerves and 11.7×10^{-5} cm.²/min. in muscles. R. K. CANNAN.

Relation between lactic acid formation and oxygen consumption in muscle contraction. O. MEYERHOF and W. SCHULZ (Pflüger's Archiv, 1927, 217, 547—573; Chem. Zentr., 1928, i, 821).—From the difference of the increase of lactic acid in oxygen and in nitrogen, for equal work, divided by the respired oxygen, the oxidation quotient of the lactic acid (lactic acid disappeared/lactic acid equivalent oxidised) was determined for frog's gastrocnemius. The mean value was 4.7 (cf. Embden, Lehnartz, and Henschel, A., 1927, 589). The significance of the value is discussed. A. A. ELDRIDGE.

Rôle of magnesium and calcium in the acidification or fatigue of muscle. (Behaviour of alkaline-earth phosphates of muscle in acid and alkaline rigor.) L. WACKER (Biochem. Z., 1928, 196, 426—440).—The ash content of muscles left *in situ* declines with the onset of rigor, the loss being greater in acid than in alkaline rigor. In spite of the decrease of total ash content, the soluble mineral constituents of muscle increase during post-mortem acid formation at the cost of the insoluble mineral matter, magnesium and calcium phosphates being chiefly concerned in these changes. The curare-like action of magnesium administered parenterally, the sedative influence in muscular convulsions, and the increase of magnesium ions in the muscle during activity and other evidence are cited in favour of the view that the condition known as fatigue is due to the effect of the increase of magnesium ions in the muscle during the increase in acidity.

P. W. CLUTTERBUCK.

Anaërobic resynthesis of phosphocreatine after stimulation of isolated frog's muscle. H. GORODISSKY (Z. physiol. Chem., 1928, 175, 261—291).—After tetanic stimulation for short periods of the isolated frog gastrocnemius, there is a decrease in the phosphocreatine (phosphagen), and in the subsequent recovery in oxygen resynthesis of this compound occurs, results which confirm those of Eggleton and Eggleton (A., 1927, 271, 990). If the stimulation is not too prolonged, resynthesis of phosphocreatine in the recovery process can take place either anaërobically or aërobically, whereas Eggleton and Eggleton found that resynthesis occurred only under aërobic conditions; after more severe stimulation (for 25 sec., compared with 12 sec. previously) the resynthesis occurs only in the presence of oxygen. The resynthesis of phosphocreatine, like that of lactacidogen (cf. Embden and Hentschel, A., 1926, 427), takes place more readily in the presence of oxygen, although it is not an oxidative process. A. WORMALL.

Natural guanidinophosphoric acids (phosphagens) in striped muscle. I. Physiological behaviour of phosphagens. II. Physico-chemical properties of guanidinophosphoric acids. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1928, 196, 22—48, 49—72).—I. The hydrolysis of creatine-phosphoric acid by muscle enzyme is adversely influenced by carbohydrate and fluoride. The velocity of reaction is strongly influenced by p_H . Below p_H 8 synthesis occurs in fresh muscle extract; this can be increased by addition of creatine.

The general behaviour of arginine-phosphoric acid (present in crustacean muscle) is similar to that of creatine-phosphoric acid. It is split on muscle contraction and re-formed when oxygen is supplied. In muscle extract, the tendency to synthesis predominates at the neutral point and is a maximum at p_H 8. For comparison the enzymic hydrolysis of amino-phosphoric acid is also studied.

II. The isolation of arginine-phosphoric acid from crab muscle and the identification of the fission products are described. The purification of the phosphagen depends on the fractional precipitation, by means of alcohol, of the barium salt, and later of the sulphate of the free acid complex. The barium salt has $[\alpha]_D^{20} + 2^\circ$ and the free acid $[\alpha]_D^{20} + 5^\circ$. The α -amino-group of the complex is free. Measurements of the heat of hydrolysis of creatine-phosphoric acid, arginine-phosphoric acid, and aminophosphoric acid were made at acid reaction (h_a) and at neutral reaction (h_n); the respective values obtained for the three acids were: h_a 12,000—13,000, 11,000—12,000, 16,000 g.-cal. per mol.; h_n 10,000—11,000, 8000—10,000, 15,000 g.-cal. per mol. The dissociation curves of the three acids were also studied. The hydrolysis of the compounds in muscle at about the neutral point has practically no effect on p_H , but the hydrolysate has a strong buffering action.

J. H. BIRKINSHAW.

Decomposition of creatine-phosphoric acid in relation to the activity of muscle. I. D. NACHMANSOHN (Biochem. Z., 1928, 196, 73—97).—The amount of creatine-phosphoric acid (phosphagen) hydrolysed is compared with the lactic acid formed and

with the tonus under varied conditions. Phosphagen decomposition is the same for direct as for indirect stimulation, but much less with curarised muscle. There is an anaërobic resynthesis closely connected with relaxation which is complete in 20 sec.; about 30% of the phosphagen is reconstituted. During anaërobic reconstitution no lactic acid is formed and no ammonia disappears. J. H. BIRKINSHAW.

Effect of feeding creatinine on growth and on its distribution in the liver and muscles of normal mice. A. CHANUTIN and H. H. BEARD (J. Biol. Chem., 1928, 78, 167—180).—Addition of creatine to a normal diet has no effect on the growth of young mice. Administration of creatine causes a rapid but slight increase in the creatine of the muscles, and a slower and more irregular but greater increase in that of the liver. The creatine of the muscles attained a maximum which was independent of the amount of creatine fed and of the duration of the experiment. Cessation of the administration of creatine is followed by a rapid disappearance of the excess from the liver, whilst the creatine content of the muscles remains high for some time.

C. R. HARRINGTON.

Behaviour of creatinol in the animal body. F. PETERS (Z. physiol. Chem., 1928, 174, 177—178).—Following the subcutaneous injection of 7 g. of creatinol [α -methyl- α -(β -hydroxyethyl)guanidine] into a dog kept on a nitrogen-deficient diet, the increase in the total nitrogen of the urine for the same day accounts for practically all the nitrogen of the creatinol. Very small amounts only of unchanged creatinol are excreted and the creatinine and the nitrogenous bases of the urine precipitated by phosphotungstic acid increase to a very slight extent.

A. WORMALL.

Metabolism of amino-acids. I. Changes in nitrogenous constituents of the blood following administration of amino-acids. M. W. JOHNSTON and H. B. LEWIS (J. Biol. Chem., 1928, 78, 67—82).—The changes in the non-protein nitrogenous constituents of the blood of rabbits following oral administration of various amino-acids vary with the nature of the amino-acid. Glycine and alanine produce a marked rise in the amino-nitrogen of the blood, which, in the case of glycine especially, is prolonged, indicating that these amino-acids are rapidly absorbed but slowly deaminated. Glutamic and aspartic acids on the other hand cause very little increase in the amino-nitrogen, but a steady rise in the carbamide-nitrogen of the blood, so that, in these cases, absorption is slow and deamination rapid. The residual nitrogen of the blood is considerably increased after glycine, possibly owing to synthesis of peptides.

C. R. HARRINGTON.

Variations in the amino-acid content of some Lepidoptera while in chrysalis. A. COURTOIS (Compt. rend., 1928, 186, 1575—1576).—The amino-acid content of many chrysalides falls to a constant minimum during this stage of metamorphosis. It is suggested that the amino-acids are utilised in the formation of the imago. G. A. C. GOUGH.

Uric acid formation. G. NAITO and T. NISHIOKA (J. Biochem. Japan, 1927, 8, 225—233).—Oral

administration of urea causes in man an accelerated synthesis and increased excretion of uric acid.

CHEMICAL ABSTRACTS.

Fate of *o*-nitrocinnamic acid in the dog. A. A. CHRISTOMANOS (*Z. physiol. Chem.*, 1928, 176, 74—75).—Administration of *o*-nitrocinnamic acid to a dog *per os* does not lead to an increased excretion of kynurenic acid as expected, but a small percentage of the administered substance and traces of *o*-nitrohippuric acid are excreted in the urine. After the administration of 3.5 and 4.0 g. of the substance, 0.33 and 0.62 g. respectively of *o*-nitrocinnamic acid and 0.12 and 0.14 g. of *o*-nitrohippuric acid were isolated from the urine. Intravenous injection of *o*-nitrocinnamic acid causes a transient lowering of the blood pressure, whereas cinnamic acid has no similar effect.

A. WORMALL.

Water and fat metabolism. I. L. ELEK and E. ROTH (*Arch. exp. Path. Pharm.*, 1928, 132, 246—252).—Serum containing a large amount of fat when compared with a normal serum shows an increased tendency to bind water. Experiments in which the serum was dialysed against distilled water, sodium chloride, or calcium chloride solutions indicate abnormal behaviour of the calcium ions in the case of the serum containing much fat. W. O. KERMACK.

Influence of unphysiological nutrition on the composition of the organs and on metabolism. I. Unbalanced fat diet. W. BICKENBACH and P. JUNKERSDORF (*Arch. exp. Path. Pharm.*, 1928, 132, 129—144).—Administration of much fat to dogs following a period of starvation results in a fall of the blood-sugar followed by a steep rise to a hyperglycæmic level. This result is attributed to a disturbance of the blood-sugar-regulating mechanism of the liver following fat infiltration.

