

BRITISH CHEMICAL ABSTRACTS

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General, Physical, and Inorganic Chemistry.

Highly accurate method for interferometric wave-length determinations, and its application to a preliminary determination of krypton lines for a German standard metre in terms of light waves. A. P. WEBER (Physikal. Z., 1928, 29, 233—239).—In view of the use of interferometric methods in fixing standards of length, the relative merits of the Fabry-Perot etalon and the Koster absolute interference comparator methods have been studied at the Physikalisch-Technischen Reichsanstalt. The krypton spectrum possesses advantages over the cadmium spectrum in that the latter shows only one entirely suitable line, the standard red line, whereas several lines are available in the discharge from pure krypton. The following wave-lengths have been measured relative to the cadmium line 6438.5033 Å. (in air at 20°, 760 mm., and 10 mm. moisture): green cadmium, 5085.8490, red krypton, 6456.3241, yellow, 5870.9463, yellowish-green, 5649.5924, violet, 4502.3790, green, 5400.5919, the two lines last named being measured relative to the other krypton lines. Pending further investigations in different countries on the krypton yellowish-green line, the use of the cadmium red line as a standard is continued.

R. A. MORTON.

Coefficient of absorption in lead of the γ -rays from thorium-C'' and radium-C. L. BASTINGS (Phil. Mag., 1928, [vii], 5, 785—793).—Measurements of the absorption in lead of the γ -rays from thorium-C'' and radium-C have shown that the absorption coefficient in the case of the former increases with the thickness of the lead penetrated, whilst in the case of the latter it decreases. This result is in general agreement with Compton's theory of scattering of radiation, since whilst the γ -rays from radium-C are distributed over a moderate range of wave-lengths with no outstanding gaps or preponderating concentration of energy, those from thorium-C'' are almost monochromatic.

A. E. MITCHELL.

Reversal of helium lines. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 83—91).—See this vol., 209.

Spectra and atoms. A. FOWLER (J.C.S., 1928, 764—780).—A lecture.

Spark spectrum of neon. H. N. RUSSELL, K. T. COMPTON, and J. C. BOYCE (Proc. Nat. Acad. Sci., 1928, 14, 280—283).—A new series of lines of considerably shorter wave-length than those previously described has been discovered in the spark spectrum of neon. A vacuum spectrograph was used, the spectrum being excited by electron impacts at con-

trolled voltages between a Wehnelt cathode and a wire-grid anode, the pressure in the spectrograph being kept at less than 0.005 of that in the discharge tube. This work, together with previous observations of de Bruin, has enabled 203 lines to be classified in 59 multiplets. A table is given stating the term values of all the states of Ne II so far identified. The mean quantum defects of the various states are also given, and compared with those of O II, to which they show close similarity. The ionisation potential was found to be 40.9 ± 0.05 volts. A. J. MEE.

Spark spectrum of argon. I. T. L. DE BRUIN (Z. Physik, 1928, 48, 62—66).—Theoretical. The deepest quadruplet term of the A II spectrum has been determined. An analogy is drawn between the spectrum of A II and Ne II.

W. E. DOWNEY.

Energy levels of the hydrogen atom according to the Dirac quantum theory of electrons. W. GORDON (Z. Physik, 1928, 48, 11—14).—Mathematical. It is shown that Dirac's theory leads to Sommerfeld's fine-structure formula.

W. E. DOWNEY.

Natural vibrations in the infra-red of beryllium oxide, magnesium oxide, calcium oxide, and zinc oxide. S. TOLKSDORF (Z. physikal. Chem., 1928, 132, 161—184).—The infra-red transmission spectra of the above oxides have been studied in the range 2—22 μ . In every case the lattice vibration is anharmonic. Magnesium oxide and calcium oxide give, corresponding with their simple cubic lattice structure, simple spectra, each having one fundamental. The hexagonal lattices of beryllium oxide and zinc oxide each appear to possess three fundamentals. Using the values obtained for the natural frequencies, ν , to calculate the values of $\beta\nu$, where β is the quotient of Planck's constant by Boltzmann's constant, gives results in fair agreement with those derived from m. p., compressibilities, and specific heats, respectively.

R. CUTHILL.

Structure of the fluorine spectrum (F I). T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 944—951).—A theoretical term scheme has been deduced for the fluorine spectrum (F I) on the basis of the theory of complex spectra developed by Heisenberg (A., 1925, ii, 729), Hund (*ibid.*, 912), and Pauli (*ibid.*, 339). This is in fairly good agreement with experimental results.

M. S. BURR.

Structure of the second order spectrum of sulphur (S II). J. GILLES (Compt. rend., 1928, 186, 1109—1111; cf. Bloch and Bloch, A., 1927, 1117).—

Five multiplets of rays corresponding with the combinations $ans.^4P-anp.^4P^4$, $ans.^4P-anp.^4D$, $anp.^4P-and.^4D$, $anp.^4D-and.^4D$, and $anp.^4D-and.^4F$ have been recognised for the S II spectrum, and are tabulated. The S II and O II spectra are analogous.

J. GRANT.

Absorption spectra of nitric oxide. M. LAMBREY (Compt. rend., 1928, 186, 1112—1114; cf. A., 1927, 808).—The absorption spectrum of nitric oxide is made up of two families of doublets located in the long and short wave-length regions, respectively, some of the doublets of the latter being partly superposed on those of the former. Each of the components is a resolvable band, and there is a single absorption minimum corresponding with a null ray. Formulæ are given representing the rays.

J. GRANT.

Origin of the spectrum of the solar corona. M. SAHA (Nature, 1928, 121, 671—672).—A discussion of the method whereby certain light elements may give rise to the coronal spectrum. For lithium, beryllium, and boron, the force of radiation would more than balance the force of gravity, so that the element could be retained in the solar atmosphere only in the ionised form; corresponding lines for the non-ionised elements are not found in the Fraunhofer spectrum, but the identification of lines of the ionised elements is doubtful. The possibility of silicon, carbon, and other elements giving rise to prohibited transitions is also discussed, and the author's views are supported by experimental evidence derived from the behaviour of thallium.

A. A. ELDRIDGE.

Stark effect and series limits. [Miss] J. M. DEWEY and H. P. ROBERTSON (Nature, 1928, 121, 709—710).—An upper limit is obtained for the energy of quantised orbits in a hydrogen-like atom, and it is shown that various types of unquantised orbits having negative energies exist.

A. A. ELDRIDGE.

Excitation of the auroral green line in active nitrogen. J. KAPLAN (Nature, 1928, 121, 711).—The auroral green line has been excited in active nitrogen produced by a condensed discharge in a mixture of nitrogen and oxygen (4%); the wave-length was determined as 5577.5 Å. With decreasing amounts of oxygen the line, at first intense, gradually disappeared. A red line, 6654.8 Å., possibly identical with an unclassified oxygen line at that wave-length, was also observed. The dissociation of the oxygen molecule and the excitation of the atom are considered not to occur in a single act.

A. A. ELDRIDGE.

Mn II spectrum excited by rare gas ions. J. G. BLACK and O. S. DUFFENDACK (Science, 1927, 66, 401—402).—Rare gas ions on contact with manganese atoms ionise them and excite them to the degree that the ionising potential of the rare gas exceeds that of manganese (7.4 volts). Argon (ionisation potential 15.4 volts) gives manganese lines originating in the 7P and 5P levels; with neon (ionisation potential 21.5 volts), 7P — 7D lines were strong.

A. A. ELDRIDGE.

Extension of the violet CN band system to include the CN tail bands. F. A. JENKINS (Physical Rev., 1928, 121, 539—558).—Wave-

numbers of band-lines are tabulated for thirteen of the CN tail bands as excited by interaction of acetylene with active nitrogen. The tail bands are merely members of the ordinary CN sequences, with high vibrational quantum numbers. The constants B' and B'' were evaluated. The vibrational term-differences obtained from the calculated band-origins satisfy the combination principle. The assignment of the tail bands to the violet CN system makes this the first known system having some bands shaded towards the violet and others towards the red; also the frequencies of the bands of a given sequence may pass through a maximum.

A. A. ELDRIDGE.

Certain multiplets in the spectra of Nb III and Nb IV. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], 31, 520—526).—By applying the irregular doublet law to known data for the triad of multiplets 3DF , $^3DD'$, and 3DP ($ds-dp$) in the two-electron systems Sr I and Y II, the corresponding multiplets for Zr III and Nb IV have been identified; similarly the triad of multiplets $^4F'D'$, $^4F'F$, and $^4F'G'$ (d^2s-d^2p) in the three-electron systems Y I and Zr II has been extended to Nb III, and the stronger lines of the $^4F'G'$ multiplet to Mo IV.

A. A. ELDRIDGE.

Zeeman effect and Stark effect of hydrogen in wave mechanics. Force equation and virial theorem in wave mechanics. A. E. RUARK (Physical Rev., 1928, [ii], 31, 533—538).—Theoretical. The Zeeman levels of hydrogenic atoms are determined by a new method. The formulæ for the first-order Stark effect and for the Paschen-Back effect can be obtained similarly.

A. A. ELDRIDGE.

Absorption and scattering of mercury vapour for the line 2536 Å. J. Z. ZIELINSKI (Physical Rev., 1928, [ii], 31, 559—568).—The absorption coefficient of the radiation (λ 2536 Å.) excited in mercury vapour by a beam from a mercury arc is unchanged by admission of air up to 4 mm. pressure, although the resonance radiation is strongly quenched; in a vacuum the scattering coefficient is equal to the absorption coefficient.

A. A. ELDRIDGE.

Intensities in the hydrogen spectral series. F. G. SLACK (Physical Rev., 1928, [ii], 31, 527—532).—Theoretical intensities of the components of the most important lines of the first six series of the hydrogen spectrum are computed and tabulated, together with the probability coefficients for the components and lines.

A. A. ELDRIDGE.

Series spectra of potassium and calcium. I. S. BOWEN (Physical Rev., 1928, [ii], 31, 497—502).—Series designations are given for some extreme ultra-violet lines in the spectra of K III, K IV, Ca IV, and Ca V; additional lines in the K II spectrum are identified. The series lines in the spectrum of Ca III are tabulated with series designations. The term values give the ionisation potential of K II as 31.7 volts, and that of Ca III as 51.0 volts.

A. A. ELDRIDGE.

Reflexion of atoms by a crystal. A. ELLETT and H. F. OLSON (Physical Rev., 1928, [ii], 31, 643—647).—For cadmium and mercury atoms striking a rock-salt surface the incident and reflected beams are

equally inclined to the normal. Sodium is not reflected. Hydrogen gives irregular results.

A. A. ELDRIDGE.

Continuous absorption in sodium vapour. B. TRUMPY (*Z. Physik*, 1928, 47, 804—813).—From measurements of the continuous absorption by sodium vapour in the neighbourhood of the convergence frequency of the principal series, it is shown that the coefficient for the continuous absorption diminishes rapidly with increasing frequency, and at 2300 Å. attains a value approximately one half that obtaining at the convergence frequency. The results are discussed from the point of view of Sugiura's theory.

J. W. SMITH.

Behaviour of hydrogen and mercury at the electrode surfaces of spectrum tubes. M. C. JOHNSON (*Proc. Roy. Soc.*, 1928, A, 118, 695—708).—If an aluminium cathode is exposed to mercury vapour and then washed for a long time in streams of hydrogen without further admission of mercury, the resulting domination of mercury lines over the hydrogen spectra, and the increase in rate of cathode disintegration, are accompanied by a decrease in the proportion of the spectrum of hydrogen due to neutralisation of protons, as deduced from the Doppler effect. With aluminium electrodes, the mercury spectrum appears instantaneously; it is almost instantaneous with a nickel cathode if there is gas connexion with a second tube containing aluminium, but with an isolated nickel cathode the mercury spectrum is fainter and requires a greater mercury pressure. In badly-contaminated tubes, the gradual saturation of the absorbing sodium or silver and the gradual weakening of the mercury spectrum at the electrodes are functions of the time during discharge, not of the intervals of time between. Admission of mercury to all tubes continues to decrease the resistance of the tube after admission has ceased for as long as 10 min. When solid, a mercury cathode can be made to disintegrate electrically in a way distinct from its thermal disintegration, but the disintegration layer from the aluminium cathode after mercury contamination is of aluminium, and is due neither to thermal nor to electrical disintegration of mercury. It is suggested that when a gas known to be liable to multiple ionisation is admitted to the tube, the increased energy of its ions effects what has been impossible for the steady proton bombardment, viz., a partial break-up of the protective layer of oxygen on the aluminium cathode, thus allowing the gases in the aluminium structure to diffuse out.

L. L. BIRCUMSHAW.

Emission of light by flames containing sodium and the absorption of light by mercury vapour. H. A. WILSON (*Proc. Roy. Soc.*, 1928, A, 118, 362—366).—The relative light intensities due to 1, 4, and 9 sensibly equal Bunsen flames, arranged in a row and supplied with sodium by the same sprayer, were found to be 1:2:3, within the limits of error. Using solutions with concentrations of sodium proportional to 1, 4, 9, and 16 in the sprayer, the light intensities for any number of flames from 1 to 9 were found to be as 1:2:3:4. These results confirm Gouy's conclusion (*Ann. Chim. Phys.*, 1879, 18, 5)

that $I \propto \sqrt{\rho d}$ (when ρd is not extremely small), where I is the light intensity emitted in a direction perpendicular to the flame surface, d is the flame thickness, and ρ the amount of sodium per unit volume. Gouy's square-root law may be simply explained by taking into account the fact that the sodium atoms absorb the light at the centres of the D lines much more strongly than that at the edges. The experimental results on the emission of light by sodium flames and on the absorption of resonance radiation in mercury vapour (Hughes and Thomas, A., 1927, 1118) are shown to be consistent with the view that the atoms absorb light like simple damped oscillators.

L. L. BIRCUMSHAW.

Theory of scattering of slow electrons. J. HOLTSMARK (*Z. Physik*, 1928, 48, 231—243).—Using a method previously developed (Faxén and Holtsmark, A., 1927, 1119), the scattering of slow electrons in argon and the effective cross-section of the argon atom for small electron velocities are calculated. A general agreement is found with the data of Rusch (A., 1926, 989) and of Brüche (A., 1927, 1119). The minimum scattering cross-section is obtained approximately. The calculations are made on the basis of the field worked out by Pauling (A., 1927, 394) and by Hartree (this vol., 216). The minimum appears to be a general property for all centrally symmetrical atoms, in agreement with the latest experimental results of Brüche. The calculation for neon is not in such good agreement as for argon. The diffusing cross-section is also calculated.

A. J. MEE.

Corona discharge in helium and neon. L. G. H. HUXLEY (*Phil. Mag.*, 1928, [vii], 5, 721—737).—Measurements of the potentials necessary to start a discharge between a cylinder and a coaxial wire in pure helium and in pure neon have been made. It has been found that the starting potential depends on the polarity of the electrodes and that whilst at pressures less than about 8 mm. the starting potential is greater when the wire is positive, the reverse is the case for higher pressures. This result is not in agreement with the theory that the discharge is maintained by the action of electrons in ionising the gas molecules by collision and of the positive ions in liberating electrons from the cathode, since the negative discharge would then be started always by the smaller potential. The velocities of the positive ions in helium and neon have been measured and the molecules are shown to present towards positive ions of certain velocities large reductions in effective diameter, and the mean free paths in neon of the positive ions are shown to be about five times those in helium.

A. E. MITCHELL.

Electrical properties of monatomic gases. J. S. TOWNSEND and S. P. MACCALLUM (*Phil. Mag.*, 1928, [vii], 5, 695—700).—In an investigation of the electrical properties of neon it has been found that small traces of diatomic impurities may be removed in a few seconds by the action of a high-frequency discharge from either internal or external electrodes. The effect of impurities on the electrical properties of the gas has been shown to be more noticeable in a wide tube, where the force required to maintain the

discharge is comparatively small, than in a narrow tube, where a larger force is required. The purification is explained on the previous results of Townsend and Donaldson (*ibid.*, 179) that in similar discharges the positive ions and electrons do not recombine to any appreciable extent in the gas. The disappearance of ions from the gas is then attributable primarily to the diffusion of the electrons to the walls of the tube, leaving the gas positively charged. The repulsion of the positive ions to the wall quickly establishes a stable distribution in which positive ions and electrons reach the wall simultaneously. Losses are balanced by the process of ionisation of molecules by electron collision and a steady state is maintained. The easily ionised molecules of diatomic gases are thus driven by the force of the positive charges into contact with the tube wall, where they remain for a considerable time and do not affect the electrical properties of the free monatomic gas. It is thus concluded that atoms of monatomic gases are ionised by electron collisions and that the development of heavy currents in these gases is chiefly due to this process, a conclusion which is in disagreement with other theories.

A. E. MITCHELL.

Quantum theory of the Ramsauer effect. J. R. OPPENHEIMER (Proc. Nat. Acad. Sci., 1928, 14, 261—262).—The Ramsauer effect can be accounted for by consideration of electronic resonance and spin. Two first-order cross-sections for the elastic collision of an electron and a hydrogenic atom can be calculated, corresponding with initial orbital wave-functions respectively symmetric and antisymmetric in the co-ordinates of the impacting electron and the atomic electron. The symmetric wave-function gives a greater cross-section than that calculated without resonance, whilst the anti-symmetric function gives a cross-section vanishing for some small velocity for each angle of deflexion. The total cross-section shows a sharp minimum at about 1 volt. In the general case, both symmetric and antisymmetric wave functions will occur, but for atoms having only paired electrons (*e.g.*, helium, argon, methane) the cross-section is given by the antisymmetric function alone and may, therefore, pass through a minimum for sufficiently low velocities. For any particular case the whole problem must be solved. Minima in cross-sections have been observed for argon and krypton.

A. J. MEE.

Electric moment of alkali atoms. J. J. WEIGLE (Physical Rev., 1928, [ii], 31, 672—675).—The electric moments of sodium, potassium, and rubidium atoms, respectively, are computed by an "inaccurate" method as 0.18, 0.24, and 0.27×10^{-18} g.cm.³sec.⁻², respectively. The values, being negligible, are in accord with Bohr's theory.

A. A. ELDRIDGE.

Low-voltage arcs in iodine. H. F. FRUTH (Physical Rev., 1928, [ii], 31, 614—628).—The minimum radiating potential of the iodine atom is 6.5 volts, the ionising potential of the atom 8.0, and the ionising potential of the molecule 9.5 volts. At 4.9 volts the spectrum contained the lines 2062, 2535, and 3135 Å., the continuous band 3460 Å., and

several groups of bands. Arc lines appear at slightly higher voltages, and spark lines at 8 volts. The continuous bands at 4080, 4300, and 4800 Å. are observed for molecular, but not atomic, iodine. A band system at 2224—2050 Å., and two groups at 2880, 2833, 2776, 2716 Å. and 2480, 2379, 2290, 2243 Å., were observed.

A. A. ELDRIDGE.

Positive ion kinetics. G. P. HARNWELL (Physical Rev., 1928, [ii], 31, 634—642).—Measurements of the mean free path and energy loss per collision of positive ions of potassium and caesium in helium, neon, argon, hydrogen, and nitrogen accord with a free path approximately equal to the kinetic theory value and with an energy loss considerably less than would be expected.

A. A. ELDRIDGE.

Motion of conducting electrons. A. E. MALINOVSKI (Z Physik, 1928, 47, 859—885).—A detailed description of the experiments previously recorded (A., 1927, 504). The negative results obtained are theoretically discussed and the conclusion is reached that the magnitude of the electromagnetic motion of the conducting electrons is not influenced by the self-induction of the conductor.

J. W. SMITH.

Electrical conductivity in flames. P. LENARD (Ann. Physik, 1928, 85, [iv], 730—744).—A general review.

W. E. DOWNEY.

Ion rays. E. WEITKAMP (Physikal. Z., 1928, 29, 217—223).—For salts from which the same ion is emitted, a parallelism is shown to exist between the m. p. and the temperature at which emission begins. At lower temperatures the emission falls off with time, but at and above the m. p. the emission is constant. Addition of graphite to the salt-containing anode results in a reduction of the emission to as little as 1/10 to 1/20 of the original current. Small additions of iodine slightly increase, and larger quantities of iodine markedly decrease the emission. In the case of cadmium iodide, no difference appears when dry air is admitted after the substance has been maintained and allowed to cool in a vacuum, whereas moisture greatly increases the emission.

R. A. MORTON.

Origin of magnetism based on the structure of atoms. K. HONDA (Proc. Imp. Acad. Tokyo, 1928, 4, 12—15).—A qualitative discussion of the author's theory that ferro- and para-magnetism is due to nuclear electrons, whilst diamagnetism is attributed to the outer, or optical, electrons of the atom. Diamagnetic atoms have definite magnetic moments comparable with those of the ferro- or para-magnetic atoms, but owing to their large angular moments, they cannot be magnetised. In the latter case, it is assumed (after Rutherford) that the angular moments of protons and electrons in the nucleus, revolving in opposite directions, almost cancel one another, whilst the theory of the gyroscope is applied to show that in the former case a diatomic model cannot be magnetised but may be diamagnetised.

J. GRANT.

Reflexion of positive rays by a platinum surface. G. E. READ (Physical Rev., 1928, [ii], 31, 629—633).—A study of the relative amount of reflexion of lithium and potassium ions at a platinum

surface under various conditions, and of the angle distribution of the reflected rays.

A. A. ELDRIDGE.

Revision of at. wt. of uranium. Analysis of uranous chloride. O. HÖNIGSCHMID and W. E. SCHILZ (*Z. anorg. Chem.*, 1928, 170, 145—160).—By preparing and analysing uranous chloride by the methods previously used for the bromide (A., 1914, ii, 662; 1916, ii, 484) the value of the ratio $UCl_4 : 4Ag$ has been found to be 0.880524, giving 238.14 for the at. wt. of uranium. For the fused chloride, d_{4}^{25} is 4.725.

R. CUTBILL.

Precision measurements in radioactivity. L. BASTINGS (*J. Sci. Instru.*, 1928, 5, 113—122).—The factors introducing error into gold-leaf electrometer measurements are discussed. An experimental technique and a gold-leaf electrometer are described, by means of which results can be obtained consistent to 1 in 1000.

C. W. GIBBY.

β -Rays of proto-actinium. O. HAHN and A. VON GROSSE (*Z. Physik*, 1928, 48, 1—10).—The absorption curves for the secondary β -radiation of proto-actinium have been measured and μ , the absorption coefficient in aluminium, is found to be 126 cm^{-1} . Comparison of the curves with those for radio-actinium suggests that the β -radiation of proto-actinium is not due to impurity. The γ -radiation which accompanies secondary β -rays was detected. This γ -radiation of proto-actinium is found to be more penetrating than the β -rays from the active precipitate of actinium.

W. E. DOWNEY.

Velocities of α -particles from radium-C, thorium-C and -C'. G. H. BRIGGS (*Proc. Roy. Soc.*, 1928, A, 118, 549—557).—The value of $H\rho = MV/E$ for an α -particle from radium-C has been redetermined, the apparatus for producing the magnetic deflexion being modified (cf. A., 1927, 392, 393). From the value found, 3.993×10^5 e.m.u., and the theoretical value of E/M , 4814.8, calculated from recent determinations of the at. wt. of helium and the value of the Faraday, taking into account the relativity correction for the increase in mass of the α -particle, the initial velocity of α -particles from radium-C is found to be 1.923×10^9 cm./sec. The values found by Rutherford and Robinson were $H\rho = 3.983 \times 10^5$ and $V = 1.922 \times 10^9$ (cf. A., 1914, ii, 789). The initial velocities of α -particles from thorium-C and -C' are found to be 1.705×10^9 and 2.053×10^9 cm./sec. respectively. These results are compared with those deduced from the Geiger relation $V^3 = kR$, and found to be in good agreement. A table is given showing the velocities of α -particles from other radioactive substances, the results being deduced from the author's velocity curve for α -particles from radium-C (*loc. cit.*) and from Geiger's determination of the ranges (*Z. Physik*, 1921, 8, 45).

L. L. BIRCUMSHAW.

Energy stages of atoms and molecules and their relationship to chemical union. J. FRANCK (*Ber.*, 1928, 61, [B], 445—459).—A lecture.

H. WREN.

Penetrating radiation. J. CLAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1927, 30, 1115—1127).—Measurements of the penetrating or ultra- γ -radiation

have been made at Bandoeng, Java, from February to July. There appears to be a daily variation in intensity with a minimum at about 8 a.m., which is always maintained, although the average value for the day may vary with the season. Absorption experiments indicate that there are at least two different kinds of rays, with possible mass absorption coefficients of $17 \times 10^{-3} cm^{-1}$ and $4 \times 10^{-3} cm^{-1}$, which are greater than those found by Millikan and Cameron (*Physical Rev.*, 1926, [ii], 28, 851). The wavelengths calculated from these are 3×10^{-11} and $0.8 \times 10^{-11} cm.$, respectively. The intensity of the radiation appears to decrease with increasing altitude at first and then to increase. A penetrating radiation was also observed in a rock-salt mine in Stassfurt.

M. S. BURR.

Non-appearance of the recombination luminescence in the reaction between alkali and halogen atoms. V. KONDRATJEV (*Nature*, 1928, 121, 571—572).—The exciter of chemiluminescence in the reaction between alkali atoms and halogens is considered to be a molecule, $NaCl^*$, having an excess of energy and existing as an energy-rich molecule for a sufficiently long time to meet a sodium atom. The curves for the potential energy of the systems $(M)(X)$ and $(M^+)(X^-)$ as a function of the distance r between two nuclei intersect at a point r_c at which the valency electron of the metal can be "adiabatically" transferred to the halogen atom. The molecule M^+X^- (MX^*) formed in this way from the neutral atoms can exist for a comparatively long time in a high vibrational state. The energy of vibration of such a molecule can be increased by the absorption of the temperature radiation to a quantity $Q + J - E$, where Q is the heat of reaction $M + X = MX$, J the ionising potential of the cation, and E the electron affinity of the anion; in the chemiluminescence spectrum, lines the excitation energy of which exceeds Q do in fact appear. In the region $r < r_c$, spontaneous transition followed by emission of light may be expected, but visible radiation is not observed. Radiation may be expected in recombination of one normal and one excited atom, the curves $(M')(X)$ or $(M)(X')$ and $(M^+)(X^-)$ of which do not intersect. The curves $(K)(I)$ and $(K^+)(I^-)$ do not intersect, whereas the curves $(Na)(I')$ and $(Na^+)(I^-)$ intersect; in the chemiluminescence spectrum of the former, but not the latter, reaction, a large continuous band is observed.

A. A. ELDRIDGE.

Disappearance of gases into glass under the action of the electric discharge. J. TAYLOR (*Nature*, 1928, 121, 708—709).—In experiments in which positive ions obtained in various gases at low pressures by means of an electrodeless discharge were pulled out by an electric field to the walls of a glass bulb immersed in molten sodium nitrate, (a) for hydrogen, oxygen, and nitrogen the quantity of gas disappearing is directly proportional to the quantity of electricity transferred through the glass walls, (b) for hydrogen, every electron charge passed involves the disappearance of one hydrogen molecule, (c) for oxygen and nitrogen, every two electron charges passed involve the disappearance of one atom, (d) for helium, no disappearance of gas occurred. The

effect is not an accelerated diffusion, but appears to arise from an electrolytic decomposition of the glass probably resulting, with hydrogen, in the formation of water which penetrates deeply into the glass structure.

A. A. ELDRIDGE.

Energy of the helium atom and of the positive ion of the hydrogen molecule. B. N. FINKELSTEIN and G. E. HOROWITZ (*Z. Physik*, 1928, 48, 118—122).—Mathematical.

W. E. DOWNEY.

Statistical theory of the transition between two excited states of an atom. K. BOLLERT (*Z. Physik*, 1928, 48, 98—110).—Theoretical.

W. E. DOWNEY.

Wave mechanics of rotating electrons. J. FRENKEL (*Z. Physik*, 1928, 47, 786—803).—Mathematical. An extension of a former theory (A., 1926, 773).

J. W. SMITH.

Wave equations of the electron. C. G. DARWIN (*Proc. Roy. Soc.*, 1928, A, 118, 654—680).—Mathematical. Dirac's recent work on the quantum theory of the electron (this vol., 344, 456) is discussed, and his system is treated by the ordinary methods of wave calculus instead of by the non-commutative algebraical methods. The relationship of his equations to previous theories is considered, and it is shown that Schrödinger's equation and the pair of equations derived empirically by the author (cf. A., 1927, 916) are successive approximations to Dirac's. The equations are solved for the motion of an electron in a central field, and are shown to be expressible in terms of spherical harmonics and to lead to a doublet structure for the spectrum. The discussion of the radial functions is shown to lead exactly to the original Sommerfeld expression for the energy levels in the case of hydrogen. A few points connected with the free electron, the emission of radiation from an atom, and its magnetic moment are reviewed, the rules of combinations are considered, and a discussion of the Zeeman effect is outlined.

L. L. BIRCUMSHAW.

Statistical method for estimating some properties of atoms and its application to the theory of the periodic system of the elements. E. FERMI (*Z. Physik*, 1928, 48, 73—79).—Theoretical. The electrons in heavy atoms may be considered as a kind of atmosphere, and their distribution round the nucleus may be calculated by a statistical method.

W. E. DOWNEY.

Anomalous effective cross-section of similar atoms when suffering collisions of the second kind. W. SCHÜTZ (*Z. Physik*, 1928, 48, 67—72).—Polemical against Orthmann and Pringsheim (this vol., 338) and von Keussler (A., 1927, 491).

W. E. DOWNEY.

Change of wave-length in light scattering. C. V. RAMAN (*Nature*, 1928, 121, 619).

Absorption coefficients. H. G. DE LASZLO (*J. Physical Chem.*, 1928, 32, 503—506).—A summary of the methods used to measure absorption coefficients of solutions and pure liquids.

L. S. THEOBALD.

Absorption spectra of formaldehyde and carbon monoxide: close relationship between these two molecules. V. HENRI and S. A. SCHOV (*Compt. rend.*, 1928, 186, 1050—1052).—The ultra-

violet absorption spectrum of formaldehyde corresponds with a bivalent molecule, and is analogous in many respects to that of carbon monoxide, having a system of triplets with the same intervals. The inter-combination absorption bands $^1S-^3P$ occurring in the latter correspond with the resonance rays of the bivalent atoms.

J. GRANT.

Arc spectrum of Kasolo uraninite. J. VERHAEGHE (*Bull. Acad. roy. Belg.*, 1928, [v], 14, 18—30).—Crude uraninite may be utilised to give a continuous arc spectrum suitable for the investigation of absorption spectra in the ultra-violet. Uraninite itself is insoluble in hydrochloric acid, whilst the crust of secondary minerals dissolves easily. Arc spectra obtained with the solution exhibit the complete spectrum of lead, whilst only the more persistent lines (indicating concentrations between the limits 0.001—2.0%) are recorded for iron, cobalt, nickel, molybdenum, chromium, manganese, vanadium, titanium, lanthanum, magnesium. The following elements can be present only in traces, since only "raies ultimes" were detectable: potassium, strontium, caesium, tungsten, and thorium. The proportion of iridium present remains doubtful.

R. A. MORTON.

Infra-red absorption spectra of acetylene, ethylene, and ethane. A. LEVIN and C. F. MEYER (*J. Opt. Soc. Amer.*, 1928, 16, 137—164).—The spectra of acetylene, ethylene, and ethane were investigated between 2 and 15 μ . Each gas shows a characteristic type of structure for its vibrational-rotational bands. The three main absorption regions of acetylene have been resolved into individual lines which are alternately intense and faint. These lines have the same average spacing in the three bands. The two minor absorption regions of acetylene were also investigated, and the molecular moment of inertia was computed from the spacing of the fine structure of the principal bands. The value is in agreement with that computed from the classical theory on the assumption of a linear molecular model. Seven regions of absorption were investigated for ethylene. Two were resolved into individual lines with a strong *Q* branch present in one case and absent in the other. Four of the remaining regions reveal "envelopes" of an identical type, characterised by a sharp *Q* branch together with *P* and *R* branches. The bands in the region of 2.3 μ lack *Q* branches. The main absorption regions of ethane reveal bands, each consisting of a single succession of absorption maxima.

C. J. SMITHELLS.

Spectroscopic criterion for the benzenoid structure in some types of triphenylmethane derivatives. R. C. GIBBS and C. V. SHAPIRO (*Proc. Nat. Acad. Sci.*, 1928, 14, 251—252).—It is shown that in every case where the benzenoid structure was to be expected (with one exception), the absorption spectra of the compounds in neutral alcoholic solution include a pair of bands having an average separation of 100 mm^{-1} , and lying in the region between frequency numbers (mm^{-1}) 3500 and 3700. These bands are usually weak, and are sometimes superimposed on the general absorption. The average molecular absorption coefficient for these bands is of the same order of magnitude for all the triphenylmethane derivatives

studied. This observation was applied to coloured solutions, and confirmed the view that benzenoid or lactonoid derivatives were actually present in the solutions even although they might be in equilibrium with quinonoid modifications. *p*-Hydroxytriphenylcarbinol was studied in this way, together with hydration products of benzaurin and aurin etc. There is one exception—dichlorosulphonefluoran, a colourless compound, known to be lactonoid in structure, which, however, gives the above bands.

A. J. MEE.

New diffuse radiations. Y. ROCARD (Compt. rend., 1928, 186, 1107—1109).—An attempt is made to explain the new diffuse radiations described by Raman (this vol., 461) on the basis of the author's theory (this vol., 354), as the optical beats due to the various oscillation frequencies of the electric moment of the molecules.

J. GRANT.

Absorption spectra of anthracene derivatives. I. E. DE B. BARNETT, J. W. COOK, and T. E. ELLISON (J.C.S., 1928, 885—890).—Substitution in the *meso*-positions of anthracene has very little effect on the spectrum (in alcohol), which is merely shifted as a whole, but is independent of the mass of the substituent. Destruction of the bridge linking by reduction to 9:10-dihydroanthracene, however, causes the spectrum to become similar to that of an alkyl derivative of benzene. Derivatives of anthrone in which tautomeric change is impossible owing to replacement of the methylene hydrogen atoms of anthrone by non-mobile groups give a characteristic absorption curve. As would be expected from considerations of transannular tautomerism (this vol., 52), 1:5-dichloroanthrone has bands of both the anthracene type and the anthrone type. It is established that the reactive bromo-compound of 1:5-dichloro-9-benzylanthracene has a structure corresponding with those of the colourless series of compounds derived from it, but it is not possible to decide between the two alternative structures for these compounds (cf. *loc. cit.*).

R. CUTHILL.

Optical analogue of the Compton effect. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, 121, 711).—The presence in the light scattered by fluids of wave-lengths differing from those of the incident light is demonstrated. It is suggested that an incident quantum of radiation may be scattered by the molecules of a fluid either as a whole or in part.

A. A. ELDRIDGE.

Shape and intensities of infra-red absorption lines. D. M. DENNISON (Physical Rev., 1928, [ii], 31, 503—519).—An expression for the shape of an infra-red absorption line is developed. The absorption coefficient may be expressed by means of two damping curves involving the number of molecules per unit volume, the temperature, and the effective diameter. Formulae are derived which are capable of interpreting the absorption lines of the infra-red hydrogen chloride spectrum; the value 10.8×10^{-8} cm. is obtained for the effective diameter. The meaning of this value and the validity of the assumptions are discussed. The effective moving charge of the hydrogen chloride molecule is $\epsilon = (0.199) \times 4.77 \times 10^{-10}$ e.s.u.

A. A. ELDRIDGE.

Changes produced in the absorption bands of certain organic fluorescent dye solutions by alterations of concentration and temperature. W. E. SPEAS (Physical Rev., 1928, [ii], 31, 569—578).—Increase in concentration of solutions of rhodamin *B* or eosin produces the same general effect on the absorption bands as a fall of temperature, and *vice versa*. Increase in concentration of alcoholic rhodamin *B* causes an increase in the absorption per molecule and a shift of the bands towards the red. Experiments were also performed with fluorescein, uranin, and resorcinol-benzoin. A. A. ELDRIDGE.

Chemiluminescence between alkali metal vapours and tin halides. M. PÓLÁNYI and G. SCHAY (Z. Physik, 1928, 47, 814—818).—Highly diluted flames of alkali metals burning in stannic chloride, bromide, and iodide emit intense luminescence and continuous bands. The bands extend from 400 to 550 μ with potassium and stannic chloride, from 405 to 540 μ with sodium and stannic chloride, from 440 to 600 μ with sodium and stannic bromide, and from 500 to 620 μ with sodium and stannic iodide. The intensity is greatest in the middle of the band and decreases symmetrically on each side. From the data the heats of formation of the tetra-chloride and trichloride of tin are deduced. The chemiluminescence is explained by supposing a trihalide to be first formed and that this decomposes into the di- and tetra-halides with evolution of light energy.

J. W. SMITH.

Band spectrum of water vapour. II. D. JACK (Proc. Roy. Soc., 1928, A, 118, 647—654; cf. A., 1927, 808).—The water-vapour band λ 3428 has been measured and analysed. Comparison of the term differences in this band with those in the bands previously analysed shows that the initial terms are the same for the bands λ 3428 and λ 3064, and the final terms are the same for the bands λ 3428, λ 3122, and λ 2875. This is in agreement with the scheme already proposed (*loc. cit.*). The band λ 3428 corresponds with the transition $0 \rightarrow 1$ of the vibrational quantum number. Accurate values are calculated for the moments of inertia of all the bands, to replace the relative values previously given. The values for the state of no vibration are $I_0' = 1.633$ and $I_0'' = 1.498 \times 10^{-40}$ g.-cm.², whilst the corresponding nuclear separations are $r_0' = 1.022 \times 10^{-8}$ cm. and $r_0'' = 0.979 \times 10^{-8}$ cm. in the case of the hydroxyl ion.

L. L. BIRCUMSHAW.

Variation of the absorption coefficients of fluorite and quartz with temperature in the short-wave infra-red. O. REINKOBER and H. KIPCKE (Z. Physik, 1928, 48, 205—215).—The absorption coefficients of fluorite in the region between 8 μ and 12.5 μ , and of quartz between 3 μ and 6.5 μ , were measured at a series of wave-lengths at different temperatures from 20° to the temperature of liquid air. The curves between absorption coefficient and temperature show that the former decreases in both cases as the temperature is lowered. Extrapolation indicates that at the absolute zero there will still be some absorption. The graph connecting wave-length and the ratio of the absorption coefficients at 20° and at -180° (this being used instead of the exact

temperature coefficient) is drawn, and it is found that for fluorite the relationship is linear. The results agree very well with those of Rubens and Hertz. For quartz the ratio increases rapidly with the wavelength as this approaches the chief absorption region, and there is a minimum in the curve between 3μ and 7μ .

A. J. MEE.

Widening of absorption bands with pressure. M. C. TEVES (*Z. Physik*, 1928, 48, 244—258).—The effect of mixing an inert foreign gas with a vapour on the absorption spectrum of the latter was investigated. The vapours used were benzene and *o*- and *p*-dichlorobenzene (which all have spectra with series of sharp edges showing fine structure due to rotation) and the foreign gas was nitrogen. For pressures of nitrogen up to 10 atm. the broadening of the rotation lines was in accord with the Lorentz collision damping theory. At higher pressures, however, there was a displacement as well as broadening, an increase of absorption energy, and finally appearance of new edges. A curve is given showing the change in $1/\lambda$ for given pressures, and photographs showing the spectrum of benzene, and that with the addition of nitrogen at pressures from 20 to 100 atm. For a given gas added, there is a proportionality between the displacement of the lines and the molecular concentration. Possible causes of the broadening of the lines are discussed, including the Doppler effect, the effect of molecules of the same kind on one another, collision damping (Lorentz theory), and, in detail, the Stark effect due to molecular fields. There appears to be a strong analogy with the Stark effect for atoms, but the effect is of a much greater order of magnitude. The appearance of new edges is analogous to the appearance of normally forbidden lines in the Stark effect. A direct connexion of the displacement with the polarisation is not found.

A. J. MEE.

Measurement of spectral photographs. W. HIRSCHL (*Z. Physik*, 1928, 48, 293—294).—The spectral photograph is measured under the microscope by means of a photographed scale. A. J. MEE.

Problem of the normal hydrogen molecule in the new quantum mechanics. S. C. WANG (*Physical Rev.*, 1928, [ii], 579—586).—Theoretical. The following data are obtained for the configuration corresponding with the normal hydrogen molecule: heat of dissociation 3.76 volts, moment of inertia 4.59×10^{-41} g. cm.², nuclear vibration frequency 4900 cm.⁻¹

A. A. ELDRIDGE.

Connexion between positive rays and the abrupt change of potential at the cathode for the thermal emission from an oxide cathode. Method of obtaining the energy of emission. G. SCHMERWITZ (*Z. Physik*, 1928, 48, 259—275).—Experimental details are given for the determination of the positive-ray current, the anode current, and the abrupt change of potential at the cathode for a tube with a cathode coated with calcium oxide. The electron stream showed no relationship with the change of potential at the cathode; the positive-ray current showed a linear relationship with it for high values, but at about 2.4 volts there was an abrupt change in the curve. Below this voltage there was

practically no positive-ray current. In high vacua the same result was obtained, the value being independent of the temperature, and thus of the number of electrons emitted. It is shown that this critical voltage is the equivalent of the energy of emission of the electrons from the calcium oxide. Similar results were obtained with barium oxide and strontium oxide, and these agree with the values obtained by Spanner.

A. J. MEE.

High-frequency glow discharge in hydrogen. E. HIEDEMANN (*Ann. Physik*, 1928, [iv], 85, 649—686).—Glow discharges excited by constant waves or modulated constant waves show a much sharper separation of the various phases of a discharge than those excited by means of damped waves (*i.e.*, a spark coil as source). A characteristic of these high-frequency discharges is a splitting of the positive column, with the formation of a dark space, shortly before the disappearance of the column. Another characteristic is that a visible glow can be observed at gas pressures of 0.001 mm. Glass fluorescence, on the other hand, is observable at 55 mm. gas pressure. The discharge in hydrogen has been quantitatively studied. Under certain conditions a stratified discharge is obtained. The potentials between the layers under various conditions show relationships to the ionisation potentials of the hydrogen molecule and atom.

W. E. DOWNEY.

Dielectric constants and magnetic susceptibilities in the new quantum mechanics. III. Application to dia- and para-magnetism. J. H. VAN VLECK (*Physical Rev.*, 1928, [ii], 31, 587—613).—Theoretical. The general mathematical theory is modified. It is admitted that Pauli's formula for diamagnetic susceptibility can be applied to molecules as well as to atoms. The paramagnetism of atoms and molecules is discussed. The experimental susceptibilities of oxygen and chlorine dioxide accord with the assumption that the normal states are respectively ³S and ²S terms. Calculation of the paramagnetic susceptibility of nitric oxide gives a value in agreement ($\pm 1.5\%$) with the experimental value (cf. A., 1927, 609, 812).

A. A. ELDRIDGE.

Migration of ions from aqueous solutions into glass. F. QUITNER (*Ann. Physik*, 1928, [iv], 85, 745—769).—The migration of cations from metal salt solutions and of hydrogen ions from acid solutions into four Schott glasses at 52° and $2-6 \times 10^5$ volts/cm. field strength has been investigated. The percentage of the total current carried by alkali metal ions is characteristic for the various glasses and rises with increasing concentration of the solution used as anode. Silver ions wander the most freely, whilst calcium, barium, zinc, and copper, when at all, wander only feebly. With an acid solution or a barium hydroxide solution as anode, the current for the greater part is due to hydrogen ions.

W. E. DOWNEY.

Molecular and atomic volumes. XVII. Volumes and magnetic properties of solid cyanides. W. BILTZ [with W. ESCHWEILER and A. BODENSIEK] (*Z. anorg. Chem.*, 1928, 170, 161—183; cf. A., 1927, 920).—The volume of the cyanide radical in both simple and complex cyanides has been studied

with the aid of density measurements on the solid cyanides. In the cyanides of the univalent metals, the volume is 20—24, which agrees with the value for the zero volume derived from data for other compounds containing the cyanide radical, and is taken as the normal value; in the cyanides of bivalent metals, with the exception of nickel, the volume is greater. The volume in the double cyanides of potassium decreases with increase in the size of the complex, ultimately falling below the normal figure. Replacement of the metal atom in the complex by a metal of higher at. wt. in the same group of the periodic system causes a rise in the volume of the cyanide group, and also, in general, in the solubility in 87—88% alcohol. Substitution of nickel or zinc for the potassium usually gives rise to a considerable expansion, the formation of these cyanides from the component simple cyanides being in some instances attended by an increase in volume. It appears probable here, however, that polymerisation plays some part. The volume of the cyanide radical in other hydrated complex cyanides, calculated from existing data, is nearly normal. Comparison of the molecular volumes of a few fulminates with those of the corresponding cyanides shows that the volume of the oxygen is here less than the zero volume. In the thiocyanates, on the other hand, the sulphur appears to have undergone little, if any, contraction. Measurements of the magnetic susceptibilities of the complex potassium cyanides show that, in accordance with the views of Welo and others, a complex which contains a metal atom in itself paramagnetic is not paramagnetic if it possesses the inert gas configuration. The behaviour of these cyanides as a whole is in excellent agreement with the rule suggested by Sidgwick, according to which there is a tendency for the formation of those complexes with effective atomic numbers equal to the atomic numbers of the following inert gases. In a few instances, however, ferromagnetic metals in complexes having effective atomic numbers not equal to the atomic numbers of inert gases are found to be diamagnetic. The complex cyanides, $\text{ZnNi}(\text{CN})_4$ (yellow), $\text{NiAu}_2(\text{CN})_4$ (white), and $\text{Ni}_2\text{W}(\text{CN})_8$ (brown), have been obtained from the corresponding potassium salts by precipitation.

R. CUTHILL.

Theory of the birefringence induced by flow in fluids. C. V. RAMAN and K. S. KRISHNAN (Phil. Mag., 1928, [vii], 5, 769—783).—It is shown, from the results of Stokes, that the tensions and pressures in a fluid in a state of viscous flow are such as to cause the orientation of elongated molecules so that their greatest length lies in the direction of the axis of tension and their shortest length along the axis of pressure. It is then shown that the orienting tendency is opposed by the thermal agitation of the molecules resulting in a state of statistical equilibrium determined from Boltzmann's principle. The optical anisotropy of the molecules combined with the orienting tendency is claimed to give rise to the birefringence of the medium, the magnitude of which is proportional to the product of the viscosity and the velocity gradient. This proportionality constant has been designated the Maxwell constant for the liquid and has been expressed in terms of the optical

and geometrical anisotropy of the molecule, the refractive index, density, and mol. wt. of the liquid, and Boltzmann's constant. The theory has been used to explain satisfactorily the general features of the phenomena observed from the published results for 172 liquids and quantitative values of the Maxwell constant have been determined. A. E. MITCHELL.

Thermal variation of magnetic rotatory power when the magnetisation coefficient is positive and independent of temperature. H. ÖLLVIER (Compt. rend., 1928, 186, 1001—1003).—Paramagnetic substances may be classified according as they obey Curie's, Weiss', or other similar laws, or have paramagnetism independent of the temperature. Becquerel showed that according to Langevin's theory of the orientation of paramagnetic atoms in a field, paramagnetic rotation of the plane of polarisation occurs, which is proportional to the coefficient of mass magnetisation. Assuming the simple additive law expressing this in terms of Verdet's constant, the variation in magnetic potential, and the observed rotation, it is shown for sodium dichromate—a compound shown by Weiss and Collet (A., 1926, 230, 234) to have a constant paramagnetism—that Verdet's constant (referred to unit mass) is independent of temperature between 7° and 61°. A solution of iodine-free zinc iodide ($d^{20} 2.482$) was found preferable to carbon disulphide as a comparison substance. It has a Verdet constant 1.36 times as great at 16°, using yellow or mercury green light. It is transparent up to $\lambda 0.3 \mu$.

J. GRANT.

Production of optical activity by circularly polarised light. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, 132, 313—319).—By the action of circularly polarised light on a film of sensitive silver chloride, there is formed colloidal silver which manifests both circular dichroism and circular double refraction. The curves connecting these magnitudes with the frequency of the light are similar to those obtained for the linear anisotropy of the sensitive chloride (cf. this vol., 583).

R. CUTHILL.

Refractivity and dispersivity of normal saturated monobasic acids. H. I. WATERMAN and S. H. BERTRAM (Rec. trav. chim., 1928, 47, 576—577).—The work of Nekrassov (A., 1927, 922) is cited by the authors in support of their contention that oscillations occur in the physical constants of homologous series in the liquid state. They maintain that the refraction of the normal monobasic acids shows alternation in the liquid state.

W. A. RICHARDSON.

Anomalous dispersion of ionised gases. IV. Anomalous dispersion of hydrogen; true intensity ratio of the hydrogen lines H_α and H_β . A. CARST and R. LADENBURG (Z. Physik, 1928, 48, 192—204).—Hydrogen in a discharge tube was highly ionised by passing through it a current of 0.2—1 amp./cm.², and the anomalous dispersion of the hydrogen lines H_α and H_β was photographed and measured. The mean of the measurements gave for the ratio of the number of dispersion electrons corresponding with the two lines the value 4.66. According to the quantum theory dispersion formula, this ratio should be equal to a first approximation to the

"strength," f_a/f_β , of the corresponding quantum switch. The value of f_a/f_β calculated from quantum mechanics is 5.37. The difference between the experimental value for the ratio and that obtained theoretically is beyond the range of experimental error, and can be explained by the influence of negative dispersion. The probability of this is high because of the strong excitation. When corrected the experimental value of f_a/f_β comes to be less than 5.91, but greater than 4.66, between which values lies that obtained theoretically. A. J. MEE.

Rectilinear diameter of ethylene. E. MATHIAS, C. A. CROMMELIN, and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 1054—1056).—The densities of liquid ethylene and its saturated vapour have been determined between -145.07° and 7.98° . The rectilinear diameter $y=0.22179-0.00061277t$, where t is the temperature on the centigrade scale. The critical temperature deduced from this formula is 9.5° and the critical density is 0.21597. The critical coefficient $RT_c/p_c v_c=3.524$. The deviations of the observed from the calculated values of the rectilinear diameter may exceed 1%. In the neighbourhood of the critical point the curve of diameters is slightly concave, and at lower temperatures convex to the temperature axis. M. S. BURR.

Apparent large diameters of molecules for deactivation by collision. B. LEWIS (Science, 1927, 66, 331—332).—Tolman, Yost, and Dickinson's calculation for nitrogen pentoxide (A., 1927, 604) is erroneous. Whilst collisions between inactive molecules are not considered to occur any more frequently than is usual in the kinetic theory, collisions between active and inactive molecules which cause a transfer of energy and may result in deactivation occur 50 to 66 times as often as required by the kinetic theory; hence the apparent abnormality in diameter for deactivation by collision can be accounted for by increased numbers of collisions. A. A. ELDRIDGE.

Ionised hydrogen molecule. A. H. WILSON (Proc. Roy. Soc., 1928, A, 118, 635—647).—Mathematical. The ionised hydrogen molecule is represented by a system which is a particular case of the three-body problem. Applying Schrödinger's method to the system, a wave equation is obtained which is separable in elliptic co-ordinates, and the resulting differential equations can be solved exactly. The relations between the differential equations defining the system are discussed and values obtained for the energies of the various states. The unexpected result appears that no solution is in general possible; solutions will occur only for certain distances apart of the nuclei. It seems probable that these states are illusory, and that there are no positive distances of the nuclei which give states. L. L. BIRUMSHAW.

Simple method of determining the orientation and structure of crystals with X-rays. W. E. DAWSON (Phil. Mag., 1928, [vii], 5, 756—767).—An X-ray goniometer has been devised the operation of which depends on the observation of Weissenberg (Z. Physik, 1924, 23, 229) that if the rotation of a crystal be accompanied by a proportional movement of the recording film the angle traversed by the

crystal between successive reflexions may be obtained and thus sufficient data are provided, from one photograph, for the absolute determination of the normal to each set of atomic reflecting planes, and hence also the orientation and space-lattice of the crystal. The method has been employed for the examination of aluminium crystals prepared by the method of Carpenter (B., 1926, 792). The results are in fair agreement with those of Yoshida and Tanaka (A., 1927, 95) for similar crystals except that they tend to show that in such crystals the orientation is at random about the direction of stretching.

A. E. MITCHELL.

Phosphorescence of calcium tungstate induced by X-rays. F. E. SWINDELLS (J. Opt. Soc. Amer., 1928, 16, 165—173).—The rate of decay of a very phosphorescent sample of calcium tungstate, determined photographically, was found to fit the Becquerel equation, $I^x=a+bt$, from 30 sec. to 5 min. after exposure to X-rays. The phosphorescence of this sample could be detected after 50 hrs. under conditions when the phosphorescence of normal calcium tungstate disappeared in 1 min. The intensity of the phosphorescence was found to be closely proportional to the product of the intensity of the X-rays and the time of exposure up to a limiting value, beyond which there was a negligible increase.

C. J. SMITHELLS.

X-Ray examination of manganese arsenide, iron telluride, nickel stannide, and platinum stannide. I. OFTEDAL (Z. physikal. Chem., 1928, 132, 208—216).—The values in Å. of a and c , respectively, for the hexagonal elementary cells of the above compounds are: manganese arsenide, 3.716 ± 0.003 , 5.704 ± 0.006 ; platinum stannide, 4.103 ± 0.003 , 5.428 ± 0.005 ; iron telluride, 3.800 ± 0.003 , 5.651 ± 0.005 ; nickel stannide, 4.081 ± 0.002 , 5.174 ± 0.003 . From the intensity data, the first two definitely appear to have the nickel arsenide structure, and this is probably so with the other two as well.

R. CUTHILL.

Reflexion of X-rays by plane surfaces. H. E. STAUSS (Physical Rev., 1928, [ii], 31, 491—496).—Measurements of the reflexion of molybdenum $K\alpha_1$ radiation by plane surfaces of glass and quartz, and by sputtered films of nickel, platinum, and silver suggest that the densities of sputtered films of nickel and platinum are less than those of the massive metals, and that that of nickel is smaller the thinner is the film. The surface density of quartz appears to be less than the average density.

A. A. ELDRIDGE.

X-Ray investigation of the structure of some naphthalene derivatives. J. M. ROBERTSON (Proc. Roy. Soc., 1928, A, 118, 709—727).—The crystal structures of 1:2:3:4-tetrachloro-1:2:3:4-tetrahydronaphthalene and of 1:2:3:4:5:8-hexachloro-1:2:3:4-tetrahydronaphthalene examined by the rotating crystal method are found to be closely similar. The former has a 7.9, b 10.3, c 14.2 Å., β $112^\circ 40'$, d 1.67; the latter a 7.8, b 12.3, c 13.9 Å., β $116^\circ 14'$, d 1.87. The lattices are monoclinic body-centred with four asymmetric molecules in the unit cell, and the most probable space-group is C_2^1 . This involves a polar molecule. By means of Bernal's

method of interpretation, indices are assigned to all the reflexions. Information is also obtained as to the approximate location of the halogen atoms, which virtually lie on a different type of lattice. A qualitative examination and comparison of the intensities of the most important reflexions indicate that the two additional substituted chlorine atoms in the hexachlorotetrahydronaphthalene must lie somewhere beneath the other halogens when the structure is viewed along the c axis. The facts are accounted for if it is assumed that the long axis of the molecule coincides with the c axis of the crystal. The intensity distribution in the higher orders of certain planes requires an almost flat carbon ring, as in the graphite structure.

L. L. BIRCUMSHAW.

X-Ray study of some simple ethane derivatives.

I. and II. (MISS) K. YARDLEY (Proc. Roy. Soc. 1928, A, 118, 449—484, 485—497).—I. A detailed investigation has been made of crystals of hexachloroethane, hexabromoethane, tetrachlorodibromoethane (two forms), pentabromofluoroethane, trichlorobromoethane, and β - γ -tetrabromo- n -butane (two unstable orthorhombic forms, one obtained below 0°). These substances form an isomorphous series, crystallising in the space-group Q_h^{16} . Hexachloroethane $a : b : c = 1.1350 : 1 : 0.6302$; hexabromoethane $a : b : c = 1.1278 : 1 : 0.6270$; tetrachlorodibromoethane (symmetrical form), $a : b : c = 1.1308 : 1 : 0.6270$; (asymmetrical form), $a : b : c = 1.1220 : 1 : 0.6288$; pentabromofluoroethane, $a : b : c = 1.1012 : 1 : 0.6098$; trichlorotribromoethane, $a : b : c = 1.1270 : 1 : 0.6262$; tetrabromobutane (low-temperature form), $a : b : c = 1.073 : 1 : 0.601$; (ordinary temperature form), $a : b : c = 1.1206 : 1 : 0.6296$. There are four molecules in the unit cell, each possessing a plane of symmetry parallel to (010). This plane passes through the two carbon atoms and two of the halogen atoms (or the two methyl groups in the case of tetrabromobutane), with the other four halogen atoms arranged in pairs on either side. In the case of hexachloro- and hexabromo-ethane, and probably the tetrabromobutane, the molecules also possess a pseudo-centre which produces additional halvings not expected from space-group considerations. The symmetry of the carbon valencies is deduced from the molecular symmetry and it is shown that the carbon atom possesses two A and two B valencies, possibly identical with the two (2, 1) and two (2, 2) electrons in the outer group of neutral carbon. Composite F curves obtained for hexachloro- and hexabromo-ethane are compared with Hartree's curves for Cl^- and C^{++++} (cf. A., 1925, ii, 735). The formula of both forms of tetrachlorodibromoethane appears to be $\text{CCl}_2\cdot\text{CClBr}_2$.

II. Tetrabromobutane possesses a stable tetragonal form which bears no apparent resemblance to the two forms described above, and has a 8.80 \AA , c 11.27 \AA , d 2.818. The unit cell probably contains four molecules in face-centred positions. Dibromotetramethylethane (β - γ -dibromodisopropyl) forms needle-like tetragonal crystals having $a : c = 1 : 0.7798$ and d 1.811. There are four molecules in the unit cell occupying approximately face-centred positions, and possessing either a plane or dyad axis of symmetry or both.

The molecules themselves simulate tetragonal symmetry. There are two possible types of structure, which are illustrated. Pentamethylbromoethane forms needle-like crystals very similar to those of the tetramethyl compound. The orthorhombic cell has a 21.35, b 10.77, c 7.84 \AA , d 0.85; it may be divided into two pseudo-tetragonal parts, the arrangement of molecules in each resembling that in the unit cell of dibromotetramethylethane. The space-group is C_{2v}^{21} .

L. L. BIRCUMSHAW.

Theory of absorption and dispersion in X-ray spectra. R. DE L. KRONIG and H. A. KRAMERS (Z. Physik, 1928, 48, 174—179).—An explanation is put forward for the fact that the effective number of oscillators that must be associated with continuous absorption bands in the case of X-rays in order to give the observed dispersion and absorption, is different from the number of electrons in the shell associated with the particular absorption band concerned. In particular, the case of the K -band is considered, and it is shown why the effective number of oscillators is less than 2.

A. J. MEE.

[Crystal structures of] diselenides of iron, cobalt, and nickel. W. F. DE JONG and H. W. V. WILLEMS (Z. anorg. Chem., 1928, 170, 241—245).—The compounds NiSe_2 and CoSe_2 have been prepared by heating the monoselenides in a vacuum with selenium; it has not been possible to obtain the corresponding iron salt. In each case the structure is shown by the X-ray diagram to be of the iron pyrites type (A., 1927, 502), the length of the basal edge, the calculated density, and the distance apart of the atomic centres being 5.854 ± 0.003 \AA , 7.18, and 2.41 \AA , respectively, for the cobalt compound, and 6.022 ± 0.003 \AA , 6.69, and 2.47 \AA for the nickel compound.

R. CUTHILL.

Hexahydrated double sulphates containing thallium. A. E. H. TUTTON (Proc. Roy. Soc., 1928, A, 118, 367—392; cf. A., 1925, ii, 749).—A complete goniometrical measurement and a full optical and volume investigation have been made of perfect crystals of thallium magnesium, thallium ferrous, thallium manganese, and thallium copper sulphates. All these crystallise in the holohedral class of the monoclinic system. For thallium magnesium sulphate, $a : b : c = 0.7442 : 1 : 0.5000$, $\beta = 106^\circ 30'$; for thallium ferrous sulphate, $a : b : c = 0.7427 : 1 : 0.4999$, $\beta = 106^\circ 16'$; for thallium manganese sulphate, $a : b : c = 0.7454 : 1 : 0.4964$, $\beta = 106^\circ 22'$; for thallium copper sulphate, $a : b : c = 0.7499 : 1 : 0.5033$, $\beta = 105^\circ 33'$. The results are in line with those previously obtained for the corresponding zinc, nickel, and cobalt thallium sulphates. Thallium does not entropically replace the alkali metals potassium, rubidium, caesium, or the ammonium group, but the thallium salts are very nearly isostructural with the analogous ammonium and rubidium salts. One outstanding difference is shown, *i.e.*, a very much higher optical refraction and spectral dispersion. Attention is directed to the remarkably small effect on the crystal form and properties of interchanging the M-metals, in comparison with the marked determinative effect exerted by interchange of the five R-bases.

L. L. BIRCUMSHAW.

Hexahydrated double selenates containing thallium. Completion of the thallium salts and of the whole monoclinic series. A. E. H. TUTTON (Proc. Roy. Soc., 1928, A, 118, 393—426; cf. preceding abstract).—A full crystallographic investigation has been made of a series of double selenates, $R_2M(SeO_4)_2 \cdot 6H_2O$, containing thallium as the R-metal, and magnesium, ferrous iron, nickel, cobalt, manganese, copper, or zinc as the M-metal. The iron salt has not previously been described, probably owing to the fact that iron reduces selenic acid directly to selenium. Pure *ferrous selenate* may be prepared by the action of dilute selenic acid on ferrous sulphide, and very pale green crystals of *thallium ferrous selenate* are obtained on evaporating excess of ferrous selenate solution with thallium selenate solution under reduced pressure. For thallium magnesium selenate, $a : b : c = 0.7485 : 1 : 0.4993$, $\beta = 105^\circ 36'$; for thallium nickel selenate, $a : b : c = 0.7456 : 1 : 0.5019$, $\beta = 105^\circ 36'$; for thallium cobalt selenate, $a : b : c = 0.7463 : 1 : 0.5021$, $\beta = 105^\circ 40'$; for thallium ferrous selenate, $a : b : c = 0.7445 : 1 : 0.5011$, $\beta = 105^\circ 27'$; for thallium manganese selenate, $a : b : c = 0.7463 : 1 : 0.4993$, $\beta = 105^\circ 29'$; for thallium copper selenate, $a : b : c = 0.7531 : 1 : 0.5048$, $\beta = 104^\circ 59'$.

The results obtained are in every respect analogous to those for the double sulphates containing thallium. The replacement of sulphur by selenium causes all the constants to be slightly shifted, and the relations of the thallium double selenates to the double selenates containing potassium, rubidium, caesium, and ammonium are almost exactly the same as in the case of the double sulphates. The thallium double selenates are distinguished by exceptionally high refractive indices and molecular refractions, the maximum index of refraction in some cases exceeding that of the very highly refractive monobromonaphthalene.

L. L. BIRUMSHAW.

Longitudinal thermomagnetic potential difference in a bismuth crystal. C. W. HEAPS (Physical Rev., 1928, [ii], 31, 648—652).—The results suggest that a magnetic field produces a structural change in the atomic system of bismuth, the change in the direction normal to the field differing from that parallel to it.

A. A. ELDRIDGE.

Interpretation of the paramagnetism of the iron group. O. LAPORTE (Z. Physik, 1928, 47, 761—769).—The magneton numbers of the iron group, calculated from purely spectrographic data by means of the relative doublet formula in the manner described by Laporte and Sommerfeld (A., 1927, 86), do not agree with the observed values. The same effect is also shown by the rare earths. Possible explanations of these discrepancies are discussed.

J. W. SMITH.

Theory of Heusler's alloy. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1928, 47, 770—785).—It is shown on metallographic grounds that Richarz' theory of the Heusler alloy anomalies is untenable. The author describes experiments which indicate that the anomalies can be traced to a phase change occurring in the neighbourhood of 130° .

J. W. SMITH.

Calculation of the rotatory power of quartz. R. DE MALLEMANN (Compt. rend., 1928, 186, 1046—1048).—The experimental results of Ze (this vol., 352) are used to deduce the value of the molecular anisotropy which figures in the author's expression for the rotatory power (A., 1927, 610). A value of $30^\circ/\text{mm.}$ was obtained for quartz at $\lambda 0.546 \mu$ (observed value $25.5^\circ/\text{mm.}$). The agreement is considered satisfactory in view of the indirect method employed and the low experimental accuracy. It is improved if allowance is made for the slight inclination of the plane of principal molecular axes with respect to the ternary crystal axis, the existence of which is indicated by the work of Ze and of Bragg.

J. GRANT.

Transmission and reflexion of gold and silver films. W. V. HOUSTON and G. MOORE (J. Opt. Soc. Amer., 1928, 16, 174—176).—Measurements of the reflecting power and transmission of sputtered films of gold and silver as a function of the wave-length and thickness were made to determine the most suitable coating for the mirrors of interferometers. Between 5000 and 6000 Å. gold and silver are equally good. Above 6000 Å. gold is superior, since for the same reflecting power the transmission is higher. Below 5000 Å. silver is much superior to gold.

C. J. SMITHELLS.

Quick and slow decay of luminescence of phosphors of various types of atoms. H. MOSER (Ann. Physik, 1928, [iv], 85, 687—710).—With oxide phosphors the quick decay outweighs the slow decay, but with selenide phosphors the reverse is the case. Sulphide phosphors, in general, show both processes equally strongly. The total emission shows a strong increase from oxygen, sulphur, to selenium as generic atoms and calcium, strontium, to barium as alkaline-earth atoms.

W. E. DOWNEY.

Deformation, rupture, and hardening of crystals. M. PÓLÁNYI (Naturwiss., 1928, 17, 285—294).—See this vol., 9.

Magnetic susceptibility of aluminium. C. CHÉVENEAU (Compt. rend., 1928, 186, 1102—1104).—Very small amounts of iron alloyed with aluminium have very little effect on its magnetic properties, and these effects follow no simple rule, as the iron behaves differently according as it is present in the metallic or ionic state. Iron-free aluminium should be paramagnetic and should have a susceptibility near that obtained for Hoopé's "extra-pure" aluminium (Al 99.87%, Fe 0.06%), viz., +0.58.

J. GRANT.

Electrical resistance of titanium and zirconium at low temperatures. P. CLAUSING and G. MOUBIS (Physica, 1927, 7, 245—250; Chem. Zentr., 1927, ii, 2649).—With titanium and zirconium at 70 — 273° Abs., the dependence of electrical resistance on temperature is normal (cf. Koenigsberger and Schilling, A., 1910, ii, 481). The specific resistance at 273° is 0.80×10^{-4} and 0.41×10^{-4} , respectively, and the temperature coefficient 0.00469 and 0.00438.

A. A. ELDRIDGE.

Dielectric constants of dilute solutions of polar liquids in non-polar solvents. J. D. STRANATHAN (Physical Rev., 1928, [ii], 31, 653—671).—Dielectric constants and densities have been determined at 10°

intervals between f. p. and b. p. for dilute solutions of methyl, ethyl, propyl, and amyl alcohols in benzene, and methyl alcohol in carbon tetrachloride. The electric moments are independent of temperature, being respectively 1.64, 1.74, 1.75, and 1.62×10^{-18} for benzene solutions, in agreement with Debye's theory, and in contrast with results for the pure liquid alcohols.

A. A. ELDRIDGE.

Magnetic susceptibility of solutions. J. J. WEIGLE (Physical Rev., 1928, [ii], 31, 676—679).—When a solution of ions of different magnetic susceptibilities is placed in a magnetic field, an almost imperceptible difference exists between the concentrations of the solute in and outside of the field.

A. A. ELDRIDGE.

Wave mechanical theory of metallic conduction. J. FRENKEL (Z. Physik, 1928, 47, 819—834).—Mathematical.

J. W. SMITH.

Dispersion by hydrogen-like atoms in undulatory mechanics. B. PODOLSKY (Proc. Nat. Acad. Sci., 1928, 14, 253—257).—Schrödinger's theory of dispersion is applied to the case of atomic hydrogen, terms of the order of relativistic correction being omitted. The wave-equation is obtained by the operational method of Schrödinger and Eckart, as extended by Epstein. Formulæ are developed giving a result for the dielectric constant in exact agreement with that obtained by Van Vleck, Epstein, and Pauling. Values for the refractive index obtained, however, do not agree very well with the experimental value of Langer, but this may be due to experimental difficulties.

A. J. MEE.

Anomalous dispersion of gases in the excited state. I. Dispersion formula of the quantum theory. R. LADENBURG. II. Anomalous dispersion in excited neon. III. Transition probability and density of excited atoms in neon; statistical equilibrium in the positive column. H. KOPFERMANN and R. LADENBURG (Z. Physik, 1928, 48, 15—25, 25—50, 51—61).—I. Theoretical. The connexion between the dispersion formula of the classical theory and that of the quantum theory is discussed with a view experimentally to prove the latter.

II. Anomalous dispersion of light passed through the positive column of a neon discharge tube has been detected in the region of 19 lines in the orange. The dispersion increases with increase of current strength up to 50 mm. The effect of pressure, above 1.3 mm. of mercury, is to cause the anomalous dispersion to decrease.

III. A theoretical discussion of the results obtained in the experiments described in the previous paper.

W. E. DOWNEY.

Latent heat of vaporisation as a function of temperature. R. M. WINTER (J. Physical Chem., 1928, 32, 576—582).—The variation with temperature of the total latent heat of vaporisation is expressed by the relation $\lambda = \lambda_0 (1 - T/T_c)^{0.4}$ for the 22 liquids examined. The values of λ_0 , a constant for each liquid, were found graphically from the data of Mills (A., 1909, ii, 861), as well as those of T_c which are in good agreement with observed values. Elimination of the term $1 - T/T_c$ from the above

relation and from the relationships found by Sugden for temperature, density, and surface tension (A., 1927, 920) gives $\gamma = \text{constant} \times \lambda^3$, and $\lambda = \text{constant} \times (D - d)^{4/3}$, where D and d are the densities of liquid and vapour, respectively.