W. O. KERMACK.

Effect of closing the hepatic veins on the sugar and cholesterol content of blood. J. J. ROUZAUD and L. C. SOULA (*Compt. rend.*, 1928, 186, 1378—1380).—A steadily increasing hyperglycæmia and a transitory hypocholesterolaemia result in experiments on the dog. At the end of 1 hr. the blood-sugar content is increased 100%, and at the end of 30 min. the hypocholesterolaemia begins to decrease.

E. A. LUNT.

Changes in metabolism during irradiation. III. Changes of carbohydrate metabolism. L. PINCUSSEN and D. JACOBY (*Biochem. Z.*, 1928, 195, 449—456).—The lactic acid content of the whole blood decreases by 20—30% during irradiation, but this is detected only when the animal is examined shortly after irradiation. The lactic acid content of serum, however, increases, and it is suggested that during irradiation the permeability of the corpuscles increases and a considerable part of the lactic acid they contain passes into the serum. The glycogen values for heart and muscle, if changing at all, show a slight decrease, but the total carbohydrate increases considerably. It appears, therefore, that irradiation causes a sparing of sugar, but it is not certain whether this is due to decreased breakdown of sugar or to increased formation of sugar from lactic acid.

P. W. CLUTTERBUCK.

Decomposition of sugar in the human placenta and the effect of hormones thereon. S. HAYASHI (*Biochem. Z.*, 1928, 196, 323—332).—Anaërobic decomposition of sugar in the human placenta is optimal at p_H 10. Of the hexoses, lævulose yields lactic acid most readily, then dextrose, whilst galactose is almost without effect. Of disaccharides, sucrose gives most, and sodium sucrosephosphate and lactose give less lactic acid. Of the polysaccharides, glycogen is most readily attacked. The following hormones accelerate the anaërobic decomposition of sugar by the placenta, the extent of their activity being in the order given: insulin, folliculin, thyroxine, adrenaline, thymoglandol, and hypophysin. The human placenta is able to convert methylglyoxal into lactic acid.

P. W. CLUTTERBUCK.

Metabolism of the placenta. I. E. ISHIKAWA (*Biochem. Z.*, 1928, 195, 469—474).—Incubation under aseptic conditions of rabbit's placenta or placenta extracts causes both aërobically and anaërobically an increase of reducing substances (glycogenolysis). Addition of dextrose has no effect on, and of lævulose and dihydroxyacetone causes an acceleration of glycogenolysis. Placenta pulp and extract do not attack either lævulose or dihydroxyacetone under aseptic conditions in experiments lasting a short time. Under aërobic conditions the lactic acid content is usually initially decreased and then increases, whereas under anaërobic conditions, the initial decrease is not obtained. Addition of dextrose and lævulose has no influence on the amount and course of lactic acid formation.

P. W. CLUTTERBUCK.

Calcium deposition in animal tissues. I. Form of calcium in tissues and tissue fluids. H. KLEINMANN. II. Acidity of tissue in dystrophic calcification. H. KLEINMANN and I. REMESOW. III. Experimental calcification by administration of calcium salts. H. KLEINMANN (*Biochem. Z.*, 1928, 196, 98—145, 146—160, 161—176).—I. Experiments by means of cataphoresis show that cartilage has a more strongly acid nature and therefore greater binding power for calcium than other tissues. The hydrogen carbonate and phosphate ions of serum are completely dialysable and therefore non-colloidal. Gassmann's theory of a calcium phosphate-carbonate complex in bone is contested.

The effect of the solid phase on the deposition of serum-calcium was studied under varied conditions, by shaking both serum and Ringer solution with various substances. Inoculation of serum with tertiary calcium phosphate leads to a marked decrease in serum-calcium and in the carbon dioxide content. Other solid phases such as glass and calcium carbonate have no action. The phenomenon appears to be mainly due to the crystallisation effect from a super-saturated liquid on addition of a crystal of the solute—namely, calcium phosphate. A secondary effect is present depending on the exchange of the phosphate in the solid phase for the carbonate ion in solution. This leads to a further precipitation of serum-calcium.

II. In an attempt to account for the appearance of the first crystal nuclei of calcium phosphate in calci-

fication, the acidity of dead tissue was compared with that of living tissue. One kidney of a rabbit was ligatured and the p_H of the expressed fluid and ground-up organ from the two kidneys was compared after varying intervals of time. In all cases the dystrophic organ had the more alkaline reaction.

III. Artificial calcification in the tissues of mice was produced by feeding and by subcutaneous injection of calcium salts with the addition of acid- or alkali-forming substances. Calcium was deposited with "acid" and with alternately "acid and alkaline" phosphate diet, but not with "alkaline" phosphate diet. The subcutaneous injection of calcium and phosphoric acid showed even more clearly the influence of alkali or acid on calcium deposition. Calcium and phosphoric acid metabolism experiments were carried out on rabbits to which acid and alkali were administered. Acid produced a calcium and phosphoric acid excretion in excess of the intake, alkali rather the reverse. Poisoning with mercuric chloride seems to hinder the calcium and phosphate excretion. The deposition of calcium produced by metabolic disturbances is thus closely related to dystrophic calcification.

J. H. BIRKINSHAW.

Iron content of plant and animal foods. W. H. PETERSON and C. A. ELVEHJEM (J. Biol. Chem., 1928, 78, 215—223).—Figures are given for the iron content of 150 different animal and vegetable foodstuffs.

C. R. HARRINGTON.

Importance of manganese to animals. G. BERTRAND and H. NAKAMURA (Compt. rend., 1928, 186, 1480—1483; cf. A., 1924, i, 1151).—The period of survival of mice fed on a vitamin-deficient diet is increased by the presence of manganese salts. Considerable quantities of the metal are retained in the body.

G. A. C. GOUGH.

Is sea-water a physiologically equilibrated solution for the isolated organs of warm-blooded animals? S. W. ZIGANOW (Biochem. Z., 1928, 196, 333—339).—Sea-water, diluted until isotonic and heated to body temperature, can be introduced into the circulation of mammals without adverse results, can replace part of the blood (up to 40 c.c. per kg. body-weight) in cases of hæmorrhage etc., and can be used as a physiologically equilibrated medium for the isolated intestine and heart, but in the last case the normal work is not maintained, the sympathetic innervation being depressed. P. W. CLUTTERBUCK.

Action of various gases on the hen's egg. Absorption of carbon monoxide as an inert gas. S. ANCEL (Compt. rend., 1928, 186, 1579—1580).—The germs of the eggs, which do not develop after short exposure of the egg to a toxic gas such as hydrogen sulphide, ammonia, acetylene, or carbon dioxide, develop normally after exposure for several days to hydrogen, nitrogen, or carbon monoxide. It is concluded that carbon monoxide has no toxic action on living cells and that it is toxic for highly differentiated organisms only in the sense that it deprives them of their proper supply of oxygen.

G. A. C. GOUGH.

Comparison of the pharmacological action of diacetone alcohol and acetone. D. C. WALTON,

E. F. KEHR, and A. S. LOEVENHART (J. Pharm. Exp. Ther., 1928, 33, 175—183).—2:4-Dinitrophenylhydrazine gives a red precipitate with diacetone alcohol (acetonyldimethylcarbinol) and a yellow precipitate with acetone, and the attempt is being made to utilise this reaction in the analysis of mixtures of the two substances. Experiments on rats, rabbits, and dogs showed that the carbinol is somewhat more toxic than acetone. Both substances produce a fall in blood pressure. The soporific action of the alcohol develops more rapidly and it has a more constant depressant effect on the respiration.

W. MCCARTNEY.

Influence of alcohols on the bile-stimulating action of salts of bile acids. E. PROKOP (Z. ges. exp. Med., 1927, 58, 330—339; Chem. Zentr., 1928, i, 1062).—Ethyl alcohol and amylene hydrate inhibit the action of parenterally administered *apocholic*, *bilianic*, *cholic*, or *deoxycholic*, but not *dehydrocholic*, acids.

A. A. ELDRIDGE.

Biochemical study of thiocarbamide. E. NICOLAS and J. LEBDUSKA (Compt. rend., 1928, 186, 1441—1443).—Solutions of thiocarbamide which up to a strength of 3% have no coagulating action on blood possess hæmolytic action at all concentrations, including that of the isotonic solution. Duodenal administration of 1 g. per kg. of body-weight produces, in the case of dogs, only a slow and transient rise in the blood pressure with no respiratory effects. Intravenous doses of 10 and 11 g. per kg. for dogs and rabbits respectively cause death primarily through the hæmolysis of the blood; thiocarbamide is less toxic than carbamide.

G. A. C. GOUGH.

Parenteral action of irritants. I. Intravital decomposition of protein in the liver of sensitised animals. II. Biological action of parenterally injected amino-acids. III. Histological findings in liver. R. WIGAND (Arch. exp. Path. Pharm., 1928, 132, 1—17, 18—27, 28—30).—I. The method of Hashimoto and Pick (*ibid.*, 1914, 1, 76), according to which the toxicity of parenterally injected substances is measured by determining after a certain time the ratio of the uncoagulable nitrogen to the total nitrogen in the liver of the injected animal, has not been found satisfactory.