L. S. THEOBALD.

F. p. and density of pure hydrogen peroxide. A. C. CUTHBERTSON, G. L. MATHESON, and O. MAAS (J. Amer. Chem. Soc., 1928, 50, 1120—1121).—The m. p. is -0.89° ; the liquid has a great tendency to supercool and must be kept within 0.1° below the m. p. and continuously stirred. For the pure peroxide, d^0 is 1.4649; for solutions containing $A\%$ by weight of peroxide $d = 0.9486 + 0.005163A$, provided A is 95 or more.

S. K. TWEEDY.

Measurement of the true specific heats of nickel by a direct electrical method. (MME.) C. LAPP (Compt. rend., 1928, 186, 1104—1106).—The specific heats of pure Mond nickel wire have been measured between -175° and 460° by determinations of its variations in temperature when placed in a medium at the required temperature, and heated for a known period by a measured amount of electrical energy. The specific heat increases with temperature up to the Curie point (357.6°), falls between 353.5° and 360.2° , and then increases slowly in the paramagnetic region.

J. GRANT.

Anomalous dispersion in thallium vapour. V. K. PROKOVJEV and V. N. SOLOVIEV (Z. Physik, 1928, 48, 276—285).—The anomalous dispersion of thallium vapour was investigated in the neighbourhood of the lines 3776 and 5353, at different temperatures, from 892° to 1107° . It is found that the ratio of the number of dispersion centres for these lines varies with the temperature according to the Boltzmann law. From this it is shown that the probabilities of the spontaneous transitions $2s \rightarrow 2p_1$ and $2s \rightarrow 2p_2$ (Paschen-Götze notation) are equal.

A. J. MEE.

Thermal conductivities of oxygen and nitrogen. H. GREGORY and S. MARSHALL (Proc. Roy. Soc., 1928, A, 118, 594—607).—The thermal conductivities of oxygen and nitrogen at 0° have been measured, with the object of confirming the result obtained by Gregory and Archer for air (A., 1926, 231), a wide discrepancy existing among the values obtained for this gas by various observers. The apparatus used was the vertical compensated hot-wire type previously employed for determining the thermal conductivity of carbon dioxide (A., 1927, 403). From the curves obtained by plotting absolute thermal conductivities against corresponding mean gas temperatures, it is found that $K_0 = 5.89 \times 10^{-5}$ and 5.80×10^{-5} g.-cal. $\text{cm.}^{-1} \text{sec.}^{-1} \text{deg.}^{-1}$ for oxygen and nitrogen respectively. The temperature coefficients of thermal conductivity, deduced from the slopes of the curves, are 0.00289 and 0.00293 for oxygen and nitrogen, respectively. The results are consistent with those of Gregory and Archer for air at 0° .

L. L. BIRCUMSHAW.

Parachor and chemical constitution. IX. Boron compounds. J. J. ETRIDGE and S. SUGDEN (J.C.S., 1928, 989—992; cf. this vol., 416).—Determinations of the density and surface tension of methyl and ethyl borates between 15° and 60° , taken with

Mills and Robinson's data for boron trichloride (A., 1927, 927), give a value of 16.4 for the parachor of boron. Methyl alcohol and methyl borate form a mixture of maximum vapour pressure, with b. p. 55°, and containing 30% of the ester. R. CUTHILL.

Coefficient of expansion of bromoform. A. SHERMAN and J. SHERMAN (J. Amer. Chem. Soc., 1928, 50, 1119—1120).—The specific volume of bromoform, m. p. 7.7°, between 9° and 50° is given by $0.24204 [1 + 0.00090411(t - 7.7) + 0.006766(t - 7.7)^2]$. S. K. TWEEDY.

Physical constants of bromoform. H. BUHMANN (Arch. Pharm., 1928, 266, 123—125).—Pure bromoform has d_4^{20} 2.9000, b. p. 146.3°/760 mm., setting-point, +7.4°; another sample had b. p. 147.2°/760 mm. When the latter was mixed with 1% of alcohol (d_4^{20} 0.7942) the mixture had setting-point +5.4°, b. p. 146.6°. This sample fulfils the requirements of the German pharmacopœia, but the method given there for testing bromoform is unsatisfactory. In determining the proportions volatile between the prescribed limits a Schantz apparatus should be used. W. A. SILVESTER.

Connexion between the coefficient of expansion and the coefficient of compressibility of liquids. V. S. VRKLJAN (Z. Physik, 1928, 48, 111—117; see also A., 1926, 786; 1927, 103).—Theoretical.

W. E. DOWNEY.

Viscosity of mercury. S. ERK (Z. Physik, 1928, 47, 886—894).—From a critical survey of the existing data on the viscosity of mercury, the most probable values over the temperature range -20° to 340° are deduced and are found to be in agreement with an empirical formula $\log \eta = -2.21336(t + 184.54)/(t + 230.32)$. The possibility of the mercury slipping over an unwetted surface in some series of experiments is also discussed. J. W. SMITH.

Physical properties of gas-freed sulphur. C. C. FARR and D. B. MACLEOD (Proc. Roy. Soc., 1928, A, 118, 534—541).—It is extremely difficult to prepare a sample of sulphur the viscosity of which is independent of previous thermal treatment (cf. A., 1920, ii, 343). This may be due to traces of sulphuric acid, hydrogen sulphide, or sulphur dioxide, which retard the attainment of inner equilibrium between the two varieties S_{α} and S_{β} . Methods are given for the preparation of pure gas-free sulphur by distillation in a stream of carbon dioxide, followed by distillation in a high vacuum, and the relative viscosity of the sulphur so prepared has been measured over the temperature range 163—169°, which is the interval over which sulphur shows high viscosity variations. The viscosity was measured under several conditions of thermal treatment. The results showed that the viscosities between 163° and 169° lie on the same curve whatever the previous heat treatment, and it is considered established that sulphur prepared with care and protected from exposure to air gives reproducible values of the viscosity. From sulphur purified in this way, crystals of S_{III} (mother of pearl sulphur) separate readily. The natural f. p. was found to be 103.8—103.9° (cf. Smith and Carson, A., 1911, ii, 977), the ideal m. p. about 107°. Efforts to obtain rhombic sulphur from sulphur similarly prepared were unsuccessful.

It was found possible to supercool liquid sulphur down to 80°, and measurements of the relative viscosity were obtained down to this temperature. The minimum value was at about 155°.

L. L. BIROUMSHAW.

Application of Debye's dipole theory to binary liquid mixtures. J. W. WILLIAMS (Physikal. Z., 1928, 29, 174—181).—Debye's extension of the Clausius-Mosotti relation has been applied to the calculation of electric moments from the dielectric constants and densities of suitably chosen binary liquid mixtures. Earlier data (A., 1926, 1000; 1927, 819, 1132) are tabulated and the substances investigated divided into three classes: (a) molecules exhibiting no electric moment, e.g., benzene, carbon tetrachloride, carbon disulphide, hexane, tin tetraiodide, *p*-xylene, *p*-dinitrobenzene; (b) less symmetrical molecules showing a definite dipolar moment, e.g., ethyl ether, *o*- and *m*-dinitrobenzene, etc.; (c) molecules for which the existence of a dipolar moment appears doubtful, e.g., *s*-trinitrobenzene, naphthalene, iodine. Within the limits of experimental error, the molecular polarisation and therefore the electric moment of a solute molecule is independent of the nature of a dipole-free solvent. The dipolar moment, as measured in this work, is a quantitative criterion of the polarity of a molecule. R. A. MORTON.

Viscosity of supersaturated solutions. I. I. K. TAIMNI (J. Physical Chem., 1928, 32, 604—615).—The viscosities of supersaturated solutions of sodium nitrate, sodium chlorate, copper sulphate, sodium thiosulphate, tartaric acid, and sucrose have been determined by means of a modified form of the apparatus devised by Scarpa (Gazzetta, 1920, 40, 271). The viscosity-temperature curves for the first two substances remain regular, in passing not only through the temperature of saturation, but also through that of spontaneous crystallisation as determined by Miers (J.C.S., 1906, 89, 413). The curves for the remaining substances were also regular as far as they could be traced (30—45° below saturation temperature), and only one of these substances, copper sulphate, showed any signs of spontaneous crystallisation. The curves for two different concentrations of sodium thiosulphate, tartaric acid, and sucrose show an increasing divergence with a fall in temperature, this being especially noticeable in the case of the last two substances mentioned.

L. S. THEOBALD.

Electrical conductivity of silver alloys. M. HANSEN and J. SACHS (Z. Metallk., 1928, 20, 151—152).—The curves showing the variation of the electrical conductivity with the composition of binary alloys of silver containing cadmium, zinc, magnesium, manganese, tin, antimony, or aluminium within the solid solution range are almost perfect hyperbolas which approach more closely to the axes in the order given. The electrical resistance of these alloys increases almost linearly with increase in the atomic percentage of added element, the steepness of the curves decreasing in the order: antimony, tin, aluminium, manganese, zinc, magnesium, cadmium. As is the case with solid solution alloys of copper (Norbury, B., 1925, 245), the change of resistance produced by

the presence of one atom per cent. of an element in solid solution increases with the distance from the silver group of that group in the periodic system to which the element in question belongs. For elements in the same group, the effect on the resistance is more marked the greater the difference in the atomic numbers of the solute and solvent elements. In general, the hardness-composition curves correspond roughly with the resistance-composition curves, but magnesium has an exceptionally large hardening effect on silver.

A. R. POWELL.

Solubility relations of isomeric organic compounds. VII. Mutual solubility of the dinitrobenzenes with the nitroanilines, and of the three chlorobenzoic acids. J. JOHNSTON and E. P. JONES (J. Physical Chem., 1928, 32, 593-603; cf. Collett and Johnston, A., 1926, 237).—The solubility curves of the nine binary systems formed between the nitroanilines and dinitrobenzenes lie close to the ideal. The small divergences observed bear no apparent relationship to other properties of the systems. Mixed crystals are not formed. The three binary systems of the chlorobenzoic acids are also practically ideal. The three like pairs of the chloro- and bromo-nitrobenzenes form a complete series of solid solutions, but *p*-toluic acid and *p*-chlorobenzoic acid show only partial crystal miscibility. Solubility data are given.

L. S. THEOBALD.

Critical solution temperatures and their applications. A. BOUTARIC and G. CORBET (Chaleur et Ind., 1927, 8, 565-568; Chem. Zentr., 1927, ii, 2651).—A discussion, with special reference to the addition of a third component to binary liquid mixtures, particularly hydrocarbons and alcohol, and to the attempted differentiation of fats and oils.

A. A. ELDRIDGE.

Effect of a third substance on the miscibility of binary liquid systems. C. WAGNER (Z. physikal. Chem., 1928, 132, 273-294).—Theoretical. It is shown thermodynamically that if to a binary liquid mixture there is added a third substance such that for any given ratio of the two components its partial pressure at the small concentrations considered is proportional to its concentration, the temperature range of complete miscibility will be extended or restricted according as the solubility of the third substance in the region of the critical composition is greater or less, respectively, than corresponds with additivity in respect of its solubilities in the two liquids. Equations are derived (a) for the composition of the critical phase at any given temperature, (b) for the effect of the added substance on the miscibility at constant temperature, and (c) for the change in critical solution temperature. From molecular considerations, it appears that an important cause of the solubility of a substance in a binary solvent mixture being less than the value calculated additively from the solubilities in the pure solvents is that the field of force in the vicinity of a solute molecule is generally due to more than one solvent molecule.

R. CUTHILL.

Influence of salts on the solubility of water in phenol. R. CERNĂTESCU (Z. physikal. Chem., 1928, 133, 31-38).—A continuation of previous work

(cf. A., 1927, 416). The effect of the addition of a number of alkali halides and thiocyanates on the solubility of water in phenol has been studied, the temperature at which a mixture of known weights of the 18% phenol layer and the salt becomes homogeneous being measured. The lowering of solubility of water in phenol was obtained from the Rothmund solubility curve. The formula $t=ac^b$, given by Carrington, Hickson, and Paterson for the influence of salts on the critical solution temperature of the system phenol-water (A., 1926, 18), has been applied to the experimental results, and it is found that the cations and anions of the salts investigated, in order of decreasing effect on the solubility of water in phenol, may be arranged as follows: Li^+ , Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , and Cl^- , Br^- , I^- , F^- , SCN^- . Unusual results are found with potassium fluoride and with ammonium thiocyanate, which, in the case of the latter salt, may be explained by its greater solubility in the phenol layer compared with the other salts investigated.

L. L. BIRCUMSHAW.

Solubility in mixtures of solvents. I. Solubility of picric acid. E. ANGELESCU and D. DUMITRESCU (Z. physikal. Chem., 1928, 132, 217-234).—The solubility at 12° of picric acid in binary mixtures of solvents has been determined. Taking the solubilities in g./100 g. of solvent as ordinates and the percentage compositions of the solvents as abscissæ, the curves obtained closely resemble those characteristic of the vapour pressures of binary mixtures of liquids. Mixtures of benzene with ethyl ether or ethyl alcohol and of ether with alcohol show throughout positive deviations from the mixture rule, the curve of each system possessing a maximum. This type of curve probably results from combination between the solute and one of the solvents. Mixtures of water with acetone or ethyl alcohol and of acetone with chloroform or carbon tetrachloride exhibit negative deviations throughout, minima being present in the first two systems. The curves for mixtures of alcohol with carbon tetrachloride or chloroform and of benzene with acetone or carbon tetrachloride are intermediate in character between the foregoing two types, each lying partly above the straight line and partly beneath it. For many of the systems examined the results may be expressed over considerable ranges of composition of the solvents by the formula $S_c = S_o - KC^p$, where S_o is the solubility in 100 g. of a pure solvent, S_c is the solubility in 100 g. of this solvent when mixed with C g. of a second solvent, and K and p are constants. This expression will represent every type of solubility curve except that with negative deviations accompanied by a minimum.

R. CUTHILL.

Adsorption of vapours on carbon, and the thermal dilation of the interface. F. GOLDMANN and M. PÓLÁNYI (Z. physikal. Chem., 1928, 132, 321-370).—A method is described whereby adsorption isotherms of vapours may be determined by allowing the saturated vapour to remain in contact with the adsorbent at a known temperature until equilibrium is attained, and then removing successive quantities of the vapour by condensation into a tube immersed in liquid air; by sealing off this tube the mass of

vapour removed may be determined. The equilibria are completely reproducible after many months. The adsorption of ethyl chloride, ethyl ether, and carbon disulphide by carbon at -15.3° , 0° , and 20° , and of *n*-pentane by carbon at temperatures from -63.7° to 20° was examined; in each case the pressure varied from about 90% of the saturated vapour pressure to 10^{-2} mm. No evidence could be obtained that the adsorption of vapours is caused by capillary condensation. If the vapour above the adsorbent is saturated, the adsorbed layer becomes identical with the film of liquid formed when the adsorbent is immersed in the liquid. The weights of the liquid films of different substances on the same adsorbent are in the same ratio as the densities of the liquids, whilst the volumes of the liquid films are independent of temperature. The thermal expansion of the liquid in films of ethyl chloride, ethyl ether, and *n*-pentane is about 20% less than when the substances are in the ordinary liquid phase. A film of water has a positive expansion coefficient from 0° to 5° . The heat of wetting is greater than the affinity of wetting, and in general decreases as the thickness of the film increases; as saturation is approached there is, however, a sharp increase. The results of the measurements are in good agreement with the potential theory of adsorption. When the quantity of adsorbed vapour ranges from 5 to 80% of the quantity required for wetting the adsorbent, it forms a unimolecular but discontinuous film, which tends to run together as the quantity adsorbed increases; the points on the adsorbent having the greatest potential are the first to be occupied by the vapour.

H. F. GILLBE.

Active charcoal. Amorphous state, temperature stability, and relation of adsorptive power to the physical and chemical properties of the charcoal and the adsorbed molecules. O. RUFF and P. MAUTNER (*Z. physikal. Chem.*, 1928, 26, 312—356; cf. A., 1925, ii, 1125; 1926, 346; 1927, 305, 1138).—The relation between the adsorptive power of graphite and the nature and state of division of the dissolved substance is discussed. Although the adsorptive activity increases with increase of surface area, there appears to be no simple relation between the state of division and activity. Substances in colloidal solution are more easily adsorbed than those in true solution. Results are given of experiments with four different charcoals to show that the adsorptive power decreases with rise of temperature and with increased duration of heating. From a röntgenographic investigation of supernorit at different temperatures, conclusions are reached as to the influence of temperature and length of heating on the orientation of the carbon atoms to a graphite lattice. The progressive graphitisation of the carbon caused by heating beyond 1000° results in a marked decrease of activity. The adsorption of gases and substances in solution (phenol, methylene-blue, Congo-red, molasses) by a number of commercial active charcoals has been studied, and the influence of impurities and of the porosity of the material and its form is considered. On the basis of the results, a comparison is made of a number of active charcoals

for technical purposes. The non-specific and the specific natures of the adsorption are discussed. The specific adsorption represents the sum of two specific effects, one due to the adsorbent and the other to the adsorbed material. The specific effect of the charcoal is the chief factor in molecular adsorption and in the preferential polar adsorption of acids. The polar effect is influenced by the constitutive properties of the adsorbed substance, and a summary is given of data showing the effect of the size of the molecule, ring or chain formation, the presence of double linkings, and of various types of isomerism.

L. L. BIRCUMSHAW.

Adsorption and heat of adsorption of sulphur dioxide on carbon. M. PÓLÁNYI and K. WELKE (*Z. physikal. Chem.*, 1928, 132, 371—383).—The equilibria and heat changes associated with the adsorption of sulphur dioxide by carbon have been determined for adsorbed layers ranging from a few ten-thousandths to about 3% of the maximum possible. For the lowest values the adsorbed substance is held by forces which have a high energy value (about 20 kg.-cal.), but the sphere of action is restricted. From 0.0005 to 0.0008 of the maximum the adsorption takes place with a much smaller energy change, the adsorbed substance having such mobility that it is to be regarded as a two-dimensional gas, filling the adsorption area to a considerable extent. Further adsorption results in the formation of a condensed film, the latent heat of condensation being manifested by an increase of the heat of adsorption; simultaneously the mobility of the adsorbed molecules decreases.

H. F. GILLBE.

Adsorption of gases by chabasite. F. SIMON (*Z. physikal. Chem.*, 1928, 132, 456—459).—The dehydration of chabasite which occurs on heating takes place in stages which show a stoichiometric relation between the weight of the water and that of the dehydrated silicate. Measurements have been made of the adsorption of argon and of nitrogen by the anhydrous substance at 90.2° Abs. in order to determine whether similar relations obtain. The curves derived by plotting pressure against volume of dissolved gas consist of a series of straight portions, with breaks at the points which correspond with the ratio 1 mol. gas : 1 mol. chabasite. The slope of the curve at this point changes 75% for argon and 85% for nitrogen. The curves exhibit breaks also at $1/3$ mol. of gas. The theoretical significance of these observations is discussed.

H. F. GILLBE.

Adsorption of sulphur dioxide by titania gel. S. KLOSKY and A. J. BURGGRAFF (*J. Amer. Chem. Soc.*, 1928, 50, 1045—1049).—The adsorption at -22.5° , 0° , 25° , and 50° agrees with Patrick's equation at lower pressures, but over the whole range is best represented by Póányi's formula. S. K. TWEEDY.

Adsorption of excess ions by positive and negative silver halide and silver thiocyanate sols. A. LOTTERMOSER and W. PETERSEN (*Z. physikal. Chem.*, 1928, 133, 69—121).—An exhaustive study has been made, by means of potentiometric measurements, of the adsorption of silver, halogen, and thiocyanate ions by silver halide or thiocyanate sols or gels. In each case, the silver-ion concentration

was measured by electrometric titration, and the number of adsorbed ions was given by the difference between the measured potential and that calculated from Nernst's formula. The results are represented graphically by "potential curves." The amount of adsorption is found to increase with decreasing salt solubility. The adsorption of bromine and iodine ions by negative silver bromide and iodide sols, respectively, is considerably greater than that of silver ions by the corresponding positive sols. The adsorption of thiocyanate ions by negative silver thiocyanate sols is considerably less than that of bromine ions by negative silver bromide sols, although the former are only slightly more soluble than the latter. On account of the change of potential at the equivalence point, a limit is set to the accuracy of the potentiometric titrations. Thus, for silver bromide, iodide, and thiocyanate sols, titrated with 0.1*N*-silver solution, an accuracy of $\pm 0.004\%$ may be obtained. Negative silver chloride and bromide sols are markedly sensitive to light in the neighbourhood of the equivalence point, and decompose with liberation of free halogen and colloidal silver. By determining the liberated halogen, a measure of the photo-sensitiveness of the silver halide might be possible. With positive sols and silver iodide sol, the action of light, so long as the exposure is not too long, has no effect on the potential. Silver iodide and bromide sols may be considered as colloidal electrolytes, for which the greatest part of the adsorption is due to the charging of the sol. In the case of the other sols investigated, which may also be regarded as colloidal electrolytes, the adsorption caused by charging before coagulation is so small as to be unmeasurable.

L. L. BIRCUMSHAW.

Adsorption in mixtures of solvents. E. ANGELESCU and V. N. COMĂNESCU (*Kolloid-Z.*, 1928, 44, 288—296).—Measurements have been made of the adsorption of picric acid by animal charcoal in benzene, ethyl alcohol, acetone, and in various mixtures of the following pairs of liquids: ethyl alcohol-chloroform, benzene-ethyl ether, ethyl alcohol-ethyl ether, acetone-benzene, ethyl alcohol-benzene, acetone-chloroform, acetone-ethyl alcohol, and acetone-water. The concentration of the picric acid was varied between 2 and 8%. The results show that the ordinary adsorption equation $a = kc^{1/n}$ is applicable to mixtures of solvents. The values of the exponents vary between narrow limits, and the constant k is inversely proportional to the n th root of the solubility l of picric acid in the solvent or mixture of solvents. The product $kl^{1/n}$ is a measure of the affinity between animal charcoal and picric acid and can be used as a measure of the adsorptive power of a specimen of charcoal. Exceptions to these generalisations were found in the mixtures of acetone with water or ethyl alcohol containing a high percentage of acetone.

E. S. HEDGES.

Adsorption phenomena in solutions. X. Connexion between adsorption and p_H of solutions. S. PEWSNER (*Z. physikal. Chem.*, 1928, 133, 122—128).—A study has been made of the adsorption of carbamide, dextrose, formaldehyde, arsenious acid, phenol, aniline, acetone, hydrogen cyanide, and

boric acid by charcoal, in the presence of phosphate or acetate buffer solutions of varying p_H . The curves giving the relation of adsorbed quantity to p_H show either two maxima or two minima in the region p_H 5.0—7.0. The upper limit corresponds with the p_H of pure water, whilst the lower limit, p_H about 5.0, corresponds with the p_H of water in equilibrium with charcoal containing carbon dioxide.

L. L. BIRCUMSHAW.

Adsorption from solutions. W. HEYNE and M. PÓLÁNYI (*Z. physikal. Chem.*, 1928, 132, 384—398).—Measurements have been made of the adsorption by carbon of various crystalline organic compounds from aqueous and alcoholic solutions between -21° and 50° . With rise of temperature the affinity of the adsorption process increases in all cases. The maximum quantity adsorbed decreases with temperature much more rapidly than in the case of adsorption of vapours. Both the absolute value of the affinity and the maximum quantity of substance adsorbed are very much less than is found for adsorption from the vapour phase. These differences are ascribed to the work necessary for separating the solvent and solute and for breaking down the crystal lattice. Other observations in favour of this view are that adsorption of a given substance from an organic solvent is less than from water, and that the adsorption of phenol at and near its m. p. are similar to those shown in the adsorption of vapours.

H. F. GILLBE.

Adsorption phenomena in solutions. XI. N. SCHILOV and K. TSCHMUTOV (*Z. physikal. Chem.*, 1928, 133, 188—201).—Carbon purified by ignition in air differs from that prepared by treating with hydrogen at a high temperature in that it always retains a film of adsorbed carbon dioxide. The hydrolysis of both weak and strong electrolytes brought about by adsorption on carbon has been followed by p_H measurements, and in agreement with observations of the related phenomena of cataphoresis and electro-osmosis, it is found that with a negative adsorbent the anions are adsorbed before the cations. Two stages in the process of adsorption can thus be defined: in the first the charge on the adsorbent increases owing to the adsorption of ions bearing charges of the same sign as that of the adsorbent; in the second ions of the opposite sign are adsorbed and this corresponds with molecular adsorption. This theory is in accordance with the observation that strong electrolytes undergo hydrolysis when in contact with an adsorbent, whereas weak electrolytes merely experience molecular adsorption.

H. F. GILLBE.

[Influence of] electric charge of adsorbent in adsorption. S. SASAKI (*J. Biochem. Japan*, 1927, 8, 102—106).—The sign of the charge of carbon particles was determined when these had reached a state of equilibrium with the basic dyes methylene-blue and crystal-violet at 18° and 0° . As the concentration of the dye increases beyond a certain limit, the negative charge on the carbon is reversed. The concentration at which the reversal takes place is lower the lower the temperature, and the lower the proportion of charcoal to solution. The adsorption requires about 2 hrs. to complete. It is suggested

that the mass attraction between charcoal and dye molecules is the chief cause of the adsorption, although this is undoubtedly assisted by electrical attraction.

W. A. RICHARDSON.

Theory of sorption. Mechanism of heterogeneous catalysis. O. SCHMIDT (Z. physikal. Chem., 1928, 133, 263—303).—The sorption at 1 atm. pressure and at constant temperature between 0° and 150° of gases for which the molecular diameter is less than the mean diameter of the pores of the adsorbent, is found to be expressed by $\log c = a\sqrt{\lambda} - b$, where c is the quantity of gas adsorbed per unit weight of adsorbent, λ the latent heat of evaporation, and a and b are constants which are for a given adsorbent independent of the nature of the gas, but vary with temperature and pressure. The equation, which has also been derived theoretically, is applicable to the adsorption of gases by colloids and by liquids. Deviations are found when chemical reaction takes place readily. If ionisation of the adsorbed gas occurs, forces of attraction, additional to those of van der Waals, are called into play, and the force needed for separation of the molecules of the gas is greater than the calculated values. H. F. GILLBE.

Patrick's theory of adsorption. S. J. GREGG (J. Physical Chem., 1928, 32, 616—619).—Theoretical. An examination of adsorption data shows Patrick's formula, $V = k(p\gamma/p_0)^{1/n}$ (A., 1920, ii, 417), to be unsatisfactory. The inclusion of γ is unjustifiable, and the substitution of T^{-1} gives a closer agreement with experimental data. Even then the purely empirical formula obtained forms no basis for a theory of adsorption. L. S. THEOBALD.

Surface tension and the structure of the surface of aqueous ammonia solutions. O. K. RICE (J. Physical Chem., 1928, 32, 583—592).—The surface tension of aqueous ammonia has been measured by a modified capillary-rise method over the concentration range 0—14 g.-mol./litre. Calculations of the adsorption of the ammonia at the surface of the solution appear to show that even at the highest concentration used there are insufficient molecules of ammonia to form a unimolecular layer. Further, it is estimated that the average adsorbed molecule is approximately 10^{-8} cm. from the surface. L. S. THEOBALD.

Surface tension of non-aqueous salt solutions. P. P. KOSAKEVITSCH (Z. physikal. Chem., 1928, 133, 1—14).—By means of the capillary-rise method, the surface tensions of a large number of non-aqueous salt solutions have been measured, the solvents including aliphatic alcohols, acids, and ketones, glycerol, pyridine, and furfuraldehyde. The surface tension of the pure solvents is raised by the addition of salts. For concentrated solutions the relation between the surface tension (γ) and salt concentration (C) is linear. For more dilute solutions, three types of $\Delta\gamma$ - C curves are found: (1) concave to the C -axis (chiefly ethyl and propyl alcohols); (2) convex to the C -axis (methyl alcohol); (3) a straight line passing through the origin (chiefly non-alcoholic solvents and isoamyl alcohol). The greatest negative capillary activity is observed for salt solutions in methyl alcohol; the value rapidly decreases with increase

in the length of the carbon chain in the homologous alcohol series. This phenomenon may be connected with the greater degree of association of salts in the higher alcohols. In non-alcoholic solvents, the negative capillary activity is found to vary but little. If the angle between the $\Delta\gamma$ - C line and the C -axis is taken as a measure of the negative capillary activity, the order of the alkali metals (in methyl and ethyl alcohols) is the same as that in water, viz., $\text{Li} > \text{Na} > \text{K}$. By direct comparison of the $\Delta\gamma$ values at equal concentrations of the alkali iodides, however, different results are obtained according to the chosen concentration, since the curves intersect one another. The order of the lyotropic series $\text{Cl} > \text{Br} > \text{I}$ appears to be reversed in non-aqueous solvents.

L. L. BIRCUMSHAW.

Surface tension of aqueous solutions of salts of high mol. wt. G. ETTISCH and R. KOGANEI (Biochem. Z., 1928, 193, 390—392).—The surface tension-concentration (γ - C) curves of pure aqueous solutions of sodium cholate, glycocholate, and taurocholate show a well-marked minimum, the degree of lowering of the surface tension being larger, and the molar concentration at the minimum being smaller the larger the mol. wt. With sodium cholate, the activity is due to the liberation by hydrolysis of cholic acid. With sodium oleate the γ - C curves are normal and do not show a minimum. The form of the γ - C curves for sodium cholate in serum and plasma is quite distinct from that in egg-albumin, the former resembling the course in 0.005*N*-sodium hydroxide and not possessing a minimum, whilst the latter resembles the course in distilled water. P. W. CLUTTERBUCK.

Determination of hydration from surface tension. H. FREUNDLICH and A. SCHNELL (Z. physikal. Chem., 1928, 133, 151—164).—The surface tension of aqueous isoamyl alcohol solutions containing sugar or electrolytes at various concentrations has been measured. Szyszkowski's equation is valid for the mixed solutions. From the results the degrees of hydration of dextrose and sucrose and of a number of sodium and potassium salts have been calculated; the hydration of the anions corresponds with the lyotropic series. The calculated values of the hydration are in agreement with those obtained by other workers from partition and solubility data, but for the sodium and potassium cations the values deviate widely from those derived from mobilities; in the case of the anions no such deviation exists. H. F. GILLBE.

Molecular orientation at surfaces of solids. II. Work of adhesion of the saturated fatty acids for water. A. H. NIETZ (J. Physical Chem., 1928, 32, 620—630).—Experimental results previously obtained (this vol., 358) are now discussed. For the saturated fatty acids, the curves obtained by plotting work of adhesion against the number of carbon atoms show a marked alternating effect according as the number of carbon atoms is odd or even. The β -acids with an odd number and the even members lie on a smooth curve, the α -modifications of the odd-numbered members showing the alternating higher values. This is attributed to differences in crystal structure (cf. Garner and Randall, A., 1924, ii,

385). The curves show a minimum at 12—14 carbon atoms, followed by a pronounced increase, and the general trend of the curve is attributed partly to the nature of the adhesional energy-temperature relationships, and partly to the mechanical effects of the length of the carbon chain.

L. S. THEOBALD.

Production of anisotropy on surfaces. H. ZOCHER and K. COPER (*Z. physikal. Chem.*, 1928, **132**, 295—302).—The thickness of the anisotropic layer produced on the surface of glass by rubbing (A., 1927, 931) is found by etching to be about 0.3 μ . Similar layers may be produced on almost all solid substances, although with such as readily recrystallise, e.g., lead, they become isotropic after a short time. The nature of the material used to rub the surface does not affect the result. The presence of such films is detected by utilising the fact that they induce anisotropy in thin films of methylene-blue deposited on them. Most other dyes are unsuitable for this purpose, but melted *p*-azoxyanisole and *p*-azoxyphenetole may be used. Anisotropy is also observed on a freshly-fractured surface of glass.

R. CUTHILL.

Adhesion. III. Mixtures of two lubricants. (Miss) M. E. NOTTAGE (*Proc. Roy. Soc.*, 1928, **A**, **118**, 607—616; cf. **B**, 1928, 287).—By means of the method described previously, three pairs of lubricants have been studied—palmitic acid and the normal paraffin $C_{30}H_{62}$, palmitic acid and cetyl alcohol, and phenanthrene and the paraffin $C_{30}H_{62}$. Curves are given showing the relation of adhesion and m. p. of the mixtures to mol. composition, and the structure of the crystalline plate formed on breaking the metal-lubricant joint is illustrated by means of photographs. In the case of the acid-paraffin mixture, the adhesion is in every case greater than that of the pure substances. Both the adhesion and m.-p. curves show a well-defined transition point for a mixture containing about 3 mols. of palmitic acid to 1 mol. of paraffin. From a study of the structure of the crystalline plates, it appears that the transition point is accompanied by a change from a system containing two constituents to a system containing one. Mixtures on the palmitic acid side of the transition point have a latent period of increasing adhesion, those on the paraffin side, one of decreasing adhesion. In the case of the acid-alcohol mixture, the adhesion curve shows three well-defined transition points—at about 30, 50, and 66 mols. % of cetyl alcohol. The m.-p. curve shows transition points at about 30 and 66 mols. % of cetyl alcohol. The second transition point on the adhesion curve is probably due to the presence of cetyl palmitate, and coincides with a change in structure from a two-constituent to a one-constituent system. The addition of $C_{30}H_{62}$ to phenanthrene causes the adhesion of the latter to decrease at first rapidly, then gradually, and finally rapidly again. An ill-defined transition point is shown, corresponding with 46.6 mols. % of paraffin. The m. p. of each constituent is lowered by the addition of the other, the m.-p. curve being continuous and passing through a minimum extending from about 47 to 74 mols. % of $C_{30}H_{62}$. The latent period of phenanthrene is one of decreasing adhesion.

L. L. BIRCUMSHAW.

Electron theory of surface energy at the boundary of two amorphous media. B. M. EIDELSON (*Physikal. Z.*, 1928, **29**, 200—204).—Theoretical.

R. A. MORTON.

Bubbles, drops, and Stokes' law. II. W. N. BOND and (Miss) D. A. NEWTON (*Phil. Mag.*, 1928, [vii], **5**, 794—800).—The apparently accidental variations observed in the previous work of Bond (*ibid.*, 1927, [vii], **4**, 898) have been further examined and it is shown both theoretically and experimentally that the surface tension of a drop or bubble decreases the terminal velocity. For a given drop or bubble there is a critical radius below which the drop or bubble behaves as a rigid sphere, whilst for appreciably greater radii the surface-tension effect is small. Experiments with different media give results for the critical radii in fair agreement with theory and show that surface tension is the main contributory cause of the departure from Stokes' law.

A. E. MITCHELL.

Diffusion of carbon through tungsten. C. ZWIKKER (*Physica*, 1927, **7**, 189—193).—Hot tungsten filaments were coated with carbon in an atmosphere of illuminating gas, and diffusion experiments performed at 1970° Abs.; mathematical relations are derived.

CHEMICAL ABSTRACTS.

[Semipermeable] diaphragms. I. Measurement of electro-endosmosis. K. ILLIG and N. SCHÖNFELDT (*Wiss. Veröff. Siemens-Konz.*, 1927, **6**, 171—176).—An apparatus for the measurement of the electro-endosmotic effect is described. The porous diaphragm is arranged to form the junction of two right-angled tubes, so that the whole forms a U-tube with the diaphragm in the centre of the horizontal lower portion. Copper electrodes of the same area are placed at equal distances from opposite sides of the diaphragm. Corks with right-angled capillary tubes of equal and uniform cross-section are placed in the open ends of the U-tube, which is filled with electrolyte so that the horizontal limbs of the capillaries are filled half-way to the ends. The current is supplied from accumulators, and is reversed repeatedly after equal intervals of time, the movements of liquid in the capillaries being measured.

S. I. LEVY.

Osmosis of ternary liquids. General considerations. III and IV. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 1095—1114).—The diagram showing the direction of diffusion of the components of a ternary liquid mixture is discussed, and also the way in which the changes in composition of the diffusing liquids may be determined.

M. S. BURR.

Mol. wt. of cellulose nitrate in molten camphor. C. TROCUS and M. ABD EL SHAHID (*Naturwiss.*, 1928, **16**, 315).—Cellulose nitrate containing 13.5% of nitrogen, corresponding with a mean mol. wt. of 286 (2.76 nitro-groups per $C_6H_{10}O_5$), exhibits depressions of the m. p. of camphor in concentrations up to 15% which indicate values between 280 and 315 for the observed mol. wt.

R. A. MORTON.

Von Weimarn's theory of the colloidal state. S. F. SLOKASOFF (*Anal. Asoc. Quím. Argentina*, 1927, **15**, 237—286).—A lecture.

R. K. CALLOW.

Preparation of negatively-charged sols by means of tartaric acid. I. Properties of compounds of oxides of tin and titanium with tartaric acid. A. DUMANSKI and A. KNIGA (Kolloid-Z., 1928, 44, 273—277).—Measurements have been made of the density, viscosity, optical activity, and electrical conductivity of solutions of tartaric acid containing progressively increasing quantities of stannic hydroxide and titanium hydroxide respectively. The hydroxides were used in a freshly-precipitated condition by adding sodium hydroxide to the tetrachlorides of the metals. The results indicate that the reaction between tartaric acid and stannic or titanium hydroxide can be separated into two stages: in the first stage, both the optical activity and the ionic concentration increase, and in the second stage the optical activity continues to increase whilst the ionic concentration remains constant. The density and viscosity of the solutions increase linearly throughout. It is considered that the second stage denotes a colloid-chemical process, in which the excess of metallic hydroxide is peptised by the tartaric acid. Such solutions exhibit the Tyndall effect. The colloid particles migrate to the anode under a *P.D.* The formation of colloid can be observed when the ratio of tartaric acid to stannic oxide reaches 5:1. In the coagulation of stannic oxide sol by sodium, barium, or aluminium chloride Schultze's rule is not followed quantitatively. E. S. HEDGES.

Silver hydrosols with particles of uniform size. A. GAŁECKI and R. KEMPF (Rocz. Chem., 1928, 8, 40—43).—Stable silver hydrosols are prepared by the reduction of silver nitrate by means of white phosphorus. The particles of such hydrolysis are of uniform size and can serve as nuclei for the deposition of silver from its solutions, but not of gold. On the other hand, silver will deposit on similarly prepared gold hydrosol particles. Such silver hydrosols are affected by the presence of electrolytes, and their particles possess a negative charge which diminishes with time. R. TRUSZKOWSKI.

Stability of coarse particles in solutions. III. Influence of concentration of the disperse phase and of salt on clarification. H. WERNER (Ber., 1928, 61, [B], 802—809; cf. A., 1927, 620, 1023).—The rate of sedimentation of suspensions of *Bolus alba* in water and aqueous potassium chloride solution at $20.0 \pm 0.1^\circ$ has been investigated. The formation of aggregates from suspended particles may be a reversible or an irreversible process; from coarse particles it is irreversible. It may affect the falling of the particles and the shrinking of the deposit favourably, unfavourably, or not at all, according to the concentrations. The degree of its action may vary with time. The higher the concentration of the disperse phase, the lower is that of the salt necessary to produce optimal rate of falling of the particles. Every suspension is completely clarified in a relatively short time when the salt has a certain minimum concentration which is independent of that of the suspended particles within very wide limits. The necessary concentration of the salt depends on its nature. The concentration of the salt which just

causes clarification of thick suspensions approximates closely to that which is optimal for the falling of the particles and involves the least expenditure of salt. The nature of the deposit varies with the concentration of salt and disperse phase. With high salt concentration, gentle agitation usually causes the production of a very stable layer of foam the height of which increases with the concentration of salt and disperse phase. Analogous results are obtained with suspensions of *Bolus* in magnesium chloride solution and of aluminium oxide in potassium chloride solution. H. WREN.

Charge and particle size. R. KELLER (Kolloid-Z., 1928, 44, 324—326).—The colloidal state of matter is characterised not only by the size of the particles of the disperse phase, but also by a minimal and maximal electrostatic charge with respect to the dispersion medium. The part played by the ions in the charging of a colloid is small, especially in regard to the ions of strong acids and bases. An analogy is drawn between the electrical relations of colloid particles and molecules, and it is considered that in both cases the surface charge shows itself in an electric field through selective adsorption at one of the electrodes. E. S. HEDGES.

The crystalline liquid state as a general property of matter. I. Vectorial aggregation, fluid structure, and stream-double refraction of barium sulphate ultramicrocrystals. P. P. VON WEIMARN (Kolloid-Z., 1928, 44, 279—288).—The results of a microscopical and ultramicroscopical examination of barium sulphate, precipitated by mixing concentrated solutions of manganous sulphate and barium thiocyanate, support the author's claim that the state of aggregation of the precipitate depends not so much on the properties of the precipitated substance as on the physicochemical conditions of precipitation. Five stages can be distinguished in the precipitation of barium sulphate: (1) chemical reaction, (2) formation of highly supersaturated and associated solution of barium sulphate, (3) production of very concentrated, highly disperse colloidal solution, (4) vectorial aggregation in this colloidal solution, (5) destruction in consequence of aggregative crystallisation (formation of larger ultramicro- or micro-crystals). An increase in viscosity occurs during the processes (1) to (4), the substance changing from a thick oil of syrupy consistence to a gelatinous membrane. In the case of barium sulphate, states (1) and (2) are passed through rapidly. E. S. HEDGES.

Electrokinetic and chemical behaviour of alumino-silicates. S. MATTSO (Soil Sci., 1928, 25, 289—311).—On mixing increasing quantities of sodium silicate with an aluminium chloride solution, an electropositive sol, an isoelectric precipitate, and finally (with an excess of silica) an electronegative sol are successively formed. The alumina-silica system forms isoelectric precipitates in which the proportion of silica decreases with an increase in p_H , approaching zero at p_H 7.0, at which the alumina is itself isoelectric. In the presence of active anions the alumina-silica system forms isoelectric precipitates in which the proportion of silica is lower than in the

precipitates which are formed at the same p_H but in the absence of such anions. In the presence of cations the proportion of silica in the isoelectric precipitates is correspondingly increased. The base exchange capacities of the several precipitates prepared were found to increase with the ratio of silica to alumina and to be of the same order of magnitude as those of the natural gels. The hydroxyl ion as well as the cation is absorbed by the natural gel indicating true adsorption instead of the neutralisation of an acid. The mechanism of adsorption and exchange and the pedological significance of these experiments are discussed.

H. J. G. HINES.

Immunity [towards staining] of the granule in colloidal solutions. A. BOUTARIC and F. BANÈS (Compt. rend., 1928, 186, 1003—1005).—Spectrophotometric measurements have shown that eosin is removed from aqueous solution by colloidal solutions of mastic, gold, albumin, casein, or aluminium hydroxide only when the latter are flocculated, and not when they are in the colloidal state. Flocculation was produced by aluminium chloride or by boiling. The exceptional nature of ferric hydroxide and arsenic sulphide sols may be due to flocculation in crystalline granules. The phenomenon is one of true adsorption, and not of occlusion, since the dye is removed even if added after flocculation is complete, and throws light on the selective staining of living as distinct from dead cells by dyes.

J. GRANT.

Flow of starch pastes at high and low rates of shear. F. D. FARROW, G. M. LOWE, and S. M. NEALE (J. Text. Inst., 1928, 19, 18—31T).—The flow of starch pastes and of castor oil in capillary and Couette viscosimeters has been measured at 20° over a range of shear of 300,000-fold; within this range the viscosity of castor oil is constant. A method is described whereby the results of viscosity measurements in these instruments may be used to calculate the simple shearing stress and velocity gradient at a definite point in the fluid. A graph of the values so obtained expresses in a manner independent of the instrument the variation of flow with shearing stress for the liquid investigated. The stress-shear curve for starch pastes is quite continuous and either passes through or terminates close to the origin. Whilst it does not hold even approximately over the whole of the range examined, the relation $P^N = \eta dv/dy$ appears to describe the flow of starch pastes better than any other two-constant equation and serves as a useful and accurate interpolation formula within the range usually covered by any one type of instrument. Results of measurements made in capillary tubes are expressed in terms of stress and strain, and therefore made independent of instrument dimensions and comparable with data obtained by the use of other forms of viscosimeter, by the use of a formula based on the above relation, viz., $(Pr/2l)^N = \eta(V/t)(N+3)/\pi r^3$, where r is the radius and l the length of the tube, P the driving pressure, and V the volume of liquid flowing in time t . The method is applied to results given by Freundlich and Schalek (A., 1925, ii, 112) for the flow of benzopurpurin sols in both capillary and rotating-cylinder viscosimeters, and it is shown

that the discrepancy between the apparent viscosities as determined by the two methods then disappears.

B. P. RIDGE.

Osmotic pressure of protein solutions containing salts. J. A. CHRISTIANSEN (Compt. rend. Trav. Lab. Carlsberg, 1928, 17, No. 6, 1—17).—Theoretical. An attempt is made to derive general expressions applicable to the conditions existing in an osmometer of the type used by Sørensen and his co-workers (cf. A., 1919, i, 175).

H. INGLESON.

Magnetic susceptibility and the supposed second isoelectric point of gelatin. M. FALLOT (Compt. rend., 1928, 186, 1287—1288).—Between p_H 3.69 and 8.20, the magnetic susceptibility curves of gelatin show a minimum value at p_H 4.7, and after a maximum at p_H 5.6, decrease regularly. The dispersions and refractive indices of gelatin solutions are independent of variations in the p_H value, and no evidence has been found of the supposed second isoelectric point at p_H 7.7.

J. GRANT.

Isoelectric points of protamines. S. MIYAKE (Z. physiol. Chem., 1928, 172, 225—229).—Different fractions of clupeine and salmine which have approximately equal arginine contents have the same isoelectric point. Arginine has the highest isoelectric point (p_H 10.5) of all amino-acids, and in twelve protamines examined the isoelectric point is higher or lower as the arginine content increases or decreases, the lowest being that of cyprinine. The precipitation of clupeine by alcohol shows an optimum at the isoelectric point (p_H 12.2). The mixture of amino-acids from the total hydrolysis of clupeine has an isoelectric point 9.37. The results show that the displacement of the isoelectric point towards the alkaline side by the imino-group is greater than that produced by the joint action of free carboxyl and amino-groups.

C. HOLLINS.

Dependence of the viscosity of gelatin solutions on temperature. A. FODOR and K. MAYER (Kolloid-Z., 1928, 44, 314—315).—Using the Ostwald viscosimeter, measurements were made of the viscosity of gelatin solutions with and without addition of acid or alkali between the temperatures 22° and 26°. The viscosity of an aqueous solution of gelatin has a higher temperature coefficient than that of a gelatin solution containing acid or alkali. It is inferred that solvation of the particles is not the primary cause of the increase in viscosity, and that the important feature is the formation of an adsorption compound between the gelatin and acid or alkali.

E. S. HEDGES.

Turbidity phenomena in gelatin. K. MAYER (Kolloid-Z., 1928, 44, 315—319).—The turbidity of solutions of electrolysed gelatin was measured in an "extinctionmeter" at various temperatures between 12.5° and 27.5°. For each temperature a maximum occurs at 1.8% of gelatin, and the turbidity is less at higher temperatures. The fall in turbidity with rising temperature is greatest for a 1% solution. Examination of the effect of hydrogen-ion concentration on the turbidity show that two maxima occur at p_H 5.2—5.4 and p_H 4.0—4.2. It is possible to purify gelatin by electro dialysis without previous dialysis by working with a small current density and

membranes with large pores, and maintaining a rapid flow of water in the anode and cathode chambers in order to remove the electrolytes. E. S. HEDGES.

Diffusion of silver ions [and dyes] in gels. K. YABUKI (J. Biochem. Japan, 1927, 8, 137—156).—The influence of the gel concentration, the concentration of the diffusing silver nitrate, and the chloride concentration on the velocity of diffusion of silver ions in gelatin and agar gels has been studied microscopically, employing a method in which the rate of advance of the silver chloride boundary is measured. An empirical relation $x=at^b$ was found, x being the distance travelled by the diffusing ions in time t , and a and b constants for the particular concentrations of gel, silver nitrate, and sodium chloride employed. The value of a may be taken as a measure of the velocity of diffusion. Up to 10% gelatin concentration, and 5% agar, the velocity of diffusion of the silver ion is inversely proportional to the gel concentration. With constant gel concentration the rate is greater for high than for low silver-ion concentration. Increase in sodium chloride concentration gives decreased rate of diffusion. A similar relation is observed for the diffusion of dyes in gelatin gels of 10—40% concentration. The fact that the change in rate of diffusion with gel concentration is continuous suggests that there is no essential difference in the structure of the gel within these concentration limits (Hardy, J. Physiol., 1899, 172).

W. A. RICHARDSON.

Conductivity of gel containing salt. K. YABUKI (J. Biochem. Japan, 1927, 8, 157—165).—The conductivity of potassium chloride (0.1—0.01*N*) in gelatin (2—28%) and agar (0.5—5%) gels has been measured, and it is found that the conductivity y due to the salt is a function of the concentration x of the colloid, the relation being of the form $y(ax+b)=1$, where a and b are constants. The decrease in conductivity produced by the colloid is attributed to the resistance offered by the colloid rather than to adsorption of the salt by the colloid particles. The rate of increase of resistance with concentration decreases with increasing concentration of the colloid. There appears to be no essential difference in the structure of gelatin and agar gels over the ranges examined.

W. A. RICHARDSON.

Influence of slightly soluble substances on the thixotropy of ferric oxide sols. H. FREUNDLICH and K. SOELLNER (Kolloid-Z., 1928, 44, 309—313).—The accelerating influence of metals on the thixotropic change of ferric oxide sols containing sodium chloride is explained in the following way. Direct measurements have shown that the time of setting increases with increasing hydrogen-ion concentration, and it is considered that the metals dissolve in the weakly acid ferric oxide sol containing ferric chloride to a sufficient extent to diminish the hydrogen-ion concentration, and thus the time of setting. The ions of the metal are without influence. Pure gold and platinum are not sufficiently soluble in the acid solution to produce any effect. These results are confirmed by semi-quantitative experiments in which a large number of sparingly soluble substances (elements, oxides, sulphides, silicates, etc.) were

added. A marked difference was found between the effects produced by a soluble and an insoluble steel. Substances such as graphite and sulphur were without influence, but a positive effect was produced by oxides of iron. In agreement with theory, a metal is effective when separated from the sol by a collodion membrane.

E. S. HEDGES.

Electrokinetic potential of silicic acid gels. S. GLIXELLI and J. WIETELAK (Rocz. Chem., 1928, 8, 10—21).—Measurements of the velocity of electro-osmosis of 0.001*N*-nitric acid solutions through silica gel diaphragms show that this is substantially the same when the concentration of the silica in the diaphragm changes from 1.8 to 5.3%, the mean electrokinetic potential ζ being 0.211×10^{-3} volt. The value of ζ rises with diminishing concentration of nitric acid, being 5.42×10^{-3} volt for pure water. This value of ζ is unusually low in comparison with other diaphragms; thus for powdered quartz and for ignited silicic acid ζ is respectively 12.3×10^{-3} and 23.8×10^{-3} volt. Previous shaking, concentration or dilution of the gel does not appear to affect the value of ζ obtained, which, however, diminishes rapidly with increase in the concentration of sodium silicate solution from which the original gel is precipitated. The above phenomena are explained on the basis of Eggert and Reitstötter's theory of the structure of gels (A., 1926, 1098).

R. TRUSZKOWSKI.

Coagulation of colloids by electrolytes. III. Potentiometric titration of the coagulation of ferric hydroxide sols. A. J. RABINOVITSCH and V. A. KARGIN (Z. physikal. Chem., 1928, 133, 203—232; cf. A., 1927, 654).—The chemical changes which occur during the coagulation of ferric hydroxide sols by electrolytes have been followed by potentiometric titration. The replacement of chlorine ions by ions from the colloidal particles and the adsorption of ions by the latter may be thus investigated. It is found that the adsorption and replacement of chlorine ions do not take place according to the usual adsorption isotherms, but partake more of the nature of a chemical reaction. Coagulation usually occurs only after the whole of the chlorine has been replaced by the anions, and in those cases in which it takes place previously, the replacement takes place from the precipitate. During the titration the chlorine ions are replaced by more than the equivalent quantity of other anions, the effect being greater the higher the concentration of the sol and of the coagulating electrolyte. Since there is no corresponding replacement of cations, the positive charge on the colloidal particles must be increased by the addition of electrolyte to the sol. This conclusion has been verified by cataphoretic measurements.

H. F. GILLBE.

Electric charge and coagulation of colloids. H. MÜLLER (Kolloidchem. Beih., 1928, 26, 257—311).—Smoluchowski's theory of rapid coagulation for monodisperse systems is extended to polydisperse systems. Assuming that the effective radius of the attractive forces determining the coagulation between the single particles is small compared with the radii of the colloid particles, it is shown that coagulation takes place more rapidly between particles of different

sizes than between those of equal size. The view of Wiegner and Galecki, that in the coagulation of polydisperse sols the submicrons act as coagulation nuclei for the amicrons, receives theoretical confirmation. A mathematical theory is developed, which is applicable to any polydisperse system, and the following equation is deduced: $\Sigma v = N_0 / (1 + t/T) [\lambda n_0 / \{(N_0 \lambda + n_0)(1 + t/T)^\lambda - n_0\}]$, where Σv is the total number of small particles at time t , N_0 and n_0 are the original numbers of large and small particles respectively, T is the coagulation time of the large particles, and $\lambda = (V_R^2 + 1) / 2V_R$, where V_R is the ratio of the radii of the large and small particles, respectively. The equation has been experimentally confirmed by Tuorila (A., 1926, 1005) and Wiegner (*ibid.*, 242). The deviations shown by the results of Westgren and Reitstötter (A., 1918, ii, 301) from those demanded by Smoluchowski's theory can be explained by the polydispersivity of the initial colloid.

The influence of the concentration and valency of the added electrolyte on the electrokinetic potential (ζ) and stability of the colloid is discussed from the point of view of Gouy's theory of the diffuse double layer. A graphical method is given for determining the potential gradient in the diffuse double layer round a spherical particle. By means of the theory developed, the change of electric charge within the layer can be calculated from cataphoresis measurements, and a closer study is possible of the laws of ion adsorption on the colloid particles. The ζ - c curves (c = concentration of electrolyte) obtained by Freundlich and Zeh (A., 1925, ii, 115), who investigated the influence of valency on the cataphoresis and coagulation of an arsenious sulphide sol, can be explained simply by changes in the diffuse double layer, assuming a constant micelle charge. In most cases, however, the ζ - c curves can be explained only on the assumption that a change in the particle charge, due to ion adsorption, takes place.

L. L. BIRCUMSHAW.

Influence of temperature on the speed of coagulation of colloids. K. JABECZYŃSKI and M. KNASTER (Rocz. Chem., 1928, 8, 36—39).—See this vol., 361.

Kinetics of the coagulation of colloids. K. JABECZYŃSKI and M. SOROCZYŃSKI (Rocz. Chem., 1928, 8, 31—35).—See this vol., 360.

[Influence of] salt content on aggregation of hæmoglobin in solution. S. KATO, Y. KATSU, and K. YABUKI (J. Biochem. Japan, 1927, 8, 133—136).—The relation deduced by Hill (J. Physiol., 1916, 40, Proc. iv), $y = 100Kx^n / (1 + Kx^n)$, between the percentage saturation y of oxyhæmoglobin and x , the oxygen tension, where K is a constant, and n represents the average number of molecules which compose an aggregate particle, is confirmed for hæmoglobin solutions dialysed to different degrees, and it is shown that n decreases as the specific conductance and the chlorine-ion concentration decrease, but at a slower rate.

W. A. RICHARDSON.

Organic rhythmic structures. M. COPISAROV (Kolloid-Z., 1928, 44, 319—323).—Rhythmic precipitates were obtained in the diffusion of picric acid, tannic acid, lactic acid, phenol, phosphoric acid, and

α -trinitrotoluene into gelatin. At low concentrations of the colloid, striated structures without definite ring formation were produced, the rings becoming definite at a certain higher concentration of colloid. The value of this concentration depends on the quality of the gelatin. The best qualities of gelatin, or those containing the smallest quantities of hydrolysis products, tend to form honeycomb structures, rather than stratified precipitates. The experiments with tannic acid indicated a tendency towards the formation of spirals in place of rings. Rhythmic precipitates were not produced in the diffusion of pyridine, benzaldehyde, oil of wintergreen, gallic acid, and *o*-nitrophenol into gelatin, isinglass, and agar.

E. S. HEDGES.

A physical factor in the Liesegang phenomenon. S. RAY (Kolloid-Z., 1928, 44, 277—279).—An expression is derived which gives the relation between the density and the height of a colloidal suspension. According to this there are three possible heights for certain densities. This is considered to be the primary cause of the periodicity in Liesegang rings.

E. S. HEDGES.

"Acclimatisation phenomenon" in the coagulation of arsenious sulphide sols by barium chloride. V. N. KRESTINSKAJA and V. S. JAKOVLEVA (J. Russ. Phys. Chem. Soc., 1928, 60, 295—310).—See this vol., 236.

Cataphoretic migration velocity of large particles in sols and gels. II. H. FREUNDLICH and H. A. ABRAMSON (Z. physikal. Chem., 1928, 133, 51—68; cf. A., 1927, 931; this vol., 238).—The fact previously observed (*loc. cit.*), that the cataphoretic velocity of large particles is independent of their shape, has been confirmed by measurements on quartz particles in water, in aqueous sugar and salt solutions, and in serum, and also on glass and kaolin particles in water. The velocity of quartz particles in water (very dilute suspensions) is lowered by the addition of proteins such as gelatin, albumin, and hæmoglobin at very low concentrations (10^{-7} g. per litre); this effect is not found with other hydrophilic sols (starch, sodium oleate, etc.). At higher protein concentrations (10^{-4} — 10^{-5} g. per litre) the cataphoretic velocity of quartz or glass particles is independent of the protein content, and it is assumed that the particles are now completely surrounded by a protein envelope and behave as protein particles. Measurements have been made of the cataphoresis of quartz particles in solutions of egg-albumin (10^{-3} — 10^{-4} g. per litre) at constant p_H , and the results agree with those obtained by Svedberg and Tiselius (A., 1926, 1104) for the relation between the cataphoresis of egg albumin and the p_H of the medium. Exceptions are found to the behaviour shown by quartz particles, zinc oxide, air bubbles, etc. Thus, in spite of the high albumin content of serum, the mobility of the red corpuscles is about twice as great as that of the white. In mixtures of serum with gelatin, containing enough gelatin (about 0.7%) to cause it to set to a soft gel, the mobility of the red corpuscles is about twice that of quartz particles and leucocytes. With larger admixtures of gelatin (1.2—1.5%), so that the whole sets to a solid gel, the blood corpuscles

and suspended quartz particles move at first with the same velocity, but after a time, the red corpuscles again move with twice the velocity of the other particles. This behaviour is explained as being due to a thixotropic change in the gel, caused by the repeated to-and-fro motion of the particles.

L. L. BIRCUMSHAW.

Gaseous solutions. M. RANDALL and B. SOSNICK (J. Amer. Chem. Soc., 1928, 50, 967—980).—The deviations of gaseous mixtures from the generalised Raoult law increase with the density of the gas, and are qualitatively the same as those of typical liquid pairs. In Hildebrand's simplified equation for $\log \gamma$ (cf. A., 1927, 936) the value of b will always be below the "critical mixing point," i.e., the value necessary for the co-existence of two gaseous phases in equilibrium. The fugacity of a pure supercooled vapour cannot be calculated above the pressure corresponding with the maximum in the pv isotherm. Lewis and Randall's fugacity rule applies only to a limited extent to vapours below the critical point of the solute gas, although it holds approximately as a limiting law for all gaseous solutions above the critical temperature. The activity functions of certain solute gases below the critical temperature are tabulated; from these, the values for other mixtures and at other temperatures may be derived.

S. K. TWEEDY.

Thermodynamic deduction of Maxwell's distribution law. A. SCHÜKAREV (Physikal. Z., 1928, 29, 181—182).—Maxwell's deduction is open to criticism, although the law is in accord with experience. An attempt has therefore been made to deduce the law from thermodynamic principles.

R. A. MORTON.

Statistical series of the Charlier A type and Boltzmann's equation. U. WEGNER (Z. Physik, 1927, 45, 539—547).—Mathematical. R. W. LUNT.

Deduction from two diffusion equations. W. HERZ (Z. anorg. Chem., 1928, 170, 246).—Combining Gapon's relation $D\sqrt{n}=\text{constant}$ (this vol., 134), where D is the diffusion coefficient of a substance, and n the number of atoms in the molecule, with the well-known equation $D\sqrt{M}=\text{constant}$, where M is the mol. wt., there results the relation $\sqrt{M}/\sqrt{N}=\text{constant}$, which proves to be in satisfactory agreement with the experimental data. R. CUTHILL.

Equation of state for binary mixtures of methane and nitrogen. F. G. KEYES and H. G. BURKS (J. Amer. Chem. Soc., 1928, 50, 1100—1106).—Compressibility data for three mixtures of nitrogen and methane between 0° and 200° and up to about 300 atm. are recorded. The equation of state for the mixtures is of the same form as that for the separate gases (cf. A., 1927, 507, 719), and the constants, provided the slight curvature of the isometrics is neglected, are linear functions of the weight percentage composition (W) of the mixtures and of the constants for the pure gases. Thus, $A=(A_k W_{N_2} + A_{CH_4} W_{CH_4})^2$, $\beta=\beta_{N_2} W_{N_2} + \beta_{CH_4} W_{CH_4}$, etc. The relationships may not be so simple when the molecular "diameters" of the two constituents are less nearly equal than in the present case.

S. K. TWEEDY.

Brownian displacements and thermal diffusion of grains suspended in a non-uniform fluid. S. CHAPMAN (Proc. Roy. Soc., 1928, A, 119, 34—54).—The distribution in magnitude and direction of the Brownian displacements, during any assigned interval, of small spherical grains suspended in a fluid (liquid or gaseous) is obtained for the general case of a non-uniform fluid. The non-uniformity may refer to temperature, composition, or any other property which affects the coefficient of diffusion (D) of the grains. The distribution function contains terms additional to that given by Einstein for the uniform case; some of these are definitely determined, but one term contains an undetermined constant which requires more detailed physical analysis for its evaluation. It is surmised that this coefficient vanishes in the case of Brownian particles which are large compared with the mean free path of the surrounding molecules. The steady distribution of grains in a fluid is considered for the case when the temperature (T) of the fluid is non-uniform. It is found that if the density of the grains is the same as that of the fluid, so that there is no tendency for them to settle in the lower strata, then the concentration n is inversely proportional to D , which varies with T more rapidly in liquids than in gases. In the case of a Maxwellian gas, D is independent of T , so that "Brownian" thermal diffusion, like true gaseous thermal diffusion, is not operative. In other fluids, the grains will tend towards the cooler regions. When the densities of the grains and fluid are unequal, it is shown that with a uniform temperature gradient nD is not constant, but varies as a power of T . The order of magnitude of the various effects is estimated, and it is shown how their accuracy might be experimentally tested. The present theory may be applicable to the Ludwig-Soret effect in liquid solutions for which the solute molecules are large and non-ionised.

L. L. BIRCUMSHAW.

Molecular displacements in diffusing gas mixtures. S. CHAPMAN (Proc. Roy. Soc., 1928, A, 119, 55—60).—The arguments used in the consideration of the Brownian motion of grains suspended in a fluid (cf. preceding abstract) are applied to ordinary gas mixtures. For a perfect gas mixture in which the concentration of one kind of molecule is very small, it is shown that if the molecules are rigid elastic spheres, and if the rare molecules are much the lighter, the spreading of any particular cluster of molecules will be accompanied by a movement towards the hot region; on the other hand, if the rare molecules are much the heavier the spreading will be associated with a movement towards the colder regions, unless their diameter is small (less than half that of the other kind of molecule present). The spreading is not symmetrical relative to the mean motion. In gas mixtures of small concentration, the product (concentration) \times (coefficient of diffusion) is not a constant.

L. L. BIRCUMSHAW.

Entropy and thermodynamic potentials of real gases and mixtures of real gases, and a mass action law for chemical reaction between real gases. I. General thermodynamic relations. J. A. BEATTIE (Physical Rev., 1928, [ii], 31, 680—690).—Theoretical. General thermo-

dynamic equations are deduced for the energy, heat content, entropy, and thermodynamic potentials of gas mixtures, and the chemical potential of a gas in a mixture in terms of the independent variables p and T , and V and T . Two forms of the mass action law are deduced, p and T , or V and T , being chosen as the independent variables. A. A. ELDRIDGE.

Group theory of homopolar chemical combination. W. HEITLER (Z. Physik, 1928, 47, 835—858).—Mathematical. An extension of the theory of Heitler and London (A., 1927, 923). J. W. SMITH.

Differential equations of a reacting mixture. R. D. KLEEMAN (Phil. Mag., 1928, [vii], 5, 620—629).—The results obtained from the generalised equations for a reacting mixture accord with that obtained previously (this vol., 239). The mass-action constant is usually a function of the temperature, volume, and masses of the constituents. In special cases the constant may be a function of the temperature alone. A. E. MITCHELL.

Decomposition of carbon dioxide at low pressure under the action of the electric current. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1928, 186, 1119—1121; cf. this vol., 477).—The final equilibrium is independent of the intensity of the current between 0 and 2 milliamp., but is attained most rapidly with currents of high intensities. During the first moments of the passage of a current of medium intensity the rate of dissociation is proportional to the duration and intensity of the current. It decreases when the pressure is increased, and is less for a continuous current than for a spark discharge although the temperatures developed are approximately the same (2100—3000°). J. GRANT.

Theory of the decomposition of methane. O. K. RICE (Proc. Nat. Acad. Sci., 1928, 14, 118—124; cf. this vol., 483).—The decomposition of azomethane is said to result from activation by collision, the chance of reaction of an activated molecule depending on the energy in the manner to be expected if reaction is due to energy which is localised in a particular centre. W. E. DOWNEY.

Dielectric constants of solutions of electrolytes. H. HELLMANN and H. ZAHN (Z. physikal. Chem., 1928, 132, 399—400).—Polemical (cf. this vol., 14). H. F. GILLBE.

Formation and stability of metallic complexes in solution. P. JOB (Ann. Chim., 1928, [x], 9, 113—203).—An extended account of work already published (A., 1923, i, 307, 902; 1925, ii, 389, 471, 887; 1926, 571, 791; 1927, 205, 546). H. BURTON.

Cryoscopic measurements on aqueous solutions of resorcinol and pyrocatechol. F. BOURION and C. TUTTLE (Compt. rend., 1928, 186, 1124—1126).—Solutions of resorcinol and pyrocatechol were examined at concentrations 0.75—3.0*M* and 0.375—1.25*M*, respectively. The f.p. data suggest the existence of equilibria between simple and triple molecules, whilst at 100° the equilibria are between simple and double or triple molecules at low or high concentrations, respectively. The calculated heats of association of three simple molecules to form a triple

molecule are +600 and -2400 g.-cal. (at constant volume) for resorcinol and pyrocatechol, respectively. J. GRANT.

Equilibrium between methoxide and hydroxyl ions in methyl alcohol-water mixtures. III. Calculation of the equilibrium constant from the dissociation constants of methyl alcohol and water. A. UNMACK (Z. physikal. Chem., 1928, 133, 45—50; cf. this vol., 18).—The equilibrium constant for the process $\text{OMe}' + \text{H}_2\text{O} \rightleftharpoons \text{OH}' + \text{MeOH}$ may be calculated from the equation $K' = K_M(W)/K_M(M)$, where $K_M(W)$ is the dissociation constant of water in methyl alcohol and $K_M(M)$ that of methyl alcohol (in methyl alcohol?). $K_M(W)$ is given by $K_M(W) = K_W(W) \cdot V_W^H(H) \times V_W^H(\text{OH})$, where $V_W^H(\text{OH})$ is the partition coefficient of the hydroxyl ion, and $V_W^H(H)$ the partition coefficient of the hydrogen ion between methyl alcohol and water. From this, the equation $K' = [K_W(W)/K_M(M)] [V_W^H(H)]^2 \cdot S(H)$ follows, $S(H)$ being the equilibrium constant for the solvation equilibrium of the hydrogen ion in mixtures of water and methyl alcohol. All the quantities in this equation are known. By taking values for $K_M(M)$ obtained by hydrolysis and potentiometric measurements, respectively, and values for $V_W^H(H)$ calculated by different methods, a number of values for K' are found ranging from 0.98 to 2.00. All these values are higher than those previously found. The reasons for this are discussed. L. L. BIRUMSHAW.

Influence of neutral salts on acid-salt equilibria. II. Dissociation constants of citric acid. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1928, 47, 558—575; cf. A., 1927, 829).—Measurements have been made of the p_H of mixtures of citric acid and its potassium salts at 18°, and the three dissociation constants of citric acid calculated. These are $K_1 = 8.2 \times 10^{-4}$, $K_2 = 1.77 \times 10^{-5}$, $K_3 = 3.9 \times 10^{-7}$. The effect of neutral salts on the p_H of the solutions has been studied. Anions are relatively inactive, but there is a well-marked cation effect in the order (Cs, Rb) < K = NH₄ < Na < Li. The influence of potassium chloride can be calculated approximately from the Debye-Hückel equation, but this does not give good results for sodium and lithium salts. The calculated average size of the ions in mixtures of di- and tri-citrate is 6.2×10^{-8} , but a constant value is not obtained for the citric acid-monocitrate mixtures, and it seems that the activity coefficient of the undissociated acid is much larger than unity at moderate concentrations. It is proposed to replace for practical purposes the true dissociation constants quoted above, which refer to infinite dilution, by "acid strengths," which represent the true dissociation constants corrected for the activity coefficients of the components. W. A. RICHARDSON.