II. Aliphatic amino-acids parenterally injected into guinea-pigs increase the number of leucocytes in the blood. Aspartic acid induces diuresis. Of various aliphatic and aromatic amino-acids tyrosine is peculiar in producing symptoms of profound collapse.

III. Histological findings observed in the liver of guinea-pigs injected parenterally 1—48 hrs. previously with horse-serum are described.

W. O. KERMACK.

Pharmacology of certain pyridylpyrroles and derivatives of 2-aminopyridine. E. DINGEMANSE and J. P. WIBAUT (Arch. exp. Path. Pharm., 1928, 132, 365—381).—By observing the general effect following subcutaneous injection in frogs, the anaesthetic effect on decapitated frogs, on isolated nerve-muscle preparations, and on the rabbit's cornea, and also the effect on the blood pressure of spinal cats, the pharmacology of 2-aminopyridine and its derivatives and of certain pyridylpyrroles has been inves-

tigated. 2-Aminopyridine has a strong toxic effect, produces convulsions, and raises the blood pressure. Its derivatives show on the whole similar, but weaker properties. The pyridylpyrroles have a powerful anæsthetic action (stronger than cocaine), and produce convulsions in certain cases. The effect on the blood pressure is variable. H. D. KAY.

Purine diuresis in the dog. A. M. PREBRASCHENSKI (Arch. exp. Path. Pharm., 1928, 132, 330—348).—If insufficient fluid is given to the animals, the diuretic effect of caffeine is inconstant. Theobromine, on the other hand, always produces some diuresis. If distilled water is given previously by the mouth, caffeine increases the urinary volume and also the amount of chloride excreted, whilst the blood-chloride is raised. In the same circumstances theobromine also increases the urinary volume, the excretion of chloride is raised, though to a smaller extent than with caffeine, but the blood-chloride is not increased.

Following the administration of 0.9% sodium chloride solution by mouth both caffeine and theobromine increase the urinary volume and chloride excretion; the effect of caffeine is, however, greater than that of theobromine. Subcutaneous injection of caffeine results in an earlier occurrence of the diuresis and a higher urinary concentration of chloride.

H. D. KAY.

Pharmacology of narcosis. "Narcotic range." L. LENDLE (Arch. exp. Path. Pharm., 1928, 132, 214—245).—The "narcotic range" (which lies between the minimum dose producing narcosis and the minimum lethal dose) has been determined for a number of homologous alcohols and the relations between their narcotic action and their chemical constitution are discussed. W. O. KERMACK.

Pharmacology of hydrogen cyanide in cold-blooded animals. I. Rôle of lung and skin respiration in the lightening of the colour of venous blood during poisoning by hydrogen cyanide. II. Effect of certain factors on oxidation in hydrogen cyanide poisoning. W. M. KARASSIK (Arch. exp. Path. Pharm., 1928, 132, 193—204, 205—213).—I. The lightening of the colour of the venous blood of the frog under the action of hydrogen cyanide occurs less quickly and only with much larger doses when the lung respiration is inhibited.

II. Rise of temperature tends to bring about darkening of the blood of animals poisoned by cyanide. W. O. KERMACK.

Utilisation of carbohydrate in mammals. H. HANDOVSKY (Klin. Woch., 1927, 6, 2464—2466; Chem. Zentr., 1928, i, 1059—1060).—In an atmosphere of very dilute hydrogen cyanide rabbits showed, besides inhibition of oxidation, (a) a disturbance of the skeletal muscular carbohydrate, (b) an increase of lower carbohydrates, (c) a diminution of glycogen—the ratio glycogen/lactic acid becomes 1.5 instead of 3.5, (d) an increase of the extractable muscular thiolic substances, (e) a decrease of cholesterol in muscle, but not in the liver. Injection of guanidine reduced the muscle-glycogen, values for the lower carbohydrates being fairly high. The ratio carbo-

hydrate/lactic acid was 2.0. Thiolic substances soluble in water were increased. Oral administration of synthalin (highly toxic) did not lead to significant change in the muscular carbohydrate or the blood-sugar, although the muscular water-soluble thiolic substances were increased. The effect of administration of insulin, cysteine, and dithioglycollic acid was also investigated. A. A. ELDRIDGE.

Fatal case of poisoning by scopolamine *per os* and by injected potassium cyanide. Location of the injected cyanide etc. A. SCHIRM and D. H. WESTER (Arch. Pharm., 1928, 266, 283—289).

W. A. SILVESTER.

Glycolysis in blood rendered non-coagulable by means of morphine. G. LO MONACO (Arch. Farm. speriment., 1928, 45, 1—5).—After injection of morphine into the mesenteric vein of dogs, the blood, which is rendered non-coagulable, exhibits marked hyperglycæmia. Under such conditions the glycolytic power of the blood is more pronounced than that of the normal blood of the same animal prior to the injection, regard being had to the dextrose content. T. H. PORE.

Hyperglycæmia in dogs after intravenous injection of pilocarpine nitrate. A. LE GRAND and G. BIERENT (Compt. rend. Soc. Biol., 1927, 97, 1483—1484; Chem. Zentr., 1928, i, 936).—Injection of pilocarpine (1 mg.) increases the blood-sugar by 80%, after removal of the suprarenals, 10%, and after removal of the thyroid, 40%. After removal of suprarenals and thyroid, pilocarpine (1 mg.) is without influence on the blood-sugar. A. A. ELDRIDGE.

Comparative study of synthetic and natural ephedrine. K. K. CHEN (J. Pharm. Exp. Ther., 1928, 33, 237—258).—The hydrochloride of the synthetic material (Merck's "ephedrine") has m. p. 187° and with cupric hydroxide it gives an ether-extractable purple colour which is indistinguishable from that given by the same amount of the natural product. Qualitatively synthetic ephedrine possesses all the properties of the natural substance, but quantitatively the former is in some respects less powerful. W. MCCARTNEY.

Ultra-violet absorption spectra of alkaloids of the tropane group and of some biological and pharmaceutical products. A. CASTILLE and E. RUPPOL (Bull. Soc. Chim. biol., 1928, 10, 623—668).—Ultra-violet absorption spectra have been determined for many alkaloids and other organic compounds of biological interest. The proportions of the tautomerides in acid and alkaline solutions of cyanuric acid, barbituric acid, and veronal may be determined from their spectra. The characteristic absorption spectra of alkaloids such as cocaine permit their determination in extracts of viscera containing large amounts of foreign substances.

G. A. C. GOUGH.

A case of hydrofluosilicic acid poisoning. J. DROST (Pharm. Zentr., 1928, 69, 385—386).

E. A. LUNT.

Action of arsenic and related elements. VI. Conditions of action of salts of hydrogen sulphide and hydrogen iodide on the nerve-muscle preparation of the frog. R. LABES (Arch. exp. Path.

Pharm., 1928, 131, 305—321).—The harmful action of hydrogen sulphide on a nerve-muscle preparation is increased by the presence of oxidising agents (methylene-blue and hydrogen peroxide) and it is concluded that its toxic action is due in part at least to the formation of sulphur in the tissue (cf. this vol. 548). Similarly, hydrogen iodide or alkali iodides exert a toxic action when conditions are favourable to the formation of free iodine, *e.g.*, in presence of hydrogen peroxide.

W. O. KERMACK.

Is glutathione the arsenic receptor in insects? D. E. FINK (J. Econ. Entomol., 1927, 20, 794—801).—The normal glutathione content of insects is variable; the determination is described. Injection of arsenious or arsenic acid reduces the glutathione by 41% and 32%, respectively.

CHEMICAL ABSTRACTS.

Chemical and enzymic processes in the light of stereochemical research. C. NEUBERG and M. KOBEL (Naturwiss., 1928, 16, 392—396).—The work of Neuberg and colleagues is reviewed. When an ethereal solution of acetobromo-*d*-glucose and *dl*-borneol is shaken with silver carbonate and the solution subjected to steam distillation, *l*-borneol is carried over. A partial resolution of racemic menthol can also be achieved in this way. The interaction of *dl*-menthol, quinoline, and acetobromo-*d*-glucose results in the formation of glucosides. The residue after steam distillation gives *l*-menthol on hydrolysis. Enzyme chemistry permits these purely chemical processes to be checked, since *l*-menthol- α -glucoside is practically completely decomposed by α -glucosidase (maltase), but is unattacked by β -glucosidase (emulsin). On the other hand, *d*-menthol- β -glucoside is hydrolysed to the extent of 93% by emulsin, but is perfectly stable towards maltase.

Methyl-*n*-propylcarbinol can be separated into *d*- and *l*-compounds after forming the glucoside, followed by fractional crystallisation. *d*-Amyl- β -*d*-glucoside can be obtained in this way, whilst *l*-amyl- β -*d*-glucoside remains in the mother-liquors.

The new methods of fractional fermentative hydrolysis of the glucosides of racemic alcohols, for the preparation of optical isomerides, and the asymmetric action of vegetable phosphatase on the potassium salts of racemic monoborneolorthophosphate (cf. this vol., 88) are described. By the action of glyoxalase on methylglyoxal, an excess of *l*-lactic acid is obtained, and on phenylglyoxal an almost quantitative yield of *l*-mandelic acid is obtained. In the presence of lactic acid bacteria, *d*-mandelic acid is obtained.

R. A. MORTON.

Enzymic processes in mammalian skeletal muscle. M. K. BEATTIE, J. BELL, and T. H. MILROY (J. Physiol., 1928, 65, 109—145).—When extracts of muscle are incubated at 22—45° in hydrogen carbonate solution there is, approximately, an equimolar production of phosphoric and lactic acids from the breakdown of the hexosediphosphoric ester present. When glycogen is added, formation of lactic acid and esterification of phosphoric acid occur in roughly equimolar proportions. The rates of these changes are less at 37° than at 22°. At 45° esterification is suppressed, but hydrolysis of glycogen and of phosphoric esters continues, whilst at 50°

diastatic action alone survives. In the presence of inorganic phosphate the amount of esterification exceeds the amount of lactic acid produced—most notably at the lower temperatures. In the presence of fluoride, esterification alone occurs and is greater than in the absence of the fluoride. Electrometric studies of the increased acidity and changes in buffer capacity accompanying esterification of phosphoric acid indicate that there are produced not only esters having dissociation constants about 10^{-6} but also others having lower values.

R. K. CANNAN.

Mechanism of fluoride action. F. LIPMANN (Biochem. Z., 1928, 196, 3—21).—Sodium fluoride has a specific inhibitory action on the hydrolysis of hexose- and glycerophosphoric esters by tissue and yeast enzymes. The formation of lactic acid in chopped muscle is also inhibited; this is a factor in the decrease of respiration. The oxidation quotient of lactic acid is diminished; in the presence of sufficient fluoride it approaches unity, when the whole of the lactic acid disappearing undergoes oxidation. The oxidation of glycerophosphoric acid is almost unchanged by fluoride, but the hydrolysis is depressed. Hydrocyanic acid has the opposite effect.

J. H. BIRKINSHAW.

Mechanism of oxidative processes. XIII. Oxidases and peroxidases. H. WIELAND and H. SUTTER (Ber., 1928, 61, [B], 1060—1068).—Attempts to repeat the isolation from *Lactarius vellereus* of the material which accelerates the auto-oxidation of quinol with production of hydrogen peroxide (Wieland and Fischer, A., 1926, 806) have unexpectedly led to the isolation of Bach and Sbarsky's enzyme (A., 1911, i, 824). The fungus is subjected to pressure and the expressed juice is treated with a small quantity of alcohol, whereby inert matter is precipitated, and then with more alcohol, which causes separation of the crude enzyme; after dialysis, the latter is 630 times as active as the fungus paste. Its activity is measured by observation of the rate of absorption of oxygen by buffered solutions of quinol in water; hydrogen peroxide is not thereby formed, although its presence is readily detected if Wieland and Fischer's preparation (*loc. cit.*) is added to the enzyme mixture. The activity of the enzyme is completely destroyed if its aqueous solution is heated for 3 min. at 100°, and is greatly restricted by hydrocyanic acid. The optimal p_H is 4.6. The rate of reaction is almost independent of the concentration of the quinol. It scarcely accelerates auto-oxidation of the iodine ion.

The peroxidase of horseradish, after purification by adsorption with aluminium hydroxide, does not accelerate the oxidation of quinol by molecular oxygen. Its catalytic activity is irreversibly restricted by hydrogen cyanide even at very great dilution, and even more markedly by hydrogen sulphide. Hydrazine and hydroxylamine are somewhat less restrictive, whereas ammonium sulphate, aniline hydrochloride, arsenious acid, hydrogen, oxygen, and nitrogen are inactive.

H. WREN.

Interferometric and chemical detection of Abderhalden's serum enzymes. E. KÜSTER and K. KOULEN (Fermentforsch., 1928, 9, 265—299).—

During aseptic autolysis of serum at 37°, the amino-nitrogen value increases, but not sufficiently to cause any measurable increase in interferometric value. Addition of kaolin does not accelerate autolysis. The dialysate of serum, when dialysed against distilled water, has a stronger ninhydrin reaction than when dialysed against physiological saline, but this is not accompanied by increase of amino-nitrogen. Addition of placenta substrate to serum frequently causes an increase in residual nitrogen which bears no relationship to changes in interferometric value, even when errors due to swelling are avoided. The same organ substrate may show different behaviour with serum of different individuals, and the substrates of different organs may behave differently with the same serum; the largest change of interferometric value is only of the order of experimental error. No results of diagnostic value could be obtained.

P. W. CLUTTERBUCK.

Peptic hydrolysis. S. P. L. SØRENSEN and L. KATSCHIONI-WALTHER [with a note on Indicators by K. LINDERSTRØM-LANG] (Compt. rend. Trav. Carlsberg, 1928, 17, No. 7, 24 pp.).—See this vol., 551.

Purification of pepsin. H. PENAU and J. PLÉ (J. Pharm. Chim., 1928, [viii], 7, 601—606).—The addition of acetone to pepsin solutions does not appreciably diminish the activity of this enzyme even after 48 hrs., if the p_H of the mixture is kept at 2.5 (isoelectric point of pepsin). Acetone is therefore a more suitable protein precipitant in the purification of pepsin than alcohol.

E. A. LUNT.

[Specificity and mode of action of erepsin, trypsin, and trypsin-kinase. Specificity of peptidases. II. Comparison of peptide-sugar condensation with the mode of action of erepsin.] K. JOSEPHSON (Ber., 1928, 61, [B], 1276—1279).—The author does not concur with the observation of Waldschmidt-Leitz and Rauchalles (this vol., 672, 673) that the condensation of dextrose and peptides differs greatly from that of dextrose and amino-acids in its dependence on the p_H of the solution, since a well-defined maximal p_H exists for the initial rate of condensation in the latter case.

H. WREN.

Specificity of animal proteases. XIV. Comparison of activating power of enterokinase from different sources. E. WALDSCHMIDT-LEITZ and O. SHENODA (Z. physiol. Chem., 1928, 176, 301—313).—Investigation has been made, by the caseinogen method (A., 1927, 174), of the hydrolytic action of erepsin-free trypsin from three animal sources, activated by erepsin-free enterokinase from eleven animal sources. With trypsin from the pancreas of the pig and the cat, it is found that activation is of the same value in all the cases examined. Differences are found in the hydrolytic action of sea-lion trypsin with pig and ox enterokinase, but the action is of the same order when enterokinase from the dog, rabbit, or the monkey *Cercopithecus sabaeus* is employed as the activator.

H. BURTON.

Mode of action of enzymes attacking proteins and their constituent materials (polypeptides). E. ABDERHALDEN (Naturwiss., 1928, 16, 396—399).—Dipeptides are hydrolysed by means of erepsin but

not by trypsin. Some decomposition occurs, however, by the action of trypsin-kinase on polypeptides, e.g., leucyltriglycyl-*l*-tyrosine. If a naphthalene-2-sulphonyl group is attached at the amino-group of polypeptides the action of trypsin-kinase is more marked than on the unsubstituted compound. It is possible that the points of attack in the polypeptide molecule are the amino-group for erepsin and the carboxyl group for trypsin. Some polypeptides are attacked only by erepsin, others only by trypsin. Some, however, are hydrolysed (at different rates) by both enzymes. The complications arising from this latter result are possibly due to different "trypsins," since the enzyme may be complex.

N-Alkali has a greater effect on polypeptides than *N*-acid. Glycyl chains are easily detached by alkali, and the longer chains more readily than the shorter. If substitution has occurred in the amino-group, hydrolysis by means of alkali is definitely hindered or assisted, depending on the substituent. The naphthalene-2-sulphonyl group decreases the action, whilst the benzoyl group causes an increase. The phenyl-carbimido-group is responsible for a greatly increased hydrolysis for a given concentration of alkali. Each substituent brings about a change in the optimal concentration of hydroxyl ions. Erepsin is regarded as attaching itself to the amino-group, the complex requiring such a p_H value that the process of hydrolysis occurs very easily. This idea makes the mechanism of enzymic hydrolysis a catalytic one in the Ostwald sense of an acceleration of a reaction already proceeding slowly. The erepsin-polypeptide then resembles the phenylcarbimido- rather than the β -naphthalenesulphonyl-polypeptide by the test of the action of dilute alkali. It seems clear that erepsin attacks the amino-group.

The work has implications for the investigation of the structure of proteins.

R. A. MORTON.

Influence of various amino-acids on yeast peptidase. A. FODOR and R. COHN (Z. physiol. Chem., 1928, 176, 17—28).—The effect of the following amino-acids on the action of yeast peptidase has been determined; glycine, *dl*-leucine, *l*-leucine, *l*-leucine, *d*-alanine, *l*-tyrosine, *l*-cystine, *d*-arginine, *d*-histidine, *d*-lysine, and *d*-glutamic acid, the first four being prepared synthetically and the rest used as natural products. With the exception of tyrosine, which has a slight inhibiting influence, all these amino-acids activate the hydrolysis of silk peptone by yeast maceration juice at p_H 8, and the influence of equimolecular quantities of the amino-acids is of the same order. This action appears to be due to a larger grouping, perhaps $\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, rather than to the amino- or carboxyl groups alone. The peptidase activity of a yeast macerate increases up to a maximum on being kept under sterile conditions, and this increase is attributed to autolytic processes which lead to an increase in the "zymolabile" form with a decrease in the "zymostable" system; in the "zymolabile" form the active group or "zymohaptic" substance is attached to amino-acids, whilst in the "zymostable" form it is associated with the natural proteins. Thus the stimulating action of leucine on the peptidase activity of yeast juice

decreases as the latter is kept. *d*-Leucine has a slightly greater activating influence than *dl*- or *l*-leucine and the last two have approximately equal effects. Cystine has an activating influence, whereas an inhibitory effect was previously recorded (Fodor and Schoenfeld, A., 1927, 76). A. WORMALL.