Equilibrium law of electrolytes and their conductive power. K. JABŁCZYŃSKI (Rocz. chem., 1928, 8, 22—30).—The equation $\lambda_\infty = \lambda + d\lambda^{4/3}N^{1/3}$, connecting the conductivity and the concentration of an electrolyte (compare Jabłczyński and Wisniewski, A., 1922, ii, 190), is applied to measurements made by different authors, and shown to give better results than Debye and Hückel's equation. In some cases,

e.g., sodium and lithium chloride, the equation does not hold, but this is due to hydration of the ions, and on applying the necessary corrections the behaviour of these salts is found to be normal.

R. TRUSZKOWSKI.

Vapour equilibrium of aqueous glycerol solutions. D. F. STEDMAN (Trans. Faraday Soc., 1928, 24, 289—298).—A distillation method which is described has been employed to determine the composition of vapour in equilibrium with aqueous solutions of glycerol at temperatures from 50° to 200° and pressures between 60 and 760 mm., with an accuracy of 0.1—0.5%. Values for the vapour pressure of anhydrous glycerol for the same temperature range have been determined with an accuracy of approximately 1%, and average values for the latent heat of evaporation over each 10° interval have been calculated. M. S. BURR.

Condition of strong electrolytes in concentrated solution. I and II. Nitrates. H. VON HALBAN and J. EISENBRAND (Z. physikal. Chem., 1928, 132, 401—432, 433—455).—I. The displacement of anion absorption bands in the presence of cations has been examined in detail for the nitrate ion band at 300 μ , using concentrated solutions of alkali nitrates and also dilute solutions of the nitrates in concentrated solutions of other salts. All cations influence the absorption of the nitrate ion, which is in the same condition in a concentrated nitrate solution as in a dilute nitrate solution having a high cation concentration. The less easily deformed the cation, the greater is its influence on the anion, whilst the dielectric constant of the solvent is of considerable importance as regards the magnitude of the effect. The displacement of the band decreases on passing down a group of the periodic table, and in the case of the alkali metals changes sign. No influence is manifested by heavy metal cations such as the mercuric, cupric, and nickelous ions at the low concentrations at which the alkali metals are active. Schäler's observation, that Beer's law is not valid for these nitrates at even low concentrations, is not due to a change in the absorption of the nitrate ion, but is a cationic effect. Other anions present in the solution affect the extent, but not the nature, of the displacement. For a given concentrated nitrate solution there exists a dilute nitrate solution containing a different salt of the same cation, such that the two solutions possess at all wave-lengths identical absorption.

The displacement effect is discontinuous, and is due to the formation of a new type of absorbing molecule which contains both the nitrate ion and the cation.

II. Measurements have been made of the absorption spectrum of nitric acid in solutions of widely varying concentration in water and in aqueous solutions of perchloric, sulphuric, and phosphoric acids, and also in dilute ethyl ether, acetic acid, ethyl alcohol, and hexane solution. The spectra of the dilute aqueous solutions are identical with those of the corresponding nitrate solutions. At concentrations below about 10N the extinction-wave-length curves of all the aqueous solutions intersect at a common point. The extreme variations exhibited

by the spectrum over this concentration range cannot be ascribed to the presence of undissociated molecules of nitric acid, and the possible formation of ionic pairs or of complex ions is suggested. In ether and in acetic acid solution, nitric acid exists to the extent of about 60% as associated ions; this is the case for concentrated aqueous solutions, the remainder consisting of undissociated molecules. The spectra of the solutions in hexane resemble those of the esters, the greater part of the acid being undissociated. Solutions in aqueous sulphuric acid have spectra which change from the first type to the second as the sulphuric acid concentration increases. The totally different spectrum exhibited by concentrated sulphuric acid solutions of nitric acid is ascribed to the presence of nitric anhydride.

H. F. GILLBE.

Graphical methods and empirical formulæ for the study of electrolytic dissociation. E. DENINA (Notiz. chim. ind., 1927, 2, 491—497; Chem. Zentr., 1927, ii, 2648).

p_H of buffered salt solutions. J. B. O'SULLIVAN (Trans. Faraday Soc., 1928, 24, 198—300).—The effect of salt solutions on the p_H values of buffer solutions has been investigated. In most cases a lowering of the p_H of both buffer and salt solutions was observed. The results obtained are in agreement with Haynes' observations (Biochem. J., 1921, 15, 440).

M. S. BURR.

Activity coefficients of small ions. H. MÜLLER (Physikal. Z., 1928, 29, 78—82; cf. A., 1927, 626).—Theoretical. W. E. DOWNEY.

Activity of hydrogen ions in aqueous solutions of beryllium sulphate. M. PRYTZ (Trans. Faraday Soc., 1928, 24, 281—288).—The p_H values of solutions of beryllium sulphate of different concentrations, both in water and in aqueous sulphuric acid, have been determined electrometrically at different temperatures. Making certain assumptions, values for the "percentage hydrolysis," α , of beryllium sulphate have been calculated. For the more dilute solutions α apparently increases with temperature, but decreases in more concentrated solutions. As concentration increases the value of α falls to a minimum and then increases. This may be explained by the increase in the activity of the hydrogen ions due to increasing concentration of beryllium sulphate. By comparing solutions of beryllium sulphate with equivalent solutions of magnesium sulphate containing sufficient added sulphuric acid to yield the same values of p_H , an attempt has been made to ascertain the true degree of hydrolysis of solutions of beryllium sulphate. The curve of corrected values of α plotted against concentration, however, still shows a pronounced minimum. M. S. BURR.

Activity coefficients of gases in aqueous salt solutions. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, 4, 271—284).

Activity coefficients of non-electrolytes in aqueous salt solutions from solubility measurements. Salting-out order of the ions. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, 4, 285—290).

Activity coefficients of the undissociated part of weak electrolytes. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, 4, 291—318).

Activity coefficients of nitric acid in aqueous solution. E. ABEL, O. REDLICH, and B. VON LENGYEL (Z. physikal. Chem., 1928, 132, 189—207).—From measurements of the f.-p. depression of nitric acid solutions containing 0.00526—4.009 g.-mol. of acid/1000 g. of water the authors have calculated the activities and activity coefficients of both constituents of the solutions, and the free energies of dilution of the acid. The activity coefficient of the acid is minimal in an approximately 0.4*N*-solution.

R. CUTHILL.

Activity coefficients of aqueous solutions of lead chloride at 25°. A. J. ALLMAND and E. HUNTER (Trans. Faraday Soc., 1928, 24, 300—306; cf. A., 1927, 1030).—Electrometric measurements have been made on the cell Pb(amalgamated)|aqueous PbCl₂|AgCl(solid)|Ag, under air-free conditions at 25°, at concentrations between saturation and 0.00006*M*. By plotting the logarithm of the concentration against the *E.M.F.*, a curve is obtained which is convex to the axes at high concentrations and concave at low ones. The form of the latter part of the curve is due to the solubility of silver chloride. From the results the mean activity coefficients of the dissolved lead chloride have been calculated for concentrations down to 0.0003*M*. The results are in fairly good agreement with Lewis and Randall's deductions from some of Brönsted's earlier measurements (A., 1906, ii, 834). It is suggested, however, that their values for the activity coefficients of barium and cadmium chloride solutions may need revision.

M. S. BURE.

Concentrated solutions. V. Experimental determination of the thermodynamic activity of the constituents of binary mixtures of organic compounds. (MLLE.) M. ROLAND (Bull. Soc. chim. Belg., 1928, 37, 117—140).—The vapour pressures of binary mixtures of organic compounds have been determined at various temperatures and concentrations by Kohnstamm's method, one of the constituents in each case having a negligible vapour pressure at the temperature concerned. The experimental error, which is dependent on the pressure, varied from 0.15 to 4.0%. All the systems studied had vapour pressures higher than required by the law of ideal solutions, and mixtures of acetone with diisomyl or with *sec.*-butylcyclohexane showed points of inflexion on the total pressure-concentration curves which gradually disappeared at temperatures removed from the critical solution temperature (−11.2° and −7.1°, respectively). The anomalies are less marked for mixtures of *sec.*-butyl alcohol with nitrobenzene, aniline, ethyl bromide, isopentane, or carbon disulphide, and of *sec.*-butyl chloride with nitrobenzene, and the curves all tend towards those of ideal solutions at the higher temperatures. The thermodynamic activity coefficients, calculated by the method of Lewis and Randall, are shown to be greater than unity. Since the activity of one substance considered as solvent in a very concentrated solution of the other component equals that of the

latter considered as a solute in a very dilute solution of the former, multiplied by a factor depending on the ratio of the states of reference chosen in each case, it is possible to calculate the activity of one component from that of the other. J. GRANT.

Oxygen-, acid-, and base-combining properties of blood. III. Validity of hydrogen-ion activity determinations by the hydrogen electrode in systems containing carbonic acid, carbonates, hæmoglobin, carbon monoxidehæmoglobin, and methæmoglobin. IV. The apparent first dissociation constant, pK_1 , of carbonic acid and the activity coefficient of the hydrogen carbonate ion in solutions of hæmoglobin, methæmoglobin, cyanhæmoglobin, and nitric oxide-hæmoglobin at varying ionic strengths. W. C. STADIE and E. R. HAWES (J. Biol. Chem., 1928, 77, 241—264, 265—302).—III. The values of the hydrogen-ion activity of these systems given by *E.M.F.* determinations with the hydrogen electrode differ by an indeterminate amount from the absolute values; the difference is due to faulty assumptions in regard to the hydrogen-ion activity of the reference solution and the liquid junction potentials which are involved. An approximate evaluation of the error due to liquid junction potentials is made. The junction potentials between saturated potassium chloride and solutions of the above substances of widely varying concentration are shown to be negligible when the Bjerrum extrapolation is made. The following evidence is advanced to show that the hydrogen electrode is a reversible source of *E.M.F.* in the above solutions. The *E.M.F.* is a function of the logarithm of the partial pressure of hydrogen over a wide range. Carbon monoxide is without effect on the *E.M.F.* of the electrode at partial pressures as great as 330 mm. The heats of ionisation of carbonic acid are identical in the presence and in the absence of hæmoglobin. There are no appreciable irreversible reactions in the presence of the electrode. Discrepancies are pointed out in the free energies and heats of ionisation of carbonic acid when calculated from *E.M.F.* data on the one hand and from conductivity and thermal data on the other. The hydration of the hydrogen ions in hæmoglobin solutions is discussed.

IV. Values of K_1 and $\gamma_{\text{HCO}_3^-}$ have been calculated from the hydrogen electrode determinations in solutions of varying ionic strength and varying concentration of the above derivatives of hæmoglobin. The results can be expressed in the equations, $pK_1 = pK_* - \beta\sqrt{\Gamma}$ and $\log \gamma_{\text{HCO}_3^-} = -\beta\sqrt{\Gamma}$, where $\beta = 0.54 - \sigma[\text{Hb}]$ and $pK_* = 6.33 - \rho[\text{Hb}]$. σ and ρ are constants characteristic of the hæmoglobin derivative present. It follows that $\gamma_{\text{HCO}_3^-}$ may be equated to two activity coefficients which measure respectively the effects of salts and of the hæmoglobin derivative on $\gamma_{\text{HCO}_3^-}$; and permit the calculation of pK_1 over a wide range of hæmoglobin and salt concentration. The pK_1 in the red blood-cell is calculated to be 5.98 and 5.87 for the oxidised and reduced states, respectively, and these values are confirmed by direct determinations in hæmolysed human, horse, and ox cells. R. K. CANNAN.

Oxygen-, acid-, and base-combining properties of blood. V. Extension of the Debye-Hückel theory of ionic interaction to hæmoglobin, hydrogen carbonate-sodium chloride systems. W. C. STADIE (J. Biol. Chem., 1928, 77, 303—323; cf. preceding abstract).—Equations are developed on the basis of the Debye-Hückel theory which permit the calculation of the activity coefficients of the hydrogen carbonate ion in solutions of hæmoglobin varying from 0 to 20 millimols. and salt from 0 to 0.5 mol. per litre. The values calculated agree within experimental error with those observed. Theoretical and experimental reasons are given for assigning to the colloidal hæmoglobin ion an ionic strength valency of 1. The two activity coefficients of the hydrogen carbonate ion in hæmoglobin solutions are related to the ionic diameter of the ion and to the influence of hæmoglobin on the dielectric constant of water. Hæmoglobin and its derivatives appear to raise this constant.

R. K. CANNAN.

Internal equilibrium in liquid sulphur. I. D. L. HAMMICK, W. R. COUSINS, and E. J. LANGFORD (J.C.S., 1928, 797—802).—By chilling sulphur heated at 150—300° and analysing the product, the equilibrium between S_{λ} and S_{μ} in the molten state has been studied. The temperature-composition curve does not become vertical until the amount of S_{μ} exceeds about 40%, as against 33% in Smith and Holmes' experiments (A., 1906, ii, 157). This would seem to show that the method of chilling employed by these authors did not entirely prevent the reversion of S_{μ} to S_{λ} , and that the vertical part of the curve is not a true allotropic line, but is merely a consequence of ineffective chilling.

R. CUTHILL.

Influence of electric and magnetic fields on crystallisation of supercooled liquids. W. KONDOGURI (Z. Physik, 1928, 47, 589—601).—The number of crystallisation centres in supercooled piperine and salol increases considerably under the influence of electric and magnetic fields. The action of the fields is investigated by a microscopic method. For an electric field, the number of crystallisation centres varies directly as the strength of the field. For a given field strength the number of centres increases with the time of application of the field up to a limiting value. If the field strength is then increased, the number of centres again increases until a new boundary value is reached. Similar results were obtained with the radiation from radium bromide, as well as with a magnetic field, but the action of the radiation from radium on salol gives rise to some deviation from the results obtained by other methods. The explanation of this has not yet been reached.

A. J. MEE.

Dissociation of formic acid vapour and the equilibrium between aqueous formic acid solutions and the vapour. M. S. VREVSKI and A. A. GLAGOLEVA (Z. physikal. Chem., 1928, 133, 370—376).—See this vol., 18.

Equilibrium between vapour and liquid in solutions of formic acid and benzene. M. S. VREVSKI, N. A. HELD, and S. A. SCHUKAREV (Z. physikal. Chem., 1928, 133, 377—389).—See this vol., 19.

Dissociation of acetic acid vapour and equilibrium between aqueous solutions and vapour of acetic acid. M. S. VREVSKI, K. P. MISCHTSCHENKO, and B. A. MUROMCEV (Z. physikal. Chem., 1928, 133, 362—369).—See this vol., 18.

Ice-point of the thermometer scale. A. MICHELS and F. COFFERIER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 1017—1020).—The ice-point as usually determined is subject to inconstancy due to dissolved gases or impurities from the containing vessel. By preparing ice from supercooled gas-free water, out of contact with air, the variation obtained was less than 0.001° as measured by a mercury thermometer. When determined by electrical methods the temperature was constant to 0.00023°. The influence of dissolved silicates appears to be very small. It is suggested that the triple point of water should be made the first point on the temperature scale in place of the ice-point, 0° being defined as 0.007° below the triple point of water.

M. S. BURR.

M.-p. curve of helium and Nernst's heat theorem. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 952—956).—A reply to van Laar (A., 1927, 718). The variations in pressure for 0.1° intervals of temperature have been determined for the m.-p. curve of helium between 1.2° and 3.0° Abs. On plotting d^2p/dT^2 against T a sharp maximum is obtained at 1.85° Abs. Neither this curve, however, nor the p - T curve suggests that there should be a minimum of pressure in the neighbourhood of 1° Abs. as required by van Laar (*loc. cit.*). If dp/dT for the m.-p. curve approaches zero at $T=0$, the entropies for the solid and liquid phases should be equal at $T=0$. This is in accordance with Nernst's heat theorem, and, even if there is a slight inclination of the p - T curve to the T -axis at $T=0$, this is not necessarily a serious contradiction of the theorem. According to van Laar's view dp/dT must become infinite at absolute zero.

M. S. BURR.

M.-p. line of helium and Nernst's heat theorem. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 957).—A reply to Keesom (cf. preceding abstract). Only further experiments can give with certainty the course of the m.-p. line at temperatures below 1° Abs. and determine whether or not the conclusions derived from Nernst's heat theorem are correct.

M. S. BURR.

Accurate determination of the specific heats of salt solutions up to 80°; results for potassium nitrate and chloride solutions. F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1928, 50, 1005—1016).—An improved, compact twin adiabatic calorimeter, modelled after that developed by Richards and Gucker (A., 1925, ii, 848), is described. An improved method of water standardisation is also recorded. The specific heats of the above solutions, containing 1 mol. of salt to 25 mols. of water, are sensibly constant at 20°, 50°, and 80°, and do not exhibit the increase that Zwicky's theory requires (A., 1926, 462, 668).

S. K. TWEEDY.

Heat of formation of the compound HCl, HBr. C. DEL FRESNO (Z. anorg. Chem., 1928, 170, 222—

224).—Using a cycle similar to that employed by Born (A., 1920, ii, 156), the calculated heat of formation of the solid compound HCl, HBr (Klemenc and Kohl, this vol., 130) (assumed to have the constitution H_2Cl', Br') from the liquid halides is 27.2 kg.-cal. Since the heat of formation corresponding with the constitution H_2Br', Cl' is less than this, the first formula is probably the correct one.

R. CUTHILL.

Heats of dissolution and dilution of salts between infinite dilution and saturation. IV. Lithium bromide. E. LANGE and E. SCHWARTZ (Z. physikal. Chem., 1928, 133, 129—150).—The heats of dissolution and dilution of lithium bromide in aqueous solution have been measured at 25° up to the saturation concentration, viz., 32.26 mols./100 mols. of water. The specific heats of the solution over the whole concentration range have been calculated, and the temperature coefficient of the heat of dissolution has been determined. The concentration-heat of dissolution curve of lithium bromide resembles closely that of lithium chloride, although the slope of the differential heat of dissolution curve for the former is smaller at low concentrations and greater at high concentrations than for the latter. The difference between the initial and total heat of dissolution is +9105 g.-cal./mol., and is, despite the smaller molar saturation concentration, greater than the corresponding figure for the chloride, viz., +8100 g.-cal./mol.

H. F. GILLBE.

Thermal investigation of some important metallurgical reactions in a calorimeter working at high temperatures. W. A. ROTH and P. CHALL (Z. Elektrochem., 1928, 34, 185—199).—A calorimeter is described for use at high temperatures with an accuracy of 1%. For the study of reactions in which gases are evolved a specially designed adjunct is used. The following data are given: Specific heats: HCl+24.65H₂O at 50° 0.8860, at 22.5—50° 0.8822; HF+4.181H₂O at 50° 0.8719, at 20—50° 0.8653; Thüringer glass, 10—50° 0.1923; platinum, 13—50° 0.03225; white marble, 18—50° 0.1994; quartz, 12—50° 0.1844; silica (ignited), 18—50° 0.1816. Heat of vaporisation of water at 50°, —570 g.-cal./g. Heats of dissolution in HCl+24.65H₂O at 50°: CaO, +46,150 g.-cal.; Ca(OH)₂, +30,710 g.-cal.; CaSiO₃, +23,040 g.-cal.; MgO, +34,750 g.-cal.; Mg(OH)₂, +26,560 g.-cal.; Zn, +27,225 g.-cal.; ZnO, +12,470 to +12,545 g.-cal.; Zn(OH)₂, +10,115 g.-cal.; zinc spar, —4,470 g.-cal.; data for different forms of calcium carbonate are also given; in HF+4.181H₂O at 50° of quartz, +31,040 g.-cal.; sand, +31,415 g.-cal.; silica (precip.), +34,465 g.-cal.; silica with 33% of water, +34,490 g.-cal. Heats of formation at 50°: CaO+SiO₂=CaSiO₃ +19,660 g.-cal.; CaO+CO₂=calcite+42,470 g.-cal.; CaO+CO₂=aragonite+42,520 g.-cal.; CaO+H₂O=Ca(OH)₂+15,440 g.-cal.; MgO+H₂O=Mg(OH)₂+8,190 g.-cal.; ZnO+H₂O=Zn(OH)₂+2360 to +2440 g.-cal.; ZnO+CO₂=zinc spar+16,940 to +17,020 g.-cal.; Zn+½O₂=ZnO+82,825 to +82,905 g.-cal. Heat of transformation: calcite→aragonite at 50°=+48 g.-cal.; amorphous to crystalline silica, +3425 g.-cal.

H. INGLESON.

Molecular structure of liquids and solids. G. ANTONOV (Bull. Soc. chim., 1928, [iv], 43, 163—177; cf. A., 1907, ii, 334; 1918, ii, 437; 1919, ii, 392; 1925, ii, 865; 1926, 671, 786; 1927, 304).—The author postulates that when two phases, neither of which is solid, are in equilibrium with each other, they contain the same number of molecules per unit volume. Two methods of demonstrating the truth of this postulate are described, the first of which is based on general considerations, whilst the second depends on the use of expressions already obtained by the author for surface tension and pressure normal to the surface of the liquid as functions of the number of molecules per unit volume. The physical properties of liquids are discontinuous functions of the temperatures. The law of rectilinear diameters is shown to be incorrect, the so-called rectilinear diameter being in reality a broken line. The terms "normal" and "abnormal" liquid are misnomers since all liquids are associated. It is highly probable that at the m. p. of a solid the same number of molecules are present per unit volume in the solid and liquid phases.

H. INGLESON.

Anisotropy induced in photochloride by the Weigert effect. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, 132, 303—312).—Under the influence of linearly polarised light, sensitive silver chloride similar to that examined by Weigert (A., 1921, ii, 289), but without any binding material such as gelatin, becomes dichroic and doubly refracting. Many of the other photosensitive systems do not undergo this change, but sensitive films of cuprous bromide have been prepared. In the case of silver, it seems probable that the anisotropy arises from the elongated form of the colloidal particles of metal.

R. CUTHILL.

Influence of grain size on the dissociation pressure of solids. II. Lead carbonate. M. CENTNERSZWER and J. KRUSTINSONS (Z. physikal. Chem., 1928, 132, 185—188; cf. this vol., 10).—Lead carbonate prepared by passing a rapid current of carbon dioxide through a neutral solution of lead acetate at the ordinary temperature has grains of an average diameter 30 μ, whilst carbonate formed by the action of a slow current of carbon dioxide at 40° on an acetate solution acidified with acetic acid has grains only 15 μ in diameter, yet both preparations give the same values for the dissociation pressure, *p*, at 255—270°. The corresponding values for *p* are lower, on the other hand, for the product obtained by the action of a rapid stream of gas on an acidified solution at 40°, the grains here being 7.5 μ in diameter. In either case, however, the relation between *p* and the temperature, *T*, is of the form $\log p = a/T + b \log T + c$, where *a*, *b*, and *c* are constants. From the data obtained, the surface tension at the interface solid-gas is calculated to be about 63,000 dynes/cm.

R. CUTHILL.

Thermal dissociation of cadmium nitrate. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 249—250).—Anhydrous cadmium nitrate melts with decomposition at 325° instead of at 360° as stated in the literature. The decomposition which takes place according to the equation $2Cd(NO_3)_2 \rightleftharpoons 2CdO +$

$4\text{NO}_2 + \text{O}_2$ is reversible, and the equilibrium pressures for the temperature range 200—315° are recorded. From these results the heat absorbed in the decomposition is found to be 55,881 g.-cal.

O. J. WALKER.

Rubrene. VII. Dissociation pressure of rubrene peroxide at the ordinary temperature. C. MOUREU, C. DUFRAISSE, and L. GIRARD (Compt. rend., 1928, 186, 1166—1168).—The oxidation of rubrene in solution by free oxygen under the influence of light is a reversible phenomenon; formation or dissociation of the peroxide takes place according to the pressure of the oxygen on the liquid surface. The dissociation pressure is about 0.5 cm. of mercury at 16°. An analogy with the peroxidation of hæmoglobin is indicated.

J. GRANT.

System sodium-tin. W. HUME-ROTHERY (J.C.S., 1928, 947—963).—The study of cooling curves and microscopical examination have confirmed the existence of the compounds reported by Mathewson (A., 1905, ii, 634), and have demonstrated the existence of others. The liquidus curve has maxima corresponding with the compounds Na_2Sn (m. p. 478°) and NaSn (m. p. 578°), the latter compound undergoing a polymorphic transformation at 483°. Breaks on the curve show the existence of Na_4Sn (m. p. 408°) and Na_2Sn_3 (m. p. 479°), the latter of which decomposes into NaSn and Na_2Sn below 357°. The compound Na_3Sn exists only in the solid state, and above 377° decomposes into Na_4Sn and Na_2Sn . Compounds NaSn_3 , NaSn_4 , and NaSn_6 , in addition to the compound NaSn_2 , are formed by peritectic reactions. In no case has the formation of solid solutions been observed.

R. CUTHILL.

Two kinds of martensite. K. HONDA and S. SEKITO (Nature, 1928, 121, 744).—The mechanism of the formation of α - and β -martensite is considered. It is concluded that in the outer layer of a quenched steel, where the cooling is rapid, the change austenite $\rightarrow \alpha$ -martensite (body-centred tetragonal) is partly arrested, and the change α -martensite $\rightarrow \beta$ -martensite (body-centred cubic) is completely hindered, so that this layer contains α -martensite with a little austenite. In the inner portion, where the cooling is less rapid, both changes take place almost completely, so that this portion contains almost pure β -martensite.

A. A. ELDRIDGE.

Equilibrium in the binary systems ethylenediamine-phenols. N. A. PUSHIN and L. SLADOVICH (J.C.S., 1928, 837—843).—By thermal analysis of binary mixtures of ethylenediamine with phenols, the formation of compounds has been detected, the numbers of mols. of phenol combining with 1 mol. of diamine being as follows (the respective m. p. are shown in parentheses): phenol, 2 (53.5°) or 4; *o*-cresol, 2 (48°); *p*-cresol, 2 (54°) or 6 (31°); pyrocatechol, 1 (73°), 2 (71°), or 3 (69.2°); guaiacol, 1 (51.5°), 2 (57.5°), or 6 (66.5°).

R. CUTHILL.

Systems hydrogen chloride-ethyl ether, and hydrogen chloride-acetone. D. McINTOSH (Bull. Chem. Soc. Japan, 1928, 3, 82—86).—Repetition of previous experiments on the above systems (A., 1913, i, 584) has confirmed the results then obtained;

the divergent results of Hirai (A., 1926, 908) are therefore to be rejected.

R. CUTHILL.

System beryllium oxide-silicon dioxide. F. MACHATSCHKI (Z. physikal. Chem., 1928, 133, 253—262).—Comparison of the Debye-Scherrer diagrams given by mixtures of beryllium oxide and silicon dioxide in proportions corresponding with the ortho- and meta-silicates indicates the existence, at temperatures between 1000° and the m. p., of the ortho-silicate phenacite. Both molten phenacite and molten mixtures of the two oxides yield when cooled rapidly crystalline beryllium oxide and a glass containing beryllium oxide; beryllium metasilicate cannot be obtained by this method, and is probably not stable in the crystalline condition.

H. F. GILLBE.

Equilibria between metals and salts in the molten state. VII. Tin, lead, stannous bromide, and lead bromide. VIII. Tin, lead, stannous chloride, and lead chloride. IX. Zinc, cadmium, zinc chloride, and cadmium chloride. R. LORENZ and G. SCHULZ (Z. anorg. Chem., 1928, 170, 247—256, 320—323, 324—326; cf. A., 1927, 518).—VII. The equilibrium $\text{Sn} + \text{PbBr}_2 \rightleftharpoons \text{SnBr}_2 + \text{Pb}$ in the molten state has been studied. Since the two metals and also the two salts are completely miscible, the system consists of three phases. At 400° and 600° the results agree satisfactorily with the requirements of the new mass law (A., 1924, ii, 761), but the classical expression yields values of the equilibrium constant which vary considerably. If bismuth is added to the metallic phase, the equilibrium is displaced somewhat, and there is a rather closer approximation to the requirements of the ideal mass law. Dilution of the salt phase with lithium bromide, on the other hand, has no appreciable effect on the equilibrium.

VIII. The equilibrium $\text{Sn} + \text{PbCl}_2 \rightleftharpoons \text{SnCl}_2 + \text{Pb}$ has been investigated at 500° and 600°, using methods more precise than those formerly employed (A., 1926, 799); the results are substantially the same.

IX. The equilibrium $\text{Zn} + \text{CdCl}_2 \rightleftharpoons \text{Cd} + \text{ZnCl}_2$ has been examined at 600°; the results are in satisfactory agreement with the new mass law, but not with the ideal law.

R. CUTHILL.

Equilibrium in the reactions of tin with water vapour and carbon dioxide. E. D. EASTMAN and P. ROBINSON (J. Amer. Chem. Soc., 1928, 50, 1106—1114).—The equilibria $\text{Sn}(l) + 2\text{H}_2\text{O}(g) = \text{SnO}_2(s) + 2\text{H}_2$ and $\text{Sn}(l) + 2\text{CO}_2 = \text{SnO}_2(s) + 2\text{CO}$ were investigated at 650—800° by a special dynamic and by static methods. The constants for the former reaction do not agree with those of Wöhler and Balz (A., 1921, ii, 633). The values for the equilibrium constant of the water-gas reaction calculated from the present results indicate that the directly determined values for this reaction are erroneous.

S. K. TWEEDY.

Equilibrium in the reduction of tungsten disulphide by hydrogen. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 189—192).—The equilibrium $\text{WS}_2 + 2\text{H}_2 = \text{W} + 2\text{H}_2\text{S}$ was investigated by the method employed for the analogous molybdenum reaction (this vol., 480). The values of $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ were measured for the range 795—1065°.

According to these results the heat of formation of tungsten disulphide is 73,400 g.-cal. Tungsten sulphide is more readily reduced than molybdenum sulphide.

O. J. WALKER.

Equilibrium (polarisation) composition of the liquid salt phase and the liquid alloy phase in a system composed of equiatomic quantities of sodium, potassium, and iodine. H. F. SILL (J. Physical Chem., 1928, 32, 466—470).—The equilibrium atomic ratios Na : K in the alloy obtained from the reactions at 700° between potassium iodide and sodium, and sodium iodide and potassium, are 11 : 1 and 9 : 1, respectively.

L. S. THEOBALD.

Effect of manganese content and speed of cooling on the separation of ferrite. R. ZOJA (Notiz. chim.-ind., 1927, 2, 559—560; Chem. Zentr., 1928, i, 248).—With constant manganese content the amount of ferrite is not a linear function of the carbon content; the deviation increases with increasing manganese content. With constant manganese content the quantity of ferrite which separates falls with increasing speed of cooling, and with constant speed of cooling it falls with increasing manganese content. The effect of the speed of cooling is the greater the higher is the manganese content.

A. A. ELDRIDGE.

Reciprocal salt pair $MgSO_4-Na_2(NO_3)_2-H_2O$. I. A. BENRATH [with H. BENRATH, W. BEU, J. CLERMONT, N. ILIEFF, S. KOJITSCH, H. PITZLER, and A. SCHLOEMER] (Z. anorg. Chem., 1928, 170, 257—287).—The above salt pair and the systems magnesium sulphate-magnesium nitrate-water, magnesium nitrate-sodium nitrate-water, sodium nitrate-sodium sulphate-water, and sodium sulphate-magnesium sulphate-water have been investigated at 15°, 25°, 50°, and 97°, and equilibrium diagrams constructed.

R. CUTHILL.

Systematic doctrine of affinity. XLVI. Measurement of oscillation of chemical affinity in crystalline dicarboxylic acids. W. BILTZ and G. BALZ (Z. anorg. Chem., 1928, 170, 342—346; cf. A., 1927, 1157).—From measurements of the dissociation pressures of crystalline ammonium salts of the dibasic fatty acids, the heats of dissociation of the acid and normal salts have been calculated. Both quantities oscillate on ascending the series, particularly near its beginning, the acids with an even number of carbon atoms giving the higher values. With the normal salts, the heat of dissociation of the first ammonia molecule is less than that of the second.

R. CUTHILL.

Salt-like hydrides. IV. J. KASARNOVSKI (Z. anorg. Chem., 1928, 170, 311—319; cf. A., 1927, 718).—From data for the heats of formation of the hydrides of lithium and the alkaline-earth metals and the electrode potentials of the metals, the normal potential at 25° of the negative hydrogen ion has been calculated to be -2.38 volts, by taking the solubilities of the hydrides to be equal to those of the corresponding fluorides. This figure leads to a value of 91.5 kg.-cal. for the energy of hydration.

R. CUTHILL.

Conductivity of electrolytes. I. Experimental and theoretical study of principles of design of the Wheatstone bridge for use with

alternating currents and an improved form of direct-reading alternating-current bridge. G. JONES and R. C. JOSEPHS (J. Amer. Chem. Soc., 1928, 50, 1049—1092).—The conditions essential for precision conductivity measurements are investigated. The best current source is a valve oscillator; a suitable circuit, giving 16 different frequencies between 500 and 2400 cycles, is given. Earthing at the mid-point of the bridge is inadmissible; an earthing system is described which maintains the telephone, when in null position, at earth potential and eliminates the variations in bridge reading observed when the current leads are reversed. Exterior disturbances should be shielded at the source. The cells should have a high constant, and the thermostat liquid must be oil. The relationship usually assumed between the resistances of the four arms of a balanced bridge is valid only if the phase angle between the voltage and the current is the same in two pairs of adjacent arms. Means of ensuring this are described. The capacity of the cell is balanced by a variable condenser in parallel with the adjacent resistance arm. The resistance of commercial resistance boxes at the frequencies used is a function of the frequency in the higher ranges and is not identical with the direct current resistance. The design and erection of boxes in which these errors are absent are considered. A direct-reading bridge is described, sensitive to 1 in 10^6 , which can be used with either direct or alternating current. The non-reactive ratio arms are readily adjusted to exact equality of resistance and the third resistance may be adjusted to 0.001 ohm.

S. K. TWEEDY.

Electrical conductance of nickel sulphate solution and ionic conductance of nickel. K. MURATA (Bull. Chem. Soc. Japan, 1928, 3, 47—53).—The conductance of aqueous solutions of nickel sulphate (0.0001—1M) was measured at 18° and 25°, and the equivalent conductance at infinite dilution calculated. The ionic conductance of nickel was found to be 45.1 at 18° and 53.0 at 25°, using Noyes and Falk's values for the sulphate ion. For 0.05M-nickel sulphate at 18° and 25° the relative viscosities are 1.0209 and 1.0175, and the degree of ionisation 0.3883 and 0.3939.

C. J. SMITHELLS.

Conductivity and catalytic action of trinitro-*m*-cresol in solution in ethyl alcohol. H. GOLDSCHMIDT, E. MARUM, and L. THOMAS (Z. physikal. Chem., 1928, 132, 257—272; cf. A., 1927, 1143).—The conductivity of a solution of the sodium salt of 2 : 4 : 6-trinitro-*m*-cresol in aqueous ethyl alcohol is greater than that of a solution of the same concentration in absolute alcohol by an amount which increases with increase in the relative amount of water. Slight alcoholysis occurs with the aniline salt, but when this is repressed by addition of aniline the behaviour is closely similar to that of the sodium salt. From conductivity determinations with trinitrocresol in aqueous and absolute alcohol, the degrees of dissociation and affinity constants, K_0 , have been calculated with the aid of Bjerrum's theory. The ratio of the values of K_0 for trinitrocresol and picric acid in solutions in which the proportion of alcohol to water is the same does not vary much with change in the relative amount of water present. Measurements

have also been made of the rate of esterification of acetic, phenylacetic, butyric, and isovaleric acids in aqueous and absolute alcohol in presence of trinitro-cresol as catalyst. As the quotient of the velocity coefficient at zero time, k_0 , by the hydrogen-ion concentration due to the catalyst has greater values than when picric acid is the catalyst, and also falls with decreasing concentration of catalyst, it appears that the catalytic action of an acid is not solely determined by the concentration of hydrogen ions or hydrogen-ion complexes. The depressing action of water on k_0 is greatest for phenylacetic and acetic acids, and least for isovaleric acid. R. CUTHILL.

Dispersion of conductivity and dielectric constant for strong electrolytes. P. DEBYE and H. FALKENHAGEN (Physikal. Z., 1928, 29, 121—132).—A relaxation time exists for ionic movements in strong electrolytes, and this quantity is important for the dispersion of conductivity and dielectric constant. The conception of a relaxation time follows from the dissymmetry of the density of charge in an ionic atmosphere, and it can be shown that a "braking" force must operate with increasing effect as the velocity of an ion increases. The consequences of dissymmetrical ionic atmospheres and variable frequencies have been worked out theoretically, but the results are as yet only qualitative, because the forces tending to retard ionic movement include a cataphoretic action (brought about by a moving ion in a solvent containing ion). This latter effect will be worked out separately.

For very small frequencies the forces on the moving ion and the Stokes frictional force are in phase, but for very high frequencies this no longer holds. The absolute value of the force on the ion steadily decreases with increasing frequency until it becomes zero with very high frequencies. The "braking" force is now composed solely of the Stokes force, so that the molecular conductivity of strong electrolytes with increasing frequency approaches the value for infinite dilution, if the cataphoretic effect is neglected. The theory is applied to the numerical data for potassium chloride. R. A. MORTON.

Electrode potential of nickel. I. Measurements in an atmosphere of hydrogen with reduced nickel powder. K. MURATA (Bull. Chem. Soc. Japan, 1928, 3, 57—69).—The potential of an electrode of powdered nickel in 0.05 and 0.005*M*-nickel sulphate solutions has been measured. By maintaining an atmosphere of hydrogen within the electrode vessel, and taking precautions to ensure the rigid exclusion of oxygen from the solution and electrode, definite and reproducible results were obtained. Calculating the ionic concentrations from the conductivity ratio, the electrode potential, in volts, for molar ionic concentration is -0.2508 at 18° , and -0.2496 at 25° . Using activities instead of concentrations, the corresponding values are -0.2492 and -0.2480 , respectively. From these figures, the change in free energy involved in the reaction $\text{Ni}^{++} + 2\text{O}^- = \text{Ni}$ has been computed. R. CUTHILL.

Calomel and silver chloride electrodes in acid and neutral solutions. Activity coefficient of aqueous hydrochloric acid and the single poten-

tial of the 0.1*M*-calomel electrode. M. RANDALL and (Miss) L. E. YOUNG (J. Amer. Chem. Soc., 1928, 50, 989—1004).—The irregular, high potentials previously recorded for the calomel electrode with 0.1*M*-hydrochloric acid are due to the presence of air (cf. Güntelberg, A., 1926, 1207); the true value is 0.3976 volt. It is predicted that hydrochloric acid below 11.62*M* will not react with mercury in absence of oxygen. From a detailed consideration of all previous f.-p., vapour-pressure, and *E.M.F.* measurements, the most probable activity coefficients of hydrochloric acid are tabulated for 1.2—16*M*-solutions at 25° , as well as the water activity in the solutions. From these results new values for standard electrode potentials are derived. The free energies of formation of HCl from the gaseous elements are: HCl (*aq.*), -31345 g.-cal., HCl (*g.*), -22741 g.-cal. The 0.1*M*-calomel electrode has a potential at 25° of -0.3341 volt in vacuum, and about -0.3354 volt in air. The conditions for the preparation of reproducible Ag|AgCl electrodes are investigated. S. K. TWEEDY.

Physical interpretation of electrolytic solution potentials. A. VON HIPPEL (Z. Physik, 1927, 45, 471—475).—The latent heat absorbed during the electrolytic transfer of 1 mol. of a metal from anode to cathode by a *N*-solution is shown to be the difference between the work associated with the chemical changes and the electrical energy. The former is equal to the difference between the difference of the heats of hydration of cations and anions and the corresponding difference of the work of removal of the positive ions. R. W. LUNT.

Potentials of manganese dioxides in electrolytes of various hydrogen-ion concentrations. T. J. MARTIN and A. J. HELFRECHT (Amer. Electrochem. Soc., April, 1928, 53; advance copy, 4 pp.).—Solutions of p_{H} value ranging from 1.2 to 7.9 were prepared by adding hydrochloric acid or ammonia to a 20% ammonium chloride solution (p_{H} 5.48), and the potentials of dry-cell electrodes, prepared from graphite and seven different samples of manganese dioxide, were measured in these various solutions. The potential of a given electrode is nearly independent of the p_{H} value of the solution over the range 2—7, but rapidly becomes more positive or more negative at lower or higher p_{H} values, respectively. In the solution of p_{H} 5.48 the electrodes prepared from samples of pyrolusite exhibited potentials ranging from 0.33 to 0.42 volt more positive than the saturated calomel electrode, but the one electrode prepared from artificial manganese dioxide gave the value 0.56 volt. H. J. T. ELLINGHAM.

Electrolytic capacitance of platinum-sulphuric acid cells. W. M. PIERCE (Physical Rev., 1928, [ii], 31, 470—475).—By recording the relation between current and time when a small, constant potential is impressed on the circuit containing the cell, it is found that the capacitance is not a function of the time constant. An empirical expression connects the capacitance with the frequency of the current flowing through it. A. A. ELDRIDGE.

Maxima on current-voltage curves. I. N. V. EMELIANOVA and J. HEYROVSKI. II. P. HERASY-

MENKO (Trans. Faraday Soc., 1928, 24, 257—267, 267—272).—See this vol., 371, 372.

Overvoltage of alloys. M. G. RAEDER and J. BRUN (Z. physikal. Chem., 1928, 133, 15—30).—From an examination of the current density-potential curves, the hydrogen overvoltage at alloy cathodes has been studied, with the object of determining the relative displacements which occur when the percentage composition of the alloy is changed, and particularly when new structural elements are formed as a result of the change in composition. The following systems were investigated: copper-nickel (homogeneous mixed crystals); silver-lead (simple eutectic system); lead-antimony and bismuth-tin (eutectic systems with incomplete mixed-crystal formation); silver-antimony (compound-forming system). In many cases, the course of the overvoltage differs from that previously assumed. In the mixed-crystal systems, the overvoltage may lie between the values for the pure components, but in some cases a pronounced rise occurs above the normal values for the components. The overvoltage of eutectic systems is not determined by the component of lowest overvoltage, but lies between the values for the components. The results for the lead-silver system are so unexpected that it is suggested that the structure of the system may be different from that usually accepted. The curves obtained for the system lead-antimony appear to confirm the existence of the compound Pb_4Sb (cf. Dean, Hudson, and Fogler, B., 1926, 93). In the compound-forming system silver-antimony, the overvoltage of the compound is practically identical with that of the component of highest overvoltage (antimony). The further course of the curve is irregular, and suggests that the structure of the alloy in this region is not fully understood.

L. L. BIRCUMSHAW.

Electrolytic decomposition of glass. P. SELÉNYI (Ann. Physik, 1928, [iv], 85, 643—644; cf. A., 1927, 1145).—In the electrolytic decomposition of glass, using a discharge tube with two copper electrodes, the whole being immersed in molten potassium nitrate, oxygen is liberated within the tube and is absorbed by the copper. The electrolysis proceeds quantitatively.

R. A. MORTON.

Electro-reduction of uranyl salts by means of the mercury dropping cathode. P. HERASYMENKO (Trans. Faraday Soc., 1928, 24, 272—279).—See this vol., 372.

Becquerel effect. G. ATHANASIU (Z. physikal. Chem., 1928, 133, 39—42).—A reply to the criticism of Lifschitz and Hooghoudt (A., 1927, 942) of the author's theoretical interpretation of Svensson's experimental results (cf. A., 1925, ii, 1067). It is stated that the author does not in general dispute Svensson's results, but emphasises the fact that the negative *E.M.F.* is not observed in the absence of polarisable electrodes.

L. L. BIRCUMSHAW.

[Becquerel effect.] J. LIFSCHITZ and S. B. HOOGHOUDT (Z. physikal. Chem., 1928, 133, 43—44).—A reply to AthanasIU (cf. preceding abstract). It had been already observed by Schmidt (Ann. Phys. Chem., 1899, 67, 563) that the Becquerel effect is not

exhibited at reversible electrodes. AthanasIU's view that the negative effect at the beginning of the exposure has its origin in the electrode is strongly opposed.

L. L. BIRCUMSHAW.

Kinetics of the dissociation of diatomic molecules. J. FRENKEL and N. SEMENOFF (Z. Physik, 1928, 48, 216—230).—The mechanism of the activation and deactivation of molecules and atoms is considered, and the relative part played by collisions and heat radiation is worked out on the basis of the "principle of detailed balancing." The several reactions which can take place when dissociation occurs through activation are considered, and by making use of the above principle, the relation between the velocity coefficients of the opposing reactions is obtained. The initial velocity of the whole reaction is calculated. The kinetics of the reaction without activation are then considered, as well as catalytic adsorption reactions, and the initial velocities are compared with each other and with that calculated for the reaction with activation.

A. J. MEE.

Autoxidation during slow combustion. E. W. J. MARDLES (J.C.S., 1928, 872—885; cf. B., 1926, 617).—Two experimental methods were employed. In the first the products of reaction of fuel-air mixtures passing through a suitably heated tube could be identified; in the second the mixtures were heated in a closed bulb to observe the rate of reaction as the temperature was slowly raised. Evidence was obtained of the formation of unstable peroxides of the fuels. Benzene and aniline are oxidised when added to hexane-air mixtures at temperatures below those at which they can be oxidised in the absence of the fuel. These effects are not due to the presence of hydrogen peroxide, since this substance when added to the fuel-air mixture exerts an effect similar to that shown by water. The hydrogen peroxide produced during combustion is a decomposition product of the very active unstable peroxides previously formed. Detonation in an engine using liquid fuel is due to the formation of organic peroxides which become concentrated in the nuclear drops during compression and ignite them when the temperature of detonation of the peroxide is reached. Detonation inducers, e.g., nitrogen peroxide or amyl nitrite, lower the temperature of spontaneous ignition, whilst organo-metallic compounds such as iron carbonyl and lead tetraethyl have the opposite effect. The last compound owes its effect to the formation of metallic lead by thermal decomposition.

H. INGLESON.

Burning of carbon disulphide. II. Velocity of uniform movement of flame in carbon disulphide-second combustible-air mixtures. A. G. WHITE (J.C.S., 1928, 751—763; cf. *ibid.*, 1922, 121, 2561; A., 1927, 115, 317, 524).—It has been previously shown that the burning of carbon disulphide near the limits for the propagation of flame is markedly hindered by the presence of other combustibles and that the limit combustion is probably catalysed by one of the products of its combustion. This behaviour is now observed over the whole range of inflammability. The mixtures containing about 1% of water vapour were fired in a long, horizontal tube closed at one end, measurements of flame velocity

being made photographically. The maximum flame speed (123 cm./sec. in a tube of 2.5 cm. diam.) is given by a mixture containing 8 vol.-% of carbon disulphide. The flame speed can be varied as much as 500% by alteration in the means of ignition, more powerful ignition increasing it. Flame speeds in dilute carbon disulphide-air mixtures are far more sensitive to oxygen content than in similar mixtures of normal combustibles, e.g., methane. The law of flame speeds of Payman and Wheeler (A., 1926, 689) breaks down for light petroleum-carbon disulphide-air mixtures, as values calculated from it are often more than 100% higher than the experimental ones. The reason for the failure of the law is probably that one combustible interferes with the burning of the other.

H. INGLESON.

Velocity coefficient for bimolecular reactions in solution. L. S. KASSEL (Nature, 1928, 121, 746—747).—Two factors, other than those mentioned by Norrish and Smith (this vol., 249), would lead to small and variable values of the probability coefficient P : the solvation and the complexity of the reactant molecules.

A. A. ELDRIDGE.

Thermal decomposition of hydrogen peroxide in aqueous solutions. B. H. WILLIAMS (Trans. Faraday Soc., 1928, 24, 245—255; cf. Rice and Reiff, A., 1927, 1035).—The decomposition is due to adsorption of molecules of hydrogen peroxide on the walls of reaction vessels and on dust present in solution. Glass that has been treated with cleaning agents possesses an activity comparable with that of dust. Preformed active points are present in silica vessels, and, with glass, active points in addition to those already present are formed by the action of the peroxide. An upper limit to the magnitude of the decomposition due to adsorption on the surface of the dust present has been determined by using a wax vessel. The decomposition in glass vessels is, for its first portion, a zero order reaction, which becomes unimolecular as the concentration of hydrogen peroxide in the bulk of the solution decreases. This can be explained from considerations of the relative rates of decomposition of molecules of hydrogen peroxide on the surface and that of their replacement. The decomposition of hydrogen peroxide in silica vessels follows a similar course except with high concentrations of hydrogen peroxide, when secondary effects probably come into action. L. F. GILBERT.

Oxidation of stannous hydroxide in sodium carbonate solution by means of air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, 3, 43—47).—The oxidation velocity of stannous hydroxide suspended in sodium carbonate solution is independent of the quantity of stannous hydroxide. Oxidation must therefore take place in solution and not in the solid phase. The effect of temperature and concentration of sodium carbonate on the reaction velocity is small. Sodium stannite is oxidised rapidly, whilst stannous hydroxide is oxidised very slowly by means of air.

C. J. SMITHELLS.

Oxidation of sodium sulphite in sodium carbonate solution with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, 3, 76—82; cf. A., 1927,

525).—The rate of oxidation when a current of air is passed through a mixed solution of sodium sulphite and sodium carbonate at 20° is independent of the sulphite concentration, but decreases with increase in the carbonate concentration, the relation between the velocity coefficient and the carbonate concentration, when this exceeds about 0.02*N*, being approximately linear. It therefore appears that the velocity measured corresponds with the rate of dissolution of oxygen in the sodium carbonate solution. Raising the temperature to 30° or 40° has little effect.

R. CUTHILL.

Hydrolysis of sucrose by hydrochloric acid in presence of alkali and alkaline-earth chlorides. C. F. KAUTZ and A. L. ROBINSON (J. Amer. Chem. Soc., 1928, 50, 1022—1030).—The rate of inversion of sucrose at 25° in presence of 0.1*N*-hydrochloric acid and of chlorides of potassium, sodium, lithium, calcium, strontium, and barium at concentrations between 0.05 and 3*N* is investigated. The activity of the hydrogen ion is probably the most important factor in determining the rate of inversion, although there is no simple relationship between the increased inversion rate and the activity coefficients of the hydrogen ion in solutions of the same acid and salt concentration containing no sucrose. For salt concentrations above 0.5*M* the equation of Schmid and Olsen (A., 1927, 21), $\log K = \log K_0 + rc$, where K_0 and r are constants, applies fairly well. The equation may be derived with the aid of the Debye-Hückel interionic attraction theory in the form $\log f_{H^+} = -\log f_{H^+} = B\mu_s + (a\sqrt{\mu_0})/(1 + A\sqrt{\mu_0})$, where the symbols have their usual meanings.

S. K. TWEEDY.

Mechanism of the hydrolysis of cellulose esters of the higher fatty acids. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 21—41).—An investigation has been made of the rate of hydrolysis of the cellulose esters of the higher fatty acids with alcoholic alkali. The reaction is bimolecular and may be represented, for the monoester, as follows: $R \cdot CO_2 \cdot C_6H_9O_4 + KOH = R \cdot CO_2K + C_6H_{10}O_5$, or, for the polymerised ester or the di- and tri-esters, the ester must decompose in successive stages. Since the reaction is heterogeneous, the surface of contact of the ester must be proportional to the concentration. By shaking, the rate of hydrolysis was increased by 50%. The influence of temperature between 0° and 38° may be expressed by Arrhenius' equation $\log k = -A/T + C$. Dilution of the alcoholic alkali with water reduces the velocity coefficient to a remarkable extent, and the effect may be represented by the following equation: $\log k = mC + n$, where C is the concentration of alcohol. A neutral salt also diminishes the velocity, but its influence is not important.

M. S. BURR.

Hydrolysis of cellulose acetate by alkali. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 42—53).—The rate of hydrolysis of cellulose acetate by aqueous alkali, to the extent of 50%, is in accordance with a unimolecular reaction. After this point the rate suddenly diminishes. If, however, the mixture is shaken, the unimolecular formula is valid until 90% has been hydrolysed, and the velocity, therefore, appears to be independent of the area of

the surface of contact. In alcoholic alkali of different concentrations, without shaking, the hydrolysis proceeds very rapidly for a short time and then the rate diminishes to a marked extent. When shaken with alkali of a rather high alcohol content the reaction is bimolecular, being proportional to the concentrations of alkali and ester. Since cellulose acetate of different origin has, under the same conditions, different rates of hydrolysis, this may be used as a test of the quality of the ester. M. S. BURR.

Hydrolysis of cellulose acetate during hydration. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 54—61).—During the production of acetone-soluble cellulose acetate by hydration of the acetone-insoluble primary cellulose triacetate with acetic acid, water, and sulphuric acid, hydrolysis takes place. The mechanism of the reaction appears to be the same as for the hydrolysis by alkali. If the quantity of water is regarded as unchanged, the hydrolysis velocities of the tri-, di-, and mono-acetates may be expressed by the following equations, respectively: $dx_1/dt=3k(b-x_1)$; $dx_2/dt=2k(x_1-x_2)$; and $dx_3/dt=k(x_2-x_3)$, where b is the initial concentration of the triacetate and x_1 , x_2 , and x_3 are the quantities of tri-, di-, and mono-ester transformed after the time t . The concentrations of the different constituents after the time t are, $C_{Tri}=be^{-3kt}$; $C_{Di}=3b(1-e^{-kt})e^{-2kt}$; $C_{Mono}=3b(1-e^{-kt})^2e^{-kt}$; and $C_{Cellulose}=b(1-e^{-kt})^3$. The values calculated on the basis of these equations, and on the assumption that the mono-ester and the regenerated cellulose are acetone-insoluble, agree with the experimental results of Hess and others (A., 1925, i, 1245). M. S. BURR.

Chemical dynamics in a rigidly coherent plane. D. H. BANGHAM (Phil. Mag., 1928, [vii], 5, 737—749).—Equations of the form $S=\text{constant} \times t^{1/m}$ shown by Bangham and Burt (A., 1924, ii, 392) to represent the rate of sorption of gases on glass surfaces are of wide application to the variation with time of processes involving the disturbance of the inner equilibrium of solids provided that the solid after disturbance remains rigidly coherent. It is assumed that the condition for rearrangement is the momentary occupation, by the groups of atoms, of a volume considerably greater than the average, and calculations are made of the mode of variation, during the progress of the reaction, of the force restraining their thermal movements. An extension of Hooke's law to the conditions in the interior of a solid requires that the intensity of the stress set up by the partial occurrence of a reaction should be equal to the difference between the hydrostatic pressures with which the initial and actual states of the solid would be in equilibrium. It then follows that the index m (above) is the ratio of the difference of volume between the activated and final states of the atomic groups to the difference between their initial and final volumes. These ideas offer an explanation of the dependence of the activity of a sorbent on its past history. The sorbed molecules are regarded as distending the rigidly coherent structure of the sorbent, which thus becomes stressed. Such a distension may occur even if the structure is sufficiently open to allow easy penetration of the free gas molecules. A. E. MITCHELL.

Influence of pressure on reaction velocity and the function of the medium. A. L. T. MOESVELD and (MISS) W. A. T. DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 1039—1053).—Theoretical. The condition of substances in mixed media is considered; e.g., dissolution of bornyl acetate in mixtures of alcohol and water may be expected to result in a non-homogeneous distribution of the components of the solvent, since alcohol will be attracted to the bornyl half of the molecule and water to the acid portion. The resultant force will cause a deformation of the ester molecule and have an influence on its reactivity. It may also be shown that the deformation should be greatest when there is only just sufficient of the better solvent present to keep the solute in solution. On account of the presence of associated molecules in pure solvent, similar if smaller effects may also be produced by the latter. When the external pressure is increased the molecules approach one another more closely, and all the effects depending on mutual forces are increased. This is borne out by experiment, and the pressure coefficient is greatest when the original effect may be expected to be greatest. The pressure coefficient also increases with pressure. It is shown, further, that rise of temperature, because of increased solubility in the medium, should cause a diminution in the pressure coefficient which can be compensated by increase in the concentration of soluble reactant or by the addition of another substance which so influences the medium that the reactant again approaches its critical solubility. These predictions have been verified experimentally for the hydrolysis of bornyl acetate by sodium hydroxide in 30% alcohol. The views put forward are independent of the mechanism of the activation process considered. M. S. BURR.

Relationship between velocity of hydrolysis by alkali and structure of esters. H. OLSSON (Z. physikal. Chem., 1928, 133, 233—252).—A number of esters have been prepared in a pure state and their rates of hydrolysis in presence of alkali measured. The velocity coefficients of the hydrolysis of some eighty-five typical esters, given in the literature, have been reduced to the same units and the results compared from the same point of view of structure. The velocity coefficient is mainly influenced by the strength of the acid component of the ester, but in other cases steric hindrance influences the velocity in the opposite sense. It may be that these two influences are manifestations of one fundamental property, viz., the force of dissociation of the separate components. H. F. GILBE.

Corrosion of iron and its anodic polarisation. H. J. DONKER and R. A. DENGK (Korrosion u. Metallschutz, 1927, 3, 217—222; Chem. Zentr., 1928, i, 251).—In dilute alkaline solutions (containing chloride), the surface of iron is uniformly attacked, but in more concentrated solutions point-corrosion predominates. Alkali hydroxide is more protective than carbonate. Sulphate solutions attack iron less than chloride solutions. Iron is not markedly attacked by neutral solutions containing dichromate, or dichromate and chloride, but it is vigorously attacked if the solution is not neutralised. A. A. ELDRIDGE.

Passivity of metals. E. S. HEDGES (J.C.S., 1928, 969—978; cf. A., 1926, 581; 1927, 25).—The lowest concentration of nitric acid which can passivate iron at 30° was repeatedly found to be 86 vol.-% of the acid *d* 1.42. To obtain reproducible results, it is necessary to pass the metal rapidly through the surface of the acid. Iron previously rendered passive by nitric acid becomes active when whirled at 3000 r.p.m. after a short induction period representing the time for removal of the film of oxide which causes the passivity. These facts are not explained on Smits' theory. When passive iron is heated in concentrated nitric acid, it dissolves at 74.5—75.5° independently of the concentration of the acid. Freshly ignited ferric oxide does not dissolve appreciably until this temperature is reached. This temperature does not correspond with an allotropic change in the iron. At -11° copper becomes passive in concentrated nitric acid, being covered by a visible film of oxide. Passivity produced by anodic polarisation and by chemical means is the same phenomenon and is the result of the formation of a film of oxidised material. A theory of anodic polarisation is advanced.

H. INGLESON.

Practical problems of corrosion. III. Formation of rust and its consequences. IV. Corrosion of wrought iron in relation to that of steel. V. Corrosion and protection at the contacts of dissimilar metals. U. R. EVANS.—See B., 1928, 300.

Action of hydrochloric acid on extra-pure aluminium. J. CALVET.—See B., 1928, 302.

Corrosion of aluminium. W. GUERTLER.—See B., 1928, 302.

[Catalytic] synthesis of methyl alcohol from carbon monoxide and hydrogen. W. K. LEWIS and P. K. FROLOCH.—See B., 1928, 359.

Induction of reaction between chromic acid and a manganous salt by arsenious acid. R. LANG and J. ZWERINA (Z. anorg. Chem., 1928, 170, 389—396).—Reaction may be induced in a mixed solution of a chromate and a manganous salt in a 0.5—1*N*-solution of sulphuric or hydrochloric acid by addition of arsenite (cf. this vol., 605), the manganous salt being oxidised to the manganic state, and the chromate reduced by the arsenite. The chromic acid is thus the actor, and the manganous salt the acceptor. At the start, the induction factor has the value 0.5, independent of the concentration of the acceptor, which is most readily accounted for by supposing the main stages in the reaction to be $\text{Cr}^{\text{VI}} + \text{As}^{\text{III}} = \text{Cr}^{\text{IV}} + \text{As}^{\text{V}}$, and $\text{Cr}^{\text{IV}} + \text{Mn}^{\text{II}} = \text{Cr}^{\text{III}} + \text{Mn}^{\text{III}}$. As the reaction proceeds, the value of the induction factor falls, owing to reaction of the arsenious acid with manganic salt; this reaction may be catalytically accelerated by addition of iodine. R. CUTHILL.

Catalytic action of mineral waters. F. C. GAISSER (Z. angew. Chem., 1928, 41, 401—407).—The benzidine reaction has been investigated for a number of naturally occurring waters. Those showing a positive reaction invariably contain ferrous and/or manganous ions, but the converse does not hold. Further, waters containing iron and manganese

are the most active catalysts of the decomposition of hydrogen peroxide. The explanation of these relationships, however, remains obscure. Experiments have also been made on the catalytic activity of the waters during the hydrolysis of starch.

H. F. GILLBE.

Preparation of a catalyst by the electrolytic corrosion of nickel. S. IKI (Ind. Eng. Chem., 1928, 20, 472—473).—See this vol., 377.

Catalytic action of platinum and the law of mass action. B. BATSCHA (Z. physikal. chem. Unterr., 1927, 40, 258—261; Chem. Zentr., 1928, i, 285).—Lecture experiments are described.

A. A. ELDRIDGE.

Platinic oxide catalyst for reductions. R. ADAMS, V. VOORHEES, and R. L. SHRINER (Org. Syntheses, 1928, 8, 92—99).—Chloroplatinic acid is fused with sodium nitrate at 500—550°, the platinic oxide formed being washed with water until practically free from nitrates. The material can be re-activated by shaking with air or oxygen, but repeated re-preparation appears to result in an accumulation of poison, and to necessitate purification. A. A. ELDRIDGE.

Catalytic synthesis of ammonia. H. VALENTIN (Z. physikal. chem. Unterr., 1927, 40, 271—272; Chem. Zentr., 1928, i, 285).—In Flörke's demonstration method (*ibid.*, 1926, 39, 283) the formation of water is observed even when dry nitrogen and ammonia are used; hence the ammonia is apparently formed from combined nitrogen and hydrogen.

A. A. ELDRIDGE.

Catalytic reduction of nitro-organic compounds in the liquid system. O. W. BROWN, G. ETZEL, and C. O. HENKE (J. Physical Chem., 1928, 32, 631—635).—The catalytic reduction of nitrobenzene, 1-nitronaphthalene, *p*-nitrotoluene, *o*-nitrophenol, *p*-nitrophenol, and dinitrotoluene in the liquid phase by hydrogen under pressure with nickel as catalyst has been studied. Quantitative reduction to the amine was obtained at 215° for the first three cases and at 226° for the last and at a pressure of 500 lb./in.² 0.52 g. of catalyst was required per g. of nitro-compound reduced. With nitrobenzene dissolved in benzene, the yield of amine increased with an increase in pressure up to 500 lb./in.², and reduction was then quantitative with or without the solvents benzene and absolute alcohol. With 1-nitronaphthalene (cf. Parrett and Lowy, A., 1926, 512), benzene was a better solvent than ethyl alcohol or ethylene glycol.

L. S. THEOBALD.

Catalytic reduction of nitrobenzene to aniline in the gaseous phase. G. B. SEMERIA and M. MILONE.—See B., 1928, 327.

First report of the committee on photochemistry. Division of Chemistry and Chemical Technology, National Research Council. H. S. TAYLOR (J. Physical Chem., 1928, 32, 481).—Introductory to the following abstracts. L. S. THEOBALD.

Experimental technique for quantitative study of photochemical reactions. G. S. FORBES (J. Physical Chem., 1928, 32, 482—502).—A selective summary in which light sources, the quantitative measurement of radiation intensity, light filters,

monochromators, analytical methods, and reaction vessels are the chief topics of discussion.

L. S. THEOBALD.

Excited systems formed by the absorption of light. L. A. TURNER (*J. Physical Chem.*, 1928, 32, 507—515).—The possible stages in the processes of the absorption of light by atoms and molecules, and the properties of the resultant excited systems are discussed in relation to their bearing on photochemical reactions.

L. S. THEOBALD.

Quantum processes in photochemistry. H. S. TAYLOR (*J. Physical Chem.*, 1928, 32, 516—528; cf. following abstract).—Photochemical processes are discussed in the light of the quantum theory with especial consideration of depolarisers, the systems hydrogen-halogen, photosensitised processes, inhibition, and more complex processes such as the oxidation of quinine and the reduction of Fehling's solution. The quantum theory gives a clearer and more comprehensive view of photochemical processes than does an analogy between these and electrochemical processes. Experimental work has not widely confirmed the idea of equivalence suggested by Einstein's law, and it is now preferable to distinguish the Grothus-Draper absorption law as the first law of photochemistry, and the second as "The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption."

L. S. THEOBALD.

Displacement of equilibrium by light. W. D. BANCROFT (*J. Physical Chem.*, 1928, 32, 529—572; cf. preceding abstract).—A review of photochemical processes on the theory of the displacement of equilibrium by light. When confined to reversible equilibrium, the theory provides the simplest interpretation of the facts. Conditions must be such that the rate of photochemical change shall be greater than the sum of the rates of the reversible reaction in the dark and in the light. The functions of depolarisers and optical sensitizers are emphasised.

L. S. THEOBALD.

Relation between photochemical and ionisation reactions. S. C. LIND (*J. Physical Chem.*, 1928, 32, 573—575).—Certain photochemical and ionisation reaction mechanisms with their similarities and differences are discussed, but further experimental examination, under identical conditions, is necessary to establish a relation between the respective yields.

L. S. THEOBALD.

Photochemistry of chlorine. G. KORNFIELD (*Z. physikal. Chem.*, 1928, 132, 460—461).—Cf. this vol., 253).

H. F. GILLBE.

Reaction mechanism of photochemical decomposition of hydrogen iodide. K. F. BONHOEFFER and L. FARKAS (*Z. physikal. Chem.*, 1928, 132, 235—256).—If the first stage in the photochemical decomposition of hydrogen iodide were a molecular excitation, it would be expected that at low pressures fluorescence instead of chemical reaction would occur. Not only is this not the case, however, but the law of equivalence is valid down to low pressures. Consequently, it must be assumed that the first stage in

the process is a direct dissociation of the molecule into atoms, $\text{HI}=\text{H}+\text{I}$. This view finds confirmation in the observation that when the iodide is exposed to light there is a fall in pressure which can be attributed only to adsorption of free atoms on the walls of the containing vessel. The same experiments also indicate that the iodine molecules formed impede the reaction. Adsorption of free atoms also occurs when hydrogen bromide or iodine vapour is illuminated. Under the influence of light, it appears that hydrogen atoms may become detached from the surface of solid hydrogen iodide.

R. CUTHILL.

[Decomposition of nitrogen oxides.] I. Effect of radiation on the decomposition of ozone and nitrous oxide. II. Low-pressure decomposition of nitrogen pentoxide and nitrous oxide. J. H. HIBBEN (*J. Amer. Chem. Soc.*, 1928, 50, 937—940, 940—950).—I. The homogeneous decomposition of nitrous oxide at 610° and the heterogeneous decomposition of ozone at 0° are uninfluenced by infra-red radiation. Molecular activation is probably not caused through the absorption of single or multiple frequencies.

II. The observed decomposition velocity of nitrous oxide at very low pressures is 1000 times as great as that calculated with the aid of Hinshelwood and Burk's equation (A., 1924, ii, 751). The reaction changes from bimolecular to unimolecular, and probably is entirely heterogeneous at very low pressures (0.01 mm.). The velocity coefficients for the decomposition of nitrogen pentoxide between 0.186 and 0.0018 mm. are in agreement with the values found at higher pressures by Daniels and Johnston (A., 1921, ii, 249), and are practically independent of pressure (cf. Hirst and Rideal, A., 1926, 32). There is no evidence of initial transition between unimolecular and bimolecular reactions as required by Lindemann's theory. The assumption of 30 degrees of freedom in the molecule will not account for the observed activation rate.

S. K. TWEEDY.

Photochemical clustering. B. LEWIS (*Nature*, 1928, 121, 792).—Macdonald's views of the mechanism of the photochemical decomposition of nitrous oxide (this vol., 254, and private communication) are discussed; the agreement between the value for $M/h\nu$ and that for M/N in the α -ray reaction (Lind, above) suggests clustering, but a general theory of photochemical clustering is not proposed. The view is, however, more acceptable for reactions involving association or polymerisation.

A. A. ELDRIDGE.

Decomposition of azoimide in ultra-violet light. K. SLEU (*Ber.*, 1928, 61, [B], 702—707).—Exposure of solutions of azoimide acidified with sulphuric acid to ultra-violet light results in rapid evolution of almost pure nitrogen and formation of hydroxylamine accompanied by a very small proportion of ammonia which is not derived by secondary photolysis of hydroxylamine; the course of the change is largely independent of the concentration of the sulphuric acid. It is suggested that the reactions involved are: $\text{HN}_3=\text{NH}+\text{N}_2$ and $\text{NH}+\text{H}_2\text{O}=\text{NH}_2\cdot\text{OH}$. Support for this hypothesis is found in the observation that in hydrochloric acid solution the

process of reaction is considerably affected by the concentration of mineral acid. Increase in the latter favours the production of ammonia to a remarkable extent and the change induced in the ratio N:H suggests the simultaneous formation of nitrous oxide. The reaction is represented: $N_3H=NH+N_2$; $NH+HCl=NH_2Cl$; $NH_2Cl+2HCl=NH_4Cl+Cl_2$. Production of nitrous oxide is ascribed to slow oxidation of hydroxylamine by chlorine. If aqueous solutions of azoimide, free from mineral acid, are illuminated to such an extent that the residual azoimide is more than sufficient to neutralise the basic nitrogen compounds obtained, nitrogen and hydroxylamine are the predominating products but ammonia and small quantities of hydrazine are also obtained; other substances are not formed. Solutions of pure sodium azide become alkaline when illuminated and contain large amounts of hydrazine in addition to ammonia and hydroxylamine; the evolved gases contain nitrogen and hydrogen. Pre-addition of sodium hydroxide does not influence appreciably the course of the reaction.

H. WREN.

Light-sensitivity of dyes. A. STEIGMANN (Kolloid-Z., 1928, 44, 326—329).—A summary and discussion of a series of papers by the author on the light-sensitivity of dyes.

E. S. HEDGES.

Laws of photographic blackening when the luminous source is a series of electric sparks. (MLLE.) M. HANOT and H. GUILLEMET (Compt. rend., 1928, 186, 1048—1050).—Although the densities of plates exposed for the same time to continuous and spark sources of light are known to differ, their blackening curves (density plotted against log. time of exposure or number of sparks) are exactly parallel for measurements between 0.415 and 0.537 μ , the relative error in measurement being 0.04%. The Schwarzschild exponent ($p=0.87$) is of the same order in the two cases, and the brightness of the spark approaches a maximum when the energy expended is increased.