Enzymic proteolysis. VII. Influence of ions on the stability of trypsin. P. RONA and H. KLEINMANN (Biochem. Z., 1928, 196, 177—196).—The influence of electrolytes in stabilising aqueous trypsin solution at p_H 5—6 was examined. The action is due to the cation; the higher its valency, the lower is the concentration necessary for stabilisation. The optimum for sodium chloride and sulphate is about 2*N*, for magnesium chloride and sulphate about 0.02—0.1*N*, and for aluminium sulphate about 0.01*N*. The addition of salts has thus a stabilising effect similar to the action of hydrogen ions. Addition of cations at the optimum p_H (1.7) has a harmful effect; the stability of unpurified trypsin solution thus depends on the total cation content. The harmful action of boiled gastric juice of normal acidity (p_H 1.5—2) on trypsin solution is due to its electrolytes. J. H. BIRKINSHAW.

Enzymic proteolysis. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, 196, 197—222).—Caseinogen solutions after a short hydrolysis by trypsin were subjected to dialysis at a collodion membrane. Although caseinogen itself is not adsorbed by the membrane, the fission products are strongly adsorbed, as shown by the loss of nitrogen from the liquid. The increase in amino-nitrogen is, on the other hand, very small. It therefore appears that the caseinogen is first broken down into large fragments without hydrolysis of the $\cdot\text{CO}\cdot\text{NH}\cdot$ linking. J. H. BIRKINSHAW.

Evaluation of the power of enzymic mordants by their action on elastin. J. SCHNEIDER, jun., and A. HÁJEK (Biochem. Z., 1928, 195, 403—414).—A method for the preparation of elastin from the ligamentum nuchæ is outlined and the influence of the following factors on its degradation by trypsin is investigated and the results are tabulated: p_H , time of disintegration, fineness of the elastin threads, temperature, variation of relative amounts of elastin and enzyme. P. W. CLUTTERBUCK.

Inactivation of urease. E. G. SCHMIDT (J. Biol. Chem., 1928, 78, 53—61).—Figures are given for the concentration of various salts which inhibit the action of urease. In the case of mercuric chloride a direct proportionality was observed between the amount of the salt present and the amount of enzyme inactivated; solutions of carbamide containing varying amounts of mercuric chloride may therefore be used for the standardisation of solutions of urease. The mercury in the blood of patients suffering from poisoning with mercuric chloride was not sufficient to affect the action of urease. C. R. HARRINGTON.

Alcoholic fermentation. XIV. Zymin fermentation. S. KOSTYTSCHEV and V. FAËRMANN. **XV. Fermentation by yeast macerate.** S. KOSTYTSCHEV and A. CHOMITSCH (Z. physiol. Chem., 1928, 176, 46—54, 55—73).—XIV. Fermentation

by zymin (prepared by the acetone method) differs from that by dried yeast, which is attributed to the presence of living yeast cells (cf. Kostytschev and others, A., 1927, 902), in having no "induction" period, whilst zymin, unlike dried yeast, does not stimulate the growth of yeast cells. The second difference, however, is due to the inability of the stimulating substances to diffuse out of the cells of the zymin, and heated zymin has this stimulating action. Under special conditions, e.g., by adding zymin to 10% sucrose solution and keeping at 30° for 14 hrs. and then diluting gradually over 7 hrs. to a 2% sugar concentration and inoculating on plates, good growth can be obtained from zymin. The conclusion is reached that zymatic cells are present in zymin and that zymin does not effect a cell-free fermentation.

XV. Fermentation by yeast maceration juice is essentially due to bacteria and there is no evidence of cell-free fermentation by this juice. Rapid filtration of the juice through a filter candle yields a solution which can ferment, but this is due to the passage of bacteria through the filter, and slow filtration gives an inactive solution. A. WORMALL.

Alcoholic fermentation. XVII. Pyruvic acid as an intermediate product of alcoholic fermentation. S. KOSTYTSCHEV and S. SOLDATENKOV (Z. physiol. Chem., 1928, 176, 287—291).—During the fermentation of a 10% sucrose solution by pure yeast, semicarbazide acetate was added at intervals. Examination of the product after 3 weeks demonstrated the presence of pyruvic acid semicarbazone.

H. BURTON.

Methylglyoxalase and co-zymase. A. GOTTSCALK (Z. physiol. Chem., 1928, 176, 314—316).—Co-zymase-free, dry bottom yeast has no appreciable action on solutions of methylglyoxal, whilst a yeast with a low co-zymase content effects about 20% transformation (cf. Neuberg and Kobel, A., 1927, 592). Thus, the activity of methylglyoxalase is related to the presence of co-zymase.

H. BURTON.

Production of glycerol by fermentation. V. Effects of sulphites on the yeast cell and on fermentation. Y. TOMODA (J. Soc. Chem. Ind. Japan, 1928, 31, 9—20).—The effects of sulphites on the yeast cell and on fermentation have been studied by staining the cell with methylene-blue and determining the decrease of sugar in the fermenting medium respectively. Sodium hydrogen sulphite is very injurious to both the cell and fermentation. The inhibiting action of sodium hydrogen sulphite is reversible to some extent. The activity of the yeast cell which has been injured by this salt can be restored if sodium carbonate or sodium hydrogen carbonate is added within 20 hrs. In a synthetic medium, which contains sodium sulphite, the velocity coefficient of the fermentation is a linear function of the number of yeast cells in unit volume. In a natural medium, however, such as molasses solution, the velocity coefficient becomes a linear function of the logarithm of the number of yeast cells. The inhibiting action of sodium hydrogen sulphite can be eliminated by adding acetaldehyde, but not by adding co-zymase. Y. NAGAI.

Aldehyde-mutation of acetic bacteria. K. MYRBÄCK, H. VON EULER, and E. SANDBERG (Z. physiol. Chem., 1928, 175, 316—320).—Acetic bacteria, which can effect the dismutation of acetaldehyde, contain the co-enzyme (co-enzyme) which is necessary for yeast and animal mutases, but the amount of co-enzyme present in a heated suspension of the bacteria is not very large. A. WORMALL.

Metabolism of the anaërobes. I. Proteolysis by *Clostridium putrefaciens* compared with that of other anaërobes. II. Relation between the volatile acid and ammonia production during metabolism of *C. putrefaciens*. III. Volatile acids produced by *C. putrefaciens* in cooked-meat medium. L. B. PARSONS and W. S. STURGES (J. Bact., 1927, 14, 181—215).—At all ages there is molar equivalence between the ammonia and volatile acids produced. There appears to be a high degree of specificity in the deamination of amino-acids by *C. putrefaciens*. The volatile acids are acetic (85 mol.-%), butyric (6%), and valeric (9%).

CHEMICAL ABSTRACTS.

Action of *Bacillus diphtheriae* and some related organisms on glucosamine. W. C. NOBLE, jun., and (Miss) F. E. D. KNACKE (J. Bact., 1928, 15, 55—65).—Glucosamine is not a source of nitrogen for *B. diphtheriae*, *B. xerosis*, or *B. Hofmanni*; it is not as easily fermented as dextrose. Ability to ferment glucosamine is not related to ability to produce toxin.

CHEMICAL ABSTRACTS.

Light-activated hæmolysin produced by *Bacillus influenzae*. H. K. WARD (J. Bact., 1928, 15, 51—54).—*B. influenzae* grown on blood-agar plates containing hæmatin in light shows hæmolysis after a time depending on the intensity of the light.

CHEMICAL ABSTRACTS.

Toxic substances produced by the *Salmonella* group of organisms. E. E. ECKER and C. RIMINGTON (J. Hyg., 1927, 27, 44—48).—The toxin in the dialysate of the filtered and concentrated medium was precipitated by neutral lead acetate. Ammonium sulphate decomposed the lead precipitate without impairing its toxicity. The concentrated preparations contained 0.3—0.4% N; carbohydrates were present.

CHEMICAL ABSTRACTS.

Fermentative metabolism of bacteria. V. *Staphylococcus*. H. W. NICOLAI and N. KAGEURA (Biochem. Z., 1928, 196, 246—256).—Under anaërobic conditions staphylococci ferment dextrose and lævulose producing two molecules of fixed acid. Maltose and sucrose give four molecules of acid. The velocity of fermentation and the rate of respiration are proportional to the cell concentration. The optimum p_H is that of blood; the temperature coefficients of respiration and of glycolysis (anaërobic) are 2.27 and 2.6, respectively. Glycolysis and respiration are sensitive to elevation of osmotic pressure; calcium and especially magnesium chlorides have a detrimental effect, whilst potassium is less harmful than sodium chloride.