J. GRANT.

Chemical action of Röntgen rays on dilute ferrous sulphate solutions as a measure of dose. H. FRICKE and S. MORSE (Amer. J. Roentgenol. Rad. Therapy, 1927, 18, 430—432).—The oxidation of a dilute solution of ferrous sulphate satisfies the essential conditions.

CHEMICAL ABSTRACTS.

Lithium chlorate and its hydrates. L. BERG (J. Russ. Phys. Chem. Soc., 1927, 59, 1093—1103).—See A., 1927, 1042.

Composition of crystals obtained from solutions containing sodium sulphate and iodides. II. (SIGNA.) E. FABRIS (Annali Chim. Appl., 1928, 18, 115—122).—Crystallisation at 16—25.5° of solutions containing sodium sulphate and either potassium, sodium, or ammonium iodide (cf. A., 1927, 939) shows that the content of iodine in the crystals separating increases progressively with the amount of iodide present. Curves are given which show the conditions necessary to obtain a definite proportion of iodine in sodium sulphate.

T. H. POPE.

Action of sodium hydroxide on carbon disulphide. J. G. WEELDENBURG (Rec. trav. chim.,

1928, 47, 496—512).—When carbon disulphide is shaken with excess of 20% sodium hydroxide solution a deep red solution is obtained. Reaction proceeds slowly at the ordinary temperature, is more rapid at 80°, and still more rapid in presence of emulsifying agents. In freshly-prepared solutions sodium sulphide, polysulphides, and thiosulphate are not present. The diluted reaction product can be titrated with hydrochloric acid towards phenolphthalein without decomposition of the sodium trithiocarbonate produced, but not towards methyl-red. Titration with iodine gives a neutral reaction mixture. The red solution is oxidised by hydrogen peroxide, chlorine, and bromine, forming sulphates, whilst salts of the heavy metals yield coloured precipitates which when moist are unstable, giving carbon disulphide and the metallic sulphide.

Determination of the constituents of the red reaction mixture by detailed methods shows that no dithiocarbonate is present, whilst the amount of carbonate and trithiocarbonate satisfies the equation $3CS_2+6NaOH=2Na_2CS_3+Na_2CO_3+3H_2O$. When carbon oxysulphide is kept over sulphuric acid very slight decomposition occurs. Reaction with aqueous alkali hydroxides is slow, but rapid with alcoholic potassium hydroxide, and the resulting product can be titrated with iodine, one atom of iodine being equivalent to 1 mol. of carbon oxysulphide. There is no reaction between carbon oxysulphide and iodine, neutral or acid copper sulphate solutions, cadmium acetate and acetic acid, or ethereal triethylphosphine.

H. BURTON.

Alteration of concentrated solutions of sodium hydrogen sulphate. E. ISNARD.—See B., 1928, 296.

Action of copper on sulphuric acid. G. FOWLES (Chem. News, 1928, 136, 257—259; cf. Druce, this vol., 378).—A critical discussion of previous work. The following series of reactions is suggested: $Cu+H_2SO_4=SO_2+H_2O+CuO(CuSO_4)$, followed by two simultaneous reductions: $4Cu+SO_2=Cu_2S+2CuO(2CuSO_4)$; $Cu+CuSO_4=Cu_2SO_4$. Sulphuric acid is then reduced by cuprous sulphide, $Cu_2S+H_2SO_4=Cu_2SO_4+H_2S$; $H_2S+H_2SO_4=2H_2O+SO_2+S$; $S+2H_2SO_4=2H_2O+3SO_2$, and simultaneously by cuprous sulphate, $Cu_2SO_4+2H_2SO_4=2CuSO_4+SO_2+2H_2O$. The result of combining these equations is $Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$.

C. W. GIBBY.

Hydrogen content of metals and alloys containing a trace of oxide. GUICHARD, CLAUSMANN, and BILLON (Compt. rend., 1928, 186, 1121—1123).—The phenomena observed when copper or one of its silver alloys (containing a trace of oxide) is fused in a current of hydrogen are due to the reduction of the crystals of copper oxide, with the formation of water vapour. This forms bubbles which diffuse out slowly, and at the point of fusion escape violently and scatter particles of the metal. Below the fusion point there is a gradual loss in weight and increase in volume of the alloy, but in the absence of the oxide these phenomena do not occur.

J. GRANT.

Production of tenorite and crystalline oligist and cobaltous oxide. DUBOIN (Compt. rend., 1928, 186, 1133—1135; cf. this vol., 257).—Large

crystals of tenorite (d^0 6.3) were produced by the addition of potassium chloride to a fused mixture of potassium hydrogen fluoride and copper oxide or chloride. After 2—3 days at red heat the mass was cooled and extracted with water. Crystals of cobaltous oxide (d^0 6.05) and of oligist (d^0 5.16) were obtained analogously from pure crystalline potassium cobalt fluoride and from ferrous chloride, respectively. The oxides are readily reduced by hydrogen.

J. GRANT

Hexabromostannates of rubidium, caesium, and beryllium. G. I. COSTEANU (Bul. Chim. Soc. Române Chim., 1927, 30, 31—34).—See A., 1927, 741.

Decomposition of alkaline-earth sulphates. L. E. BHATT and H. E. WATSON.—See B., 1928, 296.

Behaviour of metals towards dry salts at high temperatures. B. GARRE (Korrosion u. Metallschutz, 1927, 3, 194—200; Chem. Zentr., 1927, ii, 2657).—When a polished zinc rod is heated in powdered cupric oxide at 400° , the boundaries of the zinc crystallites are strongly attacked; when a piece of tin is similarly heated at 220° , it becomes covered with a thick layer of copper, and the grain boundaries are specially attacked. Silver powder does not react with copper oxide. In other experiments magnesium and aluminium were heated with sodium, potassium, or lithium carbonate, lithium hydroxide, copper, cadmium, zinc, or iron oxide; zinc with copper oxide or lead oxide; lead with copper oxide; tin with lead oxide; nickel with copper oxide.

A. A. ELDRIDGE.

Preparation of mercurammonium iodide in the crystalline state. M. FRANÇOIS (Compt. rend., 1928, 186, 1205—1207).—On the analogy of his early experiments on dimercurammonium iodide (A., 1900, ii, 346) the author has found that in the presence of a suitable quantity of a 10% solution of pure ammonia at 21° , a 10% solution of the white additive compound, $3\text{HgI}_2 \cdot 4\text{NH}_3$ (produced from the action of an excess of ammonia on the compound $\text{HgI}_2 \cdot 2\text{NH}_3$), deposits spherical groups of dark purple, short, hexagonal microscopical prisms of the compound $\text{Hg}_9\text{N}_4\text{I}_6$. The reaction is: $3(3\text{HgI}_2 \cdot 4\text{NH}_3) + n\text{NH}_3 \rightleftharpoons \text{Hg}_9\text{N}_4\text{I}_6 + 12\text{NH}_4\text{I} + (n-4)\text{NH}_3$.

J. GRANT.

Mercury-thallium molecule. R. K. WARING (Nature, 1928, 121, 675).—Volatilisation and absorption spectral observations indicate that when mercury and thallium vapours are mixed, mercury-thallium molecules are produced.

A. A. ELDRIDGE.

Rare earths. XXVII. I. Fractional precipitation of the cerium group earths by electrolysis. II. Solubility of rare-earth oxalates in nitric acid. J. W. NECKERS with H. C. KREMERS (J. Amer. Chem. Soc., 1928, 50, 950—954).—Lanthanum, in the form of hydroxide, may be separated from the other cerium-group metals by electrolysis of a neutral solution, preferably containing 5% of sodium chloride. Samarium and yttrium-group metals concentrate in the first cathodic deposits. The solubilities at 90° of some rare-earth oxalates in nitric acid solutions, both pure and containing oxalic acid, are recorded. The results are of the same order as at 25° .

S. K. TWEEDY.

Rare earths. XXVIII. Separation of cerium. J. W. NECKERS with H. C. KREMERS (J. Amer. Chem. Soc., 1928, 50, 955—958).—Addition of sodium phosphate solution to a ceric nitrate solution containing 5% of nitric acid, followed by slow addition of potassium permanganate and more sodium phosphate, causes complete precipitation of insoluble ceric phosphate. Thorium, if present, is also precipitated, but the other rare-earth phosphates are soluble. Anodic oxidation of cerium in sulphate and nitrate solutions proceeds to 90% completion with no precipitation, and in presence of the phosphate ion to 99% completion with precipitation.

S. K. TWEEDY.

Rare earths. XXIX. Preparation and properties of some anhydrous rare-earth chlorides. J. H. KLEINHEKSEL with H. C. KREMERS (J. Amer. Chem. Soc., 1928, 50, 959—967).—By dehydrating at 100 — 200° the chloride hexahydrates in a stream of hydrogen chloride under reduced pressure the anhydrous chlorides of lanthanum, cerous cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium, and thulium were prepared. The respective m. p. were: 872° , 822° , 823° , 761° , 682° , 655° , 624° , 696° , 866° , and d^{25} for coarsely-powdered material: 3.82, 3.97, 4.15, 4.17, 4.30, 3.60, 2.81, 4.25, and 4.34. The p_{H} values of solutions of the anhydrous chlorides are recorded; the values place the elements almost in the order of basicity given by Hopkins, except in the case of dysprosium, which appears to be more basic than was previously supposed. The salts will probably be completely hydrolysed at infinite dilution.

S. K. TWEEDY.

Influence of carbon dioxide under pressure on glass. O. K. BOTVINKIN.—See B., 1928, 334.

Constitution of ultramarine. E. GRUNER (Z. angew. Chem., 1928, 41, 446—450).—A review of the various theories of the constitution and of the cause of the colour of ultramarine. A. R. POWELL.

Stannic dichloride diacetate. F. FICHTER and S. HERSZBEIN (Helv. Chim. Acta, 1928, 11, 562—567).—The properties of stannic dichloride diacetate previously isolated by Fichter and Reichart (A., 1925, ii, 193) are described. It reacts with pyridine to form stannic dipyridine chloride. Stannic dichloride dipropionate and dibutyrate were also prepared. The corresponding compounds of isovaleric acid and aromatic acids could not be isolated.

F. J. WILKINS.

Displacement of metals or their oxides from solutions by hydrogen under pressure. Displacement of lead or its oxides. Crystalline modifications of lead oxide. V. IPATIEV and V. IPATIEV, jun. (Ber., 1928, 61, [B], 624—630).—The action of hydrogen under pressure on solutions of lead nitrate in water commences at 130 — 150° and at 250 — 300° a series of basic salts is produced in which the proportion of lead oxide increases with rising temperature. At 270 — 300° under a definite pressure crystalline lead oxide is the main product, whereas at higher temperatures metallic lead is formed. Hydrolysis of the salt causes liberation of nitric acid which does not accumulate in the solution since it is reduced by hydrogen to nitrogen. Addition

of nitric acid to the solution merely delays hydrolysis, the usual basic salts being produced after the added acid has been reduced. Water in the absence of hydrogen has no appreciable action on the precipitates, which are slowly affected by hydrogen, particularly at high temperatures. The effect of the addition of acetic acid to solutions of lead acetate is closely similar to that of nitric acid to solutions of lead nitrate; whereas lead oxide is precipitated from neutral solution, little change is effected in acidified solution after the same interval of time. The acetic acid is partly converted into ethyl acetate. The rate of change depends to some extent on the material (gold, quartz, glass) of which the tubes are composed, since reduction of nitric acid is accelerated by gold surfaces. In gold tubes at 250° and 80 atm. initial pressure, crystalline, blood-red lead oxide, d 8.59—8.79, is produced, whereas in quartz tubes under similar conditions the requisite temperature is 300° or more. At 260—270° in quartz tubes *yellow lead oxide* is formed in thin, crystalline leaflets, whereas at 300° and 200 atm. initial pressure *colourless lead oxide* results. Separation of metallic lead occurs at 250—275° and upwards, according to the pressure.

H. WREN.

Production of active nitrogen. J. KAPLAN (Proc. Nat. Acad. Sci., 1928, 14, 258—260).—Experiments are described in which active nitrogen has been obtained in discharge tubes containing air. The usual apparatus was used, the discharge being condensed and a spark-gap connected in series with the tube and condenser. The glow observed was blue and changed to the ordinary yellowish-green glow when the spark gap was excluded. The spectrum was photographed by means of a small Hilger quartz-spectrograph, and also with a nitrogen-filled spectrograph, covering together the region 1800—4500 Å. Many of the bands could not be identified accurately owing to their large number and the relatively small dispersion of the spectrograph. Second positive bands of N_2 were found at 2815, 2953, and 3341 Å., as well as several members of the fourth positive group of N_2 . No members of the Lyman-Birge-Hopfield bands or the predicted A—X bands were found on the plates from the nitrogen-filled spectrograph. There is therefore no evidence for transitions to the normal state of the molecule. The results of Strutt on the difference between the condensed discharge and the uncondensed discharge are confirmed. Experiments at somewhat lower voltages showed that the blue active nitrogen afterglow could be obtained when the potential at the spark-gap was only 10,000 volts.

A. J. MEE.

Formation of ammonia in the preparation of phosphorus. E. URBAIN and V. HENRI (Compt. rend., 1928, 186, 1207—1208).—In the preparation of phosphoric acid by the action of steam on natural phosphates in the presence of active carbon, the addition of a halogen acid, normally required to produce a lowering of the reaction temperature, has no effect above 600°, but in the presence of nitrogen an unstable phosphorus nitride is probably formed, which is decomposed by the steam with the formation of ammonia. A yield of 0.46 g. of ammonia (representing 2.95 g. of monoammonium phosphate) was obtained at 900° from 5 g. of phosphorus in the form of phosphoric acid impregnated on carbon.

J. GRANT.

Production of ammonium phosphates from secondary and tertiary calcium phosphates. C. MÜCKENBERGER.—See B., 1928, 297.

Allotropic modifications of phosphorus obtained under high temperatures and pressures. V. IPATIEV and V. NIKOLAJEV (Ber., 1928, 61, [B], 630—634).—Colourless, crystalline phosphorus is obtained by heating phosphorus in benzene at a temperature not exceeding 200° at 70—80 atm. pressure in an indifferent gas or by heating violet-red phosphorus at 400°/10—15 mm.; it has m. p. 44.5°, d 1.82. Crystalline, purple phosphorus (cf. A., 1926, 487) is prepared by heating yellow phosphorus in nitrogen at 260—280° and 100—150 atm. Treatment of yellow phosphorus with lead in nitrogen at 335° and 165 atm. affords violet-red phosphorus, d_{16}^{16} 2.11; determinations of density by the flotation method in potassium mercury iodide solution are untrustworthy, since the material becomes amalgamated. A ruby-red phosphorus, d_{16}^{20} 2.10, is prepared from iron powder and yellow phosphorus in nitrogen at 350° and 110 atm., and a similar product, d_{16}^{16} 2.10, from magnesium powder and yellow phosphorus at 350° and 116 atm. Black phosphorus, d_{16}^{16} 2.70, ignition temperature 481—490°, is conveniently prepared by heating yellow or technical red phosphorus for 4—5 days in nitrogen at 350° and 150—250 atm.

H. WREN.

Salt of hexafluorophosphoric acid, HPF₆. W. LANGE (Ber., 1928, 61, [B], 799—801).—If the solution obtained by dissolving phosphoric oxide in 40% hydrofluoric acid is preserved at the ordinary temperature, the difluorophosphoric acid, HPO₂F₂ (cf. A., 1927, 532), becomes hydrolysed and the residual solution yields the *nitron* salt of hexafluorophosphoric acid, C₂₀H₁₆N₄.HPF₆, m. p. 233° after softening at 228°, which does not depress the m. p. of nitron difluorophosphate. The *potassium* salt and the free acid are described. Solutions of the former do not yield precipitates with salts of the heavy metals or alkaline earths. The PF₆' ions are very stable towards boiling water and alkali hydroxides, but are slowly decomposed by concentrated acids. The PF₆' ion is also produced by dissolving phosphorus pentafluoride in cold water. Nitrosyl fluoride and phosphorus pentafluoride appear to yield the crystalline compound NOF₆.

H. WREN.

Perphosphoric acids and perphosphates. S. HUSAIN and J. R. PARTINGTON (Trans. Faraday Soc., 1928, 24, 235—245).—The action of hydrogen peroxide on phosphates (alkali, alkaline earth, ammonium, and thallium) has been investigated. Acid-reacting phosphates, such as primary phosphates, do not react with hydrogen peroxide or else give very unstable compounds. Alkaline phosphates, e.g., secondary phosphates or pyrophosphates of alkali metals, give rather stable compounds, whilst strongly alkaline phosphates, e.g., tertiary potassium phosphate, decompose hydrogen peroxide. The compounds formed by the action of hydrogen peroxide

are in no case true perphosphates, but appear to be phosphates combined with hydrogen peroxide of crystallisation. Electrolysis of orthophosphoric acid or of phosphates of lithium, sodium, and thallium does not give rise to perphosphates, whilst secondary phosphates of potassium, rubidium, caesium, and ammonium produce on electrolysis two perphosphates in solution, namely, permonophosphate and perphosphate. In contradiction to Siebold's statement (G.P. 279,306), perphosphoric acids are not obtained by the action of 30% hydrogen peroxide at 0° on phosphorus oxychloride. Doubt is thrown also on the results of many other investigators in this field. True perphosphates do not give any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether, or titanous acid, as do the phosphates containing hydrogen peroxide of crystallisation. On the other hand, they oxidise acidified manganous salt solutions to permanganic acid, acidified aniline solution to nitrosobenzene, which is then slowly oxidised to nitrobenzene, and silver nitrate solution to a black precipitate, which gradually turns yellow.

L. F. GILBERT.

Chloro-complex salts of bismuth. H. REMY and L. PELLEN (Ber., 1928, 64, [B], 862—868; cf. A., 1926, 94).—Calculations based on Coulomb's law and Goldschmidt's ionic radii (A., 1927, 611) indicate the particular stability of bismuth compounds in which the metal is co-ordinatively quinquivalent. The prediction is experimentally confirmed. The following compounds are described: methylammonium enneachlorodibismuthate, $[\text{NH}_3\text{Me}]_3[\text{Bi}_2\text{Cl}_9]$, m. p. 302°, *hendecachlorodibismuthate*, decomp. above 240°; and *heptachlorobismuthate*, m. p. above 210° (decomp.); *dimethylammonium pentachlorobismuthate*, m. p. 228°, and *heptachlorobismuthate*, m. p. 208°; *trimethylammonium enneachlorodibismuthate*, m. p. about 284° after softening at 260°, and *hexachlorobismuthate*, m. p. (indef.) 272°; *tetramethylammonium tetrachlorobismuthate*, m. p. 286° (decomp.); *ethylammonium tetrachlorobismuthate*, m. p. 158°, *pentachlorobismuthate*, m. p. 268°, *hexachlorobismuthate*, m. p. 239°, and *heptachlorobismuthate*, m. p. 199°; *propylammonium tetrachlorobismuthate*, m. p. (indef.) 157°, *pentachlorobismuthate*, m. p. 243°, and *heptachlorobismuthate*, m. p. (indef.) 170°; *butylammonium pentachlorobismuthate*, m. p. 225°, and *enneachlorobismuthate*, m. p. 180°. The salts are prepared by mixing the hydrochlorides of the ammonium bases and bismuth chloride in the requisite molecular proportions in water or dilute hydrochloric acid.

H. WREN.

Reaction between chromic acid and manganous salts. R. LANG (Z. anorg. Chem., 1928, 107, 387—388; cf. following abstract).—No reaction occurs between potassium dichromate and manganous sulphate in a *N*-solution of sulphuric acid, either in the cold or on boiling, or even when the sulphate is present in excess. If, however, an alkali fluoride or metaphosphoric acid is added to form complexes with the manganic ions, the manganous salt is oxidised with a measurable velocity, even at the ordinary temperature; if metaphosphoric acid is

used, the reaction may be reversed by the subsequent addition of hydrochloric acid. R. CUTHILL.

Action of dichromate ions on manganous ions. S. ORLOVSKI (Z. anorg. Chem., 1928, 170, 184—190).—Potassium dichromate in a solution made slightly alkaline with ammonia is reduced on boiling with manganous salts, chiefly in accordance with the equation $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{MnSO}_4 + 10\text{NH}_4\text{OH} + 7\text{H}_2\text{O} = 2\text{Cr}(\text{OH})_3 + 6\text{Mn}(\text{OH})_3 + \text{K}_2\text{SO}_4 + 5(\text{NH}_4)_2\text{SO}_4$. The whole of the manganese may be precipitated in this way, but the reaction is not suitable as a method of determination, as the precipitate appears to contain unoxidised manganous compounds. If a stronger base is used instead of ammonia, the oxidising action of the dichromate is diminished. R. CUTHILL.

Formation and decomposition of ferrite. C. E. SWARTZ and F. C. KRAUSKOPF (Amer. Inst. Min. Met. Eng. Tech. Pub., 1927, No. 40. 19 pp.).—Zinc ferrite, $\text{Zn}(\text{FeO})_2$, is formed by heating zinc oxide with ferric oxide above 650°, and is decomposed by heating with calcium or magnesium oxide at 850°. Magnesium and calcium ferrites are formed similarly. The compounds are non-magnetic.

CHEMICAL ABSTRACTS.

X-Ray studies on the "nitrides" of iron. G. HÄGG (Nature, 1928, 121, 826—827).—X-Ray examination of the products obtained by heating iron at 450° in a current of ammonia show that they are solid solutions of nitrogen in iron, and not definite chemical compounds. The structure of the products is dependent only on the nitrogen content. The γ -phase (a solid solution of nitrogen in γ -iron) lies between 5.7 and 6.1% N, corresponding approximately with Fe_3N ; the lower limit of the homogeneous ϵ -phase (a solid solution of nitrogen in a hexagonal close-packed form of iron) lies between 7.5 and 8% N, corresponding with Fe_3N , and the upper limit of attainable concentration (slightly above 11% N) corresponds with Fe_2N . It is possible that these coincidences may be related to certain concentrations of valency electrons. The catalytic effect of iron in the Haber process for combining nitrogen and hydrogen may be ascribed to the dissolved nitrogen being in the monatomic condition.

A. A. ELDRIDGE.

Thermal decomposition of complex cyanides of iron in relation to the catalytic synthesis of ammonia. A. MITASCH, E. KUSS, and O. EMERT (Z. anorg. Chem., 1928, 170, 193—212).—When ammonium ferrocyanide is heated in a vacuum, decomposition starts at about 110°, ammonium cyanide being evolved gradually until the temperature reaches 320°, when ferrous cyanide remains. It thus appears that there are in the decomposition stages intermediate between the ferrocyanide and the two simple cyanides. On heating further, decomposition starts again above 430°, nitrogen being evolved, and at 700° 95% of it has come off, the residue consisting principally of iron, along with iron carbide, carbon, and a little nitride; the formation of carbide is favoured by a low decomposition temperature and a short period of heating. When the ferrocyanide is heated in a current of hydrogen and nitrogen prepared by decomposing ammonia, the

course of the reaction up to 320° is the same as it is in a vacuum. At 320°, however, the ferrous cyanide formed is reduced to nearly pure iron, with formation of ammonia, and methane and other hydrocarbons, at a rate which increases with the pressure. Ferrous cyanide itself begins to be reduced by the mixture of nitrogen and hydrogen above 210°. At 230°, the carbon and nitrogen of the cyanide radical are reduced at approximately equal speeds, so that metallic iron only is formed. At 400°, on the other hand, the nitrogen is reduced much more rapidly than the carbon, so that the solid residue when most of the nitrogen has been removed contains iron, iron carbide, and carbon; in no case, at any temperature, is carbide unaccompanied by the metal. The fact that this mixture is not formed at 230° may be explained by supposing that the carbide FeC_2 is formed as an intermediate product, and at 400° decomposes into carbon and the carbide Fe_3C , whereas at 230° it is directly reduced. It also appears that metallic iron must be formed from the very start of the reduction. The mixture of carbide and carbon obtained at 400° is readily reduced completely by the mixture of nitrogen and hydrogen, but if the mixture is first heated in a vacuum at 400° or 500° for some time, reduction of the carbon in particular becomes much more difficult. The decomposition of the cyanide $\text{KAlFe}(\text{CN})_6$ in the nitrogen-hydrogen mixture at 450–500° under 1 atm. pressure is similar to that of ferrous cyanide at the same temperature, whilst at 360° and 95 atm. there is complete reduction to the metal; ferrous cyanide and carbide-metal mixtures must thus be intermediate products here also. This cyanide does not in itself bring about the decomposition of ammonia below 400°, or its synthesis at 360° under 95 atm. It is therefore to be concluded that the actual catalyst is the metallic iron produced in the decomposition, and activated by the substances which accompany it.

R. CUTHILL.

Reaction between monohydrated ferric oxide and hydrogen sulphide at 100°. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1928, 814–823).—The black product obtained in this reaction contains free sulphur extractable by carbon disulphide. The ratio of "sulphide" produced to oxide taken corresponds very nearly with that required for complete conversion into ferric sulphide. The course of the reaction varies considerably, but the mean composition of the product is as follows: free sulphur 2.44%, iron disulphide, 7.83%, ferric sulphide, 69.4%, ferrous sulphide, 9.76%, unchanged ferric oxide, 7.48%, moisture, 1.55%. The ferrous sulphide and disulphide are formed by the decomposition of ferric sulphide. The free sulphur results from the oxidation of the hydrogen sulphide by oxygen adsorbed on the oxide surface.

H. INGLESON.

Ruthenium. F. KRAUSS (Z. angew. Chem., 1928, 41, 413–418).—From a comprehensive review of the literature and from his own researches the author concludes that in the solution obtained by treating ruthenium tetroxide with hydrochloric acid the metal is almost entirely in the tervalent state and that by evaporation of this solution and addition of alkali chlorides derivatives of pentachlororuthenic acid are

obtained. The light yellowish-brown or colourless solution obtained as the first stage in the reduction of ruthenium trichloride in solution contains bivalent, and the blue solution obtained by more vigorous reduction univalent ruthenium. A. R. POWELL.

Application of the photo-electric cell to automatic titrations. R. H. MÜLLER and H. M. PARTRIDGE (Ind. Eng. Chem., 1928, 20, 423–425).—A circuit containing a photo-electric cell and one vacuum tube is described. Light passes through the solution being titrated and falls on the cell; the change in colour during the titration varies the intensity of the light sufficiently to actuate the cell, and through the vacuum tube operates a relay and burette release. The relay contacts may be reversed as required, and by a proper selection of indicators all cases of acidimetry and alkalimetry can be covered. Permanganate and dichromate titrations may be made by using *m*-phenylenediamine as indicator, and iodometric titrations are also possible. Certain precipitation reactions may also be followed by using reflected light. The apparatus is well adapted to precise determinations of p_{H} values, and automatic titrations were found to be more accurate than visual determinations.

D. G. HEWER.

Spectroscopic control of the end-point of indicators of the phthalein and sulphonephthalein groups. P. BRUÈRE (Bull. Soc. Chim. biol., 1928, 10, 283–290).—By spectroscopic control of the titration of coloured solutions it is possible to obtain accurate results with the usual indicators.

G. A. C. GOUGH.

Stable colorimetric standards for simple and mixed indicators. P. BRUÈRE (Bull. Soc. Chim. biol., 1928, 10, 291–293).—Permanent colorimetric standards for mixtures of indicators such as methyl-red, bromothymol-blue, and phenol-red may be prepared from mixtures of (a) potassium and cobalt dichromates (yellow), (b) cobalt and copper sulphates (blue), (c) an acetic acid solution of cobalt chloride.

G. A. C. GOUGH.

Colorimetry. H. ECKSTEIN (Chem.-Ztg., 1928, 52, 317).—The suggestion is made that the changes in colour of many of the comparison solutions used in colorimetric determinations might be avoided either by the use of suitably coloured stable dyes or of coloured glasses as comparison standards when such materials can be obtained.

H. INGLESON.

Detection of small differences in the hydrogen-ion concentration of solutions. W. KESTING (Z. angew. Chem., 1928, 41, 358–360).—Malonitrile reacts with α -naphthaquinone in solutions of $p_{\text{H}} > 2.5$ with the formation of an intensely blue solution, and the speed of the reaction increases with an increase in the p_{H} value. To compare the p_{H} of two solutions, 5 c.c. of each are placed in two test-tubes and 5 drops of a 0.2% alcoholic solution of malonitrile added to each, followed by 5 drops of a 0.3% alcoholic solution of α -naphthaquinone. After shaking, the intensities of the colours are compared; differences of only 0.2 in the p_{H} value are readily apparent after a little practice. In solutions with $p_{\text{H}} > 11.5$, the addition of the above reagents produces a green colour and the test is no longer of value; in this case

β -naphthaquinone is used instead of the α -compound and the intensities of the red colour produced in standard and test are compared. For solutions with relatively low p_{H} values benzoquinone gives more delicate colour changes than either of the naphthol derivatives. A. R. POWELL.

Non-gas electrodes for p_{H} determinations. A. J. DE LA CRUZ (Philippine Agric., 1927, 16, 307—322).—An electrode combination of aluminium and barium dioxide gave reproducible results for *E.M.F.* when used in ordinary acid-base titrations or in buffer solutions containing no protein, the optimal range being p_{H} 7—10, but not in determinations of the p_{H} value of sugar juices. The quinhydrone electrode can be used for this purpose for p_{H} values up to 10, provided the *E.M.F.* is read exactly 1 min. after addition of the quinhydrone.

CHEMICAL ABSTRACTS.

New iodoso-(iodoso-iodyl)-benzene electrode and its application to the determination of p_{OH} or p_{H} . F. GROSSMAN (Rocz. Chem., 1927, 7, 567—578).—Two new electrodes, iodosobenzene and a mixture of iodoso- and iodyl-benzene, are applied to the measurement of p_{OH} or of p_{H} between the limits 1 and 13. An iodylbenzene electrode does not appear to be applicable to the determination of p_{H} .

R. TRUSZKOWSKI.

Differential potentiometric titration. I. Simple method. II. Refined methods. B. CAVANAGH (J.C.S., 1928, 843—855, 855—872; cf. A., 1927, 1045).—The three methods described are applicable to the titration of univalent ions, e.g., Ag^+ , H^+ , Cl^- , to which a corresponding reversible electrode can be found. All the methods depend on the changes of the potential of the indicator electrode and not on particular values of the potential. The first method is applicable in cases where an absolute uncertainty of the order of one fifth or one seventh of the solubility of silver chloride (or the corresponding constant) is permissible. A first addition of the reagent is made and from the resulting potential change an approximate estimate of the amount still required is obtained by reference to a table. Nearly this amount is added and the small deficiency can then be estimated accurately by the same means. The second and third methods are used for dilute solutions where higher absolute accuracy is required. The second method is an extension of the first up to and beyond the end-point. The third method is independent of a knowledge of solubility, the end-point being deduced from two successive potential measurements by reference to a table and the use of a set of curves. Numerical examples illustrating the use of the methods are given.

H. INGLESON.

Colorimetric p_{H} determination [of water] in a neutral atmosphere. H. F. MUER and F. E. HALE.—See B., 1928, 318.

Fellenberg's method for the determination of iodine. E. JOCHMANN (Biochem. Z., 1928, 194, 454—460).—Fellenberg's method for the determination of minute amounts of iodine does not always give results as consistent as claimed.

P. W. CLUTTERBUCK.

Determination of traces of iodine. I. J. F. McCLENDON (J. Amer. Chem. Soc., 1928, 50, 1093—1099).—The sample, containing more than 0.01 mg. of iodine, is ashed in oxygen, by atomising if necessary, in a heated silica tube; the vapours are sucked through sodium hydroxide solution and a Cottrell precipitator. To the former solution the washings of the ash are added; after neutralising with phosphoric acid containing sulphurous acid the solution is boiled and on cooling the iodine is extracted with carbon tetrachloride. The latter solution is examined in a micro-colorimeter. The limit of error is 1% on samples containing more than 1 mg. of iodine and 5% on samples containing less than this.

S. K. TWEEDY.

Testing for iodine in potable waters. P. DRAWE.—See B., 1928, 350.

Determination of fluorine in zinc blende. L. FRESNIUS, K. SCHRÖDER, and M. FROMMES.—See B., 1928, 302.

Determination of dissolved oxygen in water. V. G. ANDERSON and J. R. DICKSON.—See B., 1928, 390.

Determination of sulphuric acid by the benzidine method. O. NYDEGGER (Chem.-Ztg., 1928, 52, 318—319; cf. A., 1907, ii, 196).—The chief sources of error in the method arise from the relatively large solubility of benzidine sulphate in water and from the adsorption of benzidine hydrochloride by the precipitated sulphate. Experimental details of the method are given. Results obtained are accurate, duplicate determinations agreeing to within 0.5% absolute. The presence of moderate amounts of other salts and acids is without influence on the accuracy of the determinations. H. INGLESON.

Examination of sulphuric acid for selenium. R. C. WELLS.—See B., 1928, 332.

Changes in the titre of thiosulphate solutions. C. MAYR and E. KERSCHBAUM (Z. anal. Chem., 1928, 73, 321—352).—Although carbon dioxide decomposes thiosulphate solutions with the deposition of colloidal sulphur and with the production of traces of hydrogen sulphide, this action has very little to do with the changes in the titre that take place during storage of thiosulphate solutions. Oxygen alone and exposure to direct sunlight have no action when the solution is kept in glass vessels, but photochemical decomposition takes place rapidly in quartz vessels. The principal cause of the instability of thiosulphate solutions is the presence of bacteria, of which there are three active kinds. The first type causes decomposition as follows: $2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} + \text{O} = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaOH}$; the second, according to the equations $\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{SO}_3 + \text{S}$ and $\text{Na}_2\text{SO}_3 + \text{O} = \text{Na}_2\text{SO}_4$, and the third, according to the first equation and to $\text{S} + 3\text{O} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. The presence of copper accelerates decomposition only when bacteria are also present. The protective action of alkalinity is ascribed to the restraining effect of alkalis on the growth of bacteria; a p_{H} value of 9—10 affords the greatest protection. Practically complete sterility may be produced by the addition to thiosulphate solutions of 1 vol.-% of amyl alcohol. A. R. POWELL.

Apparatus for micro-analytical determination of [ammoniacal] nitrogen. H. LEOPOLD (Chem.-Ztg., 1928, 31, 309).—A round-bottomed distillation flask, 150–200 c.c. capacity, carries a dropping funnel (containing 30% sodium hydroxide solution) and an inclined spray trap. The latter is connected with a bent tube, the vertical portion of which is enclosed by a condenser and dips into 4–6 c.c. of 0.0143*N*-hydrochloric acid. 0.002–0.005 g. of the substance is used; the distillation is carried on for 20 min., the delivery tube raised above the acid, the boiling continued for 5 min. longer, and the excess of acid titrated with 0.0143*N*-sodium hydroxide solution. D. WOODROFFE.

Hypophosphoric acid. W. D. TREADWELL and G. SCHWARZENBACH (Helv. Chim. Acta, 1928, 11, 405–416).—An electrometric precipitation method for the analysis of hypophosphoric acid is based on the very slight solubility of the uranous salt. Electrometric neutralisation curves with sodium hydroxide indicate the successive formation of disodium dihydrogen hypophosphate, trisodium monohydrogen hypophosphate, and normal sodium hypophosphate, and give values for the dissociation constants of the acid of ($\geq 10^{-2.2}$), $10^{-2.31}$, $10^{-7.27}$, $10^{-10.02}$.

F. J. WILKINS.

Determination of small amounts of carbon monoxide in air. G. M. EDELL.—See B., 1928, 365.

Determination of carbon monoxide in mines. G. S. McCAA and J. A. DAVIS (U.S. Bureau Mines Circ., 1928, No. 6057, 5 pp.).—The gas, previously passed over activated charcoal, is passed through a small glass tube containing granulated pumice saturated with a mixture of iodine and fuming sulphuric acid ("hoolamite"). The liberated iodine is determined colorimetrically, the standards being contained in a tube as part of the apparatus.

CHEMICAL ABSTRACTS.

Determination of free alkali in hypohalite solutions. E. RUPP and F. LEWY.—See B., 1928, 365.

Rapid determination of zinc. G. SPACU and J. DICK (Z. anal. Chem., 1928, 73, 356–359).—Addition of pyridine and ammonium thiocyanate to neutral solutions of zinc salts produces quantitative precipitation of white, crystalline $Zn(SCN)_2 \cdot 2C_5H_5N$, which contains 19.25% Zn. The details of precipitating, washing, and drying the compound are similar to those described for the precipitation of cadmium by the same reagents (cf. this vol., 499).

A. R. POWELL.

Nephelometric determination of small quantities of lead in presence of zinc by means of potassium chromate. L. S. VAN DER VLUGT.—See B., 1928, 336.

Detection and colorimetric determination of aluminium. I. M. KOLTHOFF (J. Amer. Pharm. Assoc., 1928, 17, 360–361).—For the detection and determination of traces of aluminium (0.5–0.02 mg. per litre), 1:2:5:8-tetrahydroxyanthraquinone in presence of a buffer solution is employed. Most metals are without influence on the reaction.

E. H. SHARPLES.

Determination of iron and sulphur in sulphides of iron. P. L. ROBINSON, L. A. SAYCE, and J. STEVENSON (J.C.S., 1928, 813–814).—The method of analysis of iron sulphide (Weyman, B., 1920, 219A) in which the solid is treated with warm aqueous copper sulphate, iron being determined in the filtrate and sulphur indirectly determined by dissolving the residue in nitric acid and precipitating the copper electrolytically, gives very untrustworthy results, especially in the presence of even small quantities of free acid. H. INGLESON.

Colorimetric determination of iron in water. P. LEHMANN and A. REUSS.—See B., 1928, 390.

Detection of cobalt in steel. J. MOIR.—See B., 1928, 301.

Gravimetric determination of titanium in iron alloys. J. CIOCHINA.—See B., 1928, 301.

Determination of antimony in bronze, brass, and similar alloys. S. A. TSCHERNICHOF.—See B., 1928, 371.

Analytical chemistry of tantalum, niobium, and their mineral associates. X. Separation of silica from earth acids. XI. Precipitation of titanium by tannin. W. R. SCHOELLER and A. R. POWELL (Analyst, 1928, 53, 258–267).—X. Volatilisation of the fluorides of tantalum and niobium is discussed and a method of separation of small quantities of silica from much earth acid by a reagent other than hydrofluoric acid is given, which involves the use of an acid flux. The mixed oxides are fused with potassium hydrogen sulphate, the cooled mass is digested with oxalic or tartaric acid, the solution (containing nearly the whole of the earth acids) filtered, and the residue (more or less pure silica) washed with hot water, ignited, and weighed. It is then evaporated with hydrofluoric acid and sulphuric acid and again ignited and weighed. The small residue is once more fused with hydrogen sulphate, the mass dissolved in the organic solvent, and the solution added to the first filtrate.

XI. Titanium may be quantitatively precipitated by tannin from oxalic or tartaric acid solution if the solution be neutralised and boiled with excess of tannin. Tantalum cannot be separated from niobium in the presence of more than an insignificant amount of titanium, *i.e.*, 1% of the tantalic oxide to be determined, as a discoloration of the yellow tantalum precipitate occurs. Thus the method may usually be used for tantalites, but in most columbites titania must first be separated from the earth acids.

D. G. HEWER.

[Analysis of platinum ores.] S. F. SHERMITSCHUSHNI and others.—See B., 1928, 302.

Micro-analytical filtration. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, 10, 495–500).—An apparatus for this operation, based on that of Pregl, is described and its application to modified determinations of potassium and sodium is detailed. G. A. C. GOUGH.

Platinum-tungsten welding. J. H. HIBBEN (J. Amer. Chem. Soc., 1928, 50, 1118).—The tungsten is cleaned with sodium nitrite and several coats of platinum are burned into it from a solution of lavender

oil and platinum chloride. It is then rapidly welded in an oxygen flame to platinum coated with borax. If cleaned tungsten is covered with borax, heated, and plunged into molten gold, it may then easily be welded to gold. Gold is an excellent flux for platinum welding.

S. K. TWEEDY.

Electrolytic gas apparatus. R. MAND (*Z. physikal. chem. Unterr.*, 1927, 40, 305; *Chem. Zentr.*, 1928, i, 285).—A demonstration apparatus is described.

A. A. ELDRIDGE.

Apparatus for the determination of gas densities. M. NIKIEL (*Metan*, 1925, 9, 203—210; *Chem. Zentr.*, 1928, i, 227—228).—The density of a gas is compared with that of air by a determination of the time taken for a liquid to flow out of a vessel attached to a gas supply, and then opened to the air. The apparatus is described and figured.

A. A. ELDRIDGE.

Registering photodensitometer. E. A. HARRINGTON (*J. Opt. Soc. Amer.*, 1928, 16, 211—222).—A direct-reading, self-recording densitometer with single thermo-couple and low-resistance D'Arsonval galvanometer, which can be used for measuring the relative opacities of photographic images of line spectra and powder photographs, is described. Quick action and small lag result from the small heat capacity of the thermo-couple and special arrangement of the galvanometer. Applications to X-ray work and ordinary spectroscopy are discussed.

C. J. SMITHELLS.

Colour glass standardisation. D. B. JUDD and G. K. WALKER (*Oil and Fat Ind.*, 1928, 5, 16—26).—A large number of red Lovibond glasses for grading vegetable oils were compared with a standard glass and graded by means of a Martens photometer. The engraved numerals were found to be only an approximate index of colour, previous findings as to inaccuracies in the region 7.0—8.0 being confirmed (samples engraved 7.6 covering a range of 1.1 red units). Results indicated that the Priest and Gibson scale departed by about 0.1 from the average Lovibond red glass of the order 7.0—8.0 used in the United States.

A. COUSEN.

Spectrocomparator. F. STANLEY (*J. Opt. Soc. Amer.*, 1928, 16, 208—210).—A comparator, which enables two spectra taken on different scales to be compared directly, is described. The optical system is arranged to give different magnifications in the two fields, and the eyepiece carries a micrometer.

C. J. SMITHELLS.

Selenium cell. R. E. MARTIN (*J. Opt. Soc. Amer.*, 1928, 16, 279—281).—A cell in which the selenium is in the form of a cylinder, and a method for making the latter by pouring viscous selenium are described.

C. W. GIBBY.

Spectroscopic demonstrator for the exhibition of emission, continuous, and absorption spectra. H. T. STETSON and H. W. GEROMANOS (*J. Opt. Soc. Amer.*, 1928, 16, 293—294).—The continuous spectrum is produced by an incandescence electric lamp supported 1 ft. from a direct-vision spectroscope. The interposition of a sodium flame gives rise to an absorption spectrum, and the latter flame alone to the two sodium lines.

C. W. GIBBY.

Light filters for the isolation of narrow spectral regions. L. A. JONES (*J. Opt. Soc. Amer.*, 1928, 16, 259—271).—Spectral absorption curves are shown for distilled water, for aqueous solutions of copper sulphate and of nickel sulphate, for Corning glasses G 986A, G 586, and G 980A, and for Wratten filters 88A, 25, 61, and 49 and combinations thereof.

C. W. GIBBY.

Refracto-dispersometer. C. CHEVENEAU and VAURABOURG (*Bull. Soc. chim.*, 1928, [iv], 43, 374—384).—A simple adaptation of the Féry refractometer to the measurement of dispersion is described. Two lines in the spectrum of the mercury vapour lamp are employed, and a disc attached to the eyepiece tube can be rotated so that suitable screens can be brought into the eyepiece in turn, and only monochromatic light of the desired wave-length transmitted. The relation between the true index of refraction n_λ and the apparent index n'_λ (the scale reading) is given by $n_\lambda = Cn'_\lambda - D$, and the method of deriving the constants C and D is given, whence the dispersion, $\Delta n = n_{\lambda_1} - n_{\lambda_2}$, is determined.

W. A. RICHARDSON.

Chamber for the study of ions and electrons in gases. L. B. LOEB and A. M. CRAVATH (*J. Opt. Soc. Amer.*, 1928, 16, 191—196).—A detailed description is given of a metal ionisation chamber suitable for use in research on the mobilities and saturation currents of ions and electrons in gases. The apparatus has been employed successfully with hydrogen sulphide.

C. J. SMITHELLS.

Devices for increasing accuracy in weighing. F. C. GUTHRIE (*Nature*, 1928, 121, 745—746).—The rider is in contact with the beam of the balance at one point only, and is moved, if possible, without raising the beam knife-edge; otherwise, the mean of several zero observations, the knife-edge being raised between each pair, is taken. Swinging is set up by a puff of air through a glass tube bent under the pan from an external bulb.

A. A. ELDRIDGE.

Laboratory thermostat. M. COPPOLA (*Annali Chim. Appl.*, 1928, 18, 97—98).—A convenient form of insulated, electrically heated thermostat with pulley-driven stirring gear is described.

T. H. POPE.

Micro-calorimeter. S. G. LIPSETT, F. M. G. JOHNSON, and O. MAASS (*J. Amer. Chem. Soc.*, 1928, 50, 1030—1033).—The construction of an adiabatic platinum micro-calorimeter on the lines of the large calorimeter previously used (*A.*, 1927, 520), and having a thermal capacity of 1 g.-cal., is described. With its aid heats of dissolution in 4 c.c. of solvent may be determined.

S. K. TWEEDY.

Simplified manometer for vacuum distillations. G. B. HEISIG (*Ind. Eng. Chem.*, 1928, 20, 382—383).—The Pyrex glass manometer is so constructed that the long (150 mm.) capillary tubing arm dips into a mercury pool (the mercury of which rises only about 0.5 mm. when the whole tube is emptied into it) on the other side of which the short arm (50 mm.) rises, bent at right angles at the top and tapering, for attachment to the distilling system. The manometer is read directly by means of a scale behind the long arm; any distillate coming over

will enter the large chamber and not interfere with the reading, and no stop-cock is necessary for attachment. The maximum error, which would be at very low pressure, is 0.5 mm.
D. G. HEWER.

Glass manometer. F. DANIELS (J. Amer. Chem. Soc., 1928, 50, 1115—1117).—The gas pressure is measured, with an accuracy of about 0.2 mm., by balancing it against a known air pressure through a glass diaphragm, the point of balance being determined electrically. The device, which is totally enclosed in glass, is claimed to be more trustworthy and easier to construct than previous, similar, devices.
S. K. TWEEDY.

Laboratory evaporator. P. OERTEL (Chem.-Ztg., 1928, 52, 302).—A steam-heated evaporating bath is described which may be worked at pressures from about 0.2 to 0.5 atm. The mean temperature is 85° and the maximum 95°, so that spurting or overheating of the material is avoided. The apparatus is so designed that little corrosion takes place and that the solution which is being evaporated cannot be contaminated with products of the corrosion of the bath.
H. F. GILLBE.

Micro-fractionating column for analytical purposes. C. M. COOPER and E. V. FASCE (Ind. Eng. Chem., 1928, 20, 420—421).—The active part of the column consists of a Pyrex tube 36×0.7 cm., constricted by projections, and vacuum-jacketed, the jacket being maintained electrically at 20° below the b. p. of the material inside, and a condenser returns reflux to the column. The Fisher organic thermometer indicates the temperature of the vapour product, which, when condensed, drops into a 5-c.c. water-jacketed burette. Permanent gases escape by a side-tube. The material remaining in the column after distillation is about 0.4 c.c. and the time required for fractionating a 10 c.c. sample is between 30 and 90 min.
D. G. HEWER.

Clamp for rubber tubing. H. W. BATCHELOR (Ind. Eng. Chem., 1928, 20, 366).—Rubber tubing is secured to glass tubing by a short glass tube of slightly larger diameter slipped over the rubber and then worked back over the junction by stretching the rubber tube. With slight modification a mercury seal may be arranged.
C. IRWIN.

Constant-volume pycnometer. H. V. ELLSWORTH (Min. Mag., 1928, 21, 431—435).—The pycnometer of 10 c.c. capacity is made of silica-glass, thus possessing several advantages over one made of ordinary glass. The stopper is perforated by a capillary and is continued into a graduated side-tube, which dips under water while the apparatus is cooling. The volume of the contained water to the graduations on the side-tube can be readily and accurately determined to 0.0002 c.c.
L. J. SPENCER.

Measuring bomb for very volatile substances. K. H. SLOTTA (Chem.-Ztg., 1928, 52, 291).—An apparatus suitable for the storage and delivery of small measured amounts of substances such as hydrogen cyanide, carbonyl chloride, methyl bromide, etc. is described.
H. INGLESON.

Rapid ashing furnace. A. FORNET (Chem.-Ztg., 1928, 52, 319).—In this apparatus, in which four ash determinations can be made simultaneously, the design brings about an intimate contact of air with the substance treated and renders stirring or addition of oxidising agents unnecessary.
H. INGLESON.

Steam still for volatile acids. D. H. CAMERON.—See B., 1928, 287.

Drying vessel. A. OPPÉ (Chem. Fabr., 1928, 241).—A vacuum-tight drying vessel capable of being weighed consists of a cap making an external joint on to the vessel, the vessel itself, an upright cylinder, and top and bottom gas connexions, the latter forming a spiral on which the vessel rests. The vessel is particularly intended for bulky hygroscopic substances and is adapted for use in a heating bath.
C. IRWIN.

Electromagnetic vacuum cut-off. J. H. HIBBEN (J. Amer. Chem. Soc., 1928, 50, 1117—1118).—A piece of soft iron enclosed in glass is suspended by means of a solenoid at the top of the sealed limb of a U-tube containing mercury. Interruption of the current causes the iron to fall; the mercury level in the other limb then rises and seals the vacuum lead from the apparatus.
S. K. TWEEDY.

Apparatus for catalytic reduction. R. ADAMS and V. VOORHEES (Org. Syntheses, 1928, 8, 10—16).—The apparatus, which is fully described, is suitable for catalytic reductions with hydrogen at 2—3 atm., the reaction vessel being continuously shaken.
A. A. ELDRIDGE.

Danger of mercury vapour. W. KRÖNER.—See B., 1928, 350.

Nomography. II. O. LIESCHE (Chem. Fabr., 1928, 228—230, 241—243; cf. this vol., 501).—The construction of charts for the reading of analytical results of the type corresponding with the relation $y=f(x)$ is developed. In the determination of barium sulphate by sedimentation the original curve is parabolic. If the relation is linear as in the iodometric determination of antimony, sulphites, etc. the chart takes the form of two scales at an angle. A more complicated linear relationship is found in the conversion of wt.-% into at.-% in alloys, e.g., of magnesium copper. The direct construction method cannot be used directly for non-linear relationships, but by breaking up the equation it may be partly applied. The method may be equally applied to empirical data as in the distillation of a mixture of water and benzene.
C. IRWIN.

Geochemistry.

Measurements of the ozone in the higher atmosphere during 1927. H. BUISSON (Compt. rend., 1928, 186, 1229—1230).—The ozone content of the higher atmosphere was determined from the absorption of rays of several wave-lengths for different heights of the sun, expressed as a function of the thickness of air traversed, and from the absorption coefficients of ozone for these wave-lengths. Expressed in mm. of pure ozone directly overhead at midday under normal conditions of temperature and pressure, it varies from 4 in spring to 2 in autumn, with minor irregular variations depending (in an inverse sense) on the atmospheric pressure. The results confirm those of Dobson and Harrison (A., 1926, 140, 493) and others. J. GRANT.

Composition of the thermal waters from Barèges. R. MASSY and P. CAZAUX (J. Pharm. Chim., 1928, [viii], 7, 340—345).—The hydrogen sulphide, total sulphur, and temperature of eighteen of these waters have been determined. The results do not agree with those obtained by Robine and Dejussieu (this vol., 267) and the reasons for the differences are discussed. E. H. SHARPLES.

Sulphate:chloride ratio of the waters of the North Pacific. T. G. THOMPSON, J. W. LANG, and L. ANDERSON (Pub. Puget Sound Biol. Sta., 1927, 5, 277—292).—The ratio was constant at 0.1396 for samples from the coasts of Alaska and Washington, from Puget Sound and Gray's Harbour.

CHEMICAL ABSTRACTS.

Occurrence of iodine in nature. XII. Geochemistry of iodine. III. Atmosphile character of iodine. T. VON FELLEBERG (Biochem. Z., 1928, 193, 384—389; cf. A., 1926, 1022; 1927, 955).—Gases escaping from various mineral springs are shown to contain iodine in spite of the alkaline nature of the fluid from which they escape. The iodine content runs parallel with the chlorine, bromine, and ammonium contents. The springs from which most gas escapes are richest in iodine, and it appears that their content of iodine is derived for the most part from the volcanic gases as they escape.

P. W. CLUTTERBUCK.

Physical factors on the sandy beach. II. Chemical changes: carbon dioxide concentration and sulphides. J. R. BRUCE (J. Marine Biol. Assoc., 1928, 15, 553—565).—The observations were made at Port Erin from 1923 to 1927. The gaseous exchanges of animals and plants cause changes in the p_{H} of the interstitial waters of the beach, but the calcareous matter present in the sand acts as an alkali reserve preventing undue rise in acidity and widening the potential range of carbon assimilation by surface flora. The black layer observed at varying depths below the surface of the sandy beach is associated with the decay of organic matter under conditions of stagnation and oxygen deficiency brought about either through gross obstruction or through the fineness of grade of the sand. Since moist ferrous sulphide to which the layer owes its dark colour oxidises very rapidly on exposure to the air, a special iodometric method was devised for its examination.

The following scheme is suggested as representing the sulphur cycle in the sea-bed and in the sandy beach: $S \xrightarrow{O} RSO_3 \xrightarrow{O} RSO_4 + \text{organic matter} \xrightarrow{\text{Bacteria}} RS \xrightarrow{CO_2} H_2S \xrightarrow{\text{Thio-bacteria}} S$ and simultaneously $H_2S + Fe_2O_3 \cdot nH_2O \xrightarrow{O} FeS + Fe_2S_3 \xrightarrow{O} Fe_2O_3 \cdot nH_2O + S$.

H. INGLESON.

X-Ray study of fluoride micas. C. MAUGUIN and L. GRABER (Compt. rend., 1928, 186, 1131—1133; cf. this vol., 463).—Fluorine atoms may replace oxygen atoms in the crystal lattice of micas, the sum of the two sets of electronegative atoms always being 12. This involves the loss of a positive and a negative elementary charge due to the departure of a hydrogen atom if the fluorine replaces a hydroxyl group, and explains the low hydrogen content of the fluoride micas. The analogy between oxygen and fluorine in geochemistry is discussed. J. GRANT.

Composition of basaltic lavas of Indo-China. A. LACROIX (Compt. rend., 1928, 186, 985—991; cf. this vol., 207).—The composition of these lavas is of importance since a fertile "red earth" is produced as the result of their decomposition. In general, they fall into a series ranging from those containing up to 8.7% of free silica (α -basalts) to those in which there is a deficit of silica sufficient to cause the appearance of nepheline (β -basalts). In the former, the pyroxene is an augite containing a relatively large amount of magnesium (pigeonite), and having a very small or zero angle between the optical axes, whilst in the latter the augite is titaniferous. The β -basalts predominate and are rich in olivine. They fall into two groups in which the silica deficit affects only the bivalent metals and the mode of combination of the alkali metals, respectively. The basalts are poor in coloured minerals, and bronzite is rare, but ilmenite is abundant. The structure is doleritic with a variable grain, which is sometimes truly holocrystalline. Glomeroporphyric associations of phenocrystals of olivine augite and bronzite were also observed. The analyses show that the volcanic glasses are poorer in ferric iron than the crystalline lavas derived from them. J. GRANT.

Crystalline carnotite from Utah. F. L. HESS and W. F. FOSHAG (Proc. U.S. Nat. Mus., 1927, 71, Art. 21, 1—6).—The specimen contained UO_3 65.62, V_2O_5 21.12, Al_2O_3 0.16, Fe_2O_3 0.04, CaO 0.64, MgO 0.22, K_2O 9.58, Na_2O 0.35, H_2O 1.35, CuO , PbO , and P_2O_5 traces, insol. 0.32, total 99.40%, corresponding with the formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 0.67H_2O$; $2V$ $50 \pm 2^\circ$, n_D 2.06—2.04, n_V 2.08—2.06. The radium:uranium ratio is discussed.

CHEMICAL ABSTRACTS.

Composition of chevkinite. L. E. KAUFMAN (Bull. Acad. Sci. Russ., 1924, 18, 315—320).—The composition of chevkinite corresponds with the formula $0.5(H, K, Na)_2O \cdot 2(Fe, Ca, Mn)_2O \cdot 2(La, Ce, Fe)_2O_3 \cdot 6(Si, Ti)_2O_2$.

CHEMICAL ABSTRACTS.

Bauxite. T. V. M. RAO (Min. Mag., 1928, 21, 407—430).—Detailed analyses are given of "laterites" from India, British Guiana, Gold Coast, etc.

The material consists of a mixture of minerals resulting from the decomposition of rocks, the principal constituent being bauxite. It is concluded that bauxite is a definite mineral species with the formula $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Experiments were made of the action on granulated basalt of dilute solutions of sodium carbonate at 30–50° during several months. Analyses of the partly decomposed products show a decrease in silica and an increase in alumina, and it is concluded that bauxite has been formed by such action.

L. J. SPENCER.

Potarite, a new mineral from British Guiana. L. J. SPENCER (Min. Mag., 1928, 21, 397–406).—The palladium mercuride described by Harrison (A., 1925, ii, 592, 593) has been found very sparingly as small nuggets and grains in the diamond-washings on the Potaro river. It is silver-white and brittle, and shows a crystalline structure with the form of cubic octahedra. The mineral has the composition PdHg, and it has since been named potarite. The supposed hexagonal modification of palladium, "allo-palladium," is perhaps potarite or simply the cubic modification of palladium.

L. J. SPENCER.

Radium and thorium content of volcanic rocks of the Hegau. H. LEDERER (Ber. naturforsch. Ges. Freiburg i. Br., 1927, 27, No. 2, 20 pp.; Chem. Zentr., 1927, ii, 2273).—The rocks of the Hegau may be classified in three groups; phonolite, basalt, and tufa, having a radium ($\times 10^{-12}$) and thorium ($\times 10^{-5}$) content as follows: 8.03–4.1, 6.18; 2.33–1.01, 0.57; 1.05–0, 1.01 g. per g.

A. A. ELDRIDGE.

Radium and thorium content of phonolite of the Kaiserstuhl. W. SEITH (Ber. naturforsch. Ges. Freiburg i. Br., 1927, 27, No. 2, 4 pp.; Chem. Zentr., 1927, ii, 2273).—Phonolite and tephrite of the Kaiserstuhl contain, respectively, 4.83 and 6.62×10^{-12} g. per g. of radium, and 4.25 and 4.33×10^{-5} g. per g. of thorium, corresponding with a uranium content of 1.55 – 2.10×10^{-5} g. per g.

A. A. ELDRIDGE.

Fresh-water lime-manganese rocks and lime-magnesia fresh-waters. H. KLAHN (Chem. Erde, 1928, 3, 453–587).—A detailed account of travertine deposits (fresh-water limestones and dolomites), with a discussion of the conditions for their formation and the composition of the waters from which they are deposited.

L. J. SPENCER.

"Cone-in-cone" marl. G. LYNCK and W. NOLL (Chem. Erde, 1928, 3, 699–721).—A discussion of "cone-in-cone" structure in marls, including "nail limestone," with descriptions of material from Thuringia and Romania. Analyses show that calcium carbonate is the main constituent, with considerable and variable amounts of clayey matter and free silica. The structure is attributed to the crystallisation of a calcium carbonate gel in the presence of much foreign matter. Comparisons are made with a similar structure in fibrous celestine pseudomorphous after gypsum from Jena.

L. J. SPENCER.

Constituents and genesis of a few minerals produced from hot springs and their vicinities in Japan. I. Akita hokutolite. II. Composition and genesis of soluble sulphates produced near a sulphur spring. I. SUGANUMA (Bull.

Chem. Soc. Japan, 1928, 3, 69–73, 73–76).—I. A deposit found near a sulphur spring in Akita-ken, Japan, resembles hokutolite (Hayakawa and Nakano, A., 1912, ii, 1123) in general composition, but contains radioactive elements of the thorium series as well as of the radium series. It is probable that the mineral owes its origin to the coagulation of colloidal silicic acid in the water of the spring by substances produced by species of *Cyanophyceae* growing in the water. Depending on the acidity and temperature of the water, the substances adsorbed by the silica vary, and the mineral has accordingly a zonal structure.

II. Specimens of halotrichite, alunogen, and melanterite found near sulphur springs have been analysed.

R. CUTHILL.

Salt formation in the Chilean desert. W. WETZER (Chem. Erde, 1928, 3, 375–436).—Microscopical examination of thin sections of Chile saltpetre (caliche) showed the presence of halite, nitratine, darapskite, gypsum, anhydrite, thenardite, glauberite, bloedite, "Chile-loeweite" [minute trigonal crystals with ϵ 1.434, ω 1.470, d 2.153, and, after deducting impurities, the composition $\text{K}_2\text{Na}_4\text{Mg}_2(\text{SO}_4)_5 \cdot 5\text{H}_2\text{O}$], "chromloeweite" (?), and leonite (?). Potassium perchlorate, although a product of extraction, could not be detected as crystals in the raw caliche. The distribution and relative ages of formation of each of these salts are discussed in detail. It is considered that the nitrates were formed by the action of atmospheric nitric acid on the alkali silicates of the rocks of the region.

L. J. SPENCER.

Comparative study of the weathering of rocks under different climatic conditions. E. BLANCK and A. RIESER (Chem. Erde, 1928, 3, 437–452).—Fragments of sandstone and of limestone were exposed to the weather during a period of five years at Göttingen and on the summit of the Brocken (1142 m.), where, owing to the difference in altitude, there are marked differences in the temperature, rainfall, and humidity. Detailed analyses of the rocks and of the portions extracted by hydrochloric acid, both before and after the experiment, showed no appreciable differences in composition.

L. J. SPENCER.

Soils [and rock weathering] in Spitzbergen. E. BLANCK and A. RIESER [with H. MORTENSEN] (Chem. Erde, 1928, 3, 588–698).—A study of rock weathering under arctic conditions. Numerous detailed analyses are given of various rocks (sandstone, quartzite, clay-slate, phyllite, diabase, and calcareous shale) and of their disintegration products, including soils and muds; analyses are also given of the portions extracted by hydrochloric acid and by sulphuric acid from the débris. Chemical action in weathering is here retarded owing to deficient water circulation, and the action of frost is of more importance in breaking down the rocks.

L. J. SPENCER.

Coals as colloid systems. L. L. FERMOR (Nature, 1928, 121, 705–706).—Evidence is adduced in support of the author's view that coals are to be regarded as colloid systems; the data refer to certain Indian coals.

A. A. ELDRIDGE.

Base exchange and the formation of coal. E. McK. TAYLOR (Nature, 1928, 121, 789–790).—

Bituminous coal appears always to occur under a roof which has undergone base exchange and containing sodium as the chief replaceable base; the "drift" and "in situ" theories may thereby be reconciled. Base exchange between the material covering the petroleum-bearing strata and solutions of sodium chloride must also have taken place. Experiments on the bacterial decomposition of fats under a roof which has undergone base exchange and hydrolysis indicate that the fat is hydrolysed, the resulting glycerol being converted into methane and the fatty acid being reduced to a corresponding paraffin. Hence both coal and petroleum may have

resulted from the bacterial decomposition of animal or vegetable fats under alkaline anaërobic conditions.

A. A. ELDRIDGE.

J. L. Smith method for the analysis of samarskite. R. C. WELLS (J. Amer. Chem. Soc., 1928, 50, 1017—1022).—Observations on the above analysis are recorded. The mineral contained helium; d^{25} 5.67—5.656; μ 2.18—2.20; it had an average age of 1040×10^6 years. The mineral is isotropic.

S. K. TWEEDY.

Minerals. H. COLLINS (Chem. News, 1928, 136, 305—306).—The author's characteristic data for atoms are applied to minerals. A. A. ELDRIDGE.

Organic Chemistry.

Catalytic hydrogenation of different types of unsaturated compounds. II. Hydrogenation of conjugated systems. S. V. LEBEDEV and A. O. YAKUBCHIK (J.C.S., 1928, 823—837, and J. Russ. Phys. Chem. Soc., 1927, 59, 981—1011; cf. A., 1925, i, 350).—The process of hydrogenation of conjugated compounds of butadiene structure in presence of platinum-black may be of four types: (I) In the first phase hydrogen adds on exclusively in the $\alpha\delta$ -position. In the second phase, proceeding at a different rate, there occurs addition to the $\beta\gamma$ -position of the ethylenic derivative formed in the first phase. The point at which the original conjugated system is consumed, the "critical point of hydrogenation," is at 50% hydrogenation. (II) In the first phase there occurs simultaneous hydrogenation of the conjugated system in the $\alpha\beta$ -, $\beta\gamma$ -, and $\gamma\delta$ -positions of the ethylenic products. The "critical point" is then found at 68—77% hydrogenation. In the second phase, the remainder of the ethylenic compounds formed in the first phase are hydrogenated. (III) It is theoretically possible, although not actually observed, that the addition of 2 mols. of hydrogen might take place simultaneously, giving a saturated compound directly. (IV) Addition of hydrogen occurs exclusively in the $\alpha\beta$ - and $\gamma\delta$ -positions. The double linkings of the formally conjugated system are hydrogenated independently, either consecutively at different rates, or concurrently, according to the type of substitution. The position of the "critical point of hydrogenation" is characteristic of the type of reaction.

The hydrogenation of isoprene was studied, using the methods previously described (*loc. cit.*). The process is of type (II). The hydrogenation curve, depicting rate of addition of hydrogen, is a horizontal line up to the "critical point" at 70% hydrogenation; after this, it shows three sections corresponding with the successive hydrogenation, at different rates, of the ethylenic products formed before the "critical point," viz., β -methyl- $\Delta\gamma$ -butene, β -methyl- $\Delta\alpha$ -butene, and β -methyl- $\Delta\beta$ -butene. *iso*Pentane is formed in the first phase, probably from β -methyl- $\Delta\gamma$ -butene. The total concentration of methylbutenes increases regularly with time, but excess of β -methyl- $\Delta\beta$ -butene was found in the first part of the curve, probably owing to its formation from the other products by isomeris-

ation under the influence of the sulphur dioxide used to separate the isoprene for analysis. In the second phase of the hydrogenation the reactions are no longer "conjugated" by the isoprene, and the methylbutenes are successively hydrogenated in the order given above, which agrees with the rules previously formulated (*loc. cit.*). This was confirmed by the behaviour in the presence of added β -methyl- $\Delta\gamma$ -butene or β -methyl- $\Delta\beta$ -butene. When isoprene is hydrogenated in admixture with various ethylenic compounds, the "critical point" retains its position, although ill-defined with β -methyl- $\Delta\beta$ -butene. R. K. CALLOW.

cis-trans-Isomerism and homologous series.

B. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1928, 60, 19—46).—The physical properties of paraffin hydrocarbon chains in homologous series are reviewed, with the conclusion that the chains are zig-zag in shape, the angle not necessarily being the tetrahedral angle, but depending on the nature of the terminal groups, which are in the *cis*-position if the number of atoms forming the chain is even, and in the *trans*-position if it is odd. The m. p., solubilities, surface tensions, dielectric constants, ionic mobilities, molecular magnetic rotations, molecular volumes, and heats of combustion and fusion of the two types are compared with the same properties of corresponding *cis*- and *trans*-isomerides of the ethylene series, and shown to have the same effect relative to their respective series. The external fields of force of isomerides are shown to vary inversely as their intramolecular tension. Similar terminal groups at both ends of the chain cause mutual repulsion, whilst other combinations cause mutual attraction. Both these factors may result in a twisting of the paraffin chain in "pseudo-*cis*" and "pseudo-*trans*" forms. It is suggested that some compounds in the liquid state are equilibrium mixtures of the true and pseudo-forms, and an explanation offered why certain monobasic fatty acids with an odd number of carbon atoms crystallise in two forms.

Attempts are made to extend these considerations so as to include the *cycloparaffins*.

M. ZVEGINTZOV.

Erythrene and its dibromides. C. PRÉVOST (Compt. rend., 1928, 186, 1209—1211).—Erythrene from the dehydration of methylvinylcarbinol had b. p.

—4.75°, d_4^{20} 0.650, n_D^{20} 1.4222, and when brominated at —20° in chloroform or at —90° in methyl chloride, gave the *trans*- $\alpha\delta$ -dibromide; no *cis*-form was obtained, and only a small amount of the $\alpha\beta$ -dibromide was formed. The two products are desmotropic, and the former when maintained at 85°/10 mm. gives rise to the latter, which has b. p. 52°/10 mm., d_4^{21} 1.865, n_D^{21} 1.541. At 20°, the $\alpha\beta$ -dibromide changes slowly to the $\alpha\delta$ -form, the change at 100° being more rapid and reversible. The desmotropic nature is confirmed by the tautomerism of the $\alpha\delta$ -dibromide, which gives rise to $\alpha\beta$ - or $\alpha\delta$ -derivatives in quantities different from those of the bromides originally present. At 100°, sodium acetate gives almost entirely the diacetate of Δ^{β} -butene- $\alpha\delta$ -diol, and traces of the diacetate of the $\alpha\beta$ -diol, whilst hydrolysis of the former furnishes the $\alpha\beta$ -diol in 40% yield. Tautomerism and desmotropy are distinct, the latter usually including the former, whilst the reverse is not true (cf. A., 1926, 131; 1927, 851; this vol., 152). Hydrolysis of the above acetates with water alone gives rise to crotonaldehyde (not isolated). J. D. FULTON.

Derivatives of $\beta\gamma$ -dimethylbutadiene. A. D. MACALLUM and G. S. WHITBY (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 33—38).—The action of sulphur chloride on $\beta\gamma$ -dimethylbutadiene in carbon disulphide yielded an oily *additive product*, $(\text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{S})_2$, d_4^{26} 1.1172, n_D^{26} 1.5400. There occurred no formation of a thiophen derivative on treatment of the diene with sulphur or reaction with antimony trichloride. Bromination yielded the two dibromides, solid, b. p. 105—110°/18.5 mm., d_4^{30} 1.6912, n_D^{30} 1.5470, and liquid, b. p. 105—110°/18.5 mm., d_4^{30} 1.6502, n_D^{30} 1.5390. Ozonolysis of the solid dibromide yielded bromoacetone, and it is, therefore, an $\alpha\gamma$ -compound (cf. Kondakov, A., 1901, i, 62). The solid dibromide is highly reactive. With sodium methoxide and ethoxide at 100° $\alpha\delta$ -dimethoxy- $\beta\gamma$ -dimethyl- Δ^{β} -butene, b. p. 81—84°/33.5 mm., and $\alpha\delta$ -diethoxy- $\beta\gamma$ -dimethyl- Δ^{β} -butene, b. p. 90—95°/25 mm., respectively, were obtained. Dimethylamine and diethylamine yielded both open-chain ditertiary bases and cyclic quaternary compounds which may be either pyrrolinium compounds or have a constitution of double mol. wt. with a ten-membered ring. $\alpha\delta$ -Di-(dimethylamino)- $\beta\gamma$ -dimethyl- Δ^{β} -butene chloroaurate, m. p. 188—189°; $\alpha\delta$ -di(diethylamino)- $\beta\gamma$ -dimethyl- Δ^{β} -butene chloroaurate, m. p. 177—179°; 1:1:3:4-tetramethyl- Δ^3 -pyrrolinium chloroplatinate (?), decomp. 199°, and 3:4-dimethyl-1:1 diethyl- Δ^3 -pyrrolinium bromoaurate (?), m. p. 52.8°, were isolated. Methyl-aniline gave $\alpha\delta$ -di(phenylmethylamino)- $\beta\gamma$ -dimethyl- Δ^{β} -butene, m. p. 76—77°. Pyridine gave $\beta\gamma$ -dimethyl- Δ^{β} -butene- $\alpha\delta$ -dipyridinium dibromide, m. p. 124° (chloroplatinate, decomp. 229°). An attempt was made to allot *cis*- and *trans*-constitutions to the two dibromides. The liquid is probably the *cis*-form, for it gave with diethylamine a higher yield of a cyclic product, 3:4-dimethyl-1:1-diethyl- Δ^3 -pyrrolinium bromoaurate (?), m. p. 106—107°, than the solid dibromide, although the quaternary products were not identical. Analogy with butadiene dibromides, refractivities, and m. p., but not molecular volumes, support this conclusion. The liquid dibromide showed

no tendency to isomerise to the solid when heated or treated with acids. The solid could be isomerised to the liquid, wholly by treatment with magnesium, partly by heating with the original diene. The solid dibromide and magnesium methyl iodide yielded the diene and two *dimerides*, $\text{C}_{12}\text{H}_{20}$, one, b. p. 50°/20 mm., and the other the distillation residue.

R. K. CALLOW.

Tetramethylbutadiene [$\gamma\delta$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene]. A. D. MACALLUM and G. S. WHITBY (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 39—44).—A review of the published data leads to the conclusion that the ease of polymerisation of butadienes is diminished by increase in the number of substituent methyl groups, and more by substitution in the $\alpha\delta$ -than in the $\beta\gamma$ -positions.

The most satisfactory of numerous methods tried for the reduction of methyl ethyl ketone to $\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol was to heat with magnesium and mercuric chloride in benzene solution. Distillation of this pinacol with a little dilute sulphuric acid yielded $\gamma\delta$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene, b. p. 132—134°, 71—73°/100 mm., $d_4^{19.2}$ 0.7832, n_D^{20} 1.4630, not identical with the by-product obtained by Herschmann (A., 1893, i, 547). An unstable *dibromide* was formed with bromine at 0°. Oxidation by 3% aqueous permanganate solution yielded acetic acid alone, confirming the constitution. It showed no tendency to polymerise on heating under conditions which cause formation of caoutchouc from isoprene. The action of sulphuric acid yielded an impure *dimeride*, b. p. 170—200°, n_D^{25} 1.4915. Air, which brought about autoxidation, caused some polymerisation. An attempt was made to synthesise $\gamma\delta$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene by another method. Bromination of *n*-butyl bromide was tried under various conditions; the desired $\beta\gamma$ -dibromobutane was obtained by using iron wire as a catalyst in Reboul's method (A., 1892, i, 127). Excess of methyl-alcoholic potash yielded γ -bromo- Δ^{β} -butene, which, on treatment with magnesium, yielded only a *substance*, $\text{C}_{16}\text{H}_{34}\text{O}$, b. p. about 160°, n_D^{25} 1.4735.

R. K. CALLOW.

Law of periodicity. III. P. PETRENKO-KRITSCHENKO [with A. RAVIKOVITSCH, V. OPOTZKI, E. PUTJATA, and M. DIAKOVA] (Ber., 1928, 61, [B], 845—854; cf. A., 1927, 713).—Periodicity is observed in the action of potassium, tetramethylammonium, tetraethylammonium, barium, and thalious hydroxides, sodium ethoxide, and silver on the chloro-derivatives of methane, but not with its bromo- or iodo-derivatives or with the halogen derivatives of toluene or acetic acid. Ammonia, piperidine, water, alcohol, silver nitrate, potassium acetate, and potassium thiocyanate behave less consistently; the reagents of this group can behave differently according to conditions and to the compound on which they act. Under equivalent conditions, the following substances are hydrolysed to the indicated extent by acetic acid in benzene at 95°: $\text{CH}_3(\text{OEt})_2$, 13.6%; $\text{CH}(\text{OEt})_3$, 18%; $\text{C}(\text{OEt})_4$, 9.7%; $\text{CH}(\text{OEt})_2\cdot\text{CH}(\text{OEt})_2$, 3%. The mutual relationship of the data is the same as that recorded by Skrabal (A., 1926, 1010), but his attribution of minimum activity to maximal symmetry of structure can scarcely be maintained. Duplication of functions does not invariably lead to a strengthening

of all the influences which distinguish the simple molecules. Thus tetraphenylethylene glycol is less readily etherified than triphenylcarbinol and ethyl tartrate less easily than ethyl lactate. Diminution of activity may also be caused by accumulation of similar but not identical groups. Among carbonyl compounds duplication of function results in enhanced activity. With halogen derivatives of methane and ethane the following results are obtained by the use of potassium hydroxide as reagent: $\text{CH}_3\text{X} > [\text{CH}_2\text{X}]_2$ for chloro- and bromo-compounds, whereas the reverse holds for iodo-derivatives; $\text{CH}_2\text{X}_2 < [\text{CHX}_2]_2$ and $\text{CHX}_3 > [\text{CX}_3]_3$ —reversal is caused by accumulation of halogen; the slightly active CH_2X_2 is converted by duplication into the active $[\text{CHX}_2]_2$, whereas the active CHX_3 yields the slightly active $[\text{CX}_3]_3$. The results are considered from the point of view of Thiele's theory of conjugated double linkings. H. WREN.

Action of cuprous cyanide on methyl iodide. E. G. J. HARTLEY (J.C.S., 1928, 780—781; cf. *ibid.*, 1916, 109, 1296).—Cuprous cyanide and methyl iodide at 100° yielded a compound, $(\text{CuNC})_3\text{MeI}$, stable in air, but losing all the methyl iodide on heating or dissolution in potassium cyanide. At 100°, in excess of acetonitrile the reaction yielded the stable compound, $3(\text{CuNC}, \text{MeI})$, which was also formed in small amount at 135° in absence of the nitrile. The action of potassium cyanide on this compound yielded methyl-carbamide, whilst aqueous solutions of silver salts yielded silver iodide, silver, cupric salts, and probably compounds of the type $\text{Cu}(\text{NCMe})_2\text{SO}_4$, which, however, could not be isolated. Cuprous cyanide and certain other insoluble cyanides combine with acetonitrile to give unstable compounds, e.g., the compound CuNC, MeCN . R. K. CALLOW.

[Preparation of] *tert.*-butyl chloride. J. F. NORRIS and W. OLMSTED (Org. Syntheses, 1928, 8, 50—51).

[Preparation of] trimethylene chlorohydrin. C. S. MARVEL and H. O. CALVERY (Org. Syntheses, 1928, 8, 112—115).

Mechanism of the action of oxidising agents on alcohols. B. V. TRONOV and M. A. LUKANIN (J. Russ. Phys. Chem. Soc., 1928, 60, 181—191).—The reactions of oxidising agents with alcohols are discussed from the point of view of the relative strength of the carbon-hydrogen and hydrogen-oxygen linkings (cf. Tronov and others, this vol., 44).

The rates of reaction of primary and secondary alcohols, both saturated and unsaturated, with bromine, nitric and chromic acids, and potassium permanganate (both in acid and alkaline solution) were investigated.

It is probable that an intermediate compound, of the nature of an ester, is first formed, which then decomposes into the final product. The molecules of the inorganic oxidising agents appear to form the ester-like compounds in the non-ionised state.

M. ZVEGINTZOV.

Determination of alcohols. A. VERLEY (Bull. Soc. chim., 1928, [iv], 43, 469—472).—The method previously described (A., 1902, ii, 54) for the determination of phenols gives satisfactory results with primary alcohols and most secondary alcohols if 5% of acetyl

chloride is added to the acetic anhydride before mixing with 2 parts of pyridine. For the determination, 10 c.c. of this mixture are used and about 2—3 g. of the alcohols. Complete acetylation is obtained by heating for 1—2 hrs. with most primary alcohols and for 2—3 hrs. with secondary alcohols: the recommended periods for the determination are 3 hrs. and 4 hrs., respectively. Accurate results cannot be obtained with very volatile alcohols or if the mixture contains a tertiary alcohol, phenol, primary or secondary amines, or an aldehyde. Small amounts of aldehydes, however, do not affect the accuracy of the results, as acetylation of aldehydes under these conditions never exceeds 14—15%. On account of their volatility alcohols lower than the pentanols give results varying from 53.85% with methyl alcohol, 66.5% with ethyl alcohol, to 97.3% for *sec.*-butyl alcohol and 99.9% for *n.*-butyl alcohol. R. BRIGHTMAN.

Liberation of hydrogen from carbon compounds. Interaction with fused alkali hydroxides of: III. Monohydric alcohols and esters; IV. [with E. L. SCHULZE.] Glycol and glycerol; V. Dextrose, lævulose, sucrose, and cellulose. H. S. FRY and E. OTTO (J. Amer. Chem. Soc., 1928, 50, 1122—1131, 1131—1138, 1138—1144).—III. The mechanism proposed for the action of fused alkali hydroxides on methyl alcohol (A., 1924, i, 1277) has been confirmed by further experiments with a eutectic mixture, m. p. 185°, of sodium and potassium hydroxides at 250—450°. At temperatures below 370° the reaction residue contains methoxide, and below 300°, formate. At 370°, 85% of the methyl alcohol is converted into carbonate and hydrogen, at 450°, 100%, and using sodium or potassium hydroxide alone at 450°, 95%. Ethyl alcohol gives no acetate or ethylene at 530° (cf. A., 1926, 710), the reaction, $\text{EtOH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + 2\text{H}_2 + \text{CH}_4$, predominating. Similarly, the amounts of carbonate, hydrogen, and methane formed when (a) propyl alcohol, (b) *isopropyl* alcohol, and (c) *tert.*-butyl alcohol are oxidised by fused alkali hydroxide at 500° agree well with the schemes: (a) $\text{PrOH} + 6\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{Na}_4\text{CO}_4 + \text{CH}_4 + 5\text{H}_2$, (b) $\text{CHMe}_2\text{OH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2 + 2\text{CH}_4$, (c) $\text{CMe}_3\text{OH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + 3\text{CH}_4$. Carbonisation is (a) slight, (b) very slight, (c) nil, but with *isobutyl* alcohol it is extensive, even at 350°. Esters are first hydrolysed by the fused alkali, then oxidised in the normal way. Thus, the oxidation of methyl formate at 475° conforms to the extent of 70% to the scheme $\text{H}\cdot\text{CO}_2\text{Me} + 4\text{NaOH} \rightarrow 2\text{Na}_2\text{CO}_3 + 4\text{H}_2$ (slight carbonisation), and that of methyl acetate to the extent of 88% to the scheme $\text{CH}_3\cdot\text{CO}_2\text{Me} + 4\text{NaOH} \rightarrow 2\text{Na}_2\text{CO}_3 + \text{CH}_4 + 3\text{H}_2$. Ammonia, methyl-, dimethyl- and trimethyl-amines, and dimethyl and diethyl ethers are not attacked. These results are in accordance with the general type reactions previously developed.

IV. The general reaction mechanism accounts for the formation of the compounds obtained by Würtz (Ann. Chim. phys., 1859, [3], 55, 417) and Nef (A., 1905, i, 3) from glycol and fused alkali hydroxides. Using the author's method, reaction is complete in 20 hrs. at 250° and a little oxalate is formed, whilst at

350°, 5—7 hrs. are required and oxalate is absent. In either case at least 80% of the glycol reacts as follows: $C_2H_6O_2 + 4NaOH \rightarrow 2Na_2CO_3 + 5H_2$. The complex results obtained by Nef with glycerol were due to a deficiency of alkali hydroxide. When glycerol is added to the fused alkali at 345—360° and the reaction completed by heating to 400° and finally to 450°, 78% is oxidised according to Buisine's equation (A., 1903, i, 455), $C_3H_8O_3 + 4NaOH \rightarrow 2Na_2CO_3 + 3H_2 + CH_4 + H_2O$, and 21% according to the equation $C_3H_8O_3 + 6NaOH \rightarrow 7H_2 + 3Na_2CO_3$.

V. When dextrose or levulose is fused with alkali at 185° and the product gradually heated during about 15 hrs. to 550°, it is oxidised to the extent of 90—95%. Of this 90% is due to the reaction $C_6H_{12}O_6 + 8NaOH \rightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2$, which involves intermediate formation of lactic acid or ethyl alcohol, and the remainder to the direct oxidation, $C_6H_{12}O_6 + 12NaOH \rightarrow 6Na_2CO_3 + 12H_2$. Quantitative results could not be obtained with sucrose, owing to carbonisation. Cellulose is completely oxidised without carbonisation when made into a paste with water and alkali and heated during 8 hrs. to 550°; 95% reacts according to the equation $C_6H_{10}O_5 + 14NaOH \rightarrow 5Na_2CO_3 + Na_4CO_4 + 12H_2$, and 5% according to $C_6H_{10}O_5 + 8NaOH \rightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 + H_2O$. H. E. F. NOTTON.

Chlorine dioxide explosions. E. C. WAGNER (J. Amer. Chem. Soc., 1928, 50, 1233—1234).—The use of potassium chlorate in the oxidation of *n*-butyl alcohol by the method of Milas (this vol., 392) may lead to explosions unless the temperature is kept below 80° until sometime after the final addition of acid has been made. H. E. F. NOTTON.

Kessyl alcohol. IV. Y. ASAHINA and S. NAKA-NISHI (J. Pharm. Soc. Japan, 1928, [551], 1—20).—It was previously shown (*ibid.*, [544], 485) that deoxykessyl ketone dichloride gave with alcoholic potassium hydroxide deoxy- α -kessylene ketone, a compound with two double linkings, which was converted into deoxy- α -kessylanone by catalytic reduction. It is now found that the analogous deoxidation takes place simply on heating with palladised charcoal (1:10) or with charcoal only: α -kessyl ketone gives on treatment with the palladised charcoal *isodeoxy- α -kessylene ketone*, b. p. 153—155°/7 mm., d_4^{20} 1.0031, n_D^{20} 1.52005, $[\alpha]_D^{20} +42.60$ (*semicarbazone*, m. p. 182°), which decolorises permanganate in acetone and is converted into *isodeoxy- α -kessylanone*, b. p. 134—136°/5 mm., d_4^{20} 0.9498, n_D^{20} 1.48072, $[\alpha]_D^{20} +32.54$ (*semicarbazone*, m. p. 220—223°), by catalytic reduction. The latter compound is stable to permanganate, turns cherry-red with vanillin and hydrochloric acid, reddish-violet-blue with bromine in glacial acetic acid. Kessyl alcohol, when heated with the palladised charcoal, affords a deep blue oil, which by treatment with phosphoric acid (Ruzicka and Rudolph, A., 1926, 299) is separated into a deep blue oil, *kessazulene*, b. p. 153°/7 mm., d_4^{20} 0.9717, soluble in phosphoric acid, and a colourless oil, *kessylene*, b. p. 109—111°/9 mm., d_4^{20} 0.9115, n_D^{20} 1.48905, insoluble in acid. The absorption spectrum of kessazulene closely resembles those of Kremer's azulene (A., 1923, i, 594) and of the azulenes

of Ruzicka and Rudolph (*loc. cit.*). Analysis of the *picrate*, m. p. 123°, and *stypnate*, m. p. 106°, of kessazulene, and of many other kessyl alcohol derivatives indicates C_{15} -formulae, not C_{14} (cf. Bertram and Gildemeister, A., 1891, 238). Kessazulene, $C_{15}H_{18}$, absorbs catalytically 3 mols. of hydrogen at the ordinary temperature, and one more molecule at 70°, giving the *octahydro-derivative*, $C_{15}H_{26}$, b. p. 112—115°/7 mm., d_4^{20} 0.8930, n_D^{20} 1.47141, which is stable to permanganate, showing its tricyclic constitution, and gives with bromine first a violet and then a blue colour. Kessylene, $C_{15}H_{22}$, similarly gives a saturated *hydrocarbon*, $C_{15}H_{26}$, b. p. 105—108°/5 mm., d_4^{20} 0.8931, n_D^{20} 1.47289, which is stable to permanganate, and shows the same coloration as octahydrokessazulene.

Unsaponifiable matter from the oils of elasmobranch fish. IV. Establishment of the structure of selachyl and batyl alcohols as monoglyceryl ethers. I. M. HEILBRON and W. M. OWENS (J.C.S., 1928, 942—947).—Batyl alcohol was prepared from the liver oil of *Centrophorus granulosus* (cf. Tsujimoto and Toyama, A., 1922, i, 297; Toyama, A., 1924, i, 604) by an improved method. The *phenylurethane*, m. p. 98°, and *p-nitrobenzoate*, m. p. 53—54°, are described. The presence of an ether oxygen atom was confirmed, but, contrary to Weidemann's statement (A., 1926, 980), no methoxyl is present. Treatment with hydriodic acid yielded octadecyl iodide, m. p. 33°, the identification of which was confirmed by the preparation from it of octadecane, methyl octadecyl ether, octadecyl alcohol, and its phenylurethane. The constitution of batyl alcohol is represented by $C_{15}H_{37} \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, (I), or $C_{13}H_{37} \cdot O \cdot CH(CH_2 \cdot OH)_2$, (II), of which (II) is preferred. It follows that selachyl alcohol, $C_{21}H_{42}O_3$, is the corresponding monoglyceryl oleyl ether, whilst chimyl alcohol, $C_{19}H_{40}O_3$, will correspond with the monoglyceryl cetyl ether. R. K. CALLOW.

Configuration of pentaerythritol. J. BÖESEKEN and B. B. C. FELIX (Ber., 1928, 61, [B], 787—790).—If pentaerythritol has the tetrahedral configuration, the products, $C(C_2H_4O_2 > CRR')_2$, derived from it by condensation with 2 mols. of an aldehyde, ketone, or ketonic acid must be asymmetric and hence capable of resolution into enantiomorphous isomerides. If, however, the pyramidal structure of the solid persists in the solution, *cis-trans*-isomerides must be capable of existence. In several cases examined, the latter possibility has not been realised, but an isolated instance of the isolation of an optically active derivative is recorded. It is suggested that both forms may be present in solution and that the central carbon atom oscillates between positions within and without the tetrahedron.

Pentaerythritol and benzaldehydediethylacetal afford dibenzylidenepentaerythritol, which, apparently by spontaneous resolution, afforded the dextrorotatory compound, m. p. 188—189°, $[\alpha]_D +30$ ° in chloroform; the active material is rapidly racemised by hydrogen chloride in chloroform to the ordinary racemate, m. p. 160°. Attempts to repeat the resolution failed. *Ditrichloroethylidenepentaerythritol*, $C(C_2H_4O_2 \cdot CH \cdot CCl_2)_2$, from pentaerythritol, chloral hydrate, and concentrated sulphuric acid, has m. p. 275°. The com-

pound $C(C_2H_4O_2 \cdot CMe \cdot CH_2 \cdot CO_2Et)_2$, b. p. 145—150°/4 mm., prepared from pentaerythritol, ethyl acetate, and alcoholic hydrogen chloride, is hydrolysed to the corresponding acid, which could not be resolved by means of strychnine, brucine, codeine, or *l*-phenylethylamine; at about 100°, the acid loses carbon dioxide and affords pentaerythritol diisopropylidene ether, m. p. 115—116°. From ethyl pyruvate the substances $C(C_2H_4O_2 \cdot CMe \cdot CO_2Et)_2$, m. p. 145°/0 mm., and $(CH_2 \cdot OH)_2C \cdot C_2H_4O_2 \cdot CMe \cdot CO_2Et$, m. p. 95°, are derived, the former of which yields the corresponding acid, m. p. 238° (sodium salt). The condensation products of pentaerythritol with 2 mols. of the following substances have been prepared: lævulic acid, m. p. 186—188°; terephthalaldehydic acid; benzaldehyde-*m*-sulphonic acid; *m*-dimethylaminobenzaldehyde. H. WREN.

Sodium ethylene thiosulphate, $Na_2C_2H_4S_4O_6$. O. MAGIDSON [with W. KROL] (Trans. sci. chem.-pharm. inst., Moscow, 1923, 6, 21—28; Chem. Zentr., 1927, ii, 2542).—When ethylene dibromide and saturated aqueous sodium thiosulphate are stirred for 10—15 days at 40°, plates of sodium ethylene thiosulphate, $Na_2C_2H_4S_4O_6$, decomposing when heated, are obtained.

A. A. ELDRIDGE.

Preparation of aliphatic and aromatic sulphones with sodium hypochlorite. A. E. WOOD and E. C. TRAVIS (J. Amer. Chem. Soc., 1928, 50, 1226—1228; cf. B., 1926, 811; Birch and Norris, A., 1925, i, 1229).—(a) Ethyl, (b) propyl, (c) *n*-butyl, (d) *n*-heptyl, (e) phenyl, and (f) benzyl sulphides have been oxidised by sodium hypochlorite (2.3—9.3% of available chlorine) at the ordinary temperature. Solutions containing 2% of free sodium hydroxide attacked only (a) and (b); those with 0.2—0.1% oxidised all except (d) within 3 hrs., and those with 0.12—0.61% of sodium carbonate gave sulphones instantly with all except (d), which gave mainly sulphoxide. H. E. F. NOTTON.

Electrolysis of anhydrous formic acid. G. BAUR [with F. SOMLO and H. W. MACKINNEY].—See this vol., 489.

Determination of formic acid in acetic acid. F. G. GERMUTH (Chemist-Analyst, 1928, 17, 7).—Mercuric chloride solution (4%, 20 c.c.), potassium acetate solution (15%, 20 c.c.), and hydroxylamine hydrochloride solution (2%, 1 c.c.) are added to 2 g. of the acetic acid, and the precipitate of mercurous chloride is collected, dried, and weighed.

CHEMICAL ABSTRACTS.

Determination of small quantities of acetic acid in air in presence of carbon dioxide. V. KUNI and S. NIKOLSKI (Gigiena truda, 1927, 41—43; Chem. Zentr., 1927, ii, 2329).—The air is drawn through 0.1*N*-sodium hydroxide solution, the change in alkalinity is determined, and the carbonate precipitated as barium carbonate; the latter is determined titrimetrically or as barium sulphate.

A. A. ELDRIDGE.

[Preparation of] trimethylacetic acid. S. V. PUNTAMBEKER and E. A. ZOELLNER (Org. Syntheses, 1928, 8, 104—106).

[Preparation of] trimethylacetic acid. L. T. SANDBORN and E. W. BOUSQUET (Org. Syntheses, 1928, 8, 108—110).

[Preparation of] β -chloropropionic acid. C. MOUREU and R. CHAUX (Org. Syntheses, 1928, 8, 54—56).

[Preparation of] β -chloropropionic acid. S. G. POWELL (Org. Syntheses, 1928, 8, 58—59).

Mechanism of the transformation undergone by ricinoleic acid. Pyrogenic decomposition of methyl ricinoleate. P. S. PANIUTIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1—6).—The position and behaviour under the influence of heat of the double linking in ricinoleic acid were investigated. Pure ricinoleic acid was prepared (in a 75% yield) from castor oil by hydrolysis and precipitation as the lead salt with lead acetate. As the free acid polymerised under the action of heat, the behaviour of the methyl ester was investigated. On distillation it gave a 62% yield of heptaldehyde. By regulating the distillation rate and introducing lumps of pumice saturated with anhydrous borax as an anti-polymerising agent, 92.7% of the aldehyde and 87% of methyl undecenoate were obtained. There was no evidence of either racemisation or migration of the double linking. M. ZVEGINTZOV.

Condensation of hydroxy-acids by the simultaneous action of several catalysts in the presence of hydrogen under high pressure; α -hydroxy-*n*-butyric and α -hydroxyisovaleric acids. V. IPATIEV and G. RASUVAJEV (Ber., 1928, 61, [B], 634—637; cf. A., 1926, 1124; 1927, 1053, 1054).—The production of dibasic acids by heating the salts of α -hydroxy-acids in aqueous solution at 250—270° under high hydrogen pressure in the presence of the oxides of nickel and aluminium becomes less marked as the carbon chain of the hydroxy-acid is lengthened. Thus, sodium α -hydroxy-*n*-butyrate affords α -methyl- β -ethylsuccinic acid in 10% yield together with about 25% of *n*-butyric acid, higher monobasic acids probably derived from dicarboxylic acids by loss of carbon dioxide, and methane. Sodium α -hydroxyisovalerate does not give a dicarboxylic acid. The main products are carbon dioxide, formic acid, isobutyl alcohol, saturated acids among which propionic acid is identified, and methane; isovaleric acid could not be isolated. H. WREN.

Condensations of hydroxy- and keto-acids; β - and γ -hydroxy- or -keto-acids and acids with a tertiary hydroxyl group. G. RASUVAJEV (Ber., 1928, 61, [B], 637—640; cf. A., 1926, 1124; 1927, 1053, 1054, and preceding abstract).—The production of dibasic acids is not observed with the acids named in the title. Thus sodium β -hydroxybutyrate in aqueous solution at 245—250° in presence of nickel and aluminium oxides and hydrogen under 56 atm. gives *n*-butyric acid in about 35% yield accompanied by carbon dioxide, formic and acetic acids, methane, and a non-homogeneous liquid. Sodium lævulate, at a temperature not exceeding 230°, affords successively γ -hydroxyvaleric acid and valeric acid in yield not exceeding 20%. About 20% of the acid suffers conversion into methane, carbon dioxide, and un-

identified products; at 250°, this type of decomposition becomes more marked, and the resulting solution, when acidified, deposits a tar. Sodium α -hydroxyisobutyrate yields 60% of isobutyric acid in addition to methane, carbon dioxide, formic acid, and unidentified products. H. WREN.

Influence of groups and associated rings on the stability of certain heterocyclic systems.

IV. Substituted butyro- and valero-lactones. S. S. G. SIRCAR (J.C.S., 1928, 898—903; cf. A., 1927, 756).—The observed rates of hydrolysis of the series of butyro- and valero-lactones substituted in the β -position by the groups H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; cyclopentane, and cyclohexane show that there is a general increase in stability in the order given, but in the series of butyrolactones the Me, H member is more stable than the Et, H member, and there is a maximum of stability at the Me, Et and Et, Et members, whilst in the valerolactones the Me, H member is least stable and the cyclopentane member shows maximum stability. It is concluded that there is an "optimum condition" of stability peculiar to each ring-system, its exact position being difficult to predict on the Thorpe-Ingold modified strain theory alone. This indicates the existence of other factors in deciding ease of ring-formation and ring-stability.

The butyrolactones were prepared by heating the silver salt of the glutaric acid with iodine (cf. Windaus and Klänhart, A., 1921, i, 392), and the valerolactones by reduction of the glutaric anhydrides with sodium and alcohol. The following are new: β -methylbutyrolactone, b. p. 88°/12 mm., β -ethylbutyrolactone, b. p. 99°/12 mm.; β -methyl- β -ethylbutyrolactone, b. p. 98°/10 mm.; $\beta\beta$ -diethylbutyrolactone, b. p. 117°/12 mm.; β -cyclopentanespirobutyrolactone, b. p. 120—121°/11 mm.; β -cyclohexanespirobutyrolactone, b. p. 138°/11 mm.; β -methylvalerolactone, b. p. 90°/12 mm.; β -ethylvalerolactone, b. p. 104°/13 mm.; β -methyl- β -ethylvalerolactone, b. p. 122°/10 mm.; $\beta\beta$ -diethylvalerolactone, b. p. 143—144°/15 mm.; β -cyclopentanespirovalerolactone, b. p. 146°/12 mm.; and β -cyclohexanespirovalerolactone, b. p. 158—159°/10 mm. The silver salts of the corresponding acids were prepared. R. K. CALLOW.

Porphyrins. XVI. γ -Chloro- $\alpha\gamma$ -dimethylitaconic acid. W. KÜSTER, H. MAURER, and K. PACKENDORFF (Z. physiol. Chem., 1928, 172, 244—250; cf. Küster, Maurer, and Palm, A., 1926, 713, 1024).—Ethyl α -acetyl- $\alpha\beta$ -dimethylsuccinate (hydrolysis product of the imide, C₈H₁₁O₃N, from hæmatoporphyrin dimethyl ether) gives with phosphorus pentachloride an acid chloride, from which by treatment with sodium ethoxide and then with acid is obtained in small yield γ -chloro- $\alpha\gamma$ -dimethylitaconic acid, m. p. 127° (decomp.). Distillation in a vacuum converts this into the anhydride, m. p. 145°, b. p. 125°/15 mm., of γ -chloroitaconic acid, CH₂:CCl·CH(CO₂H)·CHMe·CO₂H; at ordinary pressure there is also formed the isomeric oily anhydride, b. p. 210—225°, of α -methyl- β -(α' -chloroethyl)maleic acid. The crystalline and the oily anhydrides are converted by sodium and barium hydroxide, respectively, into trans- γ -chloroitaconic acid, m. p. 152°. The

ammonium salt of this acid and the products of addition of 2 mols. of ammonia to the two anhydrides all give on distillation an imide, m. p. 166°.

C. HOLLINS.

Methyl- β -hydroxyethylmaleic anhydride and the hydrolysis of α -hydroxynitriles with sulphuric acid. III. W. KÜSTER [with K. MAY, R. WOLF, A. EBERLE, and G. MANDRY] (Z. physiol. Chem., 1928, 172, 230—243; cf. A., 1925, i, 922).—Ethyl 1-acetylcyclopropane-1-carboxylate (thiosemicarbazone, m. p. 160°; *p*-bromophenylhydrazone, m. p. 131°) is converted into its cyanohydrin, which, when heated with hydriodic acid (*d* 1.7) at 140—150°, gives a less impure methyl- β -iodoethylmaleic anhydride (cf. *loc. cit.*), from which the barium salt and thence the silver, copper, and calcium salts of methyl- β -hydroxyethylmaleic acid are obtained pure. Hydrolysis of the cyanohydrin with concentrated sulphuric acid water-cooled below 40° gives oily methyl- β -hydroxyethylmaleic anhydride (copper salt), which is converted by boiling 10% sodium hydroxide into a dibasic acid, C₁₀H₁₀O₅, subliming at 200°; the anhydride is accompanied by an oxidation product, γ -hydroxy- β -carbethoxy- γ -carbamyl-*n*-valeric acid, m. p. 127°. Ice-cooling during hydrolysis prevents formation of this product.

The cyanohydrin, b. p. 114—117°/3 mm., of ethyl ethylacetate yields with 70% sulphuric acid an amide-ester, α -hydroxy- β -carbethoxy- α -methyl-*n*-valeramide, m. p. 121—122°, and a by-product, m. p. 116°. From the cyanohydrin of ethyl acetylglutarate is similarly obtained the corresponding di-ester-amide, ethyl δ -hydroxy- γ -carbethoxy- δ -carbamyl- δ -methyl-*n*-hexoate, m. p. 101°, from which by hydrolysis with 40% sodium hydroxide a small amount of hæmatic acid results; under other conditions, the γ -carbethoxy-group is also hydrolysed by sulphuric acid, giving ethyl δ -hydroxy- γ -carboxy- δ -carbamyl- δ -methyl-*n*-hexoate, m. p. 186°. Hydrolysis of ethyl cyanomethylsuccinate (Küster and Hugel, A., 1923, i, 1207) with 85% sulphuric acid yields a compound, C₁₀H₁₇O₅N, m. p. 146—147°, which loses no ammonia when heated with 0.5—20% potassium hydroxide. Ethyl γ -cyanopentane- $\alpha\gamma\delta$ -tricarboxylate (*ibid.*) is converted by 85% sulphuric acid into ethyl pentane- $\gamma\delta$ -dicarboxylimide- $\alpha\gamma$ -dicarboxylate [$\alpha\gamma$ -dicarbethoxy-pentane- $\gamma\delta$ -dicarboxylimide]. C. HOLLINS.

Reducing power of chemically pure glycuronic acid. G. SCHEFF (Biochem. Z., 1928, 194, 96—104).—A method is described for determining the reducing power of pure glycuronic acid and of the ammonium salt of its menthol derivative, and comparison is made with the reducing power of arabinose and dextrose. No simple relationship, calculable from the mol. wt., exists between the reducing powers of dextrose and glycuronic acid (cf. A., 1927, 551).

P. W. CLUTTERBUCK.

Resolution of *r*- α -sulphodi-*n*-butyric acid. R. AHLBERG (Ber., 1928, 61, [B], 811—817; cf. A., 1924, i, 832).—The preparation of barium *r*- α -sulphodi-*n*-butyrate (octa-, tri-, and semi-hydrates) is best effected by dissolving the acid in barium hydroxide followed by addition of an excess of the latter and preservation of the solution for a few days. The

salt is the most sparingly soluble of the possible isomerides. To avoid isomerisation during crystallisation, sulphodibutyric or acetic acid must be added to the salt until alkalinity completely disappears. The *r*-acid can be resolved into its optical antipodes by brucine, cinchonine, or cinchonidine. The alkaloidal salts are derived from 2 mols. of base and 1 mol. of acid. With the two alkaloids first named, the (+)-acid gives the most sparingly soluble salts, whereas with cinchonidine the salt of the (-)-acid separates. The homogeneous (-)-acid is, however, isolated more conveniently and in better yield from the mother-liquors of the precipitated brucine salt. On account of the readiness with which the active α -sulphodi-*n*-butyric acids undergo isomerisation their isolation is a matter of considerable difficulty, and the success of the operations depends on their sufficient insolubility in comparison with that of the other forms and their relative stability in anhydrous ether. (+)- α -Sulphodi-*n*-butyric acid has m. p. about 156–160° (indefinite by reason of isomerisation), $[\alpha]_D^{25} +107.9^\circ$ in ether, $[\alpha]_D^{25} +88.6^\circ$ in acetone, $[\alpha]_D^{25} +84.4^\circ$ in absolute alcohol. For the (-)-acid, $[\alpha]_D^{25} -106.7^\circ$ in ether, is recorded. (+)-Sulphodi-*n*-butyric acid undergoes slow racemisation in moist ether.

H. WREN.

Kinetics of the transformation of the active α -sulphodi-*n*-butyric acids. R. AHLBERG (Ber., 1928, 61, [B], 817–826; cf. preceding abstract).—The rate of racemisation of α -sulphodi-*n*-butyric acid in aqueous solution increases with the dilution to a well-defined maximum for 0.1*M*-solutions, after which it diminishes sharply. In solutions which are 0.1*M* with respect to the organic acid but also contain 0.01–2.01 mols. of hydrogen chloride per litre, an ill-defined maximum rate of racemisation is observed in presence of 0.01 mol. of hydrogen chloride; with higher concentrations of mineral acid the rate of inactivation falls steadily. 0.1*M*-Solutions of the acid partly neutralised by sodium hydroxide show an indistinct maximal rate of racemisation if about 20% of the acid is neutralised; with further addition of alkali hydroxide the rate of racemisation falls almost linearly with the decrease of free acid until the completely neutral solutions are nearly stable. If a portion of the α -sulphodi-*n*-butyric acid in aqueous solution is replaced by the corresponding molecular amount of orthophosphoric acid, the velocity of racemisation remains unchanged or is very slightly increased.

H. WREN.

α -Ethyl- α' -sulphodipropionic acid. R. AHLBERG (Ber., 1927, 61, [B], 827–829).—A mixture of the *r*- α -ethyl- α' -thiodipropionic acids is oxidised to a mixture of *r*- α -ethyl- α' -sulphodipropionic acids one of which can be isolated by means of its sparingly soluble barium salt. This acid can be resolved into its optical isomerides by brucine or quinine, thus giving two of the four possible active acids. The rate of racemisation of the acids in aqueous solution has been studied. Among the sulphonic acids, increasing mol. wt. causes rapid diminution in the rate of inactivation. The following half-periods in hours for approximately 0.2*M*-solutions at about 25° are recorded: α -sulphodipropionic acid, 1.3; α -ethyl-

α' -sulphodipropionic acid, 2.3; α -sulphodi-*n*-butyric acid, 2.75; α -sulphodisovaleric acid, 50.

H. WREN.

Determination of acetaldehyde by different methods. J. WAGNER (Biochem. Z., 1928, 194, 441–452).—Acetaldehyde, present in standard dilute aqueous solutions or liberated from known amounts of its hydrogen sulphite compound, its thiosemicarbazone, and from *dl*-lactic acid, is comparatively determined by the usual iodine titration, by the mercuric oxide, and hydroxylamine sulphate methods. The sulphite titration method may also be used for very small concentrations of aldehyde.

P. W. CLUTTERBUCK.

Acraldehyde. J. PRITZKER (Helv. Chim. Acta, 1928, 11, 445–448).—A criticism of the structure assigned to the colouring matter forming the product of interaction of acraldehyde, hydrogen peroxide, and phloroglucinol (Powick, A., 1924, i, 487).

H. BURTON.

Pyrogenic decomposition of mixed magnesium carbonates. Preparation of ketones. D. IVANOV (Bull. Soc. chim., 1928, [iv], 43, 441–447).—The carbonated magnesium compounds obtained by the action of carbon dioxide on magnesium aralkyl or *n*-primary alkyl compounds at -20° (cf. A., 1925, i, 503) after removal of the ether by distillation afford (1) the hydrocarbon resulting from the decomposition $2R.X + Mg = R.R + MgX_2$ with (2) the ketone from the secondary decomposition $R.CO.O.MgX + R.MgX = R.CO.R.MgX_2 + MgO$; and (3), mainly, the ketone resulting from the decomposition $2R.CO.O.MgX = R.CO.R + MgX_2 + MgCO_3$, the commencement of the third stage being usually marked by the liberation of carbon dioxide. With magnesium *sec*-alkyl or aryl or hydroaryl compounds the yields of ketone are poor and the decomposition affords mainly the corresponding ethylenic hydrocarbon, water, carbon monoxide and dioxide. In the case of the carbonated magnesium aryl compounds the corresponding hydrocarbon is the chief product, and dry distillation of the corresponding calcium or barium salts affords the same products. Since decomposition of the corresponding magnesium salts at similar temperatures affords practically the same yield of ketone, the mixed magnesium carbonates are regarded as true salts of magnesium and probably possess the symmetrical structure suggested by Jolibois (A., 1912, i, 753) at high as well as at low temperatures (cf. A., 1927, 961), and the decomposition is to be represented: $(R.CO_2)_2Mg.MgX_2 = R.CO.R + MgX_2 + MgO + CO_2$. The stability of the carbonated compound is also dependent on the nature of the halide, the temperature of decomposition being lowest with the iodides and highest with the chlorides. The reaction is, however, best effected with the chlorides or bromides, these affording crystalline carbonates, whereas those derived from *sec*-bromides or iodides are oily products. The following ketones have been prepared in this way, the yields and temperature of decomposition being indicated: acetone, 330–360°, 157% (59% from magnesium acetate); diethyl ketone, 340–360°, 70% (74% from the propionate); di-*n*-propyl ketone, 330–340°, 70%; di-*n*-butyl ketone, 360–380°, 63%

(from the chloride), 50% from the bromide at 330—340°; diisomyl ketone, 390—400°, 43% from the chloride, 35% at 370—390° from the bromide; diisopropyl ketone, 380—390°, 35%, diisobutyl ketone, 360°, 28%; di-*sec.*-butyl ketone, 340—350°, traces; dibenzyl ketone, 370°, 57% (60% from magnesium phenyl acetate at 370—380°); dihexyl ketone, 390—410°, traces; benzophenone, 460—500°, 6% (30% from magnesium benzoate); di-*p.*-tolyl ketone, 450°, traces. The following m. p. are recorded for the anhydrous (probably basic) magnesium salts: *acetate*, 357°; *n-propionate*, 286°; *n-butyrate*, 275°; *n-valerate*, 258°, *isovalerate*, 224°, *benzoate*, 320°, *hexahydrobenzoate*, 492°.

R. BRIGHTMAN.

Dioximes. XLVIII. I. DE PAOLINI and A. IMBERTI (*Gazzetta*, 1928, 58, 196—202).—The method of preparing hydroxyglyoximes previously described (cf. A., 1926, 850; 1927, 135) is extended to the preparation of aminohydroxytrioxime, $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}$ (described by Wieland and Hess, A., 1909, i, 370, as *isonitrosomalono-hydroxamic acid amine-oxime*). Ethyl oximinocynoacetate, prepared by treating a mixture of ethyl cyanoacetate and aqueous sodium nitrite solution with dilute hydrochloric acid, when treated in methyl-alcoholic solution with hydroxylamine and alcoholic ammonia solution, yields the *ammonium* salt of aminohydroxytrioxime, of which the hydrochloride has new m. p. 156° (decomp.), and the tetra-acetyl derivative, m. p. 179°. The above ammonium salt when heated in dilute sulphuric acid yields 3-amino-4-oximino-1:2:5-*isooxazolone* (cf. Wieland and co-workers, A., 1909, i, 370, 610; 1912, i, 838), which forms a *monobenzoyl* derivative, m. p. 193° (decomp.). The aminoglyoximecarboxylic acid, obtained by Wieland and Hess (*loc. cit.*) by the action of barium hydroxide on the amino-oximino-*isooxazolone*, is synthesised by the action of hydroxylamine on oximinocynoacetic acid, and has m. p. 170° (decomp.). Its *ammonium* salt, m. p. [+H₂O] 114—115°, and *silver* salt are described; it is converted by acetic anhydride into acetoximinocynoformamide (Wieland and Gmelin, A., 1909, i, 610).

E. W. WIGNALL.

Structure of carbohydrates. W. N. HAWORTH (*Helv. Chim. Acta*, 1928, 11, 534—548).—A lecture delivered to the Swiss Chemical Society.

H. BURTON.

Ultra-violet spectrograms of carbohydrates. V. HENRI and S. A. SCHOV (*Z. physiol. Chem.*, 1928, 174, 295—299).—Absorption experiments with dextrose solutions show that the absorption is less with purer dextrose preparations, and preparations which give much less absorption than that recorded by Niederhoff (A., 1927, 396, 724) are readily obtained. With the purest dextrose used, there is no detectable absorption at 2800 Å. and the absorption can be measured only below 2210 Å. In the solutions where the absorption at 2800 Å. can be measured, the values are less than one twentieth of those obtained by Niederhoff, and a comparison with the absorption coefficients of acetone leads to the conclusion that less than 1 in 300 of the molecules present in the dextrose solution have the carbonyl form. The form-

ation of an absorption band at 2800 Å. in dextrose solutions is dependent on the p_{H} , temperature, and time; the band can be detected at p_{H} values as low as 7.0 in phosphate-buffered solutions. A. WORMALL.

Ultra-violet absorption of carbohydrates. P. NIEDERHOFF (*Z. physiol. Chem.*, 1928, 174, 300—301).—The absorption band at 2800 Å. of reducing sugars in aqueous, especially alkaline, solution is not due to impurities as suggested by Kwicciński and Marchlewski (A., 1927, 1056) and by Henri and Schou (preceding abstract). The decrease in the selective absorptive power of dextrose or galactose on recrystallisation from alcohol is not due to the removal of impurities, since the mother-liquors show no selective absorption. Also, reducing sugars show a selective absorption, whereas sucrose does not.

A. WORMALL.

Reactions between sugars and amino-acids. G. QUAGLIARIELLO and P. DE LUCIA (*Boll. soc. ital. biol. sperim.*, 1927, 2, 26—30; *Chem. Zentr.*, 1927, ii, 2179).—A study of the effect of glycine on the rotation of aldehydic sugars, with which it forms compounds. The largest reduction (50%) is observed with mannose. With dextrose, the maximal fall of rotation varies with p_{H} : 0% at p_{H} 8.46, 37% at 8.95, 17.57% at 9.1, 50% at 9.5, 99% at 10.4. Simultaneously, the f. p. is changed. A. A. ELDRIDGE.

[Preparation of] l-arabinose. E. ANDERSON and L. SANDS (*Org. Syntheses*, 1928, 8, 18—21).—The authors' method (B., 1926, 169) for the preparation of *l*-arabinose from mesquite gum is modified.

A. A. ELDRIDGE.

Rhamnosan. H. VOGEL (*Helv. Chim. Acta*, 1928, 11, 442—444).—When rhamnose is heated at 150—155°/15—16 mm., there is formed a *rhamnosan* (annexed formula), m. p. 90°, $[\alpha]_{\text{D}} +2.5^\circ$ in water (*diacetate*, m. p. 102—103°, $[\alpha]_{\text{D}} +30.47^\circ$ in chloroform), which when boiled in aqueous solution regenerates rhamnose. This rhamnosan differs from that described by von Lippmann (A., 1925, i, 366).

H. BURTON.

Oxidation of dextrose in alkaline solution by air or oxygen with formation of carbon monoxide. M. NICLOUX (*Compt. rend.*, 1928, 186, 1218—1220).—A measured volume of oxygen or air was passed into an evacuated flask containing dextrose in dilute alkaline solution at the required temperature. Carbon monoxide and dioxide were formed in amounts varying with temperature, alkalinity, and time of contact of the solution with oxygen. J. D. FULTON.

Oxidation of lævulose in absence of oxygen. F. AUBEL and L. GENEVOIS (*XII Int. Cong. Physiol.*, 1926, 11—12; *Chem. Zentr.*, 1927, i, 2724—2725).—In anaërobiosis, lævulose reduces certain dyes, the rate of reduction of 10^{-3} — 10^{-6} *N*-methylene-blue solution being independent of the dye concentration, but increasing with increased p_{H} value and lævulose concentration. A. A. ELDRIDGE.

Ketonic nature of α -glucoheptulose. G. BERTRAND and G. NITZBERG (*Compt. rend.*, 1928, 186,

1172—1175).—Sorbose bacteria grown on yeast with addition of α -glucoheptitol give rise to a crystalline reducing sugar, $C_7H_{14}O_7$, named α -glucoheptulose. The sugar when heated with dilute hydrochloric acid in presence of orcinol, phloroglucinol, or resorcinol gives definite colour reactions, a characteristic of some ketonic sugars. The reducing power of the sugar is unaffected by treatment with bromine in aqueous solution. A further proof of its ketonic nature is given on reduction with 2.5% sodium amalgam in faintly acid solution, to prevent isomerisation at a temperature not above 35°, two products, *glucoheptulitol*, m. p. 144°, and α -glucoheptitol, being obtained.
J. D. FULTON.

Thiocellobiose and thiocellobiosides. F. WREDE and O. HETCHE (Z. physiol. Chem., 1928, 172, 169—178).—Cellobiose bromide hepta-acetate in hot alcohol reacts with methyl-alcoholic potassium disulphide to give *dicellobiosyl disulphide tetradeca-acetate*, m. p. 271—273°, $[\alpha]_D^{25} -79^\circ$, which is hydrolysed by methyl-alcoholic ammonia to *dicellobiosyl disulphide*, decomp. 165—170°, $[\alpha]_D^{20} -90.8^\circ$, or is reduced and acetylated by zinc dust and acetic anhydride to *thiocellobiose octa-acetate*, m. p. 205°, $[\alpha]_D^{20} -13^\circ$. *Thiocellobiose hepta-acetate*, m. p. 197° (clear at 220°), $[\alpha]_D^{20} -12.6^\circ$, obtained by reduction of the disulphide tetradeca-acetate in phenol by aluminium amalgam and aqueous-alcoholic acetic acid, gives by methylation with diazomethane the *methyl ether hepta-acetate*, m. p. 200°, $[\alpha]_D^{20} -20.2^\circ$, from which *methylthiocellobioside*, m. p. 220°, $[\alpha]_D^{20} -31^\circ$, is prepared by hydrolysis; the *ethyl ether hepta-acetate*, m. p. 193°, $[\alpha]_D^{20} -26.7^\circ$, and *ethylthiocellobioside*, m. p. 219°, $[\alpha]_D^{20} -37.7^\circ$, are similarly obtained. *Thiocellobiose*, $C_{12}H_{22}O_{10}S$, prepared from the octa-acetate and methyl-alcoholic ammonia, sinters about 110°, and in 50% alcohol shows $[\alpha]_D^{20} -33.3^\circ$, changing to $+14.8^\circ$ in 6 days; the *silver salt* gives, by treatment with methyl iodide followed by acetylation, the above methyl ether hepta-acetate.
C. HOLLINS.

Quantitative hydrolysis of starch by buffered taka-diaxase. [Determination of starch.] I. D. COLLINS (Science, 1927, 66, 430—431).—When 50 c.c. of 0.3% starch solution are kept at 40° for 36 hrs. with 1 c.c. of 10% taka-diaxase and 5 c.c. of acetate buffer (p_H 5.0), dextrose values representing 98.5—101.1% hydrolysis are obtained. Reduction of the concentration of taka-diaxase to 0.75 did not decrease the amount of dextrose formed; with 0.5 the dextrose value was 95.6—99.0. A phosphate buffer at p_H 4.5 gave 100.1% of dextrose. A. A. ELDRIDGE.

Structure of the crystalline component of cellulose. K. H. MEYER and H. MARK (Ber., 1928, 61, [B], 593—614).—The determination of the structure is based on the following considerations: (1) Cellobiose can be obtained in 60% yield from cellulose under conditions which do not permit the formation of cellobiose from dextrose; (2) cellobiose has the constitution assigned to it by Haworth and co-workers; (3) the crystalline component of cellulose has an elementary cell of which the edge in the direction of the fibre axis is 10.3 Å. long, whereas the length of the other edges is 7.9 and 8.7 Å.; the

smallest possible elementary cell contains four glucose residues. From these considerations it is deduced that the cellobiose residues are oriented in the direction of the fibre axis and are united to one another by glucosidic oxygen bridges. In the space-groups C^2 , V^3 , and V^4 , a configuration can be elucidated which explains the axial ratios and the most important intensity effects. The conclusion is reached that about forty dextrose residues in the amylenoxide ring form are united by β -glucosidic linkings in the 1:4-position to a straight, extended, main-valency chain. About forty to sixty of such chains are arranged parallel to one another and united by "micellary forces" to a cellulose particle. This conception is shown not only to be compatible with the established facts of cellulose chemistry and its Röntgen analysis, but also to afford a ready explanation of the processes of esterification, swelling, and dissolution.
H. WREN.

Sulphuric esters of cellulose. W. TRAUBE, B. BLASER, and C. GRUNERT (Ber., 1928, 61, [B], 754—767).—Cellulose, in the form of filter-paper dried at 100° in a high vacuum until constant in weight, absorbs sulphur trioxide vapour with avidity from a mixture of the latter with air. If the cellulose has absorbed only 50—75% of its weight of sulphur trioxide, the product is directly converted into its potassium salt by cautious neutralisation with potassium hydroxide. If greater absorption has occurred, the product is treated with water, followed by lead hydroxide or carbonate in amount slightly greater than is required to neutralise the free sulphuric acid. The slight excess of lead is removed as lead sulphide and the clear solution is neutralised with potassium hydroxide. *Potassium cellulose trisulphate-A* crystallises readily from the solution in yield of about 65%. It is amorphous and yields colloidal solutions in water. The copper number is 2.5—4.0. In aqueous solution it has $[\alpha]_D -5.5^\circ$ to -6.5° . The neutral, aqueous solutions are very stable when boiled; addition of hydrochloric acid causes gradual, quantitative elimination of sulphuric acid and the solution acquires strong reducing power compatible with the quantitative production of dextrose. Towards alkali hydroxides the salt *A* is very stable. Regeneration of cellulose from it has therefore not been accomplished. Solutions of the salt do not give a precipitate with silver nitrate, only a turbidity with lead acetate, and marked precipitates with basic lead acetate, nitron, and barium chloride. If the mother-liquors from the preparation of the salt *A*, which has every sign of homogeneity, are concentrated, *potassium cellulose trisulphate-B*, $C_6H_7O_5(SO_3K)_3$, separates in very varying amount; it has $[\alpha]_D +1^\circ$ to $+7^\circ$ in aqueous solution, copper number 8—9, and probably contains a varying proportion of the salt *A*.

Pre-addition of cellulose sulphate to solutions of sulphates acidified with hydrochloric acid inhibits completely the separation of barium sulphate after addition of barium chloride within certain limits; inhibition appears to be due to the formation of colloidal barium sulphate rather than to the production of complexes. Similar observations are recorded for

lead iodide, silver chromate, and mercurous chromate. In the case of sparingly soluble salts, such as potassium perchlorate, the habit of the precipitate is frequently greatly modified by the presence of potassium cellulose trisulphate.

If preparations of cellulose which have absorbed considerably more than 3 mols. of sulphur trioxide are preserved, a homogeneous, transparent, brown, viscous mass is obtained which dissolves without residue in water or alcohol. Such products when treated with water and neutralised with potassium hydroxide afford little or no potassium cellulose trisulphate-*A*, and the solutions when evaporated deposit a material containing much potassium cellulose tetrasulphate, $C_6H_6O_5(SO_3K)_4$, probably usually admixed with a little salt *B*. The tetrasulphate is not a derivative of cellulose, since in its formation a ring of the anhydro-sugar is necessarily ruptured.

Wood is also converted by sulphur trioxide into potassium cellulose trisulphate-*A* if the product is worked up immediately; if, however, it is preserved and a large excess of sulphur trioxide is used, the product is almost completely soluble in water, the lignin also appearing to be converted into water-soluble substances.

H. WREN.

Constitution of pine lignin. VII. β -Lignosulphonic acid. P. KLASON (Ber., 1928, 61, [B], 614—615; cf. A., 1920, i, 821).— α -Lignosulphonic acid is removed from the liquors by β -naphthylamine hydrochloride and the filtrate is treated with lead acetate; the precipitate is decomposed by hydrogen sulphide. The β -lignosulphonic acid thus obtained is treated with a further portion of naphthylamine to remove residual α -lignosulphonic acid and then successively with barium hydroxide and sulphuric acid. It is probable that the β -acid contains a combination of coniferaldehyde and coniferyl alcohol of the type, $R \cdot CH(OH) \cdot O \cdot CH_2R$ and formula $C_{19}H_{18}O_6$; it is impossible for the corresponding hydrosulphonic acid to yield an internal naphthylamine salt. The naphthylamine salt of the β -acid to which the structure $C_{19}H_{18}O_7 \cdot H_2SO_3 \cdot 2C_{10}H_7 \cdot NH_2$ has been ascribed (A., 1923, i, 187) probably has the composition $C_{19}H_{18}O_6 \cdot H_2SO_3 \cdot 2C_{10}H_7 \cdot NH_2 \cdot H_2O$.

H. WREN.

Primary amines from Grignard reagents and monochloroamine. G. H. COLEMAN and C. R. HAUSER (J. Amer. Chem. Soc., 1928, 50, 1193—1196).—When monochloroamine (cf. Marekwald and Wille, A., 1923, ii, 558) is treated in ethereal solution at 0° with excess of Grignard reagent, $RMgX$ (R being methyl, ethyl, *n*-propyl, *n*-butyl, isoamyl, phenyl, benzyl, or β -phenylethyl and X, chlorine, bromine, or iodine), 80—90% of it is converted into primary amine and ammonia. The yield of primary amine, which increases as that of ammonia decreases, is greatest for the same radical R when X is chlorine and least when X is iodine. Magnesium benzyl chloride gives 85% of benzylamine, whilst magnesium phenyl iodide gives 95.6% of ammonia with benzene, chloro- and iodo-benzene, and diphenyl.

H. E. F. NOTTON.

Derivatives of tetramethylenediamine, pyrrolidine, and γ -aminobutyric acid. W. KIEL (Z.

physiol. Chem., 1927, 171, 242—251).—Whereas $\alpha\delta$ -dibromobutane and δ -iodo-*n*-butylamine react with primary and secondary amines to form pyrrolidine ring systems, and with tertiary amines, forming the corresponding substituted tetramethylenediamine, γ -chloro(or -bromo)-*n*-butyronitrile reacts equally characteristically with ammonia, and with mono-, di-, and tri-methylamine, without ring formation in all cases. The following substances are described: γ -amino-*n*-butyronitrile [chloroaurate, m. p. 154° (decomp.)]; γ -methylamino-*n*-butyronitrile, b. p. 173° [hydrochloride, m. p. 162°; chloroaurate (+H₂O); picrate]; γ -dimethylamino-*n*-butyronitrile (chloroaurate, m. p. 129°; picrate, m. p. 120°); trimethyl- γ -cyanopropylammonium picrate, m. p. 126°, and chloroaurate. Hydrolysis of γ -dimethylamino-*n*-butyronitrile with hydrochloric acid affords the hydrochloride of γ -dimethylamino-*n*-butyric acid, isolated as the chloroaurate, m. p. 142°. The latter is also obtained by heating γ -iodo-*n*-butyric acid with alcoholic dimethylamine, treating the resulting iodide with thallium hydroxide and the latter with hydrochloric acid and auric chloride. Reduction of γ -methylamino-*n*-butyronitrile with sodium and alcohol gives the known δ -methylamino-*n*-butylamine, analysed as the chloroaurate. The similarly obtained δ -dimethylamino-*n*-butylamine gives a chloroaurate, m. p. 175°, a chloroplatinate, decomp. 216°, and a picrate. *NN'*-Dimethylputrescine (methyl- δ -methylamino-*n*-butylamine) is conveniently prepared from tetramethylenediamine hydrochloride and formaldehyde in presence of aqueous calcium chloride. It was identified as the chloroplatinate, m. p. 237°. Trimethyl- δ -amino-*n*-butylammonium chloroaurate, chloroplatinate, and picrate were obtained from trimethylamine and δ -iodo-*n*-butylamine hydriodide.

Rapid dry distillation of *NN'*-dimethylputrescine hydrochloride gives 1-methylpyrrolidine. The methiodide of the latter is obtained from δ -iodo-*n*-butylamine hydriodide and cold alcoholic dimethylamine.

J. STEWART.

Complex salts of bivalent platinum with $\alpha\beta\gamma$ -triaminopropane. F. G. MANN (J.C.S., 1928, 890—898; cf. A., 1927, 754).—When potassium chloroplatinitate was treated with $\alpha\beta\gamma$ -triaminopropane trihydrochloride, co-ordination occurred between the metal and the α - and β -amino-groups of the amine, giving dichloro(triaminopropane- γ -monohydrochloride)platinum monohydrate, $[Cl_2Pt(NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, HCl)]H_2O$, m. p. 290—291° (decomp., darkening at 280°). This compound is similar in type to the platinum compound previously described (*loc. cit.*), and its constitution was verified by resolution into optically active forms by fractional crystallisation of the bromocamphor-sulphonates, which were then reconverted into the hydrochlorides. *d*-Dichloro(triaminopropane-mono-*d*-bromocamphor- π -sulphonate)platinum monohydrate, $[M]_{D_{441}}^{25} + 522^\circ$, the *l*-base *l*-sulphonate, $[M]_{D_{441}}^{25} - 524^\circ$, *d*-dichloro(triaminopropane-mono-*d*-hydrochloride)platinum, $[M]_{D_{441}}^{25} + 195^\circ$, and the *l*-monohydrochloride, $[M]_{D_{441}}^{25} - 192^\circ$, were prepared. Dichloro(triaminopropane-mono-*d*-camphor- β -sulphonate)platinum, $[M]_{D_{441}}^{25} + 61^\circ$, gave no satisfactory resolution. The monohydrochloride yielded with oxalic acid dichloro-

(*triaminopropane-γ-monohydrogen oxalate*)platinum, m. p. 216—217° (decomp., darkening), and with ammonia *monochlorotriaminopropaneplatinous monochloride*, $[\text{Pt}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2)\text{Cl}]$, m. p. 282—283° (decomp.). When potassium chloroplatinite was treated with free triaminopropane, co-ordination occurred, and two new types of complex salts were separated. Treatment of the solution with acetic acid and potassium thiocyanate yielded *bis(triaminopropane-γ-monothiocyanate)platinous di-thiocyanate*, $[\text{Pt}\{\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2, \text{HCNS}\}_2](\text{SCN})_2$, m. p. 177—178°, of the same type as the cupric compound previously described (A., 1926, 1234). This should exist in racemic and *meso*-forms by virtue of two asymmetric carbon atoms, and probably the *meso*-form should be resolvable by virtue of the tetrahedral configuration about the platinum, but recrystallisation of *bis(triaminopropane-γ-mono-d-bromocamphorsulphonate)platinous di-d-bromocamphorsulphonate trihydrate*, $[\text{M}]_{\text{D}_{20}}^{25} + 1340^\circ$, gave no evidence of resolution. If the solution obtained from potassium chloroplatinite and triaminopropane was treated with potassium iodide, *bis(triaminopropane)platinous di-iodide*, $[\text{Pt}\{\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2\}_2]\text{I}_2$, m. p. 266—267° (decomp.), was formed. The *dibromide*, m. p. 270—271° (decomp.), was also prepared, and from this the *dipicrate*, which deflagrated when heated. These compounds appear to be a new type in which bivalent platinum has a co-ordination number of 6. The constitution is discussed. Ammonium chloropalladite and triaminopropane trihydrochloride yielded *dichloro(triaminopropane-γ-monohydrochloride)palladium*, m. p. 279—280° (decomp.), unstable in hot water. *Triaminopropane trihydrogen trioxalate monohydrate*, m. p. 173—174° (decomp.), is described.

R. K. CALLOW.

Oxidation of amino-acids. I. Effect of temperature on the oxidation of amino-acids by animal charcoal. II. Effect of amines. S. TOYODA (J. Biochem. Japan, 1927, 7, 209—216, 217—225).—The greatest oxidation of glycine in the Warburg charcoal model occurs at the body-temperature. Amines retard the rate of oxidation of amino-acids on charcoal to an extent dependent in homologous series on the length of the chain.

CHEMICAL ABSTRACTS.

Isomeric glycyglycine-N-carboxylic acids. F. WESSELY and E. KOMM (Z. physiol. Chem., 1928, 174, 306—318).—Hydrolysis of hydantoin-3-acetic acid with *N*-sodium hydroxide yields glycyglycine-*N*-carboxylic acid, m. p. 204—206° (decomp.), for which the formula $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (I) is suggested in contrast to $\text{CO}_2\text{H}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II) and $\text{CO}_2\text{H}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III), given by Fischer and Fournneau (A., 1901, i, 675) and by Leuchs and co-workers (A., 1907, i, 770; 1908, i, 723; 1925, i, 1248), respectively. Support for this hypothesis is given by the fact that hydantoin-3-acetic acid under the influence of ammonia yields a diamide identical with that formed from ammonia and carbonylbisglycine ester; also the ester of the glycyglycine-*N*-carboxylic acid is identical with that synthesised from carbonyl chloride and glycine ester. The carbonylbisglycine ester obtained from the acid

formed by the alkali hydrolysis of hydantoin-3-acetic acid has m. p. 147°, but after recrystallisation from water the m. p. falls considerably (even as low as 129°). This alteration in m. p. is not due to differences in the size of the crystals, and the analytical values show no alteration. Similar changes occur on recrystallisation from alcohol and ether or from benzene. Treatment of the crude product of carbonylbisglycine ester (m. p. 147°), or a recrystallised product with lower m. p., with hydrochloric acid in alcohol or ether yields a substance, m. p. 148—149°, which undergoes no change on recrystallisation. It is considered improbable that a change occurs on recrystallisation corresponding with a conversion of the ester of (I) into that of (II) or (III).

A. WORMALL.

Formation of guaninido-compounds by the action of guanidine on amino-esters. II. Formation of creatinine from sarcosine ethyl ester and guanidine or cyanamide, and of *dl*-2-imino-4-keto-5-*p*-hydroxybenzyltetrahydroglyoxaline from *dl*-tyrosine ethyl ester and guanidine. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1928, 175, 68—74; cf. this vol., 511).—Guanidine (and less easily cyanamide) reacts with sarcosine ethyl ester [ethyl methylaminoacetate] to give creatinine. From *dl*-tyrosine ethyl ester and guanidine there is obtained *2-imino-4-keto-5-p-hydroxybenzyltetrahydroglyoxaline*, m. p. 257—263°. The mechanism of the reaction is discussed.

C. HOLLINS.

Benzylidenecreatinine and related compounds.

B. H. NICOLET and E. D. CAMPBELL (J. Amer. Chem. Soc., 1928, 50, 1155—1160).—Acetyl-5-benzylidenecreatinine (cf. Erlenmeyer, A., 1895, i, 310), prepared by an improved method, is hydrolysed by acids to 5-benzylidenecreatinine (*dihydrochloride*), which is reduced by hydriodic acid to 5-benzylcreatinine (cf. Hennig, A., 1913, i, 1106; Greenwald, A., 1925, i, 839). This is hydrolysed by barium hydroxide, first to 5-benzyl-1-methylhydantoin, m. p. 106°, then to α -methylamino- β -phenylpropionic acid (Fischer and Lipschitz, A., 1915, i, 242), the yield of which from creatinine is 22% of the theoretical. Benzylidenecreatinine (I) is similarly hydrolysed to 1-methyl-5-benzylidenehydantoin, m. p. 193—194°, which is also formed from benzaldehyde and 1-methylhydantoin, and is methylated by sodium hydroxide and methyl iodide to 1:3-dimethyl-5-benzylidenehydantoin, m. p. 92°. Methylation of (I) affords methyl-5-benzylidenecreatinine, $\begin{array}{c} \text{CO}\cdot\text{C}\cdot\text{CHPh} \\ | \\ \text{NH}\cdot\text{C}\cdot\text{NMe} \end{array}$, m. p. 129°, which is hydrolysed to 1-methyl-5-benzylidenehydantoin. Attempts to condense methylcreatinine, or an (?) isomerised product obtained from this by ring opening and reclosure, with benzaldehyde were unsuccessful (cf. Kunze, A., 1911, i, 21).

H. E. F. NORRIS.

Compound of carbon monoxide with "ferrocysteine" and its decomposition by light. W. CREMER (Biochem. Z., 1928, 194, 231—232).—The compound obtained by the reaction of carbon monoxide with a mixture of ferrous sulphate and cysteine in which 1 atom of iron combines with 2 mols. of carbon monoxide (cf. this vol., 315) is decomposed by

light, but it may be distinguished from the corresponding compound of carbon monoxide and hæmin, which is similarly decomposed, by its absorption spectrum. P. W. CLUTTERBUCK.

[Preparation of] ethyl cyanoacetate. J. K. H. INGLIS (Org. Syntheses, 1928, 8, 74—76).

Action of organo-magnesium derivatives on some oxamides. R. BARRÉ (Ann. Chim., 1928, [x], 9, 204—275).—Partly an account of work already published (A., 1927, 447). The following is new. The α -form, m. p. 140—141°, of propionylformdiethylamide semicarbazone is converted by hydrochloric acid into the stable β -form, m. p. 170—171°. Propionylformdiethylamide phenylhydrazone and p-nitrophenylhydrazone have m. p. 101—102° and 124—125°, respectively. Magnesium butyl bromide and ethyl diethyloxamate react at -15° to form n-valerylformdiethylamide (90%), b. p. 120—122°/11 mm. (semicarbazone, m. p. 163°), hydrolysed by hydrochloric acid to α -ketohezoic acid, b. p. 93—94°/14 mm. (oxime, m. p. 140°; phenylhydrazone, m. p. 89°; semicarbazone, m. p. 200°). Ethyl diethyloxamate and magnesium phenyl bromide (1.6 mols.) at -15° give benzildiethylamide (63%), m. p. 95—96° (cf. McKenzie and Duff, A., 1927, 755), and benzoylformdiethylamide (15%), b. p. 183—185°/18 mm. (semicarbazone, m. p. 204—205°). When 2 mols. of the Grignard reagent are used 63% of the keto-diethylamide is obtained. Magnesium benzyl chloride and ethyl diethyloxamate furnish α -hydroxy- β -phenyl- α -benzylpropiondiethylamide (15%), m. p. 119°, and phenylacetylformdiethylamide (70%), b. p. 155—157°/7 mm. (semicarbazone, m. p. 211—212°), hydrolysed to phenylpyruvic acid, m. p. 155°.

The product of the action of diethylamine on magnesium ethyl bromide converts ethyl oxalate into tetraethyloxamide, b. p. 142°/4 mm., m. p. 31—32°. This reacts with magnesium ethyl bromide (3 mols.) in ether to form α -diethylaminobutyrdiethylamide (20%), b. p. 98—99°/3 mm. (picrate, m. p. 114—115°), also obtained from diethylamine and α -bromobutyrdiethylamide, together with propionylformdiethylamide (70%). In benzene the corresponding amounts are 36% and 55%, together with 1% of dipropionyl [disemicarbazone, m. p. 285° (decomp.)], whilst in toluene, with mechanical agitation, the percentages are 60 and 28. With magnesium ethyl iodide in benzene, the product is mainly the keto-diethylamide. Tetraethyloxamide and magnesium phenyl bromide (4 mols.) in toluene give diethylaminodiphenylacetyl-diethylamide (75%), b. p. 182—184°/3 mm. [perchlorate, m. p. 177° (decomp.)], easily hydrolysed by acid or alkali to benzildiethylamide.