J. H. BIRKINSHAW.

Antigenic complex of *Streptococcus hæmolyticus*. II. Chemical and immunological properties of the protein fractions. III. Species-

specific substance. R. C. LANCEFIELD (J. Exp. Med., 1928, 47, 469—480, 481—491).—The type-specific substance is precipitated by the usual protein reagents, is progressively destroyed by removal of the amino-group with nitrous acid, and is readily digested by trypsin and pepsin. After considerable purification it contains 14% N. The species-specific substance resists tryptic and peptic digestion, but gives Molisch's reaction; a purified sample, however, contained 4.2% N and only 28% of reducing sugars.

CHEMICAL ABSTRACTS.

Is diacetyl a product of [bacterial] metabolism? H. SCHMALFUSS and H. BARTHEMEYER (Z. physiol. Chem., 1928, 176, 282—286).—When fumaric, succinic, or malic acid is heated under the conditions previously described (A., 1927, 648), no diacetyl is produced. When a culture of *Streptococcus acidilacti*, Grotenfeldt, + *S. cremoris* is grown on sterilised milk, an odour of diacetyl is perceptible, and distillation of the culture yields a very small amount of diacetyl, identifiable by the nickel test (*loc. cit.*). The diacetyl does not arise from the lactic acid formed during the growth of the culture nor is it produced by atmospheric oxidation of acetyl-methylcarbinol.

H. BURTON.

Precipitation of the lethal principle of tuberculin by ammonium sulphate. R. R. HENLEY, M. DORSET, and H. E. MOSKEY (J. Amer. Vet. Med. Assoc., 1928, 72, 363—366).—Ammonium sulphate precipitates the lethal principle from young, alkaline cultures. With old, acid cultures there is an increase in soluble carbohydrates, a decrease in the material precipitable by acetic acid, and a change in the character and amount of the ammonium sulphate precipitate.

CHEMICAL ABSTRACTS.

Soil bacteria which decompose aromatic compounds. P. H. H. GRAY and H. G. THORNTON (Zentr. Bakt. Par., 1928, II, 73, 74—96; Chem. Zentr., 1928, i, 1052).—Bacteria (25 kinds) from English soil which decompose phenol, cresols, naphthalene, phloroglucinol, resorcinol, and toluene have been isolated.

A. A. ELDRIDGE.

Do bacteria reduce phosphate? F. LIEBERT (Zentr. Bakt. Par., 1927, II, 72, 369—374; Chem. Zentr., 1928, i, 1052—1053).—Rudakov's observation (this vol., 447) could not be repeated.

A. A. ELDRIDGE.

Effect of carbamide and of thiocarbamide on the development and vitality of bacteria. E. NICOLAS and J. LEBDUSKA (Compt. rend., 1928, 186, 1767—1769).—Thiocarbamide inhibits the development and vitality of bacteria grown in a beef broth-peptone medium of p_H 7.4 to a greater extent than carbamide. No hydrogen sulphide was evolved, and the amount of ammonia liberated was not influenced. The effect is similar to but less marked than that obtained with the higher plants (A., 1925, i, 757). On the other hand, the toxicity of carbamide towards animals is greater than that of thiocarbamide (this vol., 919).

J. GRANT.

Relative importance of additive and antagonistic effects of cations on bacterial viability. C. E. A. WINSLOW and A. F. DOLLOF (J. Bact., 1928, 15, 67—92).—The stimulating effect of sodium,

potassium, calcium, magnesium, barium, lead, and mercury ions in low concentrations on bacterial growth, and their inhibitory effect in high concentrations, are investigated quantitatively.

CHEMICAL ABSTRACTS.

Bactericidal action of dyes. A. PHILBERT and J. RISLER (*Compt. rend.*, 1928, 186, 1583—1584).—Cultures of various pathological bacteria on defibrinated human blood-serum are almost unaffected by the light of a neon lamp (the growth of staphylococci is slightly retarded). In the presence of methyl-violet (1 in 10,000), almost immediate sterilisation takes place. G. A. C. GOUGH.

Hormones and adsorption. A. ZONDEK and H. W. BANSI (*Biochem. Z.*, 1928, 195, 376—386).—Adsorption of adrenaline by animal charcoal follows the Freundlich adsorption isotherm, and is considerably inhibited by narcotics, the action of which is according to the Richardson law of homologous series. Calcium ions in high and caffeine in small concentration accelerate, whilst calcium ions in small concentration inhibit, the adsorption.

P. W. CLUTTERBUCK.

Radiation substance in the heart. H. ZWAARDEMAKER (*Pflüger's Archiv*, 1927, 218, 354—373; *Chem. Zentr.*, 1928, i, 1053).—Skeletal muscle contains a substance ("automatinogen"), dialysable and adsorbed by talc, which can be activated by irradiation to automatin. Automatin is probably identical with Demoor's "substances actives" and Haberlandt's heart hormone. Although there is only one automatinogen, natural β -automatin and artificial α -automatin are very similar but not identical.

A. A. ELDRIDGE.

Effect of insulin on acetonuria. J. H. BURN and H. W. LING (*J. Physiol.*, 1928, 65, 191—203).—The excretion of "acetone substances" by rats on a fat diet is greater in summer than in winter. In winter there is a steady rise in the glycogen content of the liver which is not compensated by a fall in the muscle-glycogen or by an increased excretion of nitrogen. Injections of insulin delay this rise for about 2 days, during which period the ketonuria is increased and then disappears. R. K. CANNAN.

Production of alcohol in the animal body. III. Influence of insulin on the amount of physiological alcohol in the blood of animals. M. AOKI (*J. Biochem. Japan*, 1927, 7, 333—344).—In birds, injection of insulin leads to a reduction of blood-alcohol in 90 min.

CHEMICAL ABSTRACTS.

Effect of insulin on faulty lipid metabolism in acute diabetes. M. LABBÉ, F. NERVEUX, and HIERNAUX (*Compt. rend.*, 1928, 186, 1445—1446).—The blood of diabetics is characterised by the low alkaline reserve, the large amounts of cholesterol and lecithin, and by the appearance of acetone derivatives which are not normally present. On the administration of insulin the latter disappear from the blood and the alkaline reserve becomes normal. In most cases the cholesterol and lecithin contents fall to the normal values. Since these symptoms are partly due to faulty lipid metabolism, insulin is probably concerned in some way in the assimilation of lipids.

G. A. C. GOUGH.

Influence of insulin and synthalin on purine metabolism. G. TAUBMANN (*Arch. exp. Path. Pharm.*, 1928, 132, 124—128).—Moderate doses of insulin administered to a dog do not cause a significant increase in the excretion of total nitrogen, but do cause an increase in the excretion of purine. Administration of synthalin markedly increases the excretion of allantoin in the urine. W. O. KERMACK.

Effect of insulin and of pancreatectomy on distribution of potassium and phosphorus in blood. S. E. KERR (*J. Biol. Chem.*, 1928, 78, 35—52).—The potassium content of the blood-serum of dogs is decreased by administration of insulin, whilst that of the corpuscles is not affected. The lipin phosphorus of the blood is not affected by excess or absence of insulin; the organic acid-soluble phosphorus of the blood corpuscles is slightly increased after pancreatectomy, but is not affected by excess of insulin. The conclusion of Kay and Robison (*A.*, 1924, i, 1368) that insulin favours the synthesis of hexosephosphoric esters in the blood is therefore not supported. C. R. HARRINGTON.

Regulation of the production of insulin. II. Action of carbohydrates (except dextrose) on the production of insulin. E. GRAFE and F. MEYTHALER (*Arch. exp. Path. Pharm.*, 1928, 131, 80—91; cf. *A.*, 1927, 1115).—By the use of the technique previously described (*loc. cit.*) it is shown that the production of insulin is stimulated not only by dextrose, but also by any reducing sugar or any carbohydrate which may give rise to reducing sugars on hydrolysis by the animal body.

W. O. KERMACK.

Detection of vitamin-A. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1928, 174, 191—195).—Comparative experiments show that there is no agreement between the antimony trichloride test for vitamin-A (Carr and Price, *A.*, 1926, 870) and feeding tests with young rats. Whale oil diluted with chloroform gives the colour reaction in concentrations of 2% and 0.2%, but not 0.02%, whereas similar dilutions of the oil (with vegetable oils) do not prevent avitaminosis when fed to rats kept on a diet deficient in vitamin-A. Doubt is expressed as to whether the colour reaction is due to vitamin-A. Crude cholesterol prepared from the oil gives an intense colour reaction, but on recrystallisation this property is lost and the material responsible for the reaction is found in the mother-liquor.