The reaction between magnesium alkyl and aryl halides and the iminochloride from oxanilide yields mainly resinous products. H. BURTON.

[Preparation of] acetamidine hydrochloride. A. W. DOX (Org. Syntheses, 1928, 8, 1—3).

[Preparation of] allyl cyanide. J. V. SUPNIEWSKI and P. L. SALZBERG (Org. Syntheses, 1928, 8, 4—6).

[Preparation of] γ -chlorobutyronitrile. C. F. H. ALLEN (Org. Syntheses, 1928, 8, 52—53).

Oxidation of alkali cyanides by permanganate. H. GALL and G. LEHMANN (Ber., 1928, 61, [B], 670—675).—During the direct oxidation of potassium cyanide by potassium permanganate in strongly alkaline solution, approximately two equivalents of oxygen are used for each molecule of cyanide; the reaction is very tedious and is accompanied by many side changes, so that it is useless for analytical purposes. Addition of copper sulphate greatly accelerates the oxidation, so that alkali cyanide may be oxidimetrically determined as follows. The solution of the cyanide is treated successively with potassium hydroxide (about 30%, 20 c.c.) and copper sulphate (5%, 20 c.c.). After addition of permanganate it is warmed for 5 min. at 60°, after which excess of the oxidising agent is determined by oxalic acid. It is essential that the cold and hot solution should exhibit the pure green colour of the manganate. If the latter disappears when the solution is warmed, more permanganate may be added. If, however, permanganate remains (shown by the blue colour of the solution), the following "cold titration" method must be used. The cyanide is treated with alkali hydroxide and copper sulphate as described above and then with so much permanganate that the solution has a pure blue colour; excess of permanganate is immediately titrated with oxalic-sulphuric acid solution. In place of oxalic acid, acidified ferrous sulphate solution may be employed. The successful use of permanganate in this connexion depends on its immediate conversion into manganate; if reaction occurs slowly, apparent consumption of permanganate ensues, due to its decomposition in alkaline solution. Manganate is used in the determination of cyanide by adding potassium hydroxide (about 30%, 20 c.c.) and copper sulphate (5%, 20 c.c.) to the solution of the cyanide followed by an excess of manganate solution. The mixture is heated nearly to boiling over a free flame, whereby the green colour must persist. Excess of manganate is titrated by ferrous sulphate or oxalic acid. The preparation of pure potassium cyanate is described in detail. H. WREN.

Grignard's reaction. J. MEISENHEIMER (Ber., 1928, 61, [B], 708—720).—The magnesium alkyl halide produced by the action of magnesium on alkyl halide may be determined by decomposing a measured volume of the ethereal solution with water and a known excess of standard nitric acid and titrating the unused acid (cf. Gilman and others, A., 1923, ii, 272). The ionic halogen is also determined by Volhard's method. In the case of the exclusive formation of magnesium alkyl halide, the ratio nitric acid : silver nitrate is 1 : 1. The method is trustworthy only if moisture and atmospheric oxygen are excluded as far as possible during the preparation of the reagent. For some unexplained reason, great dilution of solutions of magnesium methyl or ethyl iodide with ether previously to titration causes a very marked alteration in the ratio I' : OH', although the sum, I' + OH', is influenced but little if at all.

The composition generally assigned to magnesium alkyl halides is deduced from Tschelinzev's colorimetric measurements and not previously controlled by analyses. Magnesium α -naphthyl bromide has been

isolated as a crystalline *trietherate*, $\text{MgC}_{10}\text{H}_7\text{Br}\cdot 3\text{Et}_2\text{O}$, which readily loses 1 mol. of ether, forming the non-crystalline *dietherate*.

Ethereal solutions of magnesium ethyl iodide, when preserved, slowly deposit crystals of *magnesium ethoxyiodide monoetherate* owing to oxidation by the atmosphere; if moisture is also present, the deposit is mixed with magnesium iodide dihydrate. If a current of air is rapidly passed through the solution, the precipitate consists of more highly basic magnesium salts. Magnesium ethoxyiodide is readily obtained crystalline by addition of the calculated amount of anhydrous ethyl alcohol to an ethereal solution of magnesium methyl or ethyl iodide, methane or ethane being vigorously evolved. Auto-oxidation of magnesium methyl iodide solutions proceeds less smoothly, whilst magnesium ethyl bromide affords *magnesium hydroxybromide etherate* instead of the expected ethoxybromide.

The crystalline precipitates obtained by Zerewitinov from solutions of magnesium methyl iodide in amyl ether evolve little methane when treated with water and appear to consist mainly of magnesium iodide diamyletherate with varying amounts of magnesium methyl iodide (?diamyletherate) and decomposition products. If dry air is passed through the solution, crystals are gradually formed which have approximately the composition of magnesium methoxyiodide monoamyletherate and correspond most closely with Zerewitinov's magnesium methyl iodide monoamyletherate in properties. When magnesium reacts with methyl bromide in presence of a regulated amount of amyl ether, the precipitate formed appears to consist of 80.5% of magnesium methyl bromide semiamyletherate, 23.3% of magnesium bromide semiamyletherate, and 1.7% of magnesium oxide.

o-Chloro- γ -chloro-*n*-propylbenzene could not be caused to react with magnesium in ethyl ether under any conditions. Since *p*-dibromo- and *p*-di-iodobenzene are active, whereas *p*-dichlorobenzene is indifferent, it is remarkable that *o*-iodo- γ -chloro-*n*-propyl-, *o*-chloro- γ -iodo-*n*-propyl-, and *o*-iodo- γ -iodo-*n*-propyl-benzenes are indifferent. Replacement of ethyl ether by benzene induces activity in the case of the di-iodo-compound only, whereas all four halides react in boiling *isoamyl* ether; under these conditions, however, the tendency to side reactions is so pronounced that the actions do not promise usefulness in syntheses. The failure of the aliphatic halogen atom to react is unexplained, since γ -iodo-*n*-propylbenzene, *o*-iodopropylbenzene, and *o*-bromobenzyl bromide are readily active. With other reagents, the halogen atoms behave normally. *o*-Chloro- γ -chloro-*n*-propylbenzene, b. p. $112^\circ/20$ mm., prepared from γ -chloro-*n*-propylaniline, *o*-chloro- γ -iodo-*n*-propylbenzene, b. p. $142^\circ/20$ mm., from the dichloride and sodium iodide in boiling absolute alcohol, *o*-iodo- γ -chloro-*n*-propylbenzene, b. p. $102^\circ/\text{high vacuum}$, and *o*-iodo- γ -iodo-*n*-propylbenzene, b. p. $132\text{--}134^\circ/\text{high vacuum}$, do not appear to have been described previously.

Under all conditions magnesium and ethylene bromide in ether yield ethylene and homogeneous magnesium bromide dietherate. Bischoff's observation (A., 1905, i, 589), that benzil is reduced to benzoin by the product of the action of magnesium

and ethylene bromide, could not be confirmed, but may be due to reduction by metallic magnesium in the presence of magnesium bromide (cf. Gomberg and Bachmann, A., 1927, 1190). H. WREN.

Mol. wt. and constitution of Grignard's magnesium compounds. J. MEISENHEIMER and W. SCHLICHENMAIER (Ber., 1928, 61, [B], 720—729).—The structure $\text{Mg}[\text{Alk}_2\text{MgI}_2\cdot 2\text{Et}_2\text{O}]$ for magnesium alkyl halides has been suggested by Terentiev (A., 1926, 1130) in place of the constitution $\text{Alk}\cdot\text{MgI}-(\text{OEt}_2)_2$ advocated by Meisenheimer and Casper (A., 1921, i, 654) mainly on grounds of determination of the mol. wt. of magnesium methyl iodide in boiling ether. Repetition of Terentiev's experiments shows that the Grignard reagent is strongly associated in solution, but that, at sufficiently great dilution, the values for the mol. wt. approximate to those of the unimolecular compound. The experiments are not completely satisfactory, partly due to inconstancy in the b. p. of the solvent which can be avoided by using a large volume of it, but mainly owing to the ultimate formation of a precipitate in the solution. Terentiev's method of isolating the Grignard compound by evaporation of its ethereal solution and subsequent heating of the residue at 75° in a vacuum for 2 hrs. causes extensive decomposition. Magnesium ethyl bromide and magnesium methyl iodide, dried at 25° in a vacuum during 1 hr., give almost clear solutions in ether, and their mol. wt. increases with increasing concentration in a regular manner. Protracted ebullition causes some alteration in the composition of magnesium methyl iodide, as shown by alteration in the ratio $\text{I}' : \text{OH}'$ (cf. preceding abstract). Magnesium phenyl bromide is more strongly associated in ethereal solution, in which it appears to undergo little alteration when heated. The results indicate that magnesium alkyl halides are not bimolecular in solution as postulated by Terentiev. In dilute ethereal solution it is considered that magnesium ethyl bromide exists mainly as the complex $\text{Et}\cdot\text{MgBr}-(\text{OEt}_2)_2$; a very small proportion is dissociated ionically and a somewhat larger amount is doubly or more highly polymerised. Precisely similar observations are made with magnesium iodide dietherate. The interpretation placed by Ivanov on the course of the action of carbon dioxide on magnesium ethyl bromide (A., 1927, 961) and on that between magnesium methyl iodide and water or carbon disulphide by Kierzek (*ibid.*, 1176) is arbitrary and the assumption of the existence of bimolecular compounds is unnecessary. Unfortunately, the magnesium alkoxyhalides which are readily prepared pure (cf. preceding abstract) are unsuitable for mol. wt. determination, since they readily decompose when heated, but their relationship to the unimolecular Grignard compounds and unimolecular magnesium iodide renders a bimolecular structure highly improbable. H. WREN.

Condensation of cyclohexene with aromatic hydrocarbons in presence of aluminium chloride. D. BODROUX (Compt. rend., 1928, 186, 1005—1006).—*cyclo*Hexene was added to half its weight of aluminium chloride in an excess of an aromatic hydrocarbon, sometimes diluted with carbon disulphide, and the

monosubstituted product, which might be accompanied by small quantities of disubstituted product, separated by steam distillation or distillation. The following compounds were obtained: *cyclohexyltoluene* (mixture of two isomerides), b. p. 255—261°/758 mm., d^{20}_4 0.938, n^{20}_D 1.527; *2-cyclohexyl-p-xylene*, b. p. 261—262°/760 mm., d^{20}_4 0.936, n^{20}_D 1.529; *dicyclohexyl-p-xylene*, m. p. 156—157°; *5-cyclohexyl-m-xylene*, b. p. 266—268°/763 mm., d^{20}_4 0.931, n^{20}_D 1.525; *2-cyclohexyl-1:3:5-trimethylbenzene*, b. p. 283—284.5°/740 mm., d^{20}_4 0.946, n^{20}_D 1.535; *cyclohexyl-4-isopropyltoluene*, b. p. 279—283°/739 mm., d^{20}_4 0.916, n^{20}_D 1.517; *dicyclohexyl-4-isopropyltoluene*, b. p. 210—220°/22 mm.

R. K. CALLOW.

Phenylpropinenes. M. BOURGUEL (Compt. rend., 1928, 186, 1211—1213).— γ -Phenylpropinene (A., 1923, i, 429) had an anomalous value for density and refractive index when compared with its higher and lower homologues. On preparing the hydrocarbon by different methods (A., 1920, i, 603; 1925, i, 770; 1927, 47), the physical constants were in agreement amongst themselves and with those of the homologues, whilst the original values were never obtained. γ -Phenylpropinene has b. p. 68°/16 mm., d^{20}_4 0.935, n^{20}_D 1.536, and yields a silver derivative. Fractionation with cuprous chloride and sodamide shows that the product is homogeneous. Hydration gives rise to methyl benzyl ketone and oxidation with permanganate to benzoic acid. With sodamide a hydrogen atom of the methylene group is replaced by sodium to give a red derivative. α -Phenylpropinene has b. p. 73°/13 mm., d^{20}_4 0.942, n^{20}_D 1.563. J. D. FULTON.

Halogenation of aromatic compounds in aqueous solutions. D. TISCHENKO (J. Russ. Phys. Chem. Soc., 1928, 60, 153—162).—A résumé of the behaviour of aromatic compounds towards chlorine water and bromine water, and of the mechanisms suggested for the reactions.

The action of a solution of bromine in aqueous sodium carbonate was investigated. Bromine reacts with sodium carbonate in solution according to the equations $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{Br}_2 \rightleftharpoons \text{NaBr} + \text{NaHCO}_3 + \text{HBrO}$, and finally $6\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} + 6\text{Br}_2 = 6\text{NaHCO}_3 + 3\text{NaBr}_3 + 2\text{NaBr} + \text{NaBrO}_3$. The solution gives all the reactions of free bromine, and hypobromous acid cannot be detected in the presence of an excess greater than 10% of free carbonate.

The sodium hydrogen carbonate formed maintained a constant hydrogen-ion concentration during the reactions with aromatic compounds, which were carried out in 0.1N-solutions. Benzene, toluene, and the xylenes did not react, but naphthalene gave an 80% yield of very pure bromonaphthalene. Phenol gave a 70% yield of *p*-bromophenol. Resorcinol was partly oxidised, and partly yielded a dibromoresorcinol, m. p. 111°. β -Naphthol, *o*-, *m*-, and *p*-cresols gave, respectively, 1-bromo- β -naphthol, m. p. 84°, 6-bromo-*o*-cresol, m. p. 63—64°, 6-bromo-*m*-cresol, m. p. 54—55°, and a liquid monobromocresol, b. p. 110—114°/19 mm. Pyrogallol and quinol were resinified, anthraquinone and alizarin were unaffected, whilst indigotin was oxidised to indoxyl. Sodium benzoate and phthalate did not react, but the salicylate yielded a bromotrihydroxybenzoic acid. The probable brom-

inating agent in acid solutions was free bromine, in alkaline solutions hypobromous acid.

Chlorine under similar conditions gave with phenol *o*- and *p*-chlorophenols; with *o*-cresol a mixture of 4-chloro-*o*-cresol and impure 6-chloro-*o*-cresol; with *m*-cresol 6- and 4-chloro-*m*-cresol, m. p. 66°; with thymol *p*-chlorothymol, m. p. 59—60°.

Resorcinol was oxidised; β -naphthol gave a mixture of 8-chloro- β -naphthol, m. p. 101°, and $\beta\beta'$ -dinaphthol. Aniline was oxidised, acetanilide, the acetotoluidides, acetonaphthalides, α -aminoanthraquinone, and diphenylamine were unaffected, whilst dimethylaniline yielded a mixture of *o*- and *p*-chlorodimethylanilines.

Salts of carboxylic or sulphonic acids which do not contain reactive groups, such as amino- or hydroxyl groups, were not chlorinated, but sodium sulphanilate gave the sodium salt of azobenzene-4:4'-disulphonic acid.

Sodium salicylate yielded sodium chlorosalicylate, and sodium *p*-hydroxybenzoate furnished sodium 3-chloro-*p*-hydroxybenzoate.

In general, the oxidising effect in solution of chlorine is much greater than that of bromine, due to the much greater concentration of free hypochlorous acid.

M. ZVEGINTZOV.

Nitration of chlorobenzene. O. MAGIDSON [with L. KALISCHEVSKI] (Trans. sci. chem.-pharm. inst., Moscow, 1923, 6, 17—20; Chem. Zentr., 1927, ii, 2542).—Chlorobenzene and nitrating acid afford chiefly *p*-chloronitrobenzene, whilst sodium nitrate and sulphuric acid afford chiefly the *o*-compound. The latter reagent readily gives 1-chloro-2:4-dinitrobenzene at a higher temperature.

A. A. ELDRIDGE.

[Preparation of] *m*-bromonitrobenzene. J. R. JOHNSON and C. G. GAUERKE (Org. Syntheses, 1928, 8, 46).

Dinitroethylbenzenes. O. L. BRADY, J. N. E. DAY, and P. S. ALLAM (J.C.S., 1928, 978—982).—2:4:6-Trinitroethylbenzene (Schultz and Sander, A., 1909, i, 639) was reduced by ammonium sulphide to 2:6-dinitro-4-aminoethylbenzene, m. p. 175° (lit. 110°), which, on removal of the amino-group by diazotisation and treatment with alcohol, yielded 2:6-dinitroethylbenzene, m. p. 57.5°. 2-Nitro-4-acetamidoethylbenzene, m. p. 111° (cf. Cline and Reid, this vol., 162), on nitration in nitric and sulphuric acids yielded 2:3-dinitro-4-acetamidoethylbenzene, m. p. 143°, and a smaller proportion of 2:5-dinitro-4-aminoethylbenzene, m. p. 125°, was separated by hydrolysing the solid separated from the mother-liquors of the 2:3-compound. 2:3-Dinitro-4-aminoethylbenzene, m. p. 121.6°, obtained by hydrolysis, yielded, by removal of the amino-group, 2:3-dinitroethylbenzene, m. p. 58.5°. 2:5-Dinitroethylbenzene, m. p. 59.5°, was obtained similarly. 3:5-Dinitro-4-aminoethylbenzene (Pauksch, A., 1884, 1142), on removal of the amino-group, yielded 3:5-dinitroethylbenzene, m. p. 41°. The dinitroethylbenzenes were oriented by oxidation to the dinitrobenzoic acids, the methyl esters of which were also prepared. Methyl 2:3-dinitrobenzoate had m. p. 134°.

R. K. CALLOW.

Michler's "sulphones." F. BERGEL and H. DÖRING (Ber., 1927, 61, [B], 844—845; cf. Döring,

Diss., Freiburg, 1928).—The "sulphone" obtained by Michler by the action of *p*-toluenesulphonyl chloride on dimethylaniline is identified as *p*-toluenesulphonemethylanilide. A methyl group appears to be removed during the change and forms the methane carbon atom of methyl-violet and tetramethyl-diaminodiphenylmethane formed as by-products.

H. WREN.

[Preparation of] *p*-bromodiphenyl. M. GOMBERG and W. E. BACHMANN (Org. Syntheses, 1928, 8, 42—44).

Polymerisation of indene, cinnamylidene-fluorene, and some indene derivatives. G. S. WHITBY and M. KATZ (J. Amer. Chem. Soc., 1928, 50, 1160—1171).—Determination of the mol. wt., bromine absorption, and m. p. of indene polymerised by heating or treatment with stannic chloride or antimony pentachloride shows that (a) the products are complex mixtures, (b) the lower the temperature of production, the greater is the complexity of the product, (c) the polymerides, whether formed by physical or chemical means, form an unbroken series showing a smooth relation between m. p. and mol. wt. (cf. Bruson, A., 1927, 654; Stobbe and Färber, A., 1925, i, 19), (d) the polyindene molecule always combines with 2 atoms of bromine and therefore contains one double linking. Polymerisation is probably accompanied by migration of hydrogen giving a product of the general

formula, $\text{CH}_2 \cdot \text{C}_6\text{H}_4 \left[\text{CH}_2 \cdot \text{C}_6\text{H}_4 \right]_n \text{CH}_2 \cdot \text{C}_6\text{H}_4$. Cinn-

amylidene-fluorene is converted by heating or the usual catalysts into red, amorphous, non-elastic polymerides. At 200° it gives a product (C₂₂H₁₆)₂, m. p. 168—170°, and at 240—250°, (C₂₂H₁₆)₉, m. p. 356—370°, whilst antimony pentachloride gives a series of products from (C₂₂H₁₆)₄, m. p. 286—290°, to (C₂₂H₂₆)₁₂, m. p. 365—368°, the m. p. of which show a linear relationship to the mol. wts. A similar series, m. p. 245—246° to 273—275°, is obtained by thermopolymerisation of cinnamylideneindene, which gives a quadrimolecular product, m. p. 238—242°, with stannic chloride. Benzylideneindene is converted by heat into a tetrameride, m. p. 238—242°, and by antimony pentachloride into a hexameride, m. p. 252—255°, whilst hydroxybenzylbenzylideneindene gives a hexameride, m. p. 297—300°, when heated and a lower polymeride, m. p. 195—200°, with stannic chloride.

H. E. F. NOTTON.

α-Chloronaphthalene. I. Chlorination of naphthalene in the gaseous phase. P. FERRERO and R. WUNENBURGER (Helv. Chim. Acta, 1928, 11, 416—425).—An apparatus is described in which naphthalene is chlorinated in the gaseous phase either in absence or presence of a catalyst at 250—400°. Without catalyst, the maximum yield (about 60%) of α-chloronaphthalene using 1.5 mols. of chlorine at a flow of 15 litres per hr. is at 350°. At 400°, the reaction products are destroyed. In presence of 0.5% of iodine the formation of mono-substituted derivatives is favoured, whilst ferric chloride, porous earthenware, or wood charcoal activates the production of both mono- and poly-chlorinated products. The α-chloronaphthalene obtained is technically pure.

H. BURTON.

Extension of Witt's colour theory on a basis of chemical co-ordination. W. DILTHEY and R. WIZINGER (J. pr. Chem., 1928, [ii], 118, 321—348).—The colour of triphenylmethyl is ascribed to the chromophoric effect of the tervalent carbon atom. An ethylenic linking is regarded as comprising a pair of tervalent carbon atoms, and an extension of Witt's colour theory is developed from this starting-point. The weak chromophoric effect of such a pair of tervalent carbon atoms is strengthened by conversion, whilst maintaining the co-ordinative deficiency, into the heteropolar (ionic) condition. These central atoms are not to be considered as necessarily the sole or chief source of electronic vibrations (cf. Madelung and Oberwegner, this vol., 171); as ionic centres they probably give off electrons, but the further history of these is left indefinite. The co-ordination number of carbon and of nitrogen is 4; that of oxygen may be 3 or 4, but a singly-bound oxygen atom is certainly unsaturated. Thus a triply-bound carbon atom is co-ordinatively unsaturated, a distinction being drawn between co-ordination unsaturation and valency unsaturation. Thus, in crystal-violet base the central carbon atom is tervalent and hence shows valency (and also co-ordination) unsaturation, but in the colour salt this carbon atom is quadrivalent, and therefore saturated, yet there remains a co-ordination deficiency, since the negative radical occupies the second sphere and is not connected directly with the central atom. Such a condition of co-ordinative unsaturation at a heteropolar central atom in a colour salt is conveniently indicated by a dot above the atom in the formula. The introduction of auxochromes such as amino- and hydroxyl groups into a coloured substance is not in itself sufficient to endow it with dyeing properties, but in general leads to only a comparatively slight change of colour. The necessary condition for dye formation is the production of a salt. Thus, whilst triphenylmethyl is yellow and its hexamethyltriamino-derivative is orange, neither is a dye; but the salt [(NMe₂·C₆H₄)₂·C·C₆H₄·NMe₂]⁺Cl⁻ is deep violet and possesses dyeing properties. A similar effect is observed with the introduction of the antiauxochromes NO₂, NO, CN, etc.; whilst azobenzene is yellow and hexanitroazobenzene is orange, the salt [(NO₂)₃C₆H₂·N·N·C₆H₂(NO₂)₃]⁻K⁺⁺ is a dark blue dye. The effect of auxochromes and antiauxochromes in dye formation is not entirely due, however, to their salt-forming capacity, but also indirectly to their stabilising effect on the salts, which in some cases could be formed in their absence. The hydroxyl group, e.g., usually figures in the negative ions of dyes in which it is present, and in these cases alkylation destroys its effect. But it may also figure in the positive ions, thus taking no direct part in salt formation, as in *p*-hydroxytriphenylpyrylium perchlorate. Here its favourable effect lies in the increased stability of this salt to water compared with the non-hydroxylated perchlorate. In such cases alkylation does not destroy the auxochromic effect of the hydroxyl group. Since auxochromes favour formation of positive, and antiauxochromes of negative ions, in binuclear systems containing two co-ordinatively unsaturated atoms an intramolecular ionoid condition may be approached if on the one nucleus

auxochromes, and on the other antiauxochromes, are accumulated. Such a dipolar condition should show the depth and intensity of colour of a true colour salt, a deepening of colour in ionising solvents. Examples of these phenomena are given. C. HOLLINS.

Rubrene peroxide. C. MOUREU, C. DUFRAISSE, and L. GIRARD (Compt. rend., 1928, 186, 1027—1031).—The m. p. and crystalline form of rubrene peroxide (cf. A., 1926, 945) vary according to the solvent used, the following m. p. being observed: ether, 192—193°; acetone, 186—188°; ethyl acetate, 196—197°; ethyl bromide, 186—187°; ethyl iodide, 181—182°; benzene, 192—193°; toluene or chloroform, 187—188°; and bromobenzene, 165—167°. Cryoscopic measurements show that the solvent is combined only as solvent of crystallisation and that each mol. of the peroxide retains 1 mol. of bromobenzene and 0.5 mol. of benzene or ether. These proportions are confirmed by analysis and by the dissociation of the peroxide in a high vacuum, the liberated solvent being condensed in a freezing mixture of acetone and solid carbon dioxide. The gas obtained by the thermal decomposition of the peroxide consists only of oxygen and carbon dioxide, the proportion of the latter varying from 4.4 to 6.7% of the total volume of gas. Below 140°, the gas evolved is almost pure oxygen, whilst at about 180° only carbon dioxide is obtained, the two gases seemingly being the products of two different reactions. In the case of the peroxide containing benzene of crystallisation, 74—79.5% of the theoretical proportion of the oxygen is liberated as such, 4.2—6.1% as carbon dioxide, whilst 15—21% remains combined in the residue, which has a distinct phenolic odour. Similar results are obtained with a sample containing bromobenzene of crystallisation, the proportion of oxygen liberated being 72.1—74.6% of the theoretical.

J. W. BAKER.

Electrometric titration of phenols in alcoholic solution. W. D. TREADWELL and G. SCHWARZENBACH (Helv. Chim. Acta, 1928, 11, 386—405).—The dissociation constants of a number of phenols in alcoholic solution have been measured electrometrically with the following results. In absolute-alcoholic solution: phenol, $10^{-12.8}$; pyrocatechol, $10^{-12.0}$; resorcinol, $10^{-12.3}$; quinol, $10^{-12.6}$; *o*-nitrophenol, $10^{-10.7}$; *p*-nitrophenol, $10^{-10.1}$; picric acid, $10^{-5.7}$; 2:4-dinitro-naphthol, $10^{-9.0}$. In 96% alcoholic solution: *p*-nitroso-phenol, $10^{-8.1}$; 1-nitroso- β -naphthol, $10^{-8.7}$; and the following anthraquinone derivatives, α -hydroxy-, $10^{-8.3}$; β -hydroxy-, $10^{-5.7}$; 1:4-dihydroxy-, $10^{-8.8}$; 1:8-dihydroxy-, $10^{-6.9}$; 1:2-dihydroxy-, $10^{-5.4}$; 1:3-dihydroxy-, $10^{-5.3}$; 2:3-dihydroxy-, $10^{-5.7}$; 2:6-dihydroxy-, $10^{-5.6}$ and $10^{-7.4}$; 1:2:4-trihydroxy-, $10^{-3.9}$; 1:2:5-trihydroxy-, $10^{-5.7}$; 1:2:6-trihydroxy-, $10^{-4.8}$; 1:2:7-trihydroxy-, $10^{-5.2}$; 1:2:3-trihydroxy-, $10^{-4.8}$; 1:2:3:4-tetrahydroxy-, $10^{-3.1}$; also eriochrome-yellow G, $10^{-3.6}$; eriochrome-blue-black R, $10^{-5.6}$. Only in the case of 2:5-dihydroxy-anthraquinone were dissociation constants obtained for more than one hydroxyl group. F. J. WILKINS.

Catalytic reduction of nitro-organic compounds in the liquid system. O. W. BROWN, G. ETZEL, and C. O. HENKE.—See this vol., 600.

Reduction of aromatic nitro-derivatives by means of iron in the presence of magnesium chloride. S. MICEWICZ (Rocz. Chem., 1928, 8, 50—53).—Iron filings in the presence of magnesium chloride constitute a satisfactory reducing agent for the preparation of aromatic amines, no intermediate products being isolated from the reaction mixture.

R. TRUSZKOWSKI.

Chlorination of anilides. III. N-Chlorination and C-chlorination as simultaneous side-reactions. K. J. P. ORTON, F. G. SOPER, and G. WILLIAMS (J.C.S., 1928, 998—1005).—Measurements have been made of the velocities of both *N*-chlorination and *C*-chlorination in 40% acetic acid at 18°, in the reaction between chlorine and seven acetanilides which is represented by the scheme $\text{Ar}\cdot\text{NHAc} + \text{Cl}_2 \rightarrow \text{Cl}\cdot\text{Ar}\cdot\text{NHAc} + \text{HCl}$ or $\rightleftharpoons \text{Ar}\cdot\text{NClAc} + \text{HCl}$ (cf. Orton and Jones, J.C.S., 1909, 95, 1456). The reaction mixture is poured alternatively into (a) potassium iodide solution, the titre of the liberated iodine representing chlorine+chloroamine concentration, and (b) aqueous *p*-cresol which removes chlorine, the chloroamine then being determined as in (a). The ratio of the amounts of chloroamine and chloroanilide formed at any given instant is independent of time, and chloroamine formation and nuclear chlorination are therefore simultaneous side-reactions. The values of the velocity coefficients for *o*-, *m*-, and *p*-chloro- and *p*-bromo-acetanilides, aceto-*o*-, and aceto-*p*-toluidide, and acetanilide are, respectively: k_N 286, 172, 115, 123, 140, 2540, and 96; k_C 27.5, 3140, 135, 116, 1390, 18500, and 11000, the values of the ratio k_N/k_C being, 10.4, 0.0548, 0.848, 1.06, 0.102, 0.137, and 0.00873, respectively. J. W. BAKER.

Chlorination of anilides. IV. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFIELD and B. JONES (J.C.S., 1928, 1006—1012).—A quantitative study has been made of the velocities of chlorination in 99% acetic acid of a series of 21 phenolic ethers of the type $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{X}$ (*o* or *p*), in which $\text{X} = \text{Cl}$, CO_2H , or NO_2 , and $\text{R} = \text{Me}$, Et , Pr^a , Pr^b , Bu^a , CH_2Ph , (*p*) $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2$, *p*- and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$. The velocity of chlorination increases rapidly with increasing water content of the medium. An application of the concept of kinetic activation is applied to the problem of benzene substitution and, with certain assumptions, the expression $\log_{10}(r_1/2)/\log_{10}(r_2/2) = T_2/T_1$, where r_1 and r_2 are the ratios of the total *ortho*- to total *para*-compound produced at the temperatures T_1 and T_2 , respectively, is deduced. By means of this and similar expressions the ratio *o*:*m*:*p* can be calculated at any one temperature from the known values of the ratio at another temperature. Very good quantitative agreement is found with existing data. The extension of this principle to the introduction of a third substituent into a disubstituted benzene derivative is tentatively considered, and it is shown that the relative directive powers of OR and OR' as measured by the ratio of the chlorination velocity coefficients in the derivatives $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{X}$ (*o* and *p*) should be independent of the group X, a prediction which is verified experimentally. Similarly, the relative directive power of the group X is independent of the nature of R.

J. W. BAKER.

Chloroamines as halogenating agents. Iodination by a chloroamine and an iodide. A. E. BRADFELD, K. J. P. ORTON, and I. C. ROBERTS (J.C.S., 1928, 782—785).—The method of chlorination based on the interaction of hydrogen chloride and a chloroamine (Orton and King, J.C.S., 1911, 99, 1185; Orton and Bradfield, A., 1927, 655) has been extended to the preparation of a solution of iodine chloride and the iodination of various aniline derivatives. Finely-powdered sodium iodide is added in small amounts, with shaking, to a solution of "dichloramine-T" in glacial acetic acid. Little or no liberation of iodine occurs and the reduction in acidity consequent on the presence of sodium ions affects favourably the rate of iodination of anilines. Aniline with 1 equivalent of this reagent yields *p*-iodoaniline, and with 3 equivalents, tri-iodoaniline, and by similar methods the following iodoanilines are obtained from the appropriate aniline derivative: 2:4-dichloro-6-iodoaniline (*acetyl* derivative, m. p. 198—199°); 2-chloro-4-bromo-6-iodoaniline, m. p. 95—96° (*acetyl* derivative, m. p. 213°); *p*-iodoacetanilide, which by treatment with 2 mols. of bromine in 70% acetic acid at 70° yields 2-bromo-4-iodoacetanilide, m. p. 143°, hydrolysed to 2-bromo-4-iodoaniline, m. p. 75—76°. The last is chlorinated with "dichloramine-T" and hydrochloric acid forming 2-chloro-6-bromo-4-iodoaniline, m. p. 113—114° (*acetyl* derivative, m. p. 221°). By heating *o*-nitroaniline with 50% excess of the iodinating agent for 20—30 min., an 80% yield of 4-iodo-2-nitroaniline is obtained, whilst with excess of the reagent the 4:6-di-iodo-derivative is obtained. Chlorination and bromination of the former yields, respectively, 2-chloro-, m. p. 124° (*acetyl* derivative, m. p. 227°), and 2-bromo-, m. p. 117—118° (*acetyl* derivative, m. p. 222°) 4-iodo-6-nitroaniline. 4-Chloro- and 4-bromo-2-nitroanilines yield respectively, 4-chloro-, m. p. 137—138° (*acetyl* derivative, m. p. 207°), and 4-bromo-, m. p. 146—147° (*acetyl* derivative, m. p. 215°), 2-iodo-6-nitroaniline, which by diazotisation with amyl nitrite in alcoholic solution yield, respectively, 3-chloro- and 3-bromo-5-iodo-1-nitrobenzene (Körner and Contardi, A., 1913, i, 963). J. W. BAKER.

[Preparation of] **benzylaniline**. F. G. WILLSON and T. S. WHEELER (Org. Syntheses, 1928, 8, 38—40).

[Preparation of] **benzylideneaniline**. L. A. BIGELOW and H. EATNOUGH (Org. Syntheses, 1928, 8, 22—23).

Doebner reaction. VI. R. CIUSA and A. CREMONINI (Gazzetta, 1928, 58, 153—159).—*N*-Benzyl- β -naphthylamine, m. p. 67.5°, b. p. 405°, is obtained as a by-product in the Doebner reaction (cf. Ciusa and Zerbini, A., 1921, i, 195); it forms a *benzoyl* derivative, m. p. 115° (of which a dose of 1 g. per kg. causes a rise of about 1° in the body temperature of the rabbit—A. BALDONI), a *picrate*, m. p. 140—141°, and a *hydrochloride*, m. p. 219°. The nitroso-derivative (Koehler, A., 1888, 49) is reduced by zinc and acetic acid to α -benzyl- α -2-naphthylhydrazine, m. p. 79° (*hydrochloride*, m. p. 177°; *picrate*, m. p. 152°), from which the *acetone*-, m. p. 104°, *benzaldehyde*-, m. p. 178°, *o*-, m. p. 137°, and *p*-nitrobenzaldehyde-, m. p. 137°, 166°, and 168°, respectively, *vanillin*-, m. p. 170°; *piperonal*-, m. p. 156°, *anisaldehyde*-, m. p. 150°, and

cinnamaldehyde-, m. p. 214°, -*benzyl*- β -naphthylhydrazones are prepared.

1-Benzeneazo-2-benzyl-naphthylamine, m. p. 138—139°, sodium 2-benzylamino-1-naphthaleneazobenzene-*p*-sulphonate [$+3.5\text{H}_2\text{O}$], 1-*p*-nitrobenzeneazo-, m. p. 199°, and 1-*o*-nitrobenzeneazo-2-benzyl-naphthylamine, m. p. 165°, and 1- α -naphthaleneazo-2-benzyl-naphthylamine, m. p. 168°, are described. E. W. WIGNALL.

Cyclic thiocarbamides derived from fluorene. L. GUGLIAMELLI and A. NOVELLI (Anal. Assoc. Quim. Argentina, 1927, 15, 287—307; cf. A., 1926, 720).—The mechanism of formation of aromatic thiocarbamides from amines and carbon disulphide in the presence of various catalysts is discussed. The ease of formation may be influenced by the solvent and by the presence of substituents in the aromatic nucleus; thus no thiocarbamide could be obtained from *o*- and *p*-nitroanilines and carbon disulphide, even using potassium xanthate as a catalyst. Neither a dithiocarbamate nor a thiocarbamide could be obtained from 2-aminofluorene and carbon disulphide except by the method of treating the mixture containing excess of the latter with pyridine (2 mols.) and adding iodine (1 mol.). In this way, *di*-2-fluorenylthiocarbamide, m. p. 245°, was obtained. Distillation with phosphorus pentoxide yielded 2-fluorenylthiocarbimide, m. p. 70—80°. The difficulty of formation of the thiocarbamide is attributed to the effect of the methylene group. R. K. CALLOW.

Action of sodium triphenylmethyl on methoxytrimethylammonium iodide, and of triphenylmethyl halides on trimethylamine. L. W. JONES and M. W. SEYMOUR (J. Amer. Chem. Soc., 1928, 50, 1150—1154).—When sodium triphenylmethyl and methoxytrimethylammonium iodide are shaken together in dry ether, sodium iodide, trimethylamine, triphenylmethane, and $\beta\beta\beta$ -triphenylethyl alcohol are formed, probably as decomposition products of the desired triphenylmethyltrimethylammonium methoxide. Although triphenylmethyltriethylammonium iodide appears to exist (Schlubach and Miedel, A., 1923, i, 1068), attempts to prepare triphenylmethyltrimethylammonium salts from triphenylmethyl chloride or bromide and trimethylamine were unsuccessful, whilst triphenylmethyldimethylamine and methyl iodide gave only tetramethylammonium iodide and impure triphenylmethyl iodide.

H. E. F. NOTTON.

[Preparation of] **triphenylamine**. F. D. HAGER (Org. Syntheses, 1928, 8, 116—119).

Derivatives of benzyl-*p*-phenylenediamine. J. REILLY and J. J. MOORE (J.S.C.I., 1928, 47, 116T).—Benzyl-*p*-phenylenediamine prepared from benzylaniline and diazotised sulphanilic acid had m. p. 37° (lit. 30°). On diazotisation with excess of nitrous acid a nitrosodiazonium salt, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NCl}$, is formed, which couples with β -naphthol to give *p*-benzylnitrosoaminobenzeneazo- β -naphthol, m. p. 169—170°, and forms an azo dye with chromotropic acid.

Attempted synthesis of β -*m*-aminophenylethylamine. A. K. DE (J. Indian Chem. Soc., 1928, 5, 29—31).—*m*-Aminocinnamic acid, m. p. 180°,

prepared from *m*-nitrocinnamic acid, m. p. 200—201° (colourless), yields *m*-acetamidocinnamic acid, m. p. 235°, which in turn affords β -*m*-acetamidophenylpropionic acid, m. p. 162°, on reduction with sodium amalgam. The failure of the preparation of the amide of the last-named precluded the synthesis of β -*m*-aminophenylethylamine by this method. It was also not found possible to reduce *m*- ω -dinitrostyrene, m. p. 123—124°, prepared from *m*-nitrobenzaldehyde and nitromethane, to the amine. G. A. C. GOUGH.

Orientation effects in the diphenyl series. VI. Supposed isomerism of the dinitrotolidines. R. J. W. LE FÈVRE and E. E. TURNER (J.C.S., 1928, 963—969).—Nitration and subsequent hydrolysis of diacetyl-*o*-tolidine yields a mixture of 5:5'- and 6:6'-dinitro-*o*-tolidine. The former by bisdiazotisation and treatment with bromine yields a perbromide, which is decomposed by boiling glacial acetic acid to yield 4:4'-dibromo-5:5'-dinitro-3:3'-dimethyldiphenyl, m. p. 271—272°. This by heating with piperidine is converted into 4:4'-dipiperidino-5:5'-dinitro-3:3'-dimethyldiphenyl, m. p. 226—227°. The 6:6'-dinitro-compound similarly yields 4:4'-dibromo-6:6'-dinitro-3:3'-dimethyldiphenyl (I), m. p. 230—233° (softening at 225°), which does not react with boiling piperidine. Cain and Micklethwait's *o*-dinitrotolidine II, m. p. 202—203° (J.C.S., 1914, 105, 1442), is thus proved to be a mixture of 5:5'- and 6:6'-dinitrotolidines, thus explaining its supposed conversion into *o*-dinitrotolidine I and the production of the same quinoxaline (by reduction followed by condensation with benzil) from both the I and II compounds. Nitration of 6-nitrodiaacetyltolidine yields the 6:6'-dinitro-compound, since the product is converted into (I) on treatment by the perbromide method. Nitration of 4:4'-dichloro- (Schultz, Rohde, and Vicari, A., 1907, i, 244) and 4:4'-dibromo-3:3'-dimethyldiphenyl, m. p. 63—64° (Stolle, A., 1888, 699, gives 58—59°), yields, respectively, mainly 4:4'-dichloro-, m. p. 211—212°, identical with the compound obtained from 6:6'-dinitrotolidine by replacement of the amino-group by chlorine, and 4:4'-dibromo-6:6'-dinitro-3:3'-dimethyldiphenyl, identical with (I) (above). The four isomeric dinitrotolidines of the *meta* series described by Cain and Micklethwait are probably position and not space isomerides, the positions of the nitro-groups being, respectively, 6:6', 2:2', 2:6', and 6:5'.

J. W. BAKER.

α - and β -Substituted semicarbazides. α -Benzylsemicarbazide and β -benzylsemicarbazide. J. BOUGAULT and J. LEBOUCC (Compt. rend., 1928, 186, 957—960).—The benzylsemicarbazide, m. p. 235°, obtained by the method of Curtius (A., 1900, i, 610) is not 1-benzylsemicarbazide but 2-benzylsemicarbazide, $\text{NH}_2\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{CO}\cdot\text{NH}_2$, since it reacts with benzaldehyde to yield benzaldehydebenzylsemicarbazide, $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{CO}\cdot\text{NH}_2$, m. p. 159.5—160°, and with excess of potassium cyanate to yield benzylhydrazodicarboxylamide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CO}\cdot\text{NH}_2)_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 256°. Thus hydrazines containing a negative substituent react with potassium cyanate to yield 1-substituted semicarbazides, whilst those containing a less negative substituent yield the corresponding

2-compounds (cf. Young and Oates, J.C.S., 1901, 79, 659). J. W. BAKER.

Bivalent triazenes. H. KLEINFELLER (J. pr. Chem., 1928, [ii], 119, 61—73).—*m*-Phenylenediazide reacts with magnesium ethyl and phenyl bromides to form *m*-bisethyltriazenobenzene, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{N}\cdot\text{NEt})_2$, m. p. 104°, and *m*-bisphenyltriazenobenzene, m. p. 161° (silver derivative, phenylcarbimide derivative, m. p. 230°). These compounds explode when heated rapidly and are decomposed by acetic or sulphuric acid.

Magnesium acetylenyl bromide and phenyl azide react yielding bisphenyltriazenoacetylene, $(\text{NHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}\equiv)_2$, m. p. 170° (silver compound; phenylcarbimide derivative, m. p. 197°), together with an isomeric compound, $\text{C}_{14}\text{H}_{12}\text{N}_6$, m. p. 156°, which is converted into the triazeno-derivative by treatment of its chloroform solution with alkali. When the triazeno-derivative is warmed with 20% sulphuric acid there is formed 2-phenyl-1:2-dihydro-1:2:3:4-tetrazole(?), m. p. 107°, whilst similar treatment of the isomeride gives a compound, $\text{C}_8\text{H}_8\text{N}_4$, m. p. 172°. *p*-Bromophenyl azide and magnesium acetylenyl bromide yield bis-*p*-bromophenyltriazenoacetylene, m. p. 215° (silver compound, m. p. 153°), and an isomeric compound, m. p. 198°. Bromine converts the triazene in chloroform solution into a compound, $\text{C}_{14}\text{H}_{11}\text{N}_6\text{Br}_5$, which when crystallised from alcohol passes into the substance, $\text{C}_{14}\text{H}_{11}\text{ON}_6\text{Br}_3$, m. p. 204°. Similar treatment of the isomeric substance gives a compound, $\text{C}_{14}\text{H}_{11}\text{N}_6\text{Br}_5$, m. p. 176°, unchanged by crystallisation from anhydrous solvent, but passing into the substance, $\text{C}_{14}\text{H}_{10}\text{N}_6\text{Br}_3\cdot\text{OH}$, m. p. 186°, when crystallised from 96% alcohol. *m*-Phenylenediazide and magnesium acetylenyl bromide react to give small amounts of reddish-violet and yellow substances.

H. BURTON.

Migration of acyl from nitrogen to oxygen. L. C. RAIFORD and F. C. MORTENSEN (J. Amer. Chem. Soc., 1928, 50, 1201—1204).—The acyl radicals in monoacyl derivatives of 2-aminocyclohexanol and 1- α -aminobenzyl-2-naphthol, unlike those in the corresponding derivatives of *o*-aminophenols (cf. A., 1925, i, 809), do not migrate during further acylation. 2-Aminocyclohexanol, m. p. 65° (cf. Brunel, A., 1903, i, 680), benzoyl chloride, and aqueous alkali give 2-benzamidocyclohexanol, m. p. 168—169°, also formed by hydrolysing its benzoate, m. p. 204—205°, or acetate, m. p. 143—144°. Similarly, 2-acetamidocyclohexyl acetate, m. p. 117—118°, and benzoate, m. p. 198—199°, are both hydrolysed to 2-acetamidocyclohexanol. Benzoylation of 1- α -acetamidobenzyl-2-naphthol (Betti, A., 1903, i, 480) in pyridine gives 1- α -acetamidobenzyl-2-naphthyl benzoate, m. p. 176—177°, which is hydrolysed to the *N*-acetyl derivative. 1- α -Benzamidobenzyl-2-naphthyl benzoate, m. p. 118—119°, and acetate, m. p. 118—119°, are hydrolysed to 1- α -benzamidobenzyl-2-naphthol, m. p. 240—241° (Betti, loc. cit., gives m. p. 224°). H. E. F. NOTTON.

Aluminium powder as a synthetic reagent. A. C. RAY and S. DURR (J. Indian Chem. Soc., 1928, 5, 103—110; cf. J.C.S., 1920, 117, 1335).—Aluminium powder may be activated for synthetic purposes by heating it in a current of dry hydrogen at 500°. The

activation is apparently not due to the formation of a hydride nor to the removal of a film of aluminium sesquioxide, since that oxide is not reduced under the conditions employed. It is suggested that a film of a suboxide is removed in the activation. Dry distillation of phenol with the activated aluminium affords benzene and diphenyl; nitrophenols yield aminophenols, ammonia, and benzene. The powder may also be used in typical Ullmann, Freidel-Crafts, and Reformatsky reactions. When used in the reduction of a suspension of nitrobenzene in aqueous ammonium chloride, it affords β -phenylhydroxylamine at 0° and aniline at the ordinary temperature. Under the latter conditions it may be employed in the reduction of benzophenone to benzhydrol and in the reduction of azo dyes.

G. A. C. GOUGH.

Sodium and potassium phenoxides. A. N. MELDRUM and M. M. PATEL (*J. Indian Chem. Soc.*, 1928, 5, 91—94).—These compounds may be obtained in a state of purity by precipitation of solutions of the phenol in 20% alkali hydroxide with concentrated alkali solution (100—200 g. in 100 g. of water). In this way the following are prepared: sodium phenoxide, m. p. 59—60°; potassium phenoxide, m. p. 103—104°; sodium *o*-, *m*-, and *p*-tolylloxides, m. p. below 0°, and 92—94°, and 123—125°, respectively; potassium *o*-, *m*-, and *p*-tolylloxides, crystalline, m. p. about 36° and 92°, respectively; sodium *m*-xylyloxide, m. p. 41—43°; potassium *m*-xylyloxide, liquid; sodium *p*-xylyloxide, m. p. 83°; potassium *p*-xylyloxide, m. p. 35°; sodium guaiacoxide, m. p. 120°; potassium guaiacoxide, m. p. 168°; sodium eugenoxide, m. p. 115°; potassium eugenoxide, m. p. 128°; sodium α - and β -naphthoxides, m. p. 44—45° and 120°, respectively; potassium α -naphthoxide, liquid; potassium β -naphthoxide, m. p. 38—40°.

G. A. C. GOUGH.

Action of hydrogen peroxide on phenol and anisole. O. MAGIDSON and N. PREOBRAHSHENSKI (*Trans. sci. chem.-pharm. Inst.*, [Moscow], 1926, 16, 65—67; *Chem. Zentr.*, 1928, i, 35).—From phenol (31 g.), ferrous sulphate (0.1—0.2 g. in 100 c.c. of water), and 2% hydrogen peroxide are obtained, according to the temperature, 6—8 g. of pyrocatechol and 4—7 g. of quinol (with resin and excess of phenol). Anisole (36 g.) similarly yields guaiacol (1.5—2.5 g.).

A. A. ELDRIDGE.

Preparation of *p*-iodoanisole. F. F. Blicke and F. D. SMITH (*J. Amer. Chem. Soc.*, 1928, 50, 1229—1231).—A modification of the method of Brenans (*Bull. Soc. chim.*, 1901, [iii], 25, 819) gives 73% of the theoretical yield at 50—60°, and 57% at the ordinary temperature, whilst *p*-anisidine by the diazo reaction gives 75—80%. Iodination of anisole by way of its mercuration products or directly using iodine monochloride gives complex mixtures.

H. E. F. NOTTON.

Bromiodophenols produced from 5-bromo- and 3:5-dibromo-salicylic acids. P. BREMANS and C. GIROD (*Compt. rend.*, 1928, 186, 1128—1130).—Iodine reacts with 5-bromosalicylic acid (Hewitt, Kenner, and Silk, *J.C.S.*, 1904, 85, 1228; also produced from 5-aminosalicylic acid by the diazo-reaction) in the presence of sodium hydroxide or

carbonate to afford 4-bromo-2:6-di-iodophenol, m. p. 128° (*ethyl ether*, m. p. 75°), which, when heated with aqueous sodium carbonate, is converted into an amorphous red compound of unknown constitution. 3:5-Dibromosalicylic acid, when treated with less than 1 mol. of iodine under similar conditions, yields 2:4-dibromo-6-iodophenol, m. p. 104° (*ethyl ether*, m. p. 54°), which is transformed into a red compound when treated with an excess of iodine in aqueous sodium carbonate.

G. A. C. GOUGH.

[Preparation of] *m*-nitrophenol. R. H. F. MANSKE (*Org. Syntheses*, 1928, 8, 80—82).

[Preparation of] di-*o*-nitrophenyl disulphide. M. T. BOGERT and A. STULL (*Org. Syntheses*, 1928, 8, 64—65).

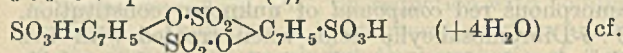
Derivatives of phenolmonosulphonyl chlorides. E. G. FÜLNEGG and A. SCHLESINGER (*Ber.*, 1928, 61, [B], 781—784).—Derivatives of phenolmonosulphonyl chlorides are obtained directly by the action of chlorosulphonic acid on the requisite ethylcarbonato-compounds. Since other groups which protect the phenolic hydroxyl group do not exert a similar effect, a specific action must be attributed to the carbethoxy-group, probably due to its negative nature. *m*-Ethylcarbonatotoluene gives (?) 5-ethylcarbonatotoluene-2-sulphonyl chloride, converted into the corresponding anilide, m. p. 149°. α -Ethylcarbonatonaphthalene affords α -ethylcarbonatonaphthalene-4-sulphonyl chloride, m. p. 83° (cf. Zincke and Ruppertsberg, *A.*, 1915, i, 135), transformed by treatment with the requisite base and subsequent hydrolysis of the product into α -naphthol-4-sulphonamide, m. p. 198° (cf. Zincke, *loc. cit.*), α -naphtholsulphon-diphenylamide, m. p. 176°, and α -naphtholsulphon- β -naphthylamide, m. p. 204°. β -Ethylcarbonatonaphthalene yields β -ethylcarbonatonaphthalene-8-sulphonyl chloride, m. p. 118°, identical with the product derived from β -naphthol-8-sulphonic acid by carbethoxylation and treatment with phosphorus pentachloride (Pollak and Halward, unpublished work); the corresponding anilide has m. p. 195°. Reduction of the sulphonyl chloride by zinc dust and sulphuric acid in presence of acetone gives 8-thiol- β -naphthol, isolated as the lead salt, (C₁₀H₇OS)₂Pb. H. WREN.

Synthetic musks. II. Elimination of side-chains during the nitration of aromatic compounds. R. DE CAPELLER (*Helv. Chim. Acta*, 1928, 11, 426—427).—The dinitro-*m*-tolyl methyl ether, m. p. 101°, formed during the nitration of 2-isobutyl-*m*-tolyl methyl ether (Barbier, this vol., 280) is 4:6-dinitro-*m*-tolyl methyl ether, the isobutyl group having been replaced by hydrogen. When heated with ammonia at 100° under pressure this yields 4:6-dinitro-*m*-toluidine. Nitration of butyl-*m*-xylene (prepared from *m*-xylene and α -butylene in presence of aluminium chloride), dibutyl-*m*-xylene, and amyl-*m*-xylene gives in each case appreciable amounts of trinitro-*m*-xylene.

H. BURTON.

Sulphonylides of cresol- and chlorophenol-disulphonic acids. C. S. SCHOEFFLE, F. J. VAN NATTA, and R. G. CLARKSON (*J. Amer. Chem. Soc.*, 1928, 50, 1171—1178).—These are obtained in high yield by heating the phenol for 6—8 hrs. at 100° with

sulphuric acid containing 20% of sulphur trioxide. In this way *p*-cresol yields tolylene-4:5-sulphonylide-3:3'-disulphonic acid (I),



Anschütz, A., 1918, i, 424); *o*-cresol, tolylene-2:3-sulphonylide-5:5'-disulphonic acid (II) (+6H₂O) (cf. Pollak, A., 1926, 514); *p*-chlorophenol, 4:4'-dichlorobenzene-1:2-sulphonylide-6:6'-disulphonic acid (+4H₂O); *o*-chlorophenol, 6:6'-dichlorobenzene-1:2-sulphonylide-4:4'-disulphonic acid (+6H₂O); and *m*-chlorophenol, 5:5'-dichlorobenzene-1:2-sulphonylide-4:4'-disulphonic acid (+8H₂O), whilst *m*-cresol does not react. The approximate solubility of the sodium salt of each acid has been measured. The sulphonylide (I) is converted through its acid chloride into its diamide, decomp. above 300°, diethyl ester, decomp. 90° (also +2MeOH), and dimethyl ester (+2MeOH), decomp. above 250°, which had half the correct mol. wt. in methyl alcohol. (II) also gives a diamide, decomp. above 300°, and methyl ester (+2MeOH), decomp. above 250°, which like the free acid (II) and methyl 4-hydroxytoluene-3:5-disulphonate, m. p. 148—149°, gives normal mol. wt. results in solvents other than methyl alcohol. Tolylene-4:5-sulphonylide (Anschütz, *loc. cit.*) and fuming sulphuric acid at the ordinary temperature yield tolylene-4:5-sulphonylide-3-sulphonic acid (+2H₂O), m. p. 220—222°.

H. E. F. NOTTON.

Reaction between phenacetin and acetaldehyde.

O. CARLETTI (Giorn. Chim. Ind. Appl., 1928, 10, 66).—If a small quantity of phenacetin, moistened with acetaldehyde in a porcelain dish, is stirred with 2—3 c.c. of concentrated sulphuric acid, the latter assumes a red colour, which intensifies gradually in the cold or more rapidly on a water-bath. Dilution of the liquid results in the separation of a bluish-brown substance, which gives the red coloration when dissolved in concentrated sulphuric acid. This reaction is given also by paraldehyde and metaldehyde, but not by formaldehyde, trioxymethylene, or hexamethylenetetramine.

T. H. POPE.

Condensation of chloral with substituted phenols. F. D. CHATTAWAY and F. CALVET (Anal. Fis. Quím., 1928, 26, 75—91; cf. A., 1927, 458, 967).—The condensation of chloral with *p*-aminophenol in excess of concentrated sulphuric acid yielded anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I), previously obtained by reduction of the 5-nitro-compound (A., 1926, 1242). Boiling alcoholic potassium hydroxide converted (I) into anhydro-5-amino-2-ββ-dichloro-α-hydroxyethenoxy-1-ββ-dichloro-α-hydroxyethylbenzene, m. p. 113—117° (acetyl derivative, m. p. 191—196°). *p*-Tolueneazophenol and 4-nitro-*m*-cresol reacted similarly with chloral, giving the 5-*p*-tolueneazo-compound (II), m. p. 153°, and the 5-nitro-4-methyl compound (III), m. p. 148—150°, respectively. Reduction of (II) by stannous chloride yielded (I) and *p*-toluidine. The action of alcoholic potassium hydroxide on (III) yielded 5-nitro-2-ethoxy-*p*-tolylglycollic acid, m. p. 155°, which was oxidised by alkaline permanganate solution to 5-nitro-2-ethoxy-*p*-toluic acid (IV), m. p. 166°, and 5-nitro-2-ethoxy-*p*-tolylglyoxylic acid, m. p. 194° (phenyl-

hydrazone, m. p. 199°). By sulphuric acid, (IV) was converted into 6-nitro-3-hydroxy-*p*-toluic acid, m. p. 225°, identical with the product of nitration of 3-hydroxy-*p*-toluic acid with fuming nitric acid in glacial acetic acid.

The formation of (III) shows that a substituent in the *m*-position to the hydroxyl group does not prevent the normal reaction. Substituents in the *o*-position, however, interfere, and 4-nitro-*o*-cresol, 5-nitrosalicylic acid, and 2:4-dinitrophenol do not condense under these conditions, probably owing to steric hindrance of the primary addition to the hydroxyl group. When the *p*-position is unoccupied, the chloral residue may enter in this position, as in the case of *m*-hydroxybenzoic acid, which yielded 5-hydroxytrichloromethylphthalide, m. p. 199—200° (cf. Fritsch, A., 1897, i, 568). Condensation of chloral with salicylic acid and *o*- and *m*-nitrophenols probably takes place in this way, but the products are resinous.

R. K. CALLOW.

Photo-oxidation of certain organic substances in presence of fluorescent dyes. C. W. CARTER (Biochem. J., 1928, 22, 575—582).—None of the aliphatic compounds employed was found to undergo photo-oxidation. Of the benzene derivatives only those containing a nuclear amino- or hydroxyl group were oxidised. Side-chains in which the groups ·NH₂ and ·CH:CH· occur are oxidised. The other side-chain compounds investigated were inactive. Certain other ring compounds, α-naphthol, tryptophan, thiophen, and to a marked degree the purine derivatives are oxidised. The carbon dioxide evolved during the oxidation was determined in a Barcroft apparatus.

S. S. ZILVA.

Derivatives of quinitol. L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1928, 186, 1007—1008; cf. this vol., 518).—The action of acetyl chloride or acetic anhydride in pyridine and chloroform at -5° on *cis*-quinitol yielded a mixture of the stereoisomeric diacetates, but *trans*-quinitol underwent no appreciable isomerisation. The monoacetates could not be isolated. As a by-product of the action of acetyl chloride, *trans*-quinitol yielded 4:4'-dihydroxydicyclohexyl ether, b. p. 132—133°/16 mm., *d*₄²⁰ 1.0920, *n*_D²⁰ 1.4574. Benzoyl chloride under similar conditions yielded *cis*-quinitol dibenzoate, m. p. 116—117°, and *trans*-quinitol dibenzoate, m. p. 151°, isomerisation during reaction of the *cis*-compound occurring only on rise of temperature. Acetic acid caused acetylation and isomerisation of *cis*-quinitol at 150°.

R. K. CALLOW.

Dyes resembling orcein. F. HENRICH and W. HEROLD (Ber., 1928, 61, [B], 767—770).—2-Amino-orcinol is not affected by dry air if dissolved in ether, benzene, or xylene; in methyl or ethyl alcohol it becomes oxidised, slowly in cold, more rapidly in hot solution, with loss of ammonia to a red dye, C₂₁H₁₃O₆N₂, regarded provisionally as a complex indophenol,

O:C₆H₂Me(OH):N:C₆HMe(OH)₂:N:C₆H₂Me(OH):O.
Oxidation appears to follow a different course in amyl alcohol. The possibility of the production of indophenols by this method is established by the formation of 4:6:6'-trihydroxy-3:3'-dimethylindo-

phenol from 5-amino-2:4-dihydroxytoluene (cf. Henrich and Götz, A., 1925, i, 913) and of a compound giving the indophenol reaction from a dilute alcoholic solution of phenol, *p*-aminophenol, and sodium. The dye is transformed by treatment with concentrated hydrochloric acid and stannous chloride at 180–200° mainly into a dark mass, which rapidly becomes oxidised and then ceases to give the reactions of the dye, but yields also about 10% of amino-orceinol hydrochloride and a little ammonium chloride. Diamino-orceinol, a possible product from the dye, yields ammonium chloride, but not amino-orceinol hydrochloride under analogous conditions. Similarly, orcein yields a product resembling that from the dye, which, however, contains much ammonium chloride and only a trace of substance which gives the same coloration as amino-orceinol with ferric chloride.

H. WREN.

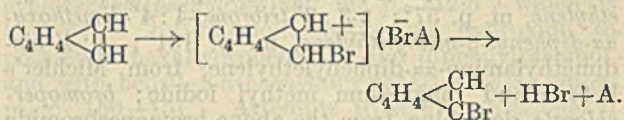
Synthesis of 3:5-dihydroxyethylbenzene. Y. ASAHINA and S. IHARA (J. Pharm. Soc. Japan, 1928, [551], 28–31).—Ethyl 3:5-dimethoxybenzoylacetate is boiled with dilute sulphuric acid for 10 hrs., and 3:5-dimethoxyphenyl methyl ketone is obtained. This ketone is reduced by zinc amalgam and hydrochloric acid to 3:5-dimethoxyethylbenzene, which yields on boiling with hydriodic and glacial acetic acids, 3:5-dihydroxyethylbenzene, m. p. 72–73°, with benzene of crystallisation. Unlike orceinol and divarinol, it develops no coloration with ferric chloride, but with vanillin and hydrochloric acid turns red and exhibits greenish fluorescence on boiling with alkali hydroxide and chloroform.

Theory of halogen substitution. P. PFEIFFER and R. WIZINGER (Annalen, 1928, 461, 132–154).—It was stated by Gattermann (A., 1889, 862) that certain $\alpha\alpha$ -dianisylethylenes gave a violet colour with bromine vapour, but that this colour rapidly disappeared, the original compounds being recovered unchanged. This statement is correct as regards the colour change, but otherwise incorrect, for the compounds undergo bromination. The bromo-derivatives behave towards bromine like the parent substances until the limit is reached when no further bromination can occur. The colours observed immediately are apparently those of unstable bromoperoxides; one of the latter, that of 4:4'-bisdimethylamino- $\alpha\alpha$ -diphenylethylene, is isolable as a deep blue solid (the corresponding iodoperiodide, also isolated, is a stable blue solid). The constitution of the coloured intermediate compounds is deduced from the fact that the depth of colour given by a compound with bromine corresponds with that given with concentrated sulphuric acid or with perchloric acid. Thus, $\alpha\alpha$ -diphenylethylene gives no colour with bromine and a greenish-yellow with the two acids, whilst $\alpha\alpha$ -di-*p*-anisylethylene, which affords a deep bluish-violet with bromine, gives deep orange colours with both acids. If the perchlorate formed in this

case is represented as $[(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\overset{+}{\text{C}}-\text{CH}_3]\overset{-}{\text{ClO}_4}$, then the coloured bromine compound will be $[(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\overset{+}{\text{C}}-\text{CH}_2\text{Br}]\overset{-}{\text{Br}_3}$, undergoing decomposition into $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\overset{+}{\text{C}}\cdot\text{CHBr} + \text{HBr} + \text{Br}_2$.

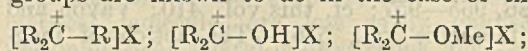
It is suggested by analogy that the bromination

of benzene in presence of a bromine carrier A (in absence of which ordinary addition occurs) may be expressed:

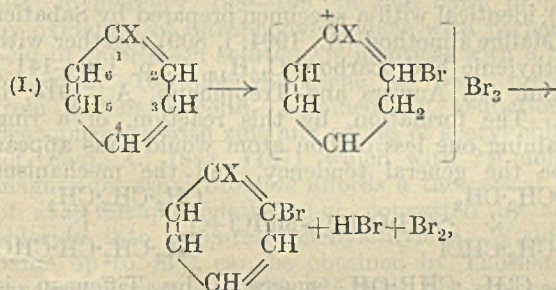


When pyridine is used as a bromine carrier, the compound $\left[\text{C}_6\text{H}_6 \left\langle \begin{array}{l} \text{CH}\cdot\text{C}_5\text{H}_5\text{N} \\ | \\ \text{CHBr} \end{array} \right\rangle \right] \text{Br}$ (cf. Meerwein, Z. angew.

Chem., 1925, 38, 816) is the intermediate formed. Again, the *ortho-para*-directive effect of certain groups X (OH, OMe, NH₂, etc.) receives explanation if it be assumed that in formula (I) the ethylenic linking 5:6 and the group X confer polar properties on the attached carbon atom (number 1) as similar groups are known to do in the case of the types:



$[\text{R}_2\overset{+}{\text{C}}-\text{NH}_2]\text{X}$; and $[(\text{NH}_2)_2\overset{+}{\text{C}}-\text{NH}_2]\text{X}$. The bromination of $\text{C}_6\text{H}_5\text{X}$ can thus be written:



p-substitution depending on a 1:4-conjugation-additive process. When X=NO₂, the "negative" effect of this group is to cause the appearance of the positive charge in the 4-position, viz., the position farthest from X. As a result, *m*-substitution occurs (position 3).

$\alpha\alpha$ -Di-*p*-anisylethylene, prepared either from dianisyl ketone and magnesium methyl iodide or from ethyl acetate and magnesium *p*-anisyl bromide, is converted by bromine (1 mol.), in benzene or carbon tetrachloride solution, into β -bromo- $\alpha\alpha$ -di-*p*-anisylethylene, m. p. 84°, the constitution of which follows from its oxidation to di-*p*-anisyl ketone. This bromo-compound is converted by bromine in carbon tetrachloride into $\beta\beta$ -dibromo- $\alpha\alpha$ -di-*p*-anisylethylene, m. p. 93–94°, also obtained by the action of methyl-alcoholic potassium hydroxide on $\beta\beta\beta$ -tribromo- $\alpha\alpha$ -di-*p*-anisylethane, m. p. 114°, which is in turn obtained by condensing bromal and anisole in presence of concentrated sulphuric acid. Dianisylethylene and the above dibromodianisylethylene are quantitatively converted by excess of bromine in glacial acetic acid solution into $\beta\beta$ -3:3'-tetrabromo-4:4'-dimethoxy- $\alpha\alpha$ -diphenylethylene, m. p. 150°, oxidised to 3:3'-dibromo-4:4'-dimethoxybenzophenone.

The following substances are described as being obtained by processes mostly similar to the above: $\alpha\alpha$ -di-*p*-anisyl- β -methylethylene (dianisylpropylene); $\alpha\alpha$ -di-*p*-anisyl- $\beta\beta$ -dimethylethylene (dianisylmethylpropylene), m. p. 64°; $\alpha\alpha$ -di-*p*-tolylethylene, from toluene

and bromoacetal in presence of concentrated sulphuric acid; α -di-*m*-xylylethylene, similarly obtained, b. p. 197—200°/17 mm.; β -bromo- α -di-*p*-anisyl- β -methyl-ethylene, m. p. 57°; β -3:3'-tribromo-4:4'-dimethoxy- α -diphenyl- β -methyl-ethylene, m. p. 131°; 4:4'-bis-dimethylamino- α -diphenylethylene, from Michler's ketone and magnesium methyl iodide; bromoperchlorate, deep blue, from the above bromoperbromide and sodium perchlorate, or, better, from the ethylene and ferric bromide, followed, after isolation of the ferribromide, by sodium perchlorate.

A table is given of the colours shown when bromine, concentrated sulphuric acid, or perchloric acid acts on a number of α -diarylethylenes of the type C_6R_2CXY , where X or Y=H, Me, Br, or Cl.

E. E. TURNER.

Molecular transpositions in the cycloheptane series. M. GODCHOT and G. CAUQUIL (Compt. rend., 1928, 186, 955—957; cf. this vol., 410; Vavon and Mitchovitch, this vol., 516).—The action of magnesium phenyl bromide on 2-chlorocycloheptanol yields phenylcyclohexylcarbinol, m. p. 48—49° (hydrogen phthalate, m. p. 163°; phenylurethane, m. p. 146—147°), identical with a specimen prepared by Sabatier and Mailhe's method (A., 1904, i, 809) together with an ethylenic hydrocarbon, $C_{13}H_{16}$, b. p. 140—141°/15 mm. (cf. Auwers and Treppmann, A., 1915, i, 789). The formation, by this reaction, of a ring containing one less carbon atom would thus appear to be the general tendency, and the mechanism

$$\begin{array}{ccc} CH_2 \cdot CH_2 \cdot CH_2 & & CH_2 \cdot CH_2 \cdot CH_2 \\ | & \searrow & | \\ CH_2 \cdot CH_2 \cdot CHCl & \xrightarrow{MgI} & CH_2 \cdot CH_2 \cdot CH \cdot CHO \\ \xrightarrow{RMgI} & & \end{array}$$

$C_6H_{11} \cdot CHR \cdot OH$, suggested by Tiffeneau, is probably correct.