A. WORMALL.

Water-soluble vitamins of group B. Probable existence of a thermostable and alkali-stable factor essential to life. (Mlle.) L. RANDOIN and R. LECOQ (*Compt. rend.*, 1928, 187, 60—62).—By using a fuller's earth of low adsorptive power to adsorb the antineuritic factor from extract of brewer's yeast two products have been obtained: (1) an extract deprived of antineuritic factor but containing the "nutrition" factor, and (2) an earth in which the antineuritic factor is concentrated. Neither this activated earth nor extract of yeast autoclaved in alkaline medium is capable of lengthening appreciably the lives of pigeons on a diet deficient in vitamin-B, but with mixtures of these two products or with

extract (1) the period of survival is considerably extended. The autoclaved extract appears to contain a water-soluble factor which is stable to heat and to alkali and is indispensable to the life of the pigeon, probably functioning in the digestion processes, and the extract obtained on removal of the antineuritic factor with fuller's earth appears to contain the same nutritive, thermostable factor. R. BRIGHTMAN.

Complex nature of vitamin-B as found in wheat and maize. C. H. HUNT (J. Biol. Chem., 1928, 78, 83-90).—Better growth was obtained in rats receiving a mixture of wheat or maize with autoclaved yeast as a source of vitamin-B than in those receiving wheat or maize alone. These cereals are therefore relatively rich in vitamin-B₁ and poor in vitamin-B₂. C. R. HARRINGTON.

Comparative influence of fats and sugar in the course of avitaminosis-B. (Mlle.) L. RANDOIN (Compt. rend., 1928, 186, 1438-1441).—Two groups of rats were fed on two separate diets deficient in vitamin-B. The first contained lard but no sugars and in the second the lard was replaced by an amount of dextrose equivalent to it in energy value. Whilst young rats eat the dextrose-containing diet more readily, in all experiments survival was longest where dextrose was withheld.

G. A. C. GOUGH.

Avitaminosis-B and the suprarenal gland. II. Behaviour of pigeons deprived of vitamin-B towards adrenaline and choline. E. SCHMITZ and H. J. POLLACK (Biochem. Z., 1928, 195, 428-441).—The protective action of an extract of the whole suprarenal gland against avitaminosis-B is not due either to the adrenaline or to the choline which it contains, but to some unknown substance.

P. W. CLUTTERBUCK.

Human milk. V. Comparison of vitamin-D in human and cow's milk. J. OUTHOUSE, I. G. MACY, and V. BREKKE (J. Biol. Chem., 1928, 78, 129-144).—Addition of human milk in amounts up to 40 c.c. daily to a diet otherwise deficient in vitamin-D failed to prevent development of rickets in rats; addition of 30 c.c. daily of cow's milk to the same diet produced healing of rickets in 7 days.

C. R. HARRINGTON.

Reactions of irradiated ergosterol (vitamin-D). A. STEIGMANN (Kolloid-Z., 1928, 45, 165-166).—Reactions of ergosterol before and after irradiation suggest that vitamin-D is an unsaturated ketone. The irradiated material gives a violet coloration with fuchsin, the colour of which has been discharged by a slight excess of sodium hydrogen sulphite. Neither ergosterol before irradiation nor ergosterol peroxide gives this reaction. The irradiated material reduces ammoniacal silver nitrate, forming a yellowish-brown colloidal sol of silver. It is considered that the silver is protected by a polymerisation product of ergosterol formed simultaneously. E. S. HEDGES.

Activation of the antirachitic factor in dried yeast. W. KIRSCH (Biochem. Z., 1928, 196, 294-300).—Dried yeast, on account of its ergosterol content, develops on irradiation with ultra-violet light a powerful antirachitic action, but this is considerably reduced by storing for seven months. The

antirachitic action of dried yeast is equally good also after irradiation with direct sunlight and in animals fed with it when they are irradiated. Rats which were irradiated daily for 1 min. for a considerable length of time were protected against rickets, but showed an inhibition of development when compared with non-irradiated animals.

P. W. CLUTTERBUCK.

Photosynthesis of the antirachitic vitamin by ultra-violet radiation of short wave-length. H. D. GRIFFITH and K. C. SPENCE (Brit. J. Actinother., 1928, 3, 69-72).—Ergosterol has been irradiated by light from a mercury-vapour lamp passed through a quartz prism to separate the waves. The sample irradiated by light of wave-length 366-313 μ did not become antirachitic when tested on rats, whilst those treated with light of 313-265 μ and of less than 265 μ were activated, the latter apparently less than the former.

W. O. KERMACK.

Factor H in the nutrition of trout. C. M. MCCAY, F. C. BING, and W. E. DILLEY (Science, 1928, 67, 249-250).—Raw liver contains a factor H, not identical with vitamin-A, B, C, D, or E, which is essential for the growth of trout.

CHEMICAL ABSTRACTS.

Orthophosphoric acid as a stimulator of the germinating power of seeds. M. GRAČANIN (Biochem. Z., 1928, 195, 457-468).—Treatment of the seeds of *Beta vulgaris*, *Secale cereale*, *Vicia sativa*, *Helianthus annuus*, *Lolium perenne*, *Festuca arundinacea*, *Trisetum flavescens*, and *Dactylis glomerata* with orthophosphoric acid accelerates the process of germination considerably, the optimal conditions consisting of treatment for 15 hrs. with an amount of acid equivalent to 0.05-1% P₂O₅ for the various seeds. The optimal concentration for the germination process is not, however, optimal for the plant embryos. Whereas only 2% of the seeds of *Hordeum vulgare* germinate after 10 days, treatment with 1% orthophosphoric acid causes the germination of 61% after 72 hrs.

P. W. CLUTTERBUCK.

Enzyme formation in ripening seeds. A. OFARIN and N. DJATSCHKOV (Biochem. Z., 1928, 196, 289-293).—The amylase content of ripening seeds increases only while they are attached to the mother plant, whereas the peroxidase and catalase contents increase even after separation therefrom.

P. W. CLUTTERBUCK.

Maintenance of semi-permeability in the plant-cell during leaching experiments. F. C. STEWARD (Proc. Leeds Phil. Soc., 1928, 1, 258-270).—Protracted leaching experiments have shown that leaching does not necessarily result in loss of semi-permeability.

W. E. DOWNEY.

Passage of boric acid and certain salts into fruits and vegetables. L. KAHLENBERG and R. TRAXLER (Plant Physiol., 1927, 2, 39-54).—A study of the permeability, under various conditions, of the outer membranes of cherries, tomatoes, plums, grapes, apples, gooseberries, peaches, cucumbers, and carrots to 0.1M-solutions of lithium chloride, nitrate, sulphate, and borate, boric acid, borax, potassium iodide, barium chloride, and strontium chloride.

CHEMICAL ABSTRACTS.

Plant colloids. XX. Behaviour of starch sols in the dark field. XXI. Distribution of phosphorus and nitrogen in starch grains. M. SAMEC (Biochem. Z., 1928, 195, 40—71, 72—78).—XX. During ageing of starch sols, Brownian movement of the ultramicroscopic particles first stops and is followed by a period of vibration and finally all movement ceases. The particles aggregate either in spherical masses, which give a blue colour with iodine, or in chains, which give a red colour with iodine. The ultrafiltrate of starch sols contains a smaller number of smaller particles than the original sol. Only quantitative differences were observed between wheat and potato starch. By heating starch sols, the number of visible particles decreases, the movement is lost, but the typical aggregation is retained. Traces of phosphorus in the starch sol appear to have a stabilising effect. Ultramicroscopic observation reveals only a small fraction of the total substance dissolved.

XXI. The outermost part of starch grains contains the greatest amount of phosphorus and nitrogen. Amylocellulose of wheat and maize starch is especially rich in these elements and also contains silica, whilst that of potato starch may be obtained free from nitrogen.

P. W. CLUTTERBUCK.

Alkaloids of Chinese *Corydalis ambigua*, Cham. et Sch. I. T. Q. CHOU (Chinese J. Physiol., 1928, 2, 203—218).—From the tubers of this plant five alkaloids have been separated. (1) *Corydalis A*, $C_{22}H_{27}O_4N$, m. p. 135° [α]_D²⁵ +295° (ethosulphate, m. p. 162°; hydrochloride, m. p. 214°; nitrate, m. p. 197°; chloroplatinate, m. p. 227°; methiodide, m. p. 228°). It is identical with corydaline. (2) *Corydalis B*, $C_{20}H_{23}O_4N$, m. p. 148—149°, optically inactive (hydrochloride, m. p. about 218°; hydrogen oxalate, m. p. 208°). (3) *Corydalis C*, $C_{20}H_{19}O_5N$, m. p. 201°, optically inactive (hydrochloride, m. p. 248°; hydrogen oxalate, m. p. 237°; chloroaurate, m. p. 195°; hydrobromide, m. p. 250°). It is possibly identical with protopine. (4) *Corydalis D*, $C_{19}H_{16}O_4N$ or $C_{19}H_{17}O_4N$, m. p. 204°, [α]_D²⁵ —295°; (hydrochloride; m. p. about 250°; hydrobromide, m. p. about 260°). (5) *Corydalis E*, m. p. 219° (hydrochloride, m. p. 246°). *Corydalis B* has narcotic and local anaesthetic properties. *Corydalis C* appears to be a cerebral stimulant.

H. D. KAY.

Constant alkaloidal content of *Datura Stramonium*, L. var. *inermis*. W. PLOSKI (Bull. Acad. Polonaise, 1927, A, 397—401).—The roots, stems, leaves, and fruit of *D. Stramonium* grown with various manures have been analysed in respect of total nitrogen and alkaloid content. In spite of the marked variation in total nitrogen, the various parts show a remarkably constant alkaloid content.