J. W. BAKER.

Mobile-anion tautomerism. I. Conditions of activation of the three-carbon system, and modes of addition to conjugated systems. H. BURTON and C. K. INGOLD (J.C.S., 1928, 904—921).—An examination has been made of the relative mobility of X (=OH, OAc, Br) and its facilitation by R (=Me, Ph, *p*-Me-C₆H₄, *p*-Cl-C₆H₄) in $R \cdot CHX \cdot CH \cdot CH_2R' \rightleftharpoons R \cdot CH \cdot CH \cdot CHX \cdot R'$, and of the effect of R on equilibrium. The order of increasing mobility is as indicated in each series, and hence corresponds with the anionic stability of X and the power of R to take up the cationic charge. The analogy with aromatic substitution and the bearing of the results on 1:4-addition to conjugated systems and related topics are discussed. Contrary to the observations of Valeur and Luce (Bull. Soc. chim., 1920, [iv], 27, 611), the conversion of α -phenylallyl alcohol (*p*-nitrobenzoate, m. p. 45—46°) into cinnamyl alcohol could not be effected, but on heating with acetic anhydride, smooth conversion into cinnamyl acetate occurs. The action of an acetic acid solution of hydrogen bromide on either alcohol yields cinnamyl bromide (Moureu and Gallacher, A., 1922, i, 34), the structure of which is proved by ozonolysis. α -*p*-Tolylethyl alcohol, b. p. 120—122°/10 mm. (*p*-nitrobenzoate, m. p. 82°), prepared by the action of magnesium *p*-tolyl bromide on acraldehyde, is readily converted by the action of acetic anhydride and subsequent hydrolysis into 4-methylcinnamyl alcohol,

m. p. 51—52° (*p*-nitrobenzoate, m. p. 131—132°), and on bromination yields 4-methylcinnamyl bromide, m. p. 64—65°. In the investigation of α -diarylated systems the structures of the various alcohols were established by ozonolysis, and by conversion under the influence of alcoholic alkali, into the isomeric ketones, $R \cdot CH(OH) \cdot CH \cdot CHR' \rightarrow R \cdot CO \cdot CH_2 \cdot CH_2R'$ Tiffeneau, Bull. Soc. chim., 1907, [iv], 1, 1209; Nomura, A., 1927, 770). α -Diphenylallyl acetate when treated with bromine in cold carbon tetrachloride deposits a bromide, m. p. 176—177°, a second bromide, m. p. 122°, being obtained from the mother-liquors. γ -Phenyl- α -*p*-tolylallyl alcohol, m. p. 78—79°, obtained by the action of magnesium *p*-tolyl bromide on cinnamaldehyde, is converted by boiling 20% alcoholic potassium hydroxide into *p*-tolyl β -phenylethyl ketone (I), m. p. 70° (oxime, m. p. 101—102°), and on acetylation yields a mixture of γ -phenyl- α -*p*-tolyl and α -phenyl- γ -*p*-tolyl acetates with a constant b. p. 210—212°/11 mm. The action of cinnamaldehyde on magnesium *p*-chlorophenyl iodide yields a mixture of the isomeric phenylchlorophenylallyl alcohols, the mixed acetates of which, b. p. 225—226°/13 mm., on treatment with bromine yield two isomeric bromides, m. p. 193—194° and 180°, respectively. Treatment of the mixed acetates with 20% alcoholic potassium hydroxide solution yields a mixture of phenyl β -*p*-chlorophenylethyl ketone (II), m. p. 58°, and *p*-chlorophenyl β -phenylethyl ketone (III), m. p. 78°, which were isolated as their oximes, m. p. 117—118° and 111—112°, respectively (below). The various reference ketones are synthesised as follows: ethyl *p*-chlorobenzoylacetate, b. p. 240°/12 mm., m. p. 54—55°, is obtained by the action of *p*-chlorobenzyl bromide on ethyl sodiobenzoylacetate, and hydrolysis with dilute sulphuric acid or barium hydroxide yields (II). Ethyl *p*-chlorobenzoylacetate, b. p. 181—182°/18 mm., m. p. 36°, obtained by the action of *p*-chlorobenzoyl chloride on ethyl sodioacetate, is similarly converted into ethyl benzyl-*p*-chlorobenzoylacetate, b. p. 228—233°/14 mm., m. p. 65°, which on hydrolysis yields (III). Ethyl *p*-toluoylacetate, b. p. 172—173°/14 mm. (Marguery, A., 1905, i, 527, gives b. p. 170°/30 mm.), is similarly converted into ethyl benzyl-*p*-toluoylacetate, b. p. 232—233°/11 mm., which by hydrolysis yields (I). Ethyl *p*-methylbenzoylacetate, b. p. 223—225°/10 mm., on hydrolysis yields phenyl β -*p*-tolylethyl ketone, low m. p., a waxy solid (oxime, m. p. 85—86°).

J. W. BAKER.

[Preparation of] benzhydrol. C. S. MARVEL and N. A. HANSEN (Org. Syntheses, 1928, 8, 24—25).—Benzophenone is reduced with technical zinc dust (85% purity), 95% alcohol, and sodium hydroxide; the benzophenone must first be heated with the alcoholic alkali.

A. A. ELDRIDGE.

Preparation of crystal-violet from oxalyl chloride and dimethylaniline. I. N. POSTOVSKI (J. Chem. Ind. [Moscow], 1927, 4, 552—553).—Powdered aluminium chloride (1 part) is added to dimethylaniline (10 parts), and oxalyl chloride (7 parts) is added gradually; the hot, green mixture is cooled with water while the remainder of the oxalyl chloride is added. The reaction is complete in 5 min. The crude mass is converted into the

carbinol with sodium hydroxide, the excess of dimethylaniline removed with steam, and the carbinol dissolved in acidified water, filtered, and recrystallised. The yield is 92—95% of the dimethylaniline taken (cf. G.P. 34,607).

CHEMICAL ABSTRACTS.

Amino-alcohols of the naphthalene series. E. FOURNEAU, TRÉFOUEL, and (Mme.) TRÉFOUEL (Bull. Soc. chim., 1928, [iv], 43, 454—458).—A number of amino-alcohols of mol. wt. approaching that of quinine and of amino-alcohols of the benzene series containing a methoxy-group or a piperidine ring have been prepared. The following are described: α -*dimethylamino- γ -1-naphthyl-*, b. p. 216—217°/28 mm. (hydrochloride, m. p. 134°); α -*diethylamino- γ -1-naphthyl-*, b. p. 214°/19 mm. (hydrochloride, m. p. 138°); α -*diamylamino- γ -1-naphthyl-*, b. p. 240°/22 mm. (hydrochloride, m. p. 114°); and α -*piperidino- γ -1-naphthyl-isopropyl alcohol*, b. p. 228°/10 mm. (hydrochloride, m. p. 145°). The foregoing compounds were all obtained from α -*chloro- γ -1-naphthylisopropyl alcohol*, b. p. 210°/25 mm. (from magnesium α -naphthyl bromide and epichlorohydrin), or from γ -1-naphthylpropylene $\alpha\beta$ -oxide, b. p. 186°/15 mm., obtained by the action of sodium hydroxide on the chlorohydrin in alcoholic solution. γ -4-Methoxy-1-naphthylpropylene $\alpha\beta$ -oxide, b. p. 225°/25 mm., α -chloro- γ -4-methoxy-1-naphthyl-, b. p. 180°/0.2 mm., and α -piperidino- γ -4-methoxy-1-naphthyl-isopropyl alcohol, b. p. 200°/0.1 mm. (hydrochloride, m. p. 193—194°), are similarly prepared. 1-Bromo-4-methoxynaphthalene, b. p. 178°/15 mm., is obtained by brominating α -methoxynaphthalene in acetic acid. γ -Chloro- α -phenylisopropyl alcohol, b. p. 135—155°/20 mm., γ -phenyl- $\alpha\beta$ -propylene oxide, b. p. 113°/39 mm., α -piperidino- γ -phenylisopropyl alcohol, b. p. 172°/12 mm. (hydrochloride, m. p. 178—179°); γ -chloro- α -p-methoxyphenylisopropyl alcohol, b. p. 188—190°/24 mm., γ -p-methoxyphenyl- $\alpha\beta$ -propylene oxide, b. p. 145—150°, and α -piperidino- γ -p-methoxyphenylisopropyl alcohol, b. p. 213°/18 mm. (hydrochloride, m. p. 164°), are described. α -Naphthol condensed with epichlorohydrin in presence of sodium hydroxide affords γ -1-naphthoxy- $\alpha\beta$ -propylene oxide, 194°/16 mm., from which α -piperidino- γ -1-naphthoxy-, b. p. 196°/0.2 mm. (hydrochloride, m. p. 177—178°), and α -diethylamino- γ -1-naphthoxy-isopropyl alcohol, b. p. 176°/0.2 mm. (hydrochloride, m. p. 125°), are obtained. γ -2-Naphthoxy- $\alpha\beta$ -propylene oxide, b. p. 200°/16 mm., α -piperidino- γ -2-naphthoxyisopropyl alcohol, b. p. 200°/0.15 mm. (hydrochloride, m. p. 172—173°), and α -diethylamino- γ -2-naphthoxyisopropyl alcohol, b. p. 190°/0.6 mm. (hydrochloride, m. p. 162°), are also described.

R. BRIGHTMAN.

Action of magnesium cyclohexyl bromide on oxalic acid derivatives. C. G. GAUERKE and C. S. MARVEL (J. Amer. Chem. Soc., 1928, 50, 1178—1182).—Ethyl oxalate and magnesium cyclohexyl bromide give the ethyl ester (I) (20% of the theoretical yield), m. p. 69° (corr.), of hydroxydicyclohexylacetic acid, m. p. 171—172°, also some dicyclohexyl, but only a small amount of tetracyclohexylethylene glycol, m. p. 151—152°, even when the Grignard reagent is in excess. Similarly, methyl and isopropyl oxalates give methyl, m. p. 48.5°, and isopropyl, m. p. 80°,

hydroxydicyclohexylacetates. Magnesium cyclohexyl bromide does not react further with the ester (I); with methyl benzilate in di-*n*-butyl ether it gives cyclohexoxyldiphenylcarbinol, m. p. 112.5°, which is hydrolysed by alcoholic potassium hydroxide to potassium hexahydrobenzoate and diphenylcarbinol, and with benzil, *s*-diphenyldicyclohexylethylene glycol, m. p. 150—151°. Attempts to reduce dicyclohexyl ketone to tetracyclohexylethylene glycol, using magnesium with iodine or mercury (cf. Gomberg, A., 1927, 245, 1190), were unsuccessful. H. E. F. NOTTON.

Tetraphenylethylene oxide (α -benzpinacol). (MLLE.) J. LÉVY and R. LAGRAVE (Bull. Soc. chim., 1928, [iv], 43, 437—441).—The reactivity of arylated ethylenic hydrocarbons towards perbenzoic acid depends partly on the mol. wt. and partly on the symmetrical or unsymmetrical nature of the molecule. Hydrocarbons such as stilbene, which possess a symmetrical molecule, are less easily oxidised than unsymmetrical triaryl-hydrocarbons (cf. A., 1926, 818; 1927, 872; Böcseken, A., 1927, 39; Lagrave, *ibid.*, 872). Tetraphenylethylene oxide, m. p. 193—194° in mercury, 198—199° in acid bath, prepared by oxidation of tetraphenylethylene with perbenzoic acid in chloroform solution, is identical with α -benzpinacolin. Tetraphenylethylene is best prepared from β -benzpinacolin, obtained by reduction of benzophenone with zinc and excess of acetyl chloride (cf. Paal, A., 1884, 1167), which with 2½ mols. of magnesium ethyl bromide affords a theoretical yield of $\alpha\alpha\beta$ -tetraphenylethan- β -ol, converted by acetyl chloride into $\alpha\alpha\beta\beta$ -tetraphenylethylene. Yields of oxide up to 43% can be obtained by Thörner and Zincke's process (A., 1878, 425, 874), but replacement of the hydrochloric acid by dilute sulphuric acid leads to benzpinacol. No benzhydrol is isolated in these reactions, but 1—2% of tetraphenylethylene is formed.

R. BRIGHTMAN.

Ether corresponding with isosafrole bromohydrin. C. MANNICH and F. SCHMITT (Arch. Pharm., 1928, 266, 84—86).—In preparing isosafrole bromohydrin from isosafrole dibromide by the action of aqueous acetone (cf. Mannich, A., 1910, i, 411) there is formed as a by-product β -bromo- α -3:4-methylenedioxyphenyl *n*-propyl ether, m. p. 134°, evidently produced by interaction of unchanged dibromide with the bromohydrin, since it can be produced in quantity by allowing these compounds to remain in contact for 10 weeks. The bromine atoms are not readily replaced (cf. the methyl ether of the bromohydrin, *loc. cit.*): thus, palladium and hydrogen, and organic bases, have no action on the compound. Hot alcoholic potassium hydroxide removes the bromine, giving what is apparently a diethylenic ether, a viscous oil, which is converted by hot 20% hydrochloric acid into 3:4-methylenedioxyphenyl ethyl ketone. The ether is also debrominated by the action of silver acetate in glacial acetic acid. The product here appears to be the diacetate of the corresponding dihydroxy-compound; when distilled it decomposes into acetic acid and isosafrole oxide. A cold 15% solution of hydrogen bromide in glacial acetic acid converts the ether into isosafrole bromohydrin.

W. A. SILVESTER.

Synthesis of amino-alcohols from isosafrole, isoeugenol, and anethole. C. MANNICH and F. SCHMITT (Arch. Pharm., 1928, 266, 73—84).—The benzoate of γ -dimethylamino- γ -3:4-methylenedioxyphenylpropan- β -ol (Mannich, A., 1910, i, 411) is a powerful but only weakly toxic anaesthetic. The following compounds were prepared in fruitless efforts to obtain a pharmacologically superior product. Dimethylaminomethylenedioxyphenylpropan- β -ol is now obtained in better yield (70%) and has m. p. 66—68°, b. p. 178—182°/16 mm. When the *methiodide*, m. p. 176°, is heated with potassium hydroxide it breaks up into trimethylamine and isosafrole oxide. This formation of isosafrole oxide is an instance of a readiness to decompose which is exhibited also in other reactions, e.g., acylation. Thus, the *benzoate* (m. p. 80—83°; *hydrochloride*, m. p. 202—208°), obtained by heating the hydrochloride of the base with benzoyl chloride at 115—125°, is accompanied by about 10% of a *by-product*, m. p. 164—165°, apparently the benzoate of γ -chloro- γ -3:4-methylenedioxyphenylpropan- β -ol, as it is decomposed by the action of alcoholic potassium hydroxide into isosafrole oxide and benzoic acid. Similarly, when the hydrochloride of the base is heated with *o*-carbomethoxybenzoyl chloride, the *o*-carbomethoxybenzoate (*hydrochloride*, m. p. 125—126°, anaesthetic) is obtained, but when the base is similarly treated, part is simply converted into its hydrochloride, part is converted into 3:4-dimethoxybenzyl methyl ketone apparently by way of isosafrole oxide, and the third product is *o*-carbomethoxybenzidimethylamide. The *p*-nitrobenzoate of the dimethylaminomethylenedioxyphenylpropanol has m. p. 223° and is reduced in dilute hydrochloric acid solution by the action of metallic copper and hydrogen sulphide to the corresponding *aminobenzoate*, m. p. 120°, which also is an anaesthetic. γ -Diethylamino- γ -3:4-methylenedioxyphenylpropan- β -ol, b. p. 175°/14 mm. (*hydrochloride*, m. p. 196°), is obtained when a cold solution of isosafrole bromohydrin and diethylamine in alcohol is kept for a month. The *benzoate*, m. p. 185°, is a potent anaesthetic. The *p*-nitrobenzoate, m. p. 220°, is also described. When the amino-alcohol is oxidised in warm glacial acetic acid solution by chromic acid, 3:4-methylenedioxybenzyl methyl ketone is obtained. γ -Piperidino- γ -3:4-methylenedioxyphenylpropan- β -ol, m. p. 77°, b. p. 235—240°/15 mm., yields a *hydrochloride*, m. p. 204°, and a *benzoate* [*hydrochloride*, m. p. 204°, (decomp.)] which is a powerful anaesthetic. γ -Dimethylamino- γ -3:4-dimethoxyphenylpropan- β -ol (Mannich, *loc. cit.*) is now found to have m. p. 51°. Its *p*-nitrobenzoate (*hydrochloride*, m. p. 198°) is obtained in mediocre yield. γ -Diethylamino- γ -3:4-dimethoxyphenylpropan- β -ol, b. p. 197—199°/14 mm., is obtained by the usual procedure in 70% yield. γ -Piperidino- γ -3:4-dimethoxyphenylpropan- β -ol cannot satisfactorily be isolated: when the syrupy crude base is distilled (b. p. 212—220°/14 mm.) it breaks up into piperidine and 3:4-dimethoxybenzyl methyl ketone. γ -Dimethylamino- γ -*p*-anisylpropan- β -ol, obtained from anethole by way of the bromohydrin in the usual way, has m. p. 39°, b. p. 162°/17 mm. The *hydrochloride*, m. p. 195°, and *p*-nitro-

benzoate [*hydrochloride*, m. p. 205° (decomp.)] are described. The latter is reduced by tin and hydrochloric acid to the *p*-aminobenzoate, m. p. 159°, which is an anaesthetic. γ -Diethylamino- γ -*p*-anisylpropan- β -ol, b. p. 210°/30 mm., yields a very hygroscopic *hydrochloride*. γ -Piperidino- γ -*p*-anisylpropan- β -ol, b. p. 203—205°/14 mm. (*hydrochloride*, m. p. 180°), yields a *p*-nitrobenzoate, m. p. 213°, (decomp.). Although the bases described above should consist of a mixture of stereoisomerides, it appears doubtful whether they really do so, those that are obtained in a crystalline form being evidently not mixtures.

W. A. SILVESTER.

Benzoic esters and electronic affinities of radicals. I. A. ZAKI (J.C.S., 1928, 983—989).—The nitration at 0° and 25° of a series of alkyl benzoates has been studied. The percentage of the *meta*-isomeride produced in the various cases is as follows: methyl, 72.6; ethyl, 69.9; *n*-propyl, 71.8; *n*-butyl, 67.9; *n*-amyl, 68.3; *n*-hexyl, 63.7; *n*-heptyl, 62.8; *n*-octyl, 60.2; *n*-cetyl, 52 (ca.); isopropyl, 64.1; isobutyl, 69.4; *sec*-butyl, 65.2; *tert*-butyl, 59.4; *sec*-octyl, 59.4% at 0°, the values for the first four of the series at 25° being, 69.7, 66.3, 68.6, and 65.1%, respectively. Branching of the carbon chains decreases the proportion of the *meta*-isomeride produced, but with the normal alkyl benzoates, alternation between the odd and even series is found. This alternation decreases as the length of the chain is increased, and it is suggested that a direct effect through space of the carbonyl oxygen atom on the more proximate odd carbon atoms of the zigzag alkyl chain is superimposed on the general inductive effect (Allan and others, A., 1926, 397) transmitted through the chain. A modification of Holleman's titration method for the determination of the percentage of *meta*-isomeride (A., 1899, i, 757; cf. Baker, A., 1927, 454) is described, an accuracy of 0.3% being claimed.

J. W. BAKER.

Carboxyphenylcarbamide derivatives. S. WEIL and (MLLE.) J. ROZENTAL (Rocz. Chem., 1928, 8, 44—49).—The following compounds of the "anaesthesine" group have been prepared: *p*-carboethoxyphenylcarbamide, m. p. 95°; *N*-acetyl-*N'*-*p*-carboethoxyphenylcarbamide, m. p. 139—140°; *N*-isovaleryl-*N'*-*p*-carboethoxyphenylcarbamide, m. p. 237°, and *N*- α -bromoisovaleryl-*N'*-*p*-carboethoxyphenylcarbamide, m. p. 134—135°. The last substance is a more powerful anaesthetic agent than "bromural."

R. TRUSZKOWSKI.

[Preparation of] perbenzoic acid. M. TIFFENEAU (Org. Syntheses, 1928, 8, 30—34).

[Preparation of] ethyl *p*-aminobenzoate. R. ADAMS and F. L. COHEN (Org. Syntheses, 1928, 8, 66).—Ethyl *p*-nitrobenzoate is catalytically reduced by hydrogen in presence of platinum oxide.

A. A. ELDRIDGE.

State of aggregation of phenylbromoacetone nitrile. A. NEKRASSOV (J. pr. Chem., 1928, [ii], 119, 108).—Phenylbromoacetone nitrile has b. p. 137—139°/15 mm., m. p. 25.4° (cf. Steinkopf, A., 1920, i, 590; Schotz, "Synthetic Organic Compounds," 310).

H. BURTON.

Dioximes. XLVII. L. AVOGADRO (Gazzetta, 1928, 58, 191—196; cf. A., 1927, 470).—Oximino-*p*-tolylacetonitrile oxide (cf. A., 1924, i, 294) is converted by benzoyl chloride or bromide into 3-*chloro*- or 3-*bromo*-5-*p*-tolyl-1:2:4-oxadiazole, m. p. 42—43° and 27—28°, respectively. It is suggested that the structures $C_6H_4Me \cdot C(OH) \cdot N \cdot C \equiv N \cdot O$ and $C_6H_4Me \cdot C(OBz) \cdot N \cdot CCl \cdot N \cdot OH$ are intermediately formed. Either halogen compound on prolonged heating with methyl-alcoholic potassium hydroxide yields 3-*hydroxy*-5-*p*-tolyl-1:2:4-oxadiazole, m. p. 199—200° (with partial sublimation), which is decomposed by nitric acid, and with *m*-4-xylidine yields *s*-*dim*-4-*xylidyl*carbamide. The hydroxy-compound yields a *sodium* salt, explodes 204°, a *silver* double salt, $C_{18}H_{15}O_4N_4Ag$, m. p. 258° (exploding), and a *cupric* salt which decomposes to a basic compound; it is alkylated by the appropriate alkyl sulphate to the 3-*methoxy*-, m. p. 47—48°, or 3-*ethoxy*-compound, m. p. 45°, also obtained by the action of an alkali ethoxide on the chloro- or bromo-compound.

The action of an aqueous sodium hydroxide solution on oximino-*p*-tolylacetonitrile oxide, followed by passage of carbon dioxide and acidification, yields 3-*hydroxy*-5-*p*-tolyl- and 5-*hydroxy*-3-*p*-tolyl-1:2:4-oxadiazoles, separated by means of the copper salt of the former (cf. Ponzio and Zanardi-Lamberti, A., 1924, i, 324); by means of its *nickel* salt is also isolated *p*-tolylmetazonic acid, m. p. 176—177°, decomp. to *p*-toluonitrile and 5-*hydroxy*-3-*p*-tolyl-1:2:4-oxadiazole. E. W. WIGNALL.

Racemisation of amino-acid derivatives. P. KARRER and M. DALLA VEDOVA (Helv. Chim. Acta, 1928, 11, 368).—When acylated amino-acids, e.g., *N*-benzoyl-*l*-leucine and *N*-benzoyl-*d*-alanine, are converted into the acid chlorides by treatment with phosphorus pentachloride in acetyl chloride at 0°, complete racemisation occurs. This must be due to the intermediate formation of a compound with a symmetrical structure, such as $NHBz \cdot CR \cdot CCl \cdot OH$.

R. K. CALLOW.

Resin acids of *Conifera*. P. LEVY [with H. BRUNOTTE and H. RAALF] (Ber., 1928, 61, [B], 616—623; cf. Aschan and Levy, A., 1927, 1067).—The acid, $C_{20}H_{32}O_4$, regarded by Levy and Brunotte (*loc. cit.*) as dihydroxyabietic acid, is shown to be identical with the dihydroxydihydro-*d*-pimaric acid of Ruzicka and Balas (this vol., 297); it is also obtained by oxidation of abietic acid prepared according to G.P. 221,889 and of crude American colophony. Abietic acid, previously regarded as homogeneous, must therefore contain isomeric resin acids (cf. Dupont, A., 1924, i, 640). This conception is confirmed by the isolation of dihydro-*d*-pimaric acid, $C_{20}H_{32}O_2$ (cf. Tschugaev and Tearu, A., 1913, i, 726), from the products of the catalytic hydrogenation of abietic acid derived from American turpentine. The production of the dihydroxy-acid and the tetrahydroxy-acid of higher m. p. or of the two tetrahydroxy-acids during the oxidation of abietic acid is closely connected with the amount of permanganate used. All three acids are shown to be homogeneous. The preparation of uniform hydroxylated acids thus

affords a certain method of establishing the number of double linkings in resin acids (contrast Jonas, A., 1922, i, 326), whereas this cannot safely be determined by catalytic hydrogenation, since the volume of hydrogen absorbed is dependent on solvent, catalyst, and temperature. H. WREN.

Derivatives of acenaphthene[5-carboxylic acid]. I. G. FARBENIND. A.-G.—See B., 1928, 293.

Esterification in presence of silica gel. A. KOROLEV (J. Chem. Ind. [Moscow], 1927, 4, 547).—Silica gel is an efficient catalyst for the esterification of salicylic acid. Salicylic acid (50 g.), methyl alcohol (120 g.), and silica gel (4 g.) are heated on a water-bath for 6—8 hrs.; the yield is 75—80% of the theoretical. CHEMICAL ABSTRACTS.

Preparation of phenyl salicylate. O. MAGIDSON and W. KROL (Trans. sci. chem.-pharm. Inst., 1926, 16, 54—63; Chem. Zentr., 1928, i, 40).—Optimally, phosphorus oxychloride (56 g.) is gradually added to a mixture of salicylic acid (138 g.) and phenol (94 g.) which is heated for 2.5 hrs., first at 60—65°, and then at 120°; the yield is 90% of the salicylic acid consumed. There is also formed an oil which on distillation in a vacuum yields 57% of phenyl salicylate.

A. A. ELDRIDGE.

Derivatives of salicylic acid. I. 3-Nitro- and 5-nitro-salicylic acids. A. N. MELDRUM and N. W. HIRVE (J. Indian Chem. Soc., 1928, 5, 95—101).—Nitration of salicylic acid by the method of Meldola, Foster, and Brightman (A., 1917, i, 453) yields a mixture of 3-nitrosalicylic acid, m. p. 148—149° (+H₂O, m. p. 128—129°), and 5-nitrosalicylic acid, m. p. 228° (22.5 g. and 50 g., respectively, from 100 g. of salicylic acid), which is best separated by crystallisation of the potassium salts. A neutral solution of the mixture in potassium hydroxide deposits the *monopotassium* salt of the 3-nitro-acid (yellow; corresponding *sodium* salt, crimson), whilst treatment of the mother-liquors with excess of potassium hydroxide yields the *dipotassium* salt of the 5-nitro-acid (yellow; corresponding sodium salt, yellow). Methyl 3-nitrosalicylate, m. p. 132° [the ester, described by Keller (A., 1908, i, 285) is probably a mixture of the isomeric esters; corresponding ethyl ester, m. p. 48.5°; corresponding amide, m. p. 155° (potassium salt, +H₂O, described)], and methyl 5-nitrosalicylate, m. p. 119° [corresponding ethyl ester, m. p. 102°; corresponding amide, m. p. 225° (potassium salt, +H₂O, described)], are prepared in the usual ways.

G. A. C. GOUGH.

Derivatives of salicylsalicylic acid. E. LEWICKA (Bull. Acad. Sci. Cracovie, 1927, A, 4 pp.; Chem. Zentr., 1928, i, 190).—The following compounds are described: acetylsalicyl chloride; *methyl* (m. p. 82—84°) and *ethyl* (m. p. 72—73°) *acetylsalicylsalicylates*; *methyl methylsalicylsalicylate*, m. p. 102—104°. A. A. ELDRIDGE.

Fission of the dioxymethylene ring. F. MAUTHNER (J. pr. Chem., 1928, [ii], 119, 74—76).—When acetopiperone is treated with aluminium chloride in boiling chlorobenzene there is formed acetopyrocatechol. Similarly, piperonylic and

guaiacol-*o*-carboxylic acids afford protocatechuic and *o*-catechuic acids.

H. BURTON.

Stereochemistry of tervalent nitrogen. J. G. JACKSON and J. KENNER (J.C.S., 1928, 573—581).—The possibility that the configuration of compounds of tervalent nitrogen is plane had been inferred from the general failure to detect the isomerism demanded by a non-planar configuration. A method of obtaining positive evidence on this point is suggested, and in this connexion experiments have been carried out on the internal condensation of β -phenylglutaric and anthranilodiacetic acids. The results in the former case directly refute Sachse's benzene formula and accord with the conception of a plane formula such as Kekulé's. If this be accepted, it is pointed out that compounds of tervalent nitrogen are described in the literature for which a plane configuration seems very probable. β -Phenylglutaric acid is readily converted, under the influence of sulphuric acid, into 1-ketohydrindene-3-acetic acid (I), m. p. 151° [semicarbazone, m. p. 268° (decomp.); methyl ester, m. p. 65° [semicarbazone, m. p. 152; 2-oximino-derivative, m. p. 167° (decomp.)]; ethyl ester, b. p. 194—200°/13 mm. [semicarbazone, m. p. 131—132°; 2-oximino-derivative, m. p. 193° (decomp.)], but no tricyclic, non-acidic, ketonic product could be isolated. Similarly, β -phenylglutaryl chloride, m. p. 46°, undergoes only partial internal condensation under the influence of aluminium chloride, yielding the compound (I). When condensation takes place in light petroleum containing aromatic components, ω -3-hydrindonylaceto-phenone, m. p. 78° [disemicarbazone, m. p. 233° (decomp.); dioxime, m. p. 179°], is also obtained. Anthranilodiacetic acid, m. p. 216° (decomp.) (lit. 212°), condenses under the influence of sodium hydroxide, giving indoxylic acid, m. p. 165° (decomp.) [*o*-methoxy-derivative, m. p. 141—142° (monohydrate)]. When sodamide is used as condensing agent, and the crude product is treated with methyl sulphate, a small yield of a compound, $C_{10}H_{10}O_2N_2$, m. p. 163°, results.

M. CLARK.

[Preparation of] ethyl benzoylformate. B. B. CORSON, R. A. DODGE, S. A. HARRIS, and K. K. HAZEN (Org. Syntheses, 1928, 8, 68—72).

Condensation products of diethyl succinylsuccinate with primary arylamines. D. MIGLIACCI and R. GARGIULO (Gazzetta, 1928, 58, 110—121; cf. Liebermann, A., 1914, i, 658; Migliacci, this vol., 289).—The interaction of diethyl succinylsuccinate with excess of primary arylamines at 125—130° yields a diethyl 2:5-diarylamino-terephthalate; at 180—200° the main product is a *NN'*-diarylcarbamide; as the proportion of ester is increased, these products are mixed with increasing amounts of a yellow substance of unknown composition. The following are described: ethyl 2:5-di-*o*-phenetidinterephthalate, m. p. 152° (dibenzoyl derivative, m. p. 249—251°); 2:5-di-*o*-phenetidinterephthalic acid, m. p. 273° (decomp.); *NN'*-di-*o*-phenetylcarbamide, m. p. 222°, and *p*-phenetyl- and *p*-anisylcarbamides; yellow substances from *o*- and *p*-phenetidine and from *p*-anisidine, m. p. 180—181°, 163—

168°, and 182—187°, respectively; ethyl 2:5-di-*o*-phenetidino- $\Delta^{1:4}$ -dihydroterephthalate, m. p. 201°, prepared at low temperature in the absence of air.

E. W. WIGNALL.

β -Phenylalanine derivatives. W. M. RODIONOV and A. M. FEDOROVA (Arch. Pharm., 1928, 266, 116—121; cf. A., 1927, 137, 451).—Continuing the investigation of pharmacologically interesting β -phenylalanine derivatives the following methoxy-compounds have been prepared. Both vanillin and protocatechualdehyde are smoothly converted into veratraldehyde by treatment with phenyltrimethylammonium hydroxide (Rodionov, A., 1926, 532), the yields being 86% and 58.3%, respectively. 2:4-Dimethoxybenzaldehyde is similarly obtained from resorcaldehyde (yield, 41.7%) and *o*-, *m*-, and *p*-methoxybenzaldehydes from salicylaldehyde, *m*-hydroxy- and *p*-hydroxy-benzaldehydes, respectively (yield, 72.8%, 88%, and 66.6%). By interaction of veratraldehyde, malonic acid, and ammonia in alcoholic solution β -amino- β :3:4-dimethoxyphenylpropionic acid (hydrochloride, m. p. 207—208°) is obtained (yield, 59%). The 2:4-dimethoxy-isomeride was also prepared in poor yield from 2:4-dimethoxybenzaldehyde. The three monomethoxy-analogues were similarly obtained, being accompanied in each case by the corresponding methoxycinnamic acid. β -Amino- β -*o*-anisylpropionic acid (yield, 33%) (hydrochloride, m. p. 208—210°), β -amino- β -*m*-anisylpropionic acid (yield, 39%) (hydrochloride, m. p. 190°), and β -amino- β -*p*-anisylpropionic acid (yield, 59%) [hydrochloride, m. p. 205° (decomp.)], are described. W. A. SILVESTER.

Synthesis of 3:4-dihydroxyphenylalanine. C. R. HARRINGTON (Biochem. J., 1928, 22, 407).—A simplified method of preparation of ethyl benzamido-3-methoxy-4-hydroxycinnamate which is employed in the synthesis of the above compound (Harrington and McCartney, A., 1927, 961) is described. The azlactone obtained by the condensation of vanillin with hippuric acid is dissolved in alcohol and boiled with sulphuric acid under a reflux condenser. After distilling off the greater part of the alcohol, the reaction mixture is treated with sodium hydrogen carbonate until slightly alkaline. The ester is then extracted with ethyl acetate and the solvent removed. The ester which crystallises from the residue is recrystallised from dilute alcohol.

S. S. ZILVA.

[Preparation of] phenylsuccinic acid. A. LAPPWORTH and W. BAKER (Org. Syntheses, 1928, 8, 88—90).

Synthesis of methyl phenylethylmalonate. M. M. RISING and T.-W. ZEE (J. Amer. Chem. Soc., 1928, 50, 1208—1213).—The overall yield of ester (43.1% of the theoretical, from phenylacetonitrile) is the highest yet attained. α -Phenylbutyronitrile is converted by absolute methyl alcohol and hydrogen chloride at -5° to -10° into the imide hydrochloride, m. p. 92°, of methyl α -phenylbutyrate. The free ester, m. p. 77—78° (cf. Neure, A., 1889, 597), yields a tautomeric sodio-derivative (cf. A., 1927, 359) which condenses with ethyl chloroformate in ether, giving methyl phenylethylmalonate. H. E. F. NOTTON.

Indicators. XI. Phenolphthalein and derivatives. A. THIEL and R. DIEHL (Sitzungsber. Ges. Naturwiss. Marburg, 1927, 62, No. 15, 472—546; Chem. Zentr., 1927, ii, 2669—2672).—Acree's view of the mechanism of the colour change of phenolphthalein (A., 1908, i, 423) is preferred, together with Pfeiffer's theory (1922) of halochromic compounds. In the chloro- and amino-phenolphthalein series the influence of the substituents on the position of the absorption maximum is additive. Phthaleins in which the hydrogen atom *ortho* to the phenolic hydroxyl group is replaced by chlorine, bromine, or an amino-group readily form oximes; 3-nitro- and 3:5-dinitro-phenolphthalein yield oximes, but not 3:3-dinitro-, 3:5:3'-trinitro-, or 3:5:3':5'-tetranitro-phenolphthalein; hence hydroxylamine does not attack the lactone ring, or act on the carbinol-carboxylic acid form. The oxime must thus be derived from the *p*-quinonoid form, it being supposed that one phenolic residue is free from, but that the two others contain, nitro-groups. The view is supported by the fact that the quinonoid ester of 3:5:3':5'-tetrabromophenolphthalein forms an oxime, as is shown by measurements of the extinction coefficient in admixture with hydroxylamine. Further, etherification of the second hydroxyl group of 3-nitrophenolphthalein prevents oxime formation, but the reduction product of the ether gives an oxime. Apparently the formation of a *p*-quinone produces a yellow colour (*e.g.*, pure phenolphthalein monomethyl ether is yellow in slightly alkaline solution), the deep colours of the phthaleins being due to the joint effect of both phenolic residues. Substitution in the phthalic acid nucleus of phthaleins also influences the absorption curves; hence the whole complex is to be regarded as a chromophore. The effect of the substitution of chlorine in the phenolic and phthalic acid portions of the molecule is discussed in terms of the tautomeric equilibrium of the indicator system. Isochromatism, optical analogy, and optical similarity of dyes are considered.

The following substances were prepared (all m. p. are corr.): 3-chlorophenolphthalein, m. p. 228—230°; 3:3'-dichlorophenolphthalein, m. p. 181°; 2-chloro-4-aminophenyl dibenzoate, m. p. 204.5—205°; 3:5-dichlorophenolphthalein, m. p. 227—229°; 3:5:3':5'-tetrabromophenolphthaleinoxime, m. p. 120°; 3-nitrophenolphthalein, m. p. 178—179°; *o*-(3-nitro-4-hydroxybenzoyl)benzoic acid, m. p. 180—181°; 3:5-dinitrophenolphthalein, m. p. 186—187°; *o*-(3:5-dinitro-4-hydroxybenzoyl)benzoic acid, m. p. 200°; 3:5:3'-trinitrophenolphthalein, m. p. 133°; 3'-amino-phenolphthalein; 3:3'-diaminophenolphthalein, m. p. 262—263°; 3:5-diamino-, 3:5:3'-triamino-, and 3:5:3':5'-tetra-amino-phenolphthalein; 3-nitro-phenolphthalein 4'-methyl ether, m. p. 140.5—141°; 3-aminophenolphthalein 4'-methyl ether, m. p. 125° (oxime, m. p. 228°); 3-nitro- and 3:5-dinitro-phenolphthaleinoxime; 3:5:3':5'-tetrabromophenolphthalein ethyl ester oxime. A. A. ELDRIDGE.

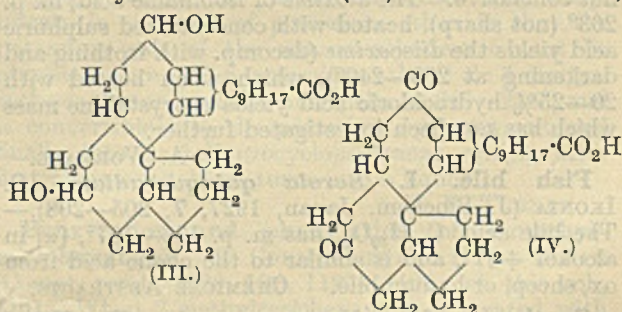
β -Phocæcholic acid. A. WINDAUS and A. VAN SCHOOR (Z. physiol. Chem., 1928, 173, 312—320).— β -Phocæcholic acid (*isocholic acid*), present in the bile

of seals and the walrus (cf. Hammarsten, A., 1909, ii, 819; 1910, ii, 879), has the same skeleton structure as cholic acid, but differs from the other bile acids in having a hydroxyl group in the side-chain (I). It is suggested that the other two hydroxyl

groups are attached to carbon atoms 3 and 12, since β -phocæcholic acid on oxidation with sodium hypobromite behaves exactly like chenodeoxycholic acid (cf. A., 1927, 56), which is 3:12-dihydroxycholic acid. In this oxidation, β -phocæcholic acid yields a hydroxy-lactonedicarboxylic acid, which on further oxidation

yields nordeoxybiliobanic acid (II). Hare and antelope bile have also been examined, and in the former, *acids* having m. p. 125°, 151°, 185°, and 222° have been found; the analytical figures for the acid having m. p.

185° suggest a tetrahydroxycholic acid. The preparation of β -phocæcholic acid from seal bile is described and the preparation and properties of the following compounds are given: an *acid*, $C_{23}H_{38}O_4$ (III), m. p. 197°, formed by oxidation of β -phocæcholic acid with potassium permanganate (*methyl ester*, m. p. 78°); an *acid*, $C_{23}H_{34}O_4$ (IV), m. p. 200°, formed by the oxidation of (III) with chromic acid,

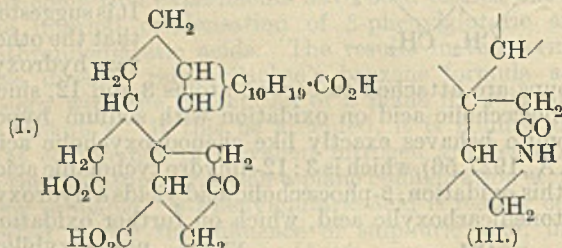


yielding on reduction with zinc amalgam and hydrochloric acid an acid identical with Wieland's norcholic acid (A., 1927, 247); a *hydroxylactonedicarboxylic acid*, $C_{21}H_{36}O_7$, m. p. 170°; *nordeoxybiliobanic acid*, m. p. 256° (*dimethyl ester*, m. p. 125°); a *hexacarboxylic acid*, $C_{22}H_{32}O_{12}$ (decomp. 225—233° with charring), formed by the action of fuming nitric acid on β -phocæcholic acid; a nitrogenous *acid*, m. p. 205°, is formed when this oxidation with fuming nitric acid is carried out at -10° . A. WORMALL.

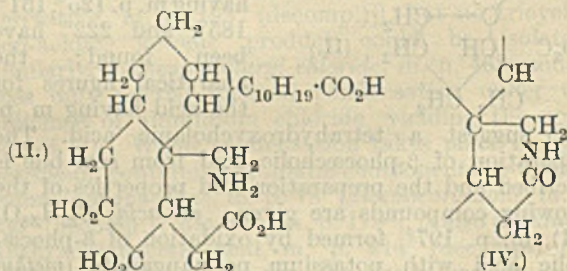
Bile acids. XVIII. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1928, 172, 159—168).—Experiments similar to those with the oxime of deoxybilianic acid (cf. A., 1927, 665) have been carried

out with nitrogenous derivatives of isodeoxybilianic acid (I).

The *oxime* of isodeoxybilianic acid is converted by heating with sulphuric acid into the *isooxime*, m. p. (after sintering) 262—264°, which is hydrolysed by heating with 20% hydrochloric acid to the corresponding *amino-acid*, $C_{24}H_{39}O_5N$ (II); the last named is reconverted, when heated at 210° for 15 min. or if warmed in acetic acid solution, into the *isooxime* or lactam [(III) or (IV), or possibly a mixture of the two].



Only one *isooxime* has so far been isolated and this is believed to have the structure (IV), a supposition supported by the fact that the amino-acid (II) on heating loses no ammonia, as would be expected from



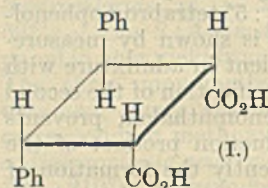
a β -amino-acid derived from (III), but this evidence is not conclusive. The *dioxime* of isobilianic acid, m. p. 263° (not sharp), heated with concentrated sulphuric acid yields the *diisooxime* (decomp. with frothing and darkening at 239—240°), which when heated with 20—25% hydrochloric acid yields a crystalline mass which has not been investigated further.

A. WORMALL.

Fish bile. I. *Serola quinqueradiata*. S. IKONIA (J. Biochem. Japan, 1927, 7, 205—208).—The bile acid, $C_{24}H_{39}O_5$, has m. p. 196—197°, $[\alpha]$ in alcohol +37°, and is similar to the cholic acid from ox, sheep, or human bile. CHEMICAL ABSTRACTS.

Synthesis of cyclic compounds. II. Ethyl *r*- and *meso*- $\beta\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylates. Synthesis of a truxinic acid. I. VOGEL (J.C.S., 1928, 1013—1022; cf. A., 1927, 959).—Reduction of ethyl benzylidenemalonate, b. p. 180°/14 mm., d_4^{25} 1.1048, n_D^{25} 1.53795, with moist aluminium amalgam (cf. A., 1927, 449) yielded 50—55% of ethyl benzylmalonate, b. p. 163°/14 mm., d_4^{20} 1.0750, n_D^{20} 1.4872, and 35—40% of a mixture, b. p. 255—270°/3 mm., which was separated completely by fractional crystallisation from alcohol into 40% of solid ethyl *r*- $\beta\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylate, m. p. 88°, and 60% of the liquid *meso*-ester. Hydrolysis by alcoholic potassium hydroxide gave the corresponding *r*- and *meso*-acids, m. p. 219—220° and 182—183° (softening at 172°), respectively. The *disodio*-deriv-

ative of the *r*-ester, obtained by treatment with sodium methoxide, reacted with 2 mols. bromine to give only ethyl *r*- $\alpha\delta$ -dibromo- $\beta\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylate, m. p. 180°, whereas the *disodio*-derivative of the *meso*-ester reacted with only 1 mol. of bromine to give an oil, presumably ethyl 2:3-diphenyl-1:1:4:4-cyclobutanetetracarboxylate, which was not purified. On hydrolysis with alcoholic potassium hydroxide this product gave a solid which, on heating at 280° until effervescence ceased, gave less than 1% yield of an acid, m. p. 239°, which could also be separated in the form of its dimethyl ester, m. p. 117°. The properties of these substances agree with those of ζ -truxinic acid (2:3-diphenylcyclobutane-1:4-dicarboxylic acid), m. p. 239° (I), and its dimethyl ester, m. p. 116° (Stoermer and Bachér, A., 1922, i, 830). The mixed *disodio*-derivatives of the mixture of ethyl $\beta\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylates reacted with the amount of bromine required by a mixture of 45% of the solid form with 55% of the liquid form, and the dibromo-compound and the dimethyl ester



could be isolated by suitable treatment. There is thus no inversion during ring formation such as occurs with ethyl *r*- and *meso*-dimethylbutanetetracarboxylates (Part I, *loc. cit.*). As the acid now synthesised has the configuration (I), it is considered probable that the *cis*-2:3-dimethyl acid described previously (*loc. cit.*) has an analogous structure, and not that then assigned to it.

R. K. CALLOW.

Aldehydes from acetylenic carbinols. I. cyclohexylideneacetaldehyde. H. RUPE, W. MESSNER, and E. KAMBLI (Helv. Chim. Acta, 1928, 11, 449—462).—The action of acetylene on sodium cyclohexanone is to furnish 1-ethynylcyclohexan-1-ol (I), b. p. 74—76°/12 mm. (*acetate*, b. p. 87°/10 mm.), together with the *glycol*, $[C_5H_{10}>C(OH)·C]_2$, m. p. 109—110° (*diacetate*, m. p. 46—47°). When (I) is heated with 86% formic acid (9 parts) for 2.5 hrs., it is converted into cyclohexylideneacetaldehyde (92.3%), b. p. 84—85°/12 mm., d_4^{20} 0.9694, n_D 1.49081 (*semicarbazone*, m. p. 214—215°; *oxime*, m. p. 61—62°; *phenylhydrazone*). Reduction of this aldehyde with hydrogen and a nickel catalyst or zinc dust and acetic acid gives cyclohexylacetaldehyde, b. p. 69°/12 mm., d_4^{20} 0.9187, n_D 1.45273 (*semicarbazone*, m. p. 171—172°). Oxidation experiments with the aldehyde and ozone, potassium permanganate, chromic acid, and hydrogen peroxide yield adipic acid, formed through the intermediate cyclohexanone. Treatment of the above *oxime* with excess of acetic anhydride gives cyclohexylideneacetaldoxime acetate, b. p. 145—147°/12 mm.

Magnesium ethyl bromide and cyclohexylideneacetaldehyde react yielding 1-ethylcyclohexyl-1-acetaldehyde, b. p. 84—85°/10—11 mm., when regenerated from the *semicarbazone*, m. p. 171—172°, together with cyclohexylidenemethylethylcarbinol (II), $C_5H_{10}>C:CH·CH_2·OH$, b. p. 96—97°/12 mm. (*benzoate*). The saturated aldehyde is formed by a 1:4-addition of the Grignard reagent with subsequent rearrangement of the substituted vinyl alcoholic grouping. When (II) is heated with acetic anhydride

and sodium acetate, elimination of water takes place, yielding α -cyclohexylidene- Δ^{β} -butylene.

$C_5H_{10} > C:C:CH_2Et$, b. p. 77—78°/12 mm.

*cyclo*Hexanone and 30% hydrogen peroxide solution yield a crystalline additive compound, $C_6H_{10}O, H_2O_2$.

H. BURTON.

Stability of benzaldehydecyanohydrin. G. BÜMMING (Arch Pharm., 1928, 266, 231—232).—Benzaldehydecyanohydrin undergoes changes on keeping, the hydrocyanic acid content decreasing, whilst resinous and insoluble oily matters make their appearance. The aqueous solution may be clarified by shaking with talc and filtering, a satisfactory pharmaceutical product being thereby obtained.

S. COFFEY.

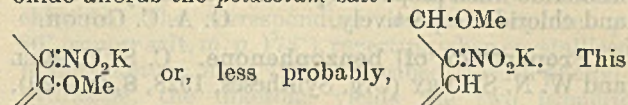
Isomerisation of hydroxyaldehydes. S. DANILOV (J. Russ. Phys. Chem. Soc., 1927, 59, 1105—1124).—See this vol., 64.

Behaviour of cyclic ketones when heated. W. TREIBS (Ber., 1928, 61, [B], 683—687).—*cyclo*-Hexanone is only slowly affected at 250°; at 300°, polymerised products, chiefly *cyclo*hexylidene*cyclo*-hexanone, result together with dodecahydrotriphenylene. Hydrocarbons of low b. p., from which *cyclo*-hexene is isolated, are formed in small amount. Carbon monoxide is formed in considerable quantity at 350°; if the action is prolonged at this temperature, the production of carbon monoxide diminishes, and mainly saturated hydrocarbons (presumably *cyclo*-hexane) result. Methyl*cyclo*hexanone (mixture of the three isomerides) is more resistant to heat than *cyclo*-hexanone. Carbon monoxide is not eliminated at 300—350°, at which temperature a bimolecular, unsaturated ketone, $C_{14}H_{22}O$, b. p. 160—164°/20 mm., $d^{20} 0.9771$, and methyl*cyclo*hexane are produced. At 375—400°, carbon monoxide is lost and (mainly) saturated hydrocarbons of low b. p. are produced. Piperitone, b. p. 236°, $d^{20} 0.934$, passed over porous earthenware at 450° gives a blue distillate and loses the *isopropyl* group. At 400° in an autoclave, it loses carbon monoxide and yields phenols among which *m*-cresol and thymol are identified. When passed over porous earthenware at 500°, thymol yields *m*-cresol and propylene; carvacrol decomposes analogously, but with greater difficulty, whilst cymene gives benzene only slowly at 600°. Carvone at 450° yields phenols containing carvacrol. Small amounts of cymene and phenols are derived from citronellal at 420°. Fenchone is much more stable towards heat than is camphor and remains unchanged to a considerable extent after 6 hrs. at 450°; carbon monoxide is lost above 400°, but elimination of water is irregular. Phenols from which carvacrol is isolated are formed in relatively small and varying amounts. From the hydrocarbon mixture, *m*-cymene and an unsaturated hydrocarbon, C_9H_{14} , are isolated. Camphor affords carbon monoxide, phenols (*m*-cresol and carvacrol), *m*- and *p*-cymene, and fenchone; the polymerised, unsaturated products from camphor and fenchone are ill-defined.

H. WREN.

Cyclic α -nitroketones. H. WIELAND, P. GARBSCH, and J. J. CHAVAN [with A. SCHÄFER] (Annalen, 1928, 461, 295—308).—1-Nitro- Δ^1 -*cyclo*-hexene forms a *dibromide*, m. p. 100—101°, which when

treated with cold methyl-alcoholic potassium hydroxide affords the *potassium* salt:



reacts with sodium nitrite to give an oximino-compound, $C_7H_{10}O_4N_2$, decomp. 122—125°, and with hydroxylamine hydrochloride to give a *substance*, m. p. 122°.

*cyclo*Hexene- ψ -nitrosite reacts (1) with alcoholic ammonia to give some 2 : 6-dinitro*cyclo*hexylamine, m. p. 96—97° [*hydrochloride*, m. p. 163°; *nitrosamine*, m. p. 145—150° (decomp.)], and (2) with alcoholic hydrazine hydrate to give a *hydrazo*-compound, $(C_6H_{10}O_2N)_2N_2H_2$, m. p. 138—140°.

Ethyl nitrate reacts with *cyclo*hexanone in presence of potassium ethoxide to give the *potassium* salt of 2-nitro*cyclo*hexanone, acidification of the aqueous solution of which may or may not lead to a crystalline specimen of 2-nitro*cyclo*hexanone, m. p. 37°, a *substance* behaving similarly to *aci*-phenylnitromethane. This *substance* forms a *bromo*-derivative when treated with bromine in methyl alcohol, gives a *semicarbazone*, m. p. 184° (decomp.), and is converted by a benzene-diazonium solution into a *product*, $C_{12}H_{15}O_4N_3$ (?), decomp. 118°. An oxime or a phenylhydrazone could not be obtained from 2-nitro*cyclo*hexanone, but with phenylhydrazine the bisphenylhydrazone of *cyclo*-hexane-1 : 2-dione, m. p. 150°, was obtained.

The above condensation using ethyl nitrate always gives rise to some of the *potassium* salt of 2 : 6-dinitro*cyclo*hexanone, this being obtained best by using twice the proportions of ethyl nitrate and potassium. When it is carefully treated with dilute acid the *potassium hydrogen* salt is obtained, whilst excess of acid affords 2 : 6-dinitro*cyclo*hexanone itself, m. p. 110.5°.

*cyclo*Pentanone so readily condenses with ethyl nitrate in presence of potassium ethoxide that the *potassium* salt of the mononitroketone cannot be obtained pure. The *potassium* salt of 2 : 5-dinitro*cyclopent*anone explodes and melts at 241—245°, and is convertible into the *potassium hydrogen* salt and finally into 2 : 5-dinitro*cyclopent*anone, which, after first being crystalline, turns into a liquid.

E. E. TURNER.

Benzylation and phenylation of 2-methyl-*cyclo*hexanone. R. CORNUBERT and H. LE BIHAN (Compt. rend., 1928, 186, 1126—1128; cf. this vol., 416).—When 2-methyl*cyclo*hexanone is treated with sodamide and benzyl halides under conditions calculated to produce monobenylation, there are produced benzyl-2-methyl*cyclo*hexanone, b. p. 167—169°/17 mm. (chief product), 2 : 6-dibenzyl-2-methyl*cyclo*hexanone, m. p. 105° (also formed by hydrogenation of the benzylidene derivative of 2-benzyl-2-methyl*cyclo*hexanone), and an *isomeride* of the last-named compound, b. p. 230—232°/15 mm. The mixture of benzyl-2-methyl*cyclo*hexanones affords 6-benzylidene-2-benzyl-2-methyl*cyclo*hexanone, m. p. 80—81° (hydrogen chloride additive compound, m. p. 124°), and the pyrone-like compound, m. p. 191°, already prepared from 6-benzyl-2-methyl*cyclo*hexanone (Cornubert and Borrel, A., 1926, 953). From the latter results it is calculated that the benzyl-2-methyl*cyclo*-

hexanones contain 9% and 10—11% of the 2:6-isomeride when prepared by the use of benzyl bromide and chloride respectively. G. A. C. GOUGH.

[Preparation of] **benzophenone**. C. S. MARVEL and W. N. SPERRY (Org. Syntheses, 1928, 8, 26—29).

[Preparation of] **benzylacetophenone** [phenyl β -phenylethyl ketone]. R. ADAMS, J. W. KERN, and R. L. SHRINER (Org. Syntheses, 1928, 8, 36—37).—Phenyl styryl ketone is catalytically reduced with hydrogen in presence of platinum oxide.

A. A. ELDRIDGE.

[Preparation of] **anthrone**. K. H. MEYER (Org. Syntheses, 1928, 8, 8—9).

[Preparation of] **nitroanthrone**. K. H. MEYER (Org. Syntheses, 1928, 8, 78—79).

Carbon rings. X. Monocyclic diketones containing sixteen, eighteen, and thirty carbon atoms in the ring. L. RUZICKA, W. BRUGGER, C. F. SEIDEL, and H. SCHINZ (Helv. Chim. Acta, 1928, 11, 496—512).—The action of heat on thorium azelate gives, in addition to cyclooctanone (A., 1926, 615), about 1% of cyclohexadecane-1:9-dione (I), b. p. 180°/2 mm., m. p. 83—84° (dioxime, m. p. 185—186°), and a very small amount of a diketone, $C_{23}H_{44}O_2$, m. p. 75—76° (semicarbazone, m. p. 128—130°). Reduction of (I) by Clemmensen's method gives a mixture of cyclohexadecane, m. p. 61°, and cyclohexadecanone. When (I) is treated with benzaldehyde in presence of sodium ethoxide, the resulting product heated with potassium hydrogen sulphate at 200—210°, and this product ozonised, there is obtained after esterification with methyl alcohol dimethyl η -ketotetradecane- α -dicarboxylate, m. p. 45° (free acid, m. p. 109—110°; cf. A., 1927, 1189). When ethyl hydrogen azelate is heated with iron powder at 280—290° and the resulting product heated with 20% hydrochloric acid, neutral and acidic substances are formed. Esterification of the acid fraction with methyl alcohol gives dimethyl θ -ketopentadecane- α -dicarboxylate, m. p. 57—59°. When the thorium salt of the acid, m. p. 115—116°, is heated (I) is obtained.

During the preparation of cyclononanone from thorium sebacate a small amount of cyclooctadecane-1:10-dione, m. p. 96—97° (dioxime, m. p. 166—168°; semicarbazone, decomp. above 230°), is obtained, which is reduced by Clemmensen's method to cyclooctadecane, m. p. 72°, and cyclooctadecanone.

As by-products in the preparation of cyclopentadecanone there are formed ditetradecyl ketone, b. p. 225—230°/2 mm., m. p. 65—66°, d_4^{20} 0.8100 (oxime, m. p. 41—42°; isooxime, m. p. 84°), and cyclotriacontane-1:16-dione, m. p. 74—75° (semicarbazone, m. p. 218—219°; dioxime, m. p. 130—131°). Oxidation of benzylidenecyclotriacontane-1:16-dione with ozone gives 14-keto-octacosane-1:28-dicarboxylic acid, m. p. 101—103°, reduced to octacosane-1:28-dicarboxylic acid, m. p. 110° (cf. Fairweather, A., 1926, 668). Reduction of the diketone gives cyclotriacontane, m. p. 53—54°, and cyclotriacontanone (semicarbazone, m. p. 149—150°).

Benzaldehyde and cyclopentadecanone react in presence of sodium methoxide, and elimination of water from the product by heating with potassium

hydrogen sulphate at 200° gives benzylidenecyclopentadecanone, b. p. 190°/1 mm., which when ozonised yields tridecane- α -dicarboxylic acid.

H. BURTON.

Ring strain and radical formation. G. WITTIG and M. LEO (Ber., 1928, 61, [B], 854—862).—The hypothesis is advanced that the strain within a suitable carbon ring assisted by sufficient loading of two carbon atoms must enhance the tendency towards rupture of the ring with resultant production of a "diradical" with two tervalent carbon atoms. Working from the reverse direction, it is shown that ring strain tends to enhance the tendency towards dissociation.

pp'-Dibenzoyldiphenylmethane, m. p. 147.5—148.5°, is prepared from benzoyl chloride, diphenylmethane, and aluminium chloride in the absence of solvent or from *pp'*-diaminodiphenylmethane by conversion by Sandmeyer's method into the corresponding nitrile and treatment of the latter with magnesium phenyl bromide. It is transformed by the Grignard reagent into *pp'*-di(hydroxydiphenylmethyl)diphenylmethane, $CH_2(C_6H_5 \cdot CPh_2 \cdot OH)_2$, which could not be caused to crystallise, but when acted on by hydrogen chloride gives *pp'*-di(chlorodiphenylmethyl)diphenylmethane, m. p. 157—160°. When shaken in benzene or ether solution with copper powder in the absence of light, the dichloro-compound yields intensely coloured solutions, decolorised by air with production of the peroxide, $C_{39}H_{30}O_2$. The free radical, $C_{39}H_{30}$, isolated by addition of light petroleum to its solution in benzene, absorbs oxygen with unusual avidity. In benzene solution it appears mainly unimolecular.

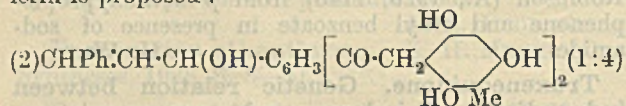
pp'-Dibenzoyl- $\alpha\beta$ -diphenylethane, m. p. 174.5—176°, prepared similarly to the methane derivative, yields *pp'*-di(hydroxydiphenylmethyl)- $\alpha\beta$ -diphenylethane, m. p. 176—178° after softening, and *pp'*-di(chlorodiphenylmethyl)- $\alpha\beta$ -diphenylethane, m. p. 184—186° (decomp.). The latter substance affords the corresponding radical, $C_{40}H_{32}$, which is largely unimolecular when dissolved in benzene; it yields a peroxide, $C_{40}H_{32}O_2$. The diradical is also produced by the action of sodium triphenylmethyl on *pp'*-di(chlorodiphenylmethyl)- $\alpha\beta$ -diphenylethane.

pp'-Dibenzoyldibenzyl is transformed by magnesium methyl iodide into *pp'*-di-(α' -hydroxy- α' -phenyl)- $\alpha\beta$ -diphenylethane, m. p. 113—114.5°, which passes in boiling glacial acetic acid into *pp'*-di-(α' -phenylethenyl)- $\alpha\beta$ -diphenylethane, m. p. 117—119°. The glycol is converted by the protracted action of cold, methyl-alcoholic hydrogen chloride into the corresponding dimethyl ether, m. p. 144—148°, transformed by sodium-potassium alloy in presence of dioxan in an atmosphere of nitrogen into the dipotassium compound. The latter compound is immediately decolorised by tetramethylethylene bromide in dioxan with production of the compound ($C_{30}H_{23}$) $_2$, m. p. (indef.) 110—115°, instead of the desired diradical; it is transformed by alcohol into *pp'*-di-(α' -phenylethyl)- $\alpha\beta$ -diphenylethane, m. p. 97—98°.

H. WREN.

Compounds with tervalent carbon. S. GOLD-SCHMIDT [with A. SADLER, E. GELBER, H. SCHÜSSLER, and A. VOGT] (Ber., 1928, 61, [B], 829—838).—In the hope of preparing $\beta\beta$ -dibenzoyl- $\alpha\alpha\alpha$ -triphenylethane,

terephthalic acids. Nitration of rottlerin hexamethyl ether under similar conditions leads to the formation of hexanitrorottlerin hexamethyl ether, decomp. on heating, which yields the same oxidation products. Hepta-acetylröttlerin, on bromination in acetic acid solution at 170°, affords *hexabromohepta-acetylröttlerin*, decomp. above 300° (*hexabromoröttlerin*, unmelting on heating, described), which may be similarly oxidised to 2:4-dibromobenzoic, phthalic, and terephthalic acids. The following probable constitution of rottlerin is proposed:



The substituting nitro-groups enter the *o*- and *p*-positions in the styryl side-chain, the 3:6-positions in the central nucleus, and the unoccupied positions in the phenolic nuclei. G. A. C. GOUGH.

Salicylic acid primeveroside. M. BRIDEL and P. PICARD (Bull. Soc. Chim. biol., 1928, 10, 381—385).—See this vol., 424.

Condensation of ketocholanic acids. I. Condensation with furfuraldehyde. K. KAZIRO (J. Biochem. Japan, 1927, 7, 283—291).

CHEMICAL ABSTRACTS.

Gossypol. III. Oxidation of gossypol. E. P. CLARK (J. Biol. Chem., 1928, 77, 81—87).—Gossypol, when oxidised with cold alkaline potassium permanganate, yielded formic, acetic, and *isobutyric* acids; the yield of the last-named, approximately one molecular proportion, is taken to indicate the presence of the *isobutyl* group in the side-chain of gossypol. C. R. HARRINGTON.

Conjugated unsaturated compounds. V. Constitution of carotin and bixin. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1928, 11, 427—431).—The resemblance of the colour reactions of carotin to those given by the unsaturated hydrocarbons described by the authors (this vol., 281) is noted. A summary of the facts relative to the structure of bixin is given. H. BURTON.

Plant-colouring matters. IV. Colouring matter from saffron. II. P. KARRER and H. SALOMON (Helv. Chim. Acta, 1928, 11, 513—525).—Details are given for the extraction from saffron of *α-crocin*, $\text{C}_{24}\text{H}_{28}\text{O}_5 \cdot 2\text{C}_{12}\text{H}_{20}\text{O}_{10} \cdot 2\text{H}_2\text{O}$, m. p. 186° (decomp.), which on acid hydrolysis gives dextrose. *α-Crocin* (see A., 1927, 571) is a dibasic acid, $\text{C}_{22}\text{H}_{26}\text{O}(\text{CO}_2\text{H})_2$, whilst *β-crocin* is its monomethyl ester. *γ-Crocin* is the dimethyl ester and is formed from both *α*- and *β*-crocin by methylation with diazomethane. Conversely, the *β*- and *γ*-crocins are converted into *α*-crocin by hydrolysis with alcoholic potassium hydroxide. Catalytic reduction of *γ*-crocin gives a *dimethyl* ester, $\text{C}_{22}\text{H}_{32}\text{O}(\text{CO}_2\text{Me})_2$, b. p. 198—200°/1 mm., whilst oxidation with ozone gives glyoxal as the only recognisable product. It is concluded that *α*-crocin is an aliphatic dicarboxylic acid with eight conjugated double linkings, and not a dihydric phenol (*loc. cit.*). H. BURTON.

Saponins and related substances. XX. Ursolic acid. II. Action of acetic anhydride

on ursolic acid. A. W. VAN DER HAAR (Rec. trav. chim., 1928, 47, 585—590).—When ursolic acid is treated with acetic anhydride there is formed a compound, m. p. 200—201°, $\alpha_D^{25} + 62.5^\circ$ in chloroform (cf. A., 1924, i, 643), consisting of 1 mol. of *diacetylursolic anhydride*, m. p. 320—322°, and 1 mol. of acetic anhydride (cf. this vol. 68). *Monoacetylursolic acid*, m. p. 279—280°, is obtained by the action of alcohol on the above compound. H. BURTON.

Formation of 3-*p*-menthone and 3-*p*-menthol from Δ^3 -*p*-menthene. A. KÖTZ and G. BUSCH (J. pr. Chem., 1928, [ii], 119, 1—42).—Treatment of 8-*p*-menthanol with potassium hydrogen sulphate at 200° gives Δ^3 -*p*-menthene, which when heated with trichloroacetic acid yields 4-*p*-menthanol. Consecutive treatment of Δ^3 -*p*-menthene with perbenzoic acid at -18° , sodium ethoxide at -10° , and sulphuric acid at -7° affords *p-menthene oxide* (91%), b. p. 70—75°/15 mm., d^{20}_4 0.8989, $\alpha_D^{25} + 45^\circ 40'$, n_D^{25} 1.44809, reduced catalytically by Willstätter's method to *p*-menthane. Hot methyl-, propyl-, butyl-, and amylalcoholic hydrochloric acid convert this oxide into 3-*p*-menthone, whilst the action of hypochlorous acid is to form an impure *menthenechlorohydrin* (*chloromenthol*). It was not possible to esterify chloromenthol, and oxidation experiments did not yield a ketone, thus indicating a tertiary hydroxyl group, *i.e.*, one in position 4. Reduction of chloromenthol with hydrogen in presence of palladium-black and dilute alcohol gives some 3-*p*-menthol (*hydrogen phthalate*, m. p. 98—100°). Most of the reduction experiments described give halogen-free products, although, in a medium of acetic acid and sodium acetate, a chlorine-containing fraction of b. p. 72—93°/11 mm. was obtained which when treated with moist silver oxide yielded a product, b. p. 200°, with a strong menthol odour (*neomenthol*?). When chloromenthol is boiled for 3 hrs., hydrogen chloride and *p*-menthene oxide are produced, whilst heating with methyl and propyl alcohols and 3-*p*-menthol under pressure at 120—200° affords 3-*p*-menthone (40—85%). Reduction of chloromenthol with zinc dust and acetic acid gives 3-*p*-menthone, and the action of acetyl chloride and pyridine is to form *chloromenthene* (89%), b. p. 92—98°/13 mm., d^{20}_4 0.9726. Δ^3 -*p*-Menthene with phosphorus pentachloride yields a small amount of chloromenthene, which when treated with an excess of silver oxide or 50% potassium hydroxide solution furnishes 3-*p*-menthone.

Reduction of 2-chlorocyclohexanol with sodium and ethyl alcohol gives 2-ethoxycyclohexanol (87%), b. p. 82—90°/15 mm., whilst similar treatment of chloromenthol affords *p*-menthene oxide (74%).

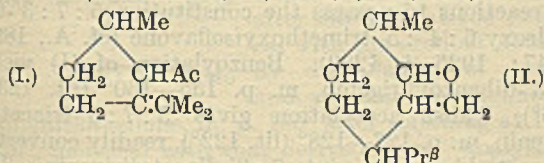
H. BURTON.

Action of menthol on phosphorus chlorides and oxychloride. T. MILOBENDZKI and (MME.) H. KOLITOVSKA (Bull. Soc. Amis Sci. Poznan, 1926, 2, 14—17).—In presence of pyridine, menthol and phosphorus trichloride give a quantitative yield of menthyl phosphite, $\text{P}(\text{OC}_{10}\text{H}_{19})_2$, m. p. 44—45°, $[\alpha]_{\text{D}} - 30^\circ$, which when heated at 240° in a vacuum affords menthene (80%), or when treated with dry hydrogen chloride affords menthyl chloride and 13% of the acid ester, $\text{P}(\text{OH})(\text{OC}_{10}\text{H}_{19})_2$. Sodium menthoxide

and phosphorus oxychloride yield quantitatively menthyl phosphate, m. p. 86°, $[\alpha]_D -100^\circ$, which when heated in a vacuum quantitatively affords menthene, or with dry hydrogen chloride affords the compound $\text{PO}(\text{OH})(\text{OC}_{10}\text{H}_{19})_2$ and menthyl chloride. Menthol and phosphorus oxychloride yield menthyl phosphate (70%), menthyl chloride (7%), and the acid phosphate. Menthol or sodium menthoxide and phosphorus pentachloride give a quantitative yield of menthyl chloride and phosphorus oxychloride; the latter then reacts as above. The reaction between menthol and phenyl dichlorophosphate was also examined.

CHEMICAL ABSTRACTS.