W. O. KERMACK.

Constitution of the anthochlorin of the yellow dahlia. L. SCHMID and A. WASCHKAU (Monatsh., 1928, 49, 83—91).—The yellow pigment "anthochlorin" (Prantl, Bot. Ztg., 1871, 29, 425) of the yellow dahlia has been isolated in quantity in a crystalline condition by extraction with 50% aqueous alcohol, evaporation of the alcohol in a vacuum, repeated (20 times) precipitation from an alcoholic

solution by addition of water, hydrolysis with 2% alcoholic hydrogen chloride, acetylation, and subsequent hydrolysis of the acetyl derivative. By a comparison of the triacetate and the dimethyl ether, the products of fusion with potassium hydroxide (*p*-hydroxyacetophenone and *p*-hydroxybenzoic acid), and by oxidation of the dimethyl ether with potassium permanganate to anisic acid, it is proved to be identical with apigenin.

J. W. BAKER.

Micro-chemistry of plants. XVII. Chromogen of a red colouring matter obtained from cacti. H. MOLISCH (Ber. deut. bot. Ges., 1928, 46, 205—211).—The occurrence of a red colouring matter, to which the name *cactorubin* has been given, is reported on the cut surfaces of cactus stem kept moist and in contact with air. It is suggested that the formation is due to the action in the dying cells of an oxidase on the chromogen of the substance. Of the 29 varieties of cactus examined 28 contained cactorubin. Cactorubin is slightly soluble in water, insoluble in alcohol, ether, and benzene, and has not yet been obtained crystalline.

E. A. LUNT.

Occurrence of a red pigment in the root of the plane tree. R. SCHAEDE (Ber. deut. bot. Ges., 1928, 46, 298—300).—The pigment, observed in a tree felled in December, was only slightly soluble in water, soluble but unstable in alkalis, soluble in methyl and ethyl alcohols, and insoluble in ether, benzene, carbon disulphide, or chloroform. It is concluded that it is a phlobaphen the function of which in the root is that of a reserve food material, since a second tree of the same age and species felled in the spring showed only traces of the substance.

E. A. LUNT.

Enzymes of oil-bearing seeds. X. Glycerophosphatases. O. FERNÁNDEZ and A. PIZARROSO (Anal. Fís. Quím., 1928, 26, 118—121).—Comparative measurements were made of the activity of glycerophosphatases in the seeds of *Amygdalus communis* (var. *dulcis*), *Corylus avellana*, *Arachis hypogaea*, *Cannabis sativa*, *Sinapis nigra*, *Pinus pinea*, and *Juglans regia*, using the method of Némec (A., 1923, i, 882). The increase of activity with slight acidity found by Némec was confirmed, but no definite regularity could be found in the effect of added glycerol.

R. K. CALLOW.

Ergosterol from the mushroom *Cortinellus Shiitake*. M. SUMI (Proc. Imp. Acad. Tokyo, 1928, 4, 116—119).—Ergosterol has been isolated from this mushroom by the usual methods and identified by its chemical and physical properties and its physiological effect after irradiation.

J. STEWART.

Biochemistry of sulphur. II. Ergothioneine from ergot of rye. B. A. EAGLES (J. Amer. Chem. Soc., 1928, 50, 1386—1387).—The isolation of the mercurichloride by the method of Tanret (A., 1909, i, 671) and its conversion into the pure base (A., 1927, 477) (0.065% of the wt. of ergot) are detailed.

H. E. F. NOTTON.

Chemical constituents of the spores of *Aspergillus oryzae*. M. SUMI (Biochem. Z., 1928, 195, 161—174).—The spores of *A. oryzae*, grown on damp soya bean, contain the following: a small amount of soluble reducing sugar and pentosan and a large

amount of mannitol; glycogen (not starch); lecithins and organic and inorganic phosphates; considerable amounts of betaine and a little stachydrine; histamine; considerable amounts of chitin; a sterol, $C_{16}H_{28}O$, m. p. 160° ; uric acid (0.6% of the air-dried material); invertase, amylase, peptase, chymase, urease, glucosidase, peroxidase, nuclease, esterase, phytase, and catalase, the first three being especially active. The following enzymes were not detected: lipase, tyrosinase, maltase, inulase, trehalase, decarboxylase, and oxidase. P. W. CLUTTERBUCK.

Biochemical differences between sexes in *Mucors*. V. Quantitative determination of sugars in (+) and (−) races. S. SATINA and A. F. BLAKESLEE (Proc. Nat. Acad. Sci., 1928, 14, 308—316; cf. this vol., 563).—The amounts of total soluble, of reducing, and of non-reducing sugars were determined for various *Mucor* species. In order to compare the amounts of sugar present in the two sexes, the determinations were made in pairs, each containing a (+) and a (−) race of a given species. In the majority of cases more sugar was found in (+) than in (−) races. The amount of reducing sugars present was not high, and was insufficient to be chiefly responsible for the reduction reaction which takes place between the alcoholic extracts of the two sexes and potassium permanganate. It is probable that the difference in reduction capacity of (+) and (−) races is mainly due to other substances possibly related to the tannins. Gravimetric tests were made for fat content in the same mycelia in which sugar was determined. The amount of fat present is relatively large, but shows no relationship to sex.

A. J. MEE.

Physiology of *Rhizopus* species. T. TAKAHASHI and K. SAKAGUCHI (Bull. Agric. Chem. Soc. Japan, 1927, 3, 35—45).—In the surface growth acid production predominates, and the ratio of carbon dioxide to alcohol is greater than in yeast fermentation; in the submerged growth the fungus behaves like yeast. Formation of alcohol from dextrose occurs when subnormal amounts of potassium and phosphoric acid are present. A decrease in potassium causes a decrease in acid formation. The fungus produces succinic acid from glycerol.

CHEMICAL ABSTRACTS.

Inhibition of enzymic action as a possible factor in the resistance of plants to disease. L. J. KLOTZ (Science, 1927, 66, 631—632).—The hydrolytic action of the diastase and invertase of the dried mycelium of *Pythiacystis citrophthora* and *Phomopsis californica* is inhibited by the bark of sour orange or tangelo more than by that of lemon; urease, however, was not so inhibited. A. A. ELDRIDGE.

Pentathionic acid, the fungicidal factor of sulphur. H. C. YOUNG and R. WILLIAMS (Science, 1928, 67, 19—20).—Sulphur contains adsorbed pentathionic acid, to which its fungicidal action is due. After destruction of the pentathionic acid with ammonia a suspension of sulphur in water soon regains

its toxicity, equilibrium being reached in presence of oxygen.

CHEMICAL ABSTRACTS.

Calibration of Barcroft's manometer. M. JOWETT (Biochem. J., 1928, 22, 717—719).—A simple method, accurate to about 1%, of calibrating the Barcroft constant-volume manometer is described.

S. S. ZILVA.

Titrimetric quinhydrone electrodes; comparison with the hydrogen electrode for p_H determinations in whole blood, plasma, and other biological fluids. G. H. MEEKER and J. G. REINHOLD (J. Biol. Chem., 1928, 77, 505—518).—For the blood-plasma and serum of man and the horse, and for biological fluids such as cerebrospinal fluid and urine, results obtained with the quinhydrone electrode, employing the authors' titrimetric technique (A., 1926, 442), agreed with those obtained with the hydrogen electrode (cf. Cullen and Earle, this vol., 438); the quinhydrone electrode is not applicable to whole blood or to the blood-serum of the dog.

C. R. HARRINGTON.

Determination of chlorides in body fluids. J. PATTERSON (Biochem. J., 1928, 22, 758—761).—The effect of the presence of protein on the determination of chloride in various body fluids by the Volhard titration can be readily overcome by use of a high concentration of nitric acid together with selected proportions and sequence of the reagents normally employed.

S. S. ZILVA.

Rapid determination of organic iodine. G. PFEIFFER (Biochem. Z., 1928, 195, 128—133).—A method is described for the determination of iodine of organic material (thyroid etc.) in which, by rapid decomposition of the tissue with concentrated sulphuric acid and hydrogen peroxide, the time of a determination is reduced to 40 min., the results being comparable with those of older methods.

P. W. CLUTTERBUCK.

Determination of uric acid in biological fluids. R. VLADESCO (Bull. Soc. Chim. biol., 1928, 10, 602—605).—The phosphotungstic acid colorimetric method for determining uric acid in biological fluids from which the proteins have been removed is unsatisfactory owing to the rapid fading of the sample and the standards, and the titration of the coloured complex with aqueous chlorine is recommended. Since the titre is not strictly proportional to the uric acid content, two titrations are made in the presence of two different volumes of standard uric acid solution.

G. A. C. GOUGH.

Dialysis with stirring. M. KUNITZ and H. S. SIMMS (J. Gen. Physiol., 1928, 11, 641—644).—The solution to be dialysed is contained in a stoppered collodion sac along with a marble or a bubble of air. The sac is placed within a test-tube which is in a rocking machine, and distilled water is led into the test-tube outside the collodion sac. The movement of the marble or bubble of air agitates the solution and accelerates dialysis.

W. O. KERMACK.