Catalytic reduction of unsaturated hydroaromatic compounds. H. RUPE and K. SCHÄFER (Helv. Chim. Acta, 1928, 11, 463—477).—Benzylmenthone, b. p. 195°/13 mm., d_4^{20} 0.9915, n_D^{20} 1.51834, n_D^{20} 1.53604, n_D^{20} 1.52279, $[\alpha]_D +12.37^\circ$, is obtained in 90% yield by reducing benzylidenepulegone with hydrogen in presence of 82% alcohol and nickel. Similar reduction of potassium pulegenate at 80°/10 atm. affords dihydropulegenic acid, b. p. 138°/11 mm., d_4^{20} 0.9642, $[\alpha]_D -0.36^\circ$. Pulegenyl chloride and zinc dimethyl react in benzene solution yielding *pulegyl methyl ketone* (I), b. p. 98°/13.5 mm., d_4^{20} 0.9126, $[\alpha]_D +40.48^\circ$ (semicarbazone, m. p. 144°; oxime, b. p. 130°/10.5 mm.). *Pulegyl ethyl ketone*, b. p. 107—112°/10 mm. (semicarbazone, m. p. 136°), and *dihydropulegyl methyl ketone*, b. p. 86°/10 mm., d_4^{20} 0.8862, $[\alpha]_D -3.56^\circ$ (semicarbazone, m. p. 174°), are described (cf. Wallach, A., 1903, i, 567, etc.).



Catalytic reduction of hydroxymethylenetetrahydrocarvone yields the *oxide* (II), b. p. 109°/11 mm., d_4^{20} 0.9232, $[\alpha]_D^{20} +31.72^\circ$, formed by elimination of water from the corresponding glycol, *methylenetetrahydrocarvone* (III), b. p. 102°/11 mm., d_4^{20} 0.9152, $[\alpha]_D -5.81^\circ$ (semicarbazone, m. p. 177°), *tetrahydrocarvyl-carbinol* (IV), b. p. 142°/11 mm., d_4^{20} 0.9947, $[\alpha]_D^{20} -40.16^\circ$ (benzoate, m. p. 105°), and a small amount of *s-di(ketotetrahydrocarvyl)ethane*, b. p. 219—220°/11 mm. When (IV) is heated with 75% sulphuric acid, dehydration into (III) takes place. Oxidation of (III) with chromic and acetic acids gives an aldehyde isolated as its *semicarbazone*, $\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}_3$, m. p. 182°.

H. BURTON.

Oxidation products of camphane, fenchane, and camphenilane derivatives with chromic acid. J. BRÉDÉ and P. PINTEN [with H. GERMAR, T. LIESER, and H. DE GREIFFE] [J. pr. Chem., 1928, [ii], 119, 81—107].—Oxidation of *i*-camphenilone in acetic acid solution with chromic acid yields after 4—5 weeks, *dl-p-ketocamphenilone* (I), b. p. 118°/13 mm., m. p. 56° [monosemicarbazone, m. p. 201—202° (decomp.)], in about 10% yield. The oxidation conditions have been determined in some detail.

Optically active *p*-ketocamphenilone, $[\alpha]_D^{20} -90.03^\circ$ in methyl alcohol, has m. p. 74°.

Bromination of (I) yields *bromoketocamphenilone* (Br=H in α' in I), m. p. 84.5°, having $[\alpha]_D -353.64^\circ$ in methyl alcohol when prepared from the optically active diketone. Heating this bromo-compound with sodium hydrogen carbonate solution causes elimination of hydrogen bromide and the formation of *keto-camphenilolenic acid*, m. p. 156° (semicarbazone, decomp. 225°), together with two *by-products* having m. p. 232—235° and 251°, respectively.

Bromination of *p*-ketofenchone (A., 1924, i, 408) gives *bromoketofenchone*, m. p. 132°, $[\alpha]_D^{20} +324.05^\circ$ in methyl alcohol, which eliminates hydrogen bromide, yielding *ketofencholenic acid*, m. p. 126—127° (oxime, decomp. 160°; semicarbazone, decomp. 212—216°). When this acid is treated with bromine, a *dibromide*, m. p. 136—137°, is formed which readily loses hydrogen bromide, yielding *bromoketofencholenic acid*, m. p. 152—153°, whilst oxidation with 1% potassium permanganate gives dimethylmalonic acid together with a γ - or δ -lactonic acid, $\text{C}_{10}\text{H}_{14}\text{O}_6$, m. p. 175—176°, derived from the acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$.

Bromination of diketocamphane (*loc. cit.*) furnishes a *bromodiketocamphane* (either *bromoketocamphor* or *epibromoketocamphor*), m. p. 144.5—145° (*dl*-bromocompounds, m. p. 128—129° and above 190°), which yields either *ketocampholenic* or *epiketocampholenic acid*, m. p. 124.5° (semicarbazone, decomp. 216—218°).

Oxidation of *dl*-bornyl acetate affords *dl-p-ketobornyl acetate*, b. p. 136—137°/9.5 mm., m. p. 73—75° (semicarbazone, decomp. 238°), which is hydrolysed by aqueous potassium hydroxide to *dl-ketoborneol*, m. p. 236°. Oxidation of this with chromic acid affords *dl-diketocamphane*, m. p. 210° (corr.). Bromination of *p*-ketobornyl acetate and *p*-ketobornyl chloride (A., 1927, 156) gives *bromoketobornyl acetate*, m. p. 100—101°, and *bromoketobornyl chloride*, m. p. 184°, respectively.

H. BURTON.

Structure of additive compounds of bornylene and halogen acids. O. ACHMATOWICZ (Rocz. Chem., 1928, 8, 55—70).—Hydrogen chloride adds on to bornylene dissolved in a number of solvents at 0° to yield a *hydrochloride*, m. p. 149—149.5°, $[\alpha]_D +15.43^\circ$, of a new isomeric hydrocarbon (*hydrobromide*, m. p. 124—125°, $[\alpha]_D +6.52^\circ$; *hydriodide*, m. p. 22—25°, $[\alpha]_D +55.18^\circ$). On heating in a sealed tube with water at 100° for 12.5 hrs., 75% of the chlorine is removed; in this respect the new hydrochloride occupies an intermediate position between bornyl and *isobornyl* hydrochlorides. The residue is identified as cyclene. Alcoholic silver nitrate removes chlorine, bromine, or iodine almost quantitatively from the corresponding hydrohalides. Bornylene hydrobromide on reduction with zinc dust yields bornylene, the ring structure of which must therefore be possessed by the hydrobromide. An additional product of reduction is *endoborneol* (A., 1927, 250); the bromine atom must therefore occupy the α -position. Magnesium forms a Grignard compound with the hydrobromide or hydriodide, which on hydrolysis yields a mixture of bornylene, borneol, a space isomeride of hydrodicamphene, and a number of unsaturated hydrocarbons. The latter on oxidation yields *i*-camphoric acid, which can have originated only from bornylene. Bornylene

hydrochloride or hydrobromide yields *endoborneol* on treatment with silver acetate. Bornylene hydrochloride when heated with aniline yields mainly cyclene, together with traces of unsaturated compounds, indicating the bridged ring structure of the hydrohalide. Thus the above group of additive compounds are *endoborneol* derivatives, as distinct from the borneol series, which are bornylene derivatives.

R. TRUSZKOWSKI.

Chemical individuality of humulene. A. C. CHAPMAN (J.C.S., 1928, 785—789).—Careful fractionation of the crude sesquiterpene obtained from clove oil shows that it consists substantially of caryophyllene with a rotation of about $[\alpha]_D -8^\circ$, together with a small proportion (5—10%) of humulene. No evidence of the existence of the so-called inactive α -caryophyllene (Deussen, A., 1911, i, 549) could be obtained. Whereas caryophyllene forms a crystalline dihydrochloride and a solid alcohol, no corresponding solid derivative can be obtained from humulene. Further comparison of derivatives of the two substances leads to the conclusion that humulene is a definite chemical individual.

M. CLARK.

Production of mercaptans of the furfuryl series. INTERNAT. NAHRUNGS- U. GENUSSMITTEL A.-G.—See B., 1928, 327.

Cyanidin. I. Comparative investigation of cyanidin chloride and 3:5:7:3':4'-pentahydroxyflavylium chloride. T. MALKIN and M. NIERENSTEIN (Ber., 1928, 61, [B], 791—799).—Whereas cyanidin chloride is oxidised by hydrogen peroxide to a yellow, crystalline substance which, contrary to Willstätter and Everest (A., 1913, i, 1371), is not a flavone, 3:5:7:3':4'-pentahydroxyflavylium chloride does not yield this substance (cf. Pratt and Robinson, A., 1925, i, 422), so that the supposed identity of the chlorides cannot be maintained. Further comparison of cyanidin chloride from cornflowers and rose leaves with 3:5:7:3':4'-pentahydroxyflavylium chloride discloses marked qualitative similarity, but almost complete quantitative differences, particularly with regard to colour reactions. The Röntgen spectra of the natural and synthetic chlorides and the absorption spectra of the compounds and the corresponding colour bases exhibit sufficient individuality to exclude the hypothesis of identity. The possible presence of impurity in the natural cyanidin chloride is discounted by the identical behaviour of the compound from the two different sources. Difficulties possibly arising in the demethylation of the intermediate substances of the synthesis of 3:5:7:3':4'-pentahydroxyflavylium chloride do not appear to arise, since the product is free from methoxyl when tested by Zeisel's method, and is completely identical with a substance prepared as follows. Protocatechuic acid is converted by cold acetic anhydride and anhydrous potassium acetate into diacetylprotocatechuic acid, m. p. 162°, and thence by phosphorus pentachloride in carbon tetrachloride into the corresponding chloride, m. p. 55°. The latter compound with diazomethane in ether affords ω -chloro-3:4-diacetoxyacetophenone, m. p. 94°, which is treated successively with potassium acetate in boiling glacial acetic acid and 2:4:6-tri-

acetoxybenzaldehyde; the product thus formed is converted by boiling hydrochloric acid into 3:5:7:3':4'-pentahydroxyflavylium chloride identical with the compound of Pratt and Robinson (*loc. cit.*). The differences between the natural and synthetic products cannot be ascribed to molecular relationships, since they have the same mol. wt. in alcohol and their dispersion in ethyl alcohol is unimolecular. Cyanidin chloride must therefore be regarded as an isomeride of the flavylium chloride to which a constitution cannot at present be ascribed. Freudenberg's reduction (A., 1925, i, 1165) of cyanidin chloride to epicatechin does not appear reconcilable with his conversion of 3:5:7-pentamethoxyflavylium chloride into pentamethylepicatechin.

H. WREN.

Colour variations of cyanidin chloride and 3:5:7:3':4'-pentahydroxyflavylium chloride as related to acidity and alkalinity. C. M. FEAR and M. NIERENSTEIN (Biochem. J., 1928, 22, 615—616).—The instantaneous production of a pure blue colour on addition of sodium carbonate takes place in the case of natural cyanidin chloride at p_H 8.04, whereas with synthetic pentahydroxyflavylium chloride this happens at p_H 11.57.

S. S. ZILVA.

Constitution of irigenin and iridin. I. W. BAKER (J.C.S., 1928, 1022—1033).—The extraction of the glucoside iridin, which occurs to the extent of 1% in Florentine orris root, is described. Hydrolysis of iridin with dilute sulphuric acid yields irigenin (I), m. p. 185° (dimorphous), shown by investigation of its reactions to possess the constitution 5:7:3'-trihydroxy-6:4':5'-trimethoxyisoflavone (cf. A., 1894, i, 47; 1925, i, 1299). Benzoylation of (I) yields 7:3'-dibenzoylirigenin, m. p. 155—160° (lit. 123—126°), whilst acetylation gives 5:7:3'-triacetylirigenin, m. p. 127—128° (lit. 122°), readily converted by partial hydrolysis into 7:3'-diacetylirigenin. The two last-named compounds are erroneously described in the literature as di- and mono-acetylirigenin, respectively. Methylation of (I) with methyl sulphate yields *irigenin trimethyl ether* (II), m. p. 163°, decomposed by alkali into 3:4:5-trimethoxyphenylacetic acid and antiarol (3:4:5-trimethoxyphenol). Demethylation of (I) yields *irigenol*, 5:6:7:3':4':5'-hexahydroxyisoflavone (+H₂O), m. p. 331° (decomp.) (*hexa-acetyl* derivative, m. p. 237—238°; *oxonium sulphate*).

Methylation of (I) with 3 mols. of methyl iodide and alkali in a sealed tube gives *irigenin 7:3'-dimethyl ether* (III), m. p. 166—167° (*acetyl* derivative, m. p. 191°), decomposed by aqueous alkali at 100° in hydrogen to 3:4:5-trimethoxyphenylacetic acid and 4:5-dimethoxyresorcinol. Further methylation of (III) with methyl sulphate gives (II). Long-continued methylation of (I) with an excess of methyl iodide and alkali gives a *compound*, m. p. 154.5°. Methylation of iridin in methyl alcohol with an excess of diazomethane gives a resinous, methylated glucoside, yielding on hydrolysis *irigenin 5:3'-dimethyl ether*, m. p. 218°. The last-named compound gives the same products on decomposition with alkali as its isomeride (III), and is converted by further methylation into (II). The dextrose nucleus in iridin is therefore present in the 7-position. The

dyeing properties of irigenin, iridin, and irigenol are described.

M. CLARK.

Stability of the double linking in dixanthylene.

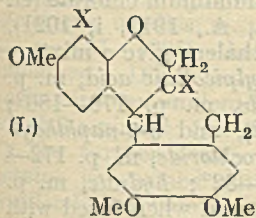
O. MAGIDSON and W. DAMASKINA (Trans. Sci. chem.-pharm. Inst., 1926, [16], 51—52; Chem. Zentr., 1928, i, 59).—Treatment of dixanthylene with phosphorus pentachloride yields a dichloro-derivative, $O:(C_6H_4)_2 \cdot CCl_2$, which, however, cannot be isolated, xanthone being obtained. The compound, $O:(C_6H_4)_2 \cdot CH \cdot CCl:(C_6H_4)_2 \cdot O$, m. p. 189—190°, is also obtained. Xanthone is also produced when dixanthylene is heated in a tube at 200° with a saturated solution of hydrogen chloride in acetic acid.

A. A. ELDRIDGE.

[Behaviour of dixanthylene when heated.] F. ARNDT and L. LORENZ (Ber., 1928, 61, [B], 869; cf. A., 1925, i, 57).—A reply to Schönberg and Schütz (this vol., 526).

H. WREN.

Brazilin and hæmatoxylin. VII. Syntheses of trimethylbrazilone and tetramethylhæmatoxyline. P. PFEIFFER, O. ANGERN, E. HAACK, and J. WILLEMS (Ber., 1928, 61, [B], 839—843; cf. this vol., 426).—Trimethylanhydrobrazilin (cf. A., 1927, 1198) suspended in glacial acetic acid is reduced by hydrogen in presence of spongy platinum to



trimethyldeoxybrazilin (I; X=H), m. p. 107—109° after softening at 106°, which is oxidised by chromic acid in glacial acetic acid to trimethylbrazilone, m. p. 167° (decomp.) after softening at 165°, identical with the product obtained by degradation of brazilin and yielding acetyltrimethyl-

anhydrobrazilone, m. p. 185° after softening at 175—176°, identical with that derived from "analytical" trimethylbrazilone. Similarly, tetramethylanhydrohæmatoxylin (cf. this vol., 426) is reduced to *tetramethyldeoxyhæmatoxylin* (I; X=OMe), m. p. 151° after softening at 147°, oxidised to tetramethylhæmatoxyline, identical with the product derived from tetramethylhæmatoxylin. Synthetic evidence in favour of the constitutions assigned on analytical grounds to brazilin and hæmatoxylin by Perkin and co-workers is thus advanced, the only uncertainty being with regard to the position of the alcoholic hydroxyl group, which, in all probability, occupies the position marked X.

H. WREN.

Derivatives of 1:3-dithiolan and of 1:3-dithian. J. C. A. CHIVERS and S. SMILES (J.C.S., 1928, 697—702; cf. A., 1926, 947).—Introduction of the alkylthiol grouping into substances such as malonic acid and deoxybenzoin may be effected by interaction of these compounds with alkyl disulphoxides (alkyl thiol sulphonates) in presence of potassium acetate. Benzyl disulphoxide reacts with deoxybenzoin yielding the benzylmercaptol of benzil, isolated, after oxidation with hydrogen peroxide, as the *dioxide*, m. p. 167°. With ethyl malonate it yields, after hydrolysis with hydrochloric acid, benzylthiolacetic acid. Ethane α -di-*p*-toluenethiol sulphonate yields with deoxybenzoin 2-benzoyl-2-phenyl-1:3-dithiolan, and with ethyl malonate it gives after hydrolysis 1:3-dithiolan-

2-carboxylic acid, m. p. 90° (*dibromide*; *di-iodide*), together with a little ethylenedithiolacetic acid. Propane α -*γ*-di-*p*-toluenethiol sulphonate, m. p. 65—67° (from α -*γ*-dibromopropane and potassium *p*-tolylthiol sulphonate), yields with deoxybenzoin 2-benzoyl-2-phenyl-1:3-dithian, m. p. 99—100°. With ethyl malonate it gives after hydrolysis 1:3-dithian-2-carboxylic acid, m. p. 115—116° (*di-iodide*). No ring closure can be induced with *pentane* α -di-*p*-toluenethiol sulphonate (from α -dibromopentane and potassium *p*-tolylthiol sulphonate) and ethyl malonate, only *pentane*- α -*dithiolacetic acid*, m. p. 91—92°, being isolated from the reaction mixture. M. CLARK.

Manufacture of substituted guanidines. CHEM. FABR. VORM. SCHERING.—See B., 1928, 327.

β -Vinylpiperidine. R. MERCHANT and C. S. MARVEL (J. Amer. Chem. Soc., 1928, 50, 1197—1201).—3-Piperidylcarbinol (cf. this vol., 427) [*chloroplatinate*, m. p. 174° (decomp.) (also +H₂O); *chloroaurate*, m. p. 153—154° (decomp.)]; 1-benzoyl derivative, m. p. 80—81°, b. p. 153°/0.01—0.02 mm., n_D^{20} 1.5690, and 48% hydrobromic acid give crude 3-bromomethylpiperidine hydrobromide, which is converted by benzylation and boiling with aqueous-alcoholic sodium cyanide into nearly pure 1-benzoyl-3-cyanomethylpiperidine, b. p. 165—175°/0.1 mm., d_4^{20} 1.1056, n_D^{20} 1.5602. When hydrolysed and esterified this yields ethyl 3-piperidylacetate, b. p. 101—103°/6 mm., n_D^{20} 1.4643, d_4^{20} 1.0131 (*chloroplatinate*, m. p. 181°), which is reduced by sodium and absolute alcohol to β -3-piperidylethyl alcohol, b. p. 121—123°/6 mm., n_D^{20} 1.4883, d_4^{20} 1.0106. 3-Vinylpiperidine, b. p. 152—155°, n_D^{20} 1.4731, d_4^{20} 0.9274 [*chloroplatinate*, m. p. 223—224° (decomp. from 220°)], is prepared in small yield by dehydrating this alcohol by means of phosphoric oxide at 180—190°. 3-Methylenepiperidine, b. p. 138°, d_4^{20} 0.9342, n_D^{20} 1.4807 (*hydrochloride*), is obtained similarly from 3-piperidylcarbinol.

H. E. F. NOTTON.

Manufacture of isatins of the naphthalene series. I. G. FARBENIND.—See B., 1928, 327.

Carbazine syntheses. V. Derivatives of C-dimethylcarbazine. VI. Derivatives of C-diethylcarbazine. H. GOLDSTEIN and W. KOPP (Helv. Chim. Acta, 1928, 11, 478—486, 486—489).—V. Magnesium methyl iodide reacts with methyl 4'-aminodiphenylamine-2-carboxylate, yielding 3-amino-5:5-dimethyldihydroacridine (*acetyl* derivative, chars at 150° after previous darkening), which is oxidised by ferric chloride to 5:5-dimethyldihydroacridine-3-imine (*perchlorate*, decomp. gradually at the ordinary temperature). Similarly, methyl 4:4'-diaminodiphenylamine-2-carboxylate gives 3:7-diamino-5:5-dimethyldihydroacridine (*diacetyl* derivative, m. p. 208° after softening), oxidised to 7-amino-5:5-dimethyldihydroacridine-3-imine (*perchlorate* +H₂O, green). Methyl 4-amino-4'-dimethylaminodiphenylamine-2-carboxylate furnishes 3-amino-7-dimethylamino-5:5-dimethyldihydroacridine (*acetyl* derivative, decomp. 180°), oxidised to 7-dimethylamino-5:5-dimethyldihydroacridine-3-imine (I) (*hydrochloride*; *perchlorate*; *diperchlorate*). When a solution of a salt of (I) is treated with alkali, partial precipitation of the

base occurs and the alkaline liquor is coloured bluish-violet. It is suggested that this phenomenon is due to the formation of an iminium hydroxide. When an aqueous-alcoholic solution of (I) is boiled with sodium carbonate solution there is produced 7-amino-5:5-dimethyl-3-carbazone, violet (acetyl derivative, red, m. p. 235°), also formed by oxidation of the reaction product from magnesium methyl iodide and methyl 4-amino-4'-hydroxydiphenylamine-2-carboxylate. If (I) is boiled with sodium hydroxide solution, 7-hydroxy-5:5-dimethyl-3-carbazone, decomp. 200°, is produced.

VI. 3-Amino- (acetyl derivative, m. p. 145°), 3:7-diamino- (diacetyl derivative, m. p. 241° after softening), and 3-amino-7-dimethylamino-5:5-diethyl-dihydroacridines [acetyl derivative, m. p. 191° (decomp.)] have been prepared from magnesium ethyl iodide and the requisite substituted diphenylamine-2-carboxylic esters. Oxidation of these with ferric chloride gives 5:5-diethyl-, 7-amino-5:5-diethyl- (perchlorate + H₂O), and 7-dimethylamino-5:5-diethyl-dihydroacridine-3-imines (perchlorate), respectively. H. BURTON.

Molecular symmetry of acetonylpyrrole. S. B. HENDRICKS (J. Amer. Chem. Soc., 1928, 50, 1205—1208).—Mol. wt. determinations on acetonylpyrrole (cf. Dennstedt and Zimmermann, A., 1887, 1052) by the method of differential vapour pressures are in agreement with the doubled formula, C₂₈H₃₆N₄. Laue and X-ray spectrum photographs on single crystals (cf. Fock, Z. Krist., 1888, 14, 541) indicate that the unit cell contains four such molecules and has the dimensions $a=b=10.09$ Å., $c=23.85$ Å. The space grouping is C₂ or C₄, the molecules being in the general positions and thus not necessarily having an element of symmetry. H. E. F. NOTTON.

Reduction potentials of organic compounds. II. Pyridine. M. SHIKATA and I. TACHI (Bull. Agric. Chem. Soc. Japan, 1927, 3, 53).—The reduction of pyridine proceeds reversibly; two waves of reduction were observed in acid and neutral solutions, the first being the reduction of pyridine ions, and the second that of undissociated molecules.

CHEMICAL ABSTRACTS.

Influence of a third substance on the rate of reaction of organic halogen derivatives with amines. B. V. TRONOV and A. T. HERSHKEVITSCH (J. Russ. Phys. Chem. Soc., 1928, 60, 171—180).—The effect on the rate of reaction of the addition of so-called inert solvents in concentrations similar to those of the reacting substances was investigated. The rates of reaction of pyridine with benzyl chloride, benzyl bromide, and trichloronitromethane were determined alone and in the presence of hydrocarbons, alcohols, ethers, aldehydes, ketones, esters, nitro-compounds, nitriles, amines, inert halogen derivatives, and carbon disulphide, at 18° and relative molecular concentrations of about 3:2. Substances which dissolved the pyridine salt accelerated the reaction, whilst those which did not retard it, some by as much as 10 times. The former were also the more active chemically and had a tendency to form loose complexes with the reacting substances.

Experiments were also performed to investigate whether the mechanism of reactions of the halogen compounds was ionic or not. M. ZVEGINTZOV.

Condensation of crotonaldehyde with ammonia in presence of alumina. A. E. TSCHITSCHIBABIN and M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1927, 59, 1125—1128).—See A., 1927, 1086.

Manufacture of 2-chloropyridine. DEUTS. GOLD- UND SILBER-SCHNEIDANSTALT.—See B., 1928, 348.

Manufacture of derivatives of 2-aminopyridine. CHEM. FABR. VORM. SCHERING.—See B., 1928, 389.

Production of new pyridine derivatives [pyridylhydrazones etc.]. DEUTS. GOLD- UND SILBER-SCHNEIDANSTALT.—See B., 1928, 389.

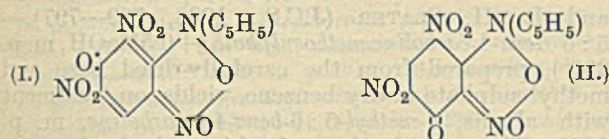
Nitroamines of the pyridine series. 3-Nitroaminopyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 338—345).—See this vol., 185.

Quaternary pyridine bases. O. MAGIDSON and G. MENSCHIKOV (Trans. Sci. Chem.-Pharm. Inst., 1926, [16], 7—20).—See A., 1926, 844.

Friedel and Crafts' reaction in the pyridine series. C. M. JEFFCOTT (J. Amer. Chem. Soc., 1928, 50, 1189—1192).—Additive compounds from pyridine or quinoline and alkyl or acyl halides do not condense with phthalic anhydride in presence of aluminium chloride. Using benzene and aluminium chloride (cf. Just, A., 1898, i, 42; Halla, A., 1911, i, 1021), quinolinic anhydride and naphthalene give a mixture of quinolinic acid, 3- α -naphthoylepicolinic acid, m. p. 155° (silver salt; hydrochloride, m. p. 179—180°; methyl ester, m. p. 100—101°), and 3- β -naphthoylepicolinic acid, m. p. 145° (hydrochloride, m. p. 172—173°; methyl ester, m. p. 80—82°; hydrate, m. p. 109°), which gives β -naphthoic acid when fused with alkali and is reduced by zinc in ammoniacal solution to β -naphthylpyridophthalide, m. p. 127°. Similarly, acenaphthene gives 3-(4'-acenaphthoylepicolinic acid, m. p. 168—169° (hydrochloride, m. p. 175°; methyl ester, m. p. 113—114°; hydrate, m. p. 121°), and diphenyl a mixture of 3-benzoylpicolinic acid (from the benzene) and 3-p-phenylbenzoylpicolinic acid, m. p. 170—171°. Phenylpyridophthalide and aluminium chloride yield with benzene 3-diphenylmethylpicolinic acid, m. p. 153° (methyl ester, m. p. 109°), which is decarboxylated at 170° to 3-pyridyl-diphenylmethane, m. p. 78—79°, and with toluene, 3-phenyl-p-tolylmethylpicolinic acid, m. p. 161°. 3-p-Toluoylpicolinic acid is reduced to p-tolylpyridophthalide, m. p. 144°. The methyl hydrogen quinolate of m. p. 123° must be the 2-carboxylic ester, since its acid chloride condenses with toluene to 3-p-toluoylpicolinic acid. The isomeric ester-acid of m. p. 108° must be a mixture, since it combines with benzene in the same way, forming 3-benzoylpicolinic acid as well as 2-benzoylnicotinic acid, m. p. 285° (methyl ester, m. p. 87°) (cf. Kirpal, A., 1910, i, 504), which is reduced to the lactone, m. p. 128°, of 3-carboxy-2-pyridylphenylcarbinol. Attempts to prepare diphenylpyridophthalide are described. 2:3-Dibenzoylpyridine, m. p. 186—187°, and 2-toluoyl-3-benzoylpyridine, m. p. 190—193°, are prepared from 3-benzoylpicolinyl chloride. H. E. F. NOTTON.

Reciprocal exchange of aromatically combined hydroxyl and halogen. III. W. BORSCHKE and E.

FESKE (Ber., 1928, 61, [B], 690—702; cf. A., 1918, i, 11; 1927, 239).—Styphnic acid, prepared by the successive sulphonation and nitration of resorcinol under defined conditions, is unexpectedly converted by *p*-toluenesulphonyl chloride in presence of pyridine into 3-hydroxy-2:4:6-trinitrophenylpyridinium betaine (I or II), m. p. about 330° (decomp.) after



darkening at 270°. It dissolves readily in fuming hydrochloric acid but is precipitated unchanged when the solution is diluted. Hydrogen chloride in glacial acetic acid at 145° converts it into a substance (?) $(\text{NO}_2)_3\text{C}_6\text{H}(\text{OH})\cdot\text{N}(\text{C}_5\text{H}_5)\cdot[\text{CH}:\text{CH}]_2\text{Cl}$, m. p. 158—159°, transformed by warm pyridine into the betaine. With diethylamine in methyl-alcoholic solution the betaine affords a compound from which 3-amino-2:4:6-trinitrophenol, m. p. 178°, is obtained by the action of hydrochloric acid. Piperidine and the betaine yield the two, interconvertible forms of the compound,

$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2\text{H}\cdot\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{N}(\text{C}_5\text{H}_5)\cdot[\text{CH}:\text{CH}]_2\text{N}(\text{C}_5\text{H}_5)$ (α -variety, needles, m. p. 124—125°; β -form, leaflets, m. p. 127—128°), the isomerism of which is not explained. Dilute sulphuric acid transforms either variety into an unidentified substance, m. p. 139°, from which 3-amino-2:4:6-trinitrophenol is readily derived by the further action of mineral acid. When the betaine is warmed with aniline, 3-hydroxy-2:4:6-trinitrodiphenylamine, m. p. 158—159°, is produced, presumably through the glutacondialdehyde derivative. Under similar conditions, *p*-toluidine yields 3-hydroxy-2:4:6-trinitrophenyl-*p*-tolylamine, m. p. 176—177° [*p*-toluidine compound, m. p. 191—193° (decomp.)], also derived from the diethylaniline compound of *p*-toluenesulphonylstyphnic acid and *p*-toluidine. 3-Chloro-2:4:6-trinitrodiphenylamine, m. p. 141—142°, is obtained from the hydroxydiphenylamine, *p*-toluenesulphonyl chloride, and diethylaniline or by the action of hot 2*N*-hydrochloric acid on trinitrodiphenylaminopyridinium-*p*-toluenesulphonate, m. p. 206—208°. Aminopicric acid, diethylaniline, and *p*-toluenesulphonyl chloride afford 3-chloro-2:4:6-trinitroaniline, m. p. 185—186°.

2:4-Dinitroresorcinol, m. p. 147—148° (the preparation from dinitrosoresorcinol is described in detail), is converted by *p*-toluenesulphonyl chloride in diethylaniline into the corresponding *p*-toluenesulphonate, m. p. 126—127°, whereas in the presence of pyridine it gives a mixture of 3-hydroxy-2:4:6-trinitrophenylpyridinium-*p*-toluenesulphonate, m. p. 134°, and 3-hydroxy-2:4:6-trinitrophenylpyridiniumbetaine, the decomp. about 325° after blackening at 300°. The betaine is converted by hydrogen chloride in glacial acetic acid into 3-chloro-2:4:6-trinitrophenol, m. p. 112—114°, by piperidine into the glutacondialdehyde derivative, $\text{C}_{21}\text{H}_{28}\text{O}_7\text{N}_8$ (labile α -form, m. p. 144—146°; stable β -variety, m. p. 171—172°), by aniline into dinitro-*m*-aminophenol, m. p. 220—222°, and phenylpyridinium chloride (additive compound with mercuric chloride, m. p. 145°), and by *p*-anisidine into *p*-anisyl-

pyridinium chloride, m. p. 127—129°. The *p*-toluenesulphonyl derivative of 2:4-dinitroresorcinol (see above) is converted by boiling aniline into 2:4-dinitro-3-hydroxyphenylamine, m. p. 124—125°, which is converted by *p*-toluenesulphonyl chloride into 2:4-dinitro-3-anilinophenylpyridinium-*p*-toluenesulphonate, $\text{NHPPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{N}(\text{C}_5\text{H}_5)\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, m. p. 216—218°, and 2:4-dinitro-3-anilinophenyl-*p*-toluenesulphonate, m. p. 151°, in presence of pyridine and diethylaniline, respectively.

4:6-Dinitroresorcinol and *p*-toluenesulphonyl chloride in pyridine afford 4:6-dinitro-3-hydroxyphenylpyridiniumbetaine, decomp. 320°, obtained by Reitzenstein and Rothschild (A., 1906, i, 454) from 1:3-dichloro-4:6-dinitrobenzene and hot pyridine (cf. Zincke and Weisspfenning, A., 1910, i, 585); it is converted by the successive action of piperidine or aniline and hydrochloric acid into 3-amino-4:6-dinitrophenol. 4:6-Dinitro-3-hydroxyphenyl-*p*-toluenesulphonate, m. p. 135° (diethylaniline salt, m. p. 109—110°), is obtained from the reactants in diethylaniline. 4:6-Dinitroresorcinol is converted by *p*-toluenesulphonyl chloride in absence of diethylaniline into a mixture of 5:5'-dichloro-2:4:2':4'-tetranitrodiphenyl ether, m. p. 232—234°, and 1:3-dichloro-4:6-dinitrobenzene.

H. WREN.

Quinoline derivatives. VIII. Derivatives of 4-hydroxy-2-phenylquinoline. IX. 4-Thiol-2-phenylquinoline and 2-phenylquinoline-4-sulphonic acid. H. JOHN [with E. WÜNSCHE]. X. 4-(2-Phenylquinolyl)aminobenzoic acids. H. JOHN (J. pr. Chem., 1928, [ii], 119, 43—48, 49—55, 56—60).—VIII. The following derivatives of 2-phenylquinoline are described: 4-acetoxy-, m. p. 70°; 4-benzoyloxy-, m. p. 90—91°; 4-ethoxy-, m. p. 100—102°; 4-phenoxy-, m. p. 252°; 4-*m*-tolylloxy-, m. p. 241—243°; 4-*p*-nitrophenoxy-, m. p. 88—90°; 4-*p*-aminophenoxy-, m. p. 81°; 4-*o*-methoxyphenoxy-, m. p. 246°, and 4-*m*-methyl-*o*-isopropylphenoxy-, m. p. 252°. Numerous salts of the above have been prepared but not characterised.

IX. 4-Chloro-2-phenylquinoline reacts with potassium hydrosulphide at 150—160° to give 4-thiol-2-phenylquinoline, m. p. 175—176° (picrate, m. p. 204°), which when exposed to air for some time passes into di-(2-phenyl-4-quinolyl) disulphide, m. p. 175—176° (picrate, m. p. 197°). 4-Methylthiol-, m. p. 64° (picrate, m. p. 225°), 4-ethylthiol-, m. p. 84.5° (picrate, m. p. 192°), 4-isoamylthiol-, m. p. 170—171°, and 4-allylthiol-, m. p. 169°, -2-phenylquinolines are described. Di-(2-phenyl-4-quinolyl) sulphide, obtained from 4-thiol-2-phenylquinoline and 4-chloro-2-phenylquinoline in presence of alcoholic potassium hydroxide, has m. p. 95°. Numerous salts of the above compounds are described.

4-Chloro-2-phenylquinoline reacts with sodium hydrogen sulphite yielding 2-phenylquinoline-4-sulphonic acid, m. p. above 290° (22 salts described).

X. 4-Chloro-2-phenylquinoline and anthranilic acid react in boiling amyl alcohol to form *o*-(2'-phenyl-4'-quinolylamino)benzoic acid, m. p. 232—236° (decomp.) (23 salts described), which when treated with hot concentrated sulphuric acid gives small amounts of alkali-soluble and -insoluble products, both

having m. p. above 305°. *m*-(2'-Phenyl-4'-quinolyl-amino)benzoic acid, m. p. 273° (ethyl ester, m. p. 174°; 23 salts described), and *p*-(2'-phenyl-4'-quinolylamino)benzoic acid, m. p. 305° (ethyl ester, m. p. 92°; 23 salts described), are prepared similarly. H. BURTON.

Condensation of acetaldehyde and paracet-aldehyde with aniline in presence of alumina. A. E. TSCHITSCHIBABIN and M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1927, 59, 1129—1134).—See A., 1927, 1086.

Doebner reaction [preparation of a benzene-azoquinoline]. A. CREMONINI (Gazzetta, 1928, 58, 127—130).—Benzylideneaminoazobenzene when heated with pyruvic acid in alcohol gives a product from which is obtainable, in 3% yield, 6-benzeneazo-2-phenylcinchoninic acid, m. p. 248° (decomp.) (soluble hydrochloride, $2C_{22}H_{15}O_2N_3 \cdot 2HCl \cdot 3H_2O$, m. p. 210°). The main product is a yellow, alkali-insoluble substance, $C_{34}H_{26}ON_6$, derived by the elimination of water from 2 mols. of aminoazobenzene, 1 mol. of benzaldehyde, and 1 mol. of pyruvic acid. By a similar condensation of 4- α -naphthaleneazo- α -naphthylamine, 6- α -naphthaleneazo-2-phenyl- α -naphthaquinoline-4-carboxylic acid, m. p. 238°, is obtained in 0.75% yield, whilst 1-benzeneazo- β -naphthylamine yields a phenylstyryl-naphthatriazole (?), $C_{25}H_{19}N_3$, m. p. 197°.

E. W. WIGNALL.

Manufacture of new polyamino-[quinoline] compounds. I. G. FARBENIND.—See B., 1928, 347.

Acridines. IV. Preparation of hydroxy-acridines and 5-substituted acridine derivatives. H. JENSEN and F. RETHWISCH (J. Amer. Chem. Soc., 1928, 50, 1144—1150).—The new acridine synthesis (A., 1927, 575) has been extended by using halogenated phenol ethers and by substituting *o*-aminophenyl ketones for *o*-aminobenzaldehyde. In this way are prepared: 3-ethoxyacridine, m. p. 99° (picrate, m. p. above 250°; hydrochloride, decomp. 200°), hydrolysed by hydriodic acid to 3-hydroxyacridine, m. p. above 250°; 1-methoxyacridine, m. p. 130—131° (picrate, decomp. 250°), hydrolysed to 1-hydroxyacridine (Matsumura, A., 1927, 467), the constitution of which is thus confirmed; 5-methylacridine, m. p. 114° (picrate, m. p. 213—214°); 5-phenyl-3-methylacridine; 1-nitro-5-phenylacridine, m. p. 189—190° (cf. Mayer and Freund, A., 1922, i, 865); 3-nitro-5-phenylacridine; 3-methylacridine picrate, m. p. 226°, and 3-ethoxy-5-phenylacridine, m. p. 105—107°. 2-Chloro-5-nitroacetophenone, unlike *o*-chloroacetophenone, readily forms with aniline, 4-nitro-2-acetyldiphenylamine, m. p. 125°, which, like 4-nitro-2'-acetyldiphenylamine, m. p. 152°, from *o*-aminobenzaldehyde and *p*-bromonitrobenzene, is converted by sulphuric and acetic acids into 3-nitro-5-methylacridine, m. p. above 300°. 3:5-Dimethylacridine (picrate, m. p. 225°, darkening at 215°), prepared by the authors' method or from acet-*p*-toluidide, has m. p. 90°, the substance obtained in the latter way by Bonna (A., 1887, 927) being probably 2:5-dimethylacridine. Acridine-5-carboxylic acid (A., 1926, 526) is not esterified by sulphuric acid or hydrogen chloride in ethyl alcohol; the ethyl ester, m. p. 78° (picrate, m. p. 226°; hydrochloride, m. p. above 250°), and methyl ester, m. p. 126.5—127.5° (picrate, m. p.

229—230°; hydrochloride, m. p. above 250°), are prepared from the acid chloride. H. E. F. NOTTON.

Syntheses in the indole series. III. Theory of anhydronium base formation and constitution of methosulphates. Fluorescence of 5:6-benz-4-carboline and its derivatives. W. O. KERMACK and R. H. SLATER (J.C.S., 1928, 789—797).—5:6-Benz-4-carboline methosulphate (+0.5MeOH, m. p. 235°), prepared from the carefully-dried base and methyl sulphate in dry benzene, yields, on treatment with alkalis, 4-methyl-5:6-benz-4- ψ -carboline, m. p. 205°. The constitution of this anhydro-base is established by the fact that it yields with methyl sulphate 1:4-dimethyl-5:6-benz-4-carbolinium methyl sulphate, m. p. 300°, identical with the salt prepared directly from 1-methyl-5:6-benz-4-carboline and methyl sulphate. 3:4-Dimethyl-5:6-benz-4- ψ -carboline, m. p. 225°, from 3-methyl-5:6-benz-4-carboline methosulphate, m. p. 270°, and alkali, yields in a similar manner 1:3:4-trimethyl-5:6-benz-4-carbolinium methyl sulphate, m. p. 292° (also prepared directly from 1:3-dimethyl-5:6-benz-4-carboline). 1-Methyl-5:6-benz-4-carboline, m. p. 142°, 3-ethyl-5:6-benz-4-carboline methosulphate, m. p. 250°, and 1:3-dimethyl-5:6-benz-4-carbolinium methyl sulphate, m. p. 296°, are described. The fluorescence of a number of carboline derivatives is examined and the influence of substituents in various positions in the ring is noted. M. CLARK.

Intermolecular condensation of acetylmethyl-anthranilic acid by means of phosphorus pentachloride and formation of a complex isocyanine dye. I. M. HELBRON, S. L. HOLT, and F. N. KITCHEN (J.C.S., 1928, 934—941; cf. A., 1923, i, 245).—Phosphorus pentachloride ($\frac{1}{3}$ mol.) reacts on heating with acetylmethylanthranilic acid (1 mol.) in presence of acetyl chloride, giving the acid chloride (I) of 3-*o*-carboxyphenylmethylcarbonyl-1:2-dimethyl-4-quinolone (II). The free acid (II) has m. p. 247° (+1H₂O, m. p. 130—131°) (methyl ester, m. p. 244°; anilide, m. p. 115°). The ethyl ester (III), m. p. 245° (+1H₂O, m. p. 124°), is hydrolysed by boiling concentrated hydrochloric acid, giving 1:2-dimethyl-4-quinolone and methylanthranilic acid. The acid chloride (I) reacts with concentrated ammonia, giving 4:4'-diketo-1:1':2'-trimethyl-1':4'-dihydro-2(3')-quinolylquinazoline, m. p. 260°, and with excess of aniline, giving 4-anilino-3-*o*-anilinophenylmethylcarbonyl-1-methyl-2-methylene-1:2-dihydroquinoline, m. p. about 165°. When acetylmethylanthranilic acid (1 mol.) is heated with phosphorus pentachloride (1.5 mols.), an acid chloride results, which is decomposed by ethyl alcohol, giving 4-chloro-3-*o*-carbomethoxyphenylmethylcarbonyl-2-methylquinoline methochloride (IV), m. p. 209° (decomp.) [methoperchlorate, m. p. 224—225° (decomp.); methiodide, decomp. 215°; methopicate, decomp. 168—169°], hydrolysed by boiling concentrated hydrochloric acid with formation of 4-hydroxy-2-methylquinoline methochloride. 4-Chloro-3-*o*-carbomethoxyphenylmethylcarbonyl-2-methylquinoline methochloride, m. p. 189—190°, yields a corresponding methiodide, m. p. 214° (decomp.). The ethyl ester (IV) reacts with aniline in acetic acid solution, giving 4-anilino-3-*o*-carbomethoxyphenylmethylcarbonyl-1-methyl-

2-methylene-1:2-dihydroquinoline, m. p. 191—192°, and with piperidine, giving the corresponding 4-piperidinomethylene base, m. p. 260°. When an alcoholic solution of the ester (IV) is heated with dilute ammonia and the resultant reddish-purple solution is treated with concentrated potassium iodide solution, 4'-chloro-3:3'-di-(o-carbethoxyphenylmethylcarbonyl)-1:2:1'-trimethylisocyanine iodide, m. p. 203° (decomp.) (perchlorate; picrate), is obtained. The following are also described: 5-bromomethylacetylanthranilic acid, m. p. 204°; 6-bromo-3-p-bromo-o-carbethoxyphenylmethylcarbonyl-1:2-dimethyl-4-quinolone, m. p. 212° (+H₂O, m. p. 123°); 4-chloro-6-bromo-3-p-bromo-o-carbethoxyphenylmethylcarbonyl-2-methylquinoline methochloride, m. p. 194°.

M. CLARK.

Manufacture of barbituric acid soporifics. I. G. FARBENIND.—See B., 1928, 389.

Pyrrrole derivatives. II. W. KÜSTER and G. KOPPENHOFER (Z. physiol. Chem., 1928, 172, 26—137; cf. A., 1922, i, 857).—Condensation of 4-carbethoxy-3:5-dimethylpyrrole-2-aldehyde with 2:5-diketopiperazine yields 2:2-bis-(4'-carbethoxy-3':5'-dimethylpyrrylmethyleno)-2:5-diketopiperazine, m. p. 268—269°, red, which in alcoholic solution gives two sharp absorption bands, one about 525 μ and a broader band with centre about 475 μ , and on reduction affords 2:2-bis-(4'-carbethoxy-3':5'-dimethylpyrrylmethyl)-2:5-diketopiperazine, colourless, m. p. 122°; on heating with 20% barium hydroxide the latter gives β -4-carbethoxy-3:5-dimethyl-2-pyrrylalanine, decomp. about 180—186°. An alternative method for the synthesis of these substituted pyrryl-amino-acids is given. 4-Carbethoxy-3:5-dimethylpyrrole-2-aldehyde when heated with rhodanine and sodium acetate in acetic acid solution yields 4-carbethoxy-3:5-dimethyl-2-pyrrylmethylenerhodanine, m. p. 253—255°, which gives a phenylhydrazone, m. p. 272—275° (decomp.), and yields on heating with 20% barium hydroxide or 15% sodium hydroxide solution β -4-carbethoxy-3:5-dimethylpyrryl- α -thiopyruvic acid, decomp. 196°. With hydroxylamine this acid gives hydrogen sulphide and an α -oxime, m. p. 218°, which on reduction gives the β -4-carbethoxy-3:5-dimethylpyrrylalanine described above. β -4-Carbethoxy-3:5-dimethylpyrryl- α -thiopyruvic acid on heating at 140° with chloroacetic acid yields β -4-carbethoxy-3:5-dimethylpyrrylpyruvic acid, m. p. 192°. Condensation of aminoacetal with ethyl 1-phenyl-2:5-dimethylpyrrole-3-carboxylate yields β -amino- α -bis-3-carbethoxy-(1-phenyl-2:5-dimethyl-4-pyrryl)ethane, m. p. 246° (sinters at 242°). The ethyl pyrrolecarbonylate, when heated in alcoholic solution with dilute hydrochloric acid and formaldehyde, yields bis-(4-carbethoxy-1-phenyl-2:5-dimethyl-3-pyrryl)methane, m. p. 102°.

A. WORMALL.

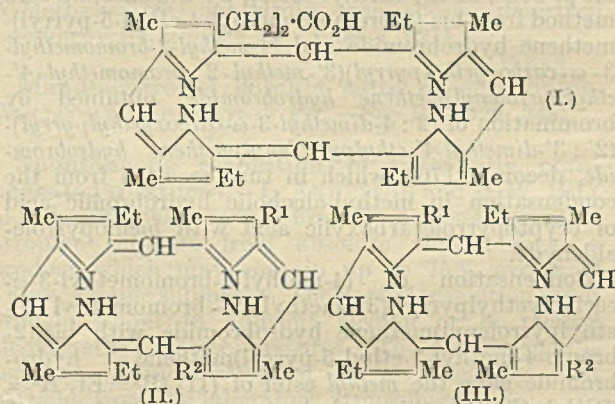
Action of cyanogen bromide on tertiary iminazoles. W. LANGENBECK (J. pr. Chem., 1928, [ii], 119, 77—80).—When 1:4-dimethylglyoxaline is treated with ethereal cyanogen bromide there is produced 2-bromo-1:4-dimethylglyoxaline, b. p. 89—90°/3 mm., m. p. 51—52° [hydrochloride, m. p. 240° (decomp.)], nitrated to 2-bromo-5-nitro-1:4-dimethylglyoxaline (Pyman and Timmis, J.C.S., 1923,

123, 494). 2-Bromopilocarpine hydrochloride, m. p. 240°, $[\alpha]_{D}^{25} + 81.9^\circ$ in water, and 2-bromoisopilocarpine hydrochloride, m. p. 201°, are prepared similarly. The pharmacological effects of 2-bromopilocarpine are given.

H. BURTON.

Dicyanotriazole. J. A. FIALKOV (J. Russ. Phys. Chem. Soc., 1927, 59, 715—725).—See A., 1927, 1205.

Porphyrin syntheses. XIV. Synthesis of porphinmonocarboxylic acids and some of their complex salts. H. FISCHER, H. GROSSEFINGER, and G. STANGLER (Annalen, 1928, 461, 221—244).—Alkali degradation of chlorophyll is known to give phyllo- and pyrro-porphyrin, i.e., two of the eight (sixteen, assuming tautomerides) possible monocarboxylic acids of aetioporphyrin. The present authors now describe the synthesis of five of these acids (or their esters). Particular attention is paid to the porphyrin (III) (R¹=Et, R²=-[CH₂]₂·CO₂H), obtained by condensing (2:4-dimethyl-3-carboxyethylpyrrolyl)-(2':4'-dimethyl-3'-ethylpyrryl)methene (cf. Fischer and Schubert, A., 1924, i, 544) with



bis-(2-bromo-3-methyl-4-ethylpyrryl)methene, using glacial acetic acid and hydrogen bromide at 165—170°. Some aetioporphyrin is formed in this condensation, owing to decomposition of the unsymmetrical methene (the bis-methene gives no porphyrin under the conditions of this condensation, whilst the unsymmetrical methene gives a basic and an acidic porphyrin). Pyridine as a condensing agent leads to the formation of basic porphyrins. By previous introduction of a bromine atom into each of the 2-methyl groups in the unsymmetrical methene (cf. this vol., 76), followed by heating the product with the bis-methene in presence of succinic acid, or, better still, with hydrobromic acid in addition, the desired porphyrin (III, as above) was obtained in good yield (35%), unaccompanied by aetioporphyrin. The crude porphyrin was purified through the methyl ester, m. p. 216°, which was converted (1) by ferrous acetate, sodium chloride, and acetic acid into the corresponding iron salt (a haemin), C₃₄H₄₀O₂N₄ClFe (also +IAcOH), (2) by magnesium methyl iodide into the corresponding phyllin, C₃₄H₄₀O₂N₄Mg (compared spectrographically with phyllophyllin), (3) by copper acetate and acetic acid into the copper salt, C₃₄H₄₀O₂N₄Cu, and (4) by concentrated potassium hydroxide in presence of a little pyridine into the free acid (III, as above) (well-defined hydrochloride; copper salt, m. p. 280°). The

properties of the acid are compared in detail with those of phyllo- and pyrro-porphyrin.

Condensation by the succinic acid method of (4-methyl-2-bromomethyl-3-ethylpyrrol)(4'-methyl-2'-bromomethyl-3'- ω -carboxyethylpyrrolenyl)methene hydrobromide with bis-(2-bromo-4-methyl-3-ethylpyrrol)methene hydrobromide gave the *methyl ester* of (I), m. p. 263° (*iron salt*, $C_{34}H_{38}O_2N_4ClFe$).

(2 : 4-Dimethyl-3-ethylpyrrol)(2' : 3'-dimethyl-4'- ω -carbomethoxyethylpyrrolenyl)methene hydrobromide, m. p. 180°, was obtained from methyl hæmopyrrolecarboxylate and cryptopyrrolealdehyde in presence of hydrogen bromide and methyl alcohol, and on bromination afforded (4-methyl-2-bromomethyl-3-ethylpyrrol)-(3'-methyl-2'-bromomethyl-4'- ω -carbomethoxyethylpyrrolenyl)methene hydrobromide, decomp. 225°. The latter, when condensed by the succinic acid method with bis-(2-bromo-4-methyl-3-ethylpyrrol)methene hydrobromide, gave the *methyl ester*, m. p. 207—208°, of (II) ($R^1=[CH_2]_2\cdot CO_2H$, $R^2=Et$), also obtained, but with m. p. 220° (*iron salt*, m. p. 263°, and *phyllin*, m. p. 200°, of the methyl ester), by the succinic acid method from bis-(2-bromo-3-methyl-4-ethyl-5-pyrrol)-methene hydrobromide and (4-methyl-2-bromomethyl-3- ω -carboxyethylpyrrol)(3'-methyl-2'-bromomethyl-4'-ethylpyrrolenyl)methene hydrobromide, obtained by bromination of (2 : 4-dimethyl-3- ω -carboxyethylpyrrol)-(2' : 3'-dimethyl-4'-ethylpyrrolenyl)methene hydrobromide, decomp. 176°, which in turn resulted from the condensation in methyl-alcoholic hydrobromic acid of cryptopyrrolecarboxylic acid with hæmopyrrolealdehyde.

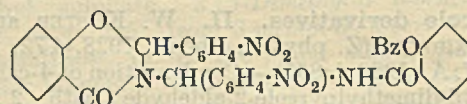
Condensation of (4-methyl-2-bromomethyl-3- ω -carboxyethylpyrrol)(3'-methyl-2'-bromomethyl-4'-ethylpyrrolenyl)methene hydrobromide with bis-(2-bromo-4-methyl-3-ethyl-5-pyrrol)methene hydrobromide gave the *methyl ester* of (II) ($R^1=Et$, $R^2=[CH_2]_2\cdot CO_2H$); this methyl ester, m. p. 238°, depresses the m. p. of the phyllo- and pyrro-porphyrin esters, m. p. 234° and 241°, respectively, and gives an *iron salt*, m. p. 258°.

Methyl hæmopyrrolecarboxylate, condensed with hæmopyrrolealdehyde in methyl-alcoholic hydrobromic acid, affords (2 : 3-dimethyl-4- ω -carboxyethylpyrrol)(2' : 3'-dimethyl-4'-ethylpyrrolenyl)methene hydrobromide, m. p. 185°, giving on bromination (3-methyl-2-bromomethyl-4- ω -carboxyethylpyrrol)(3'-methyl-2'-bromomethyl-4'-ethylpyrrolenyl)methene hydrobromide. The latter undergoes (succinic acid) condensation with bis-(2-bromo-4-methyl-3-ethylpyrrol)methene hydrobromide to give, ultimately, the *methyl ester* of (III) ($R^1=[CH_2]_2\cdot CO_2H$, $R^2=Et$) (*iron salt of ester*, m. p. 254°).

The properties of the various products are compared with those of various derivatives of phyllo- and pyrro-porphyrin. E. E. TURNER.

Condensation products from acid amides and aldehydes. Constitution of the transformation products of the benzometoxazones. E. GLAZER and S. FRISCH (*Arch. Pharm.*, 1928, 266, 103—116).—The investigation of nitro-compounds (Glaser and others, *A.*, 1923, i, 694; 1924, i, 797; 1926, 608) has been extended as follows. By simply being melted together at about 100°, *m*-nitrobenzaldehyde and

salicylamide yield *m*-nitrophenylbenzometoxazone, $C_{14}H_{10}O_4N_2$ (cf. Titherley, *J.C.S.*, 1907, 91, 1419). The condensation is also smoothly carried out in alcoholic solution in presence of a little hydrochloric acid. The product has m. p. 220° (*N*-acetyl derivative, m. p. 116°; *N*-benzoyl derivative, m. p. 173°). When it is treated with a cold solution of potassium hydroxide and acetone, it dissolves and is reprecipitated by acidifying as an amorphous form (m. p. 115—135°) of the "phenolic modification," which is more conveniently obtained, in a crystalline form (m. p. 175°), by use of other solvents, e.g., pyridine. This product solidifies again above its m. p., being reconverted into the true metoxazone, m. p. 220°. Titherley's hypothesis that *syn*- and *anti*-forms of the phenolic form exist is shown to be unfounded: the "phenolic" form is not a true tautomeric modification; it is strictly a dimeride of the formula:



This is very easily dissociated, so that the mol. wt. (in phenol) is intermediate between that of the true metoxazone and that corresponding with the formula given, and is dependent on how long the substance has been heated in phenol solution. The *O*-acetate, $C_{30}H_{22}O_9N_4$, m. p. 187—188° (decomp.), and the *O*-benzoate, $C_{35}H_{24}O_9N_4$, m. p. 161° (decomp.), show similar behaviour in mol. wt. determinations. When attempts are made to methylate the true metoxazone it is converted into the phenolic dimeride. It resists oxidation with chromic anhydride in acetic acid but is disrupted by the action of bromine in glacial acetic acid, yielding dibromosalicylamide.

m-Nitrobenzaldehyde and benzamide condense together in alcoholic solution on addition of a little hydrochloric acid, yielding *m*-nitrobenzylidenedibenzamide, m. p. 224°. The following analogues were obtained in a similar way: *o*-nitrobenzylidenedibenzamide, m. p. 217—218°; *m*-nitrobenzylidenediacetamide, m. p. 236—237°; *o*-nitrobenzylidenediacetamide, m. p. 231—232°. From ethylurethane there were prepared *m*-nitrobenzylidenediurethane, $NO_2\cdot C_6H_4\cdot CH(NH\cdot CO_2Et)_2$, m. p. 192—193°, and *o*-nitrobenzylidenediurethane, m. p. 179°.

W. A. SILVESTER.

isoOxazole ψ -bases and salts. E. P. KOHLER and A. H. BLATT (*J. Amer. Chem. Soc.*, 1928, 50, 1217—1226).—The additive product of 3 : 4 : 5-triphenylisooxazole and methyl sulphate is converted by ferric chloride and hydrochloric acid into 3 : 4 : 5-triphenyl-2-methylisooxazolinium ferrichloride, m. p. 162° (corresponding picrate, m. p. 174°). The yellow bromide (I) (decomposed at a low temperature into triphenylisooxazole and methyl bromide) of this base is formed, together with phenyl $\alpha\beta$ -diphenylstyryl ketone, when 2-methyl-3 : 4-diphenylisooxazolone (this vol., 430) is treated with magnesium phenyl bromide and the product decomposed with hydrobromic acid. It gives a *perbromide*, m. p. 152°, which is debrominated by acetone to a colourless bromide (II). The somewhat ill-defined products (I) and (II), which may represent salts of isomeric oxonium and

ammonium ions, are converted by alkali into an oily ψ -base, $\begin{matrix} \text{CPh:CPh}\cdot\text{O} \\ \text{CPh(OH)}\cdot\text{NMe} \end{matrix}$. The alkaline degradation of less highly substituted isooxazolinium salts (cf. Claisen, A., 1909, i, 185; Mumm and Münchmeyer, A., 1911, i, 79) may be explained by the intermediate formation of similar products. With picric acid the ψ -base forms the above picrate and with sodium methoxide a methyl ether, m. p. 135°. In ethereal solution it passes irreversibly with loss of water into a substance, m. p. 140—141°, tentatively regarded as $\text{CPhBz:CPh}\cdot\text{N}\cdot\text{CH}_2$. This gives, by addition to the double linking, a picrate, m. p. 184°, and a methyl alcohol additive product, m. p. 104°, which are isomeric with the picrate and methyl ether obtained from the ψ -base. It decomposes when kept, liberating formaldehyde, is hydrolysed by acids to dibenzoylphenylmethane, and ozonized to equivalent quantities of benzil and benzoic acid. With magnesium phenyl bromide it forms benzyltriphenylvinylamine, m. p. 134°, which is hydrolysed to dibenzoylphenylmethane and benzylamine. H. E. F. NOTTON.

Formation of thiazole derivatives from thiocyno-amines. H. P. KAUFMANN (Arch. Pharm., 1928, 266, 197—218).—The general method of Kaufmann and Oehring (A., 1926, 392) for the introduction of the thiocyno-group into aromatic amines has been applied to compounds in which the *ortho*-position to the amino-group is unsubstituted. *o*-Thiocynoamines result, which readily change into the corresponding thiazoles. Ethyl *p*-aminobenzoate, sodium thiocyanate, and bromine react in acetic acid solution, giving ethyl 4-amino-3-thiocyanobenzoate, m. p. 97—98°, which affords bis-(2-amino-5-carbethoxyphenyl) disulphide, m. p. 153°, when treated with alcoholic sodium hydroxide solution. The thiocyanogen compound changes quantitatively on keeping an acetic acid solution into ethyl 1-aminobenzthiazole-5-carboxylate, m. p. 241°. The following compounds are obtained in a similar manner: 5-chloro-1-aminobenzthiazole, m. p. 198°; 5-chloro-2-amino-3-methylbenzthiazole, m. p. 206°. *p*-Toluidine furnishes 3:5-dithiocyanop-toluidine, m. p. 123°; 1-amino-5-methylbenzthiazole, m. p. 136°, and 1-amino-3-thiocyano-5-methylbenzthiazole, m. p. 225°; both of these aminobenzthiazoles may be diazotised and coupled with R-salt, giving brown to reddish-brown dyes. 2-Amino- α -naphthathiazole, m. p. 261°, is obtained from 1-thiocyano- β -naphthylamine, whilst *p*-thiocyanoaniline affords 2:4-dithiocyanoaniline, m. p. 107—108°, and 1-amino-5-thiocyanobenzthiazole, m. p. 198°. Other compounds described are 2-amino-5-thiocyano-*p*-xylene, m. p. 65°, bis-(4-amino-2:5-dimethylbenzene) disulphide, m. p. 192°, 1-amino-5-thiocyano-3:6-dimethylbenzthiazole, m. p. 231°, and 2-amino-8-thiocyano- α -naphthathiazole, m. p. 272°. The above-mentioned thiazole derivatives are unchanged by sodium hydroxide or lead tartrate solutions.

S. COFFEY.

Chloroaurates of nucleic bases. F. A. HOPPESEYLER and W. SCHMIDT (Z. physiol. Chem., 1928, 175, 304—309).—Like adenine, guanine and hypoxanthine yield crystalline gold salts, the formation of which, unless accurate analytical data are obtained,

does not serve as a means of differentiating adenine from the other nucleic bases. When hypoxanthine in warm dilute hydrochloric acid solution is treated with an excess of chloroauric acid, a chloroaurate (I), $\text{C}_5\text{H}_4\text{ON}_4\cdot\text{HCl}\cdot\text{AuCl}_3$, m. p. 240—242° (decomp.), is obtained. Addition of the chloroauric acid to a hot concentrated solution in hydrochloric acid yields a second chloroaurate, $\text{C}_5\text{H}_4\text{ON}_4\cdot 2\text{HCl}\cdot\text{AuCl}_3$, m. p. 259—262° (decomp.), which is converted into (I) by crystallisation from dilute hydrochloric acid. Similarly, from guanine in hot concentrated hydrochloric acid solution is obtained the chloroaurate, $\text{C}_5\text{H}_5\text{ON}_5\cdot 2\text{HCl}\cdot\text{AuCl}_3$, m. p. 235—240° (decomp.), which is unchanged by crystallisation (cf. the almost identical composition of the adenine salt $\text{C}_5\text{H}_5\text{N}_5\cdot 2\text{HCl}\cdot\text{AuCl}_3\cdot\text{H}_2\text{O}$). The normal salt could not be obtained pure, owing, apparently, to its extreme solubility and instability. Xanthine similarly yields a very unstable salt which could not be obtained pure.

J. W. BAKER.

[Synthesis of evodiamine.] T. ASAHINA and T. OHTA (Ber., 1928, 61, [B], 869; cf. this vol., 432).—*N*-Methylisatoic anhydride has been described previously by Houben (A., 1909, i, 921).

H. WREN.

Manufacture of soluble salts of ergotoxine. WELLCOME FOUNDATION ETC.—See B., 1928, 348.

Spontaneous resolution of externally compensated mixtures. L. ANDERSON and D. W. HILL (J.C.S., 1928, 993—997).—Fractional crystallisation of atropine sulphate from absolute alcohol gives a product which may contain up to 75% excess of *l*-hyoscyamine sulphate. The partial resolution is not brought about in aqueous alcohol or in methyl alcohol-ethyl acetate mixtures. The phenomenon is ascribed to inoculation of the solution by dust particles from the laboratory atmosphere.

M. CLARK.

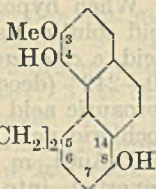
Harmine from a South American liane. O. WOLFES and K. RUMPF (Arch. Pharm., 1928, 266, 188—189).—This paper confirms and amplifies the independent work of Elger (this vol., 311). The harmine isolated was identified by its properties, composition, and by conversion into harmol, m. p. 322°. The plant from which it was isolated appears to belong to the *Malpighiaceæ*. Villalba's results (A., 1925, i, 828) are not confirmed.

W. A. SILVESTER.

Constitution of thebenine. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1928, 921—934).—14-Hydroxycodine is unaffected by boiling hydrochloric acid (*d* 1.07, the strength used in preparation of thebenine). Prolonged heating with acetic anhydride yields no triacetylthebenine, but gives a mixture of two bases, one crystalline, m. p. 304°, and the other amorphous. In consideration of these facts, Schöpf's theory of the formation of thebenine from codeinone (A., 1927, 472) appears to be improbable.

The positions of the methoxyl and hydroxyl groups of thebenine (I) have been determined by Pschorr (A., 1910, i, 423), but the evidence for placing the side-chain in position 5 is inconclusive. Conclusive evidence is now brought forward. 3:4:8-Tri-methoxy-5-vinylphenanthrene (II), obtained by the

complete alkylation and exhaustive methylation of thebenine, is converted by permanganate into 3 : 4 : 8-trimethoxyphenanthrene-5-carboxylic acid (III), m. p. 236—237° (lit. 224—226°), and 5-aldehydo-3 : 4 : 8-trimethoxyphenanthrene (IV), m. p. 151° [semicarbazone, m. p. 243—



246° (decomp.)], termed by Pschorr "oxymethebenol." The methyl ester, m. p. 149—151°, of the acid (III) readily yields the corresponding hydrazide, m. p. 177°, converted by the action of nitrous acid into the azide, which decomposes at 65° on slow heating (it explodes at 80° if suddenly heated) giving the lactone (V), m. p. 246—247°, of 4-hydroxy-3 : 8-dimethoxyphenanthrene-5-carboxylic acid.

The aldehyde (IV) yields an oxime (+ $\frac{1}{2}$ C₆H₆), softening at 140—142°, m. p. 153° (sodium salt), which gives, on dehydration by boiling with acetic anhydride and sodium acetate, 3 : 4 : 8-trimethoxy-5-cyanophenanthrene (VI), m. p. 145—146°, and 3 : 8-dimethoxythebenidine, m. p. 229—230°. The nitrile (VI) is converted, either by boiling with a mixture of hydrochloric and acetic acids or by hydrolysis of the corresponding imino-ester hydrochloride, into the lactone (V). Demethylation of the last-named compound gives the lactone of 3 : 4 : 8-trihydroxyphenanthrene-5-carboxylic acid, decomp. from 305°. The preparation of 3 : 4 : 5 : 8-tetramethoxyphenanthrene for comparison with a synthetic product of known constitution thus proves to be impracticable. Catalytic reduction of (II), however, gives 3 : 4 : 8-trimethoxy-5-ethylphenanthrene, m. p. 112—113°, identical with a specimen prepared from 2-nitroveratraldehyde and 6-methoxy-3-ethylphenylacetic acid. The side-chain is therefore in position 5 and thebenine has the constitution (I). *p*-Ethylanisole is converted by Adams and Levine's method (cf. A., 1924, i, 860) into 6-methoxy-3-ethylbenzaldehyde, b. p. 261—262° (semicarbazone, m. p. 226—227°), which reacts with hippuric acid, sodium acetate, and acetic anhydride, giving 5-keto-2-phenyl-4-(6'-methoxy-3'-ethylbenzylidene)-4 : 5-dihydro-oxazole, m. p. 159°. This azlactone is converted by long boiling with sodium hydroxide solution into 6-methoxy-3-ethylphenylpyruvic acid (VII), m. p. 185°, which reacts with *o*-phenylenediamine, giving 3-hydroxy-2-(6'-methoxy-3'-ethylbenzyl)quinoline, m. p. 184—185°. The sodium salt (+ $\frac{1}{2}$ H₂O), m. p. 184°, of the acid (VII) is oxidised by hydrogen peroxide, giving, on acidification, 6-methoxy-3-ethylphenylacetic acid, m. p. 68—69° (sodium salt), which condenses with 2-nitroveratraldehyde at 100° in presence of acetic anhydride, giving a mixture of trans- α -(6'-methoxy-3'-ethylphenyl)-2-nitro-3 : 4-dimethoxycinnamic acid (VIII), m. p. 193—194° (ammonium salt), and trans-2-nitro-3 : 4-dimethoxycinnamic acid, m. p. 229°. Reduction of (VIII) gives trans- α -(6'-methoxy-3'-ethylphenyl)-2-amino-3 : 4-dimethoxycinnamic acid, m. p. 151—152°, and an aqueous methylalcoholic solution of the diazonium sulphate of this acid yields, on boiling or on addition of copper powder, 3 : 4 : 8-trimethoxy-5-ethylphenanthrene-9-carboxylic acid, m. p. 207°. Elimination of the carboxyl group then gives 3 : 4 : 8-trimethoxy-5-ethylphenanthrene,

identical with that prepared from (II). The following are described : dimethylmethobenine methosulphate, m. p. 283—285° (lit. 268—270°); 2-amino-3 : 4-dimethoxycinnamic acid, m. p. 173—178° (decomp.) [hydrochloride; acetyl derivative, m. p. 253° (decomp.)]; 7 : 8-dimethoxycarbostryl, m. p. 166—168°; the lactone, m. p. 165°, of 8-hydroxy-3 : 4-dimethoxy-5-ethylphenanthrene-9-carboxylic acid (?), m. p. 155—157°.

M. CLARK.

Purification of brucine. F. SAUNDERS (J. Amer. Chem. Soc., 1928, 50, 1231).—Pure brucine is conveniently obtained by slow crystallisation from a solution of the hydrochloride in 20% alcohol rendered alkaline with ammonia. H. E. F. NOTTON.

Organic compounds of arsenic. XI. Action of thionyl chloride on primary and secondary arsinic acids. W. STEINKOPF and S. SCHMIDT (Ber., 1928, 61, [B], 675—678).—Phenylarsinic acid reacts vigorously with thionyl chloride, giving about half the expected quantity of phenyldichloroarsine, $\text{AsPhO}(\text{OH})_2 + 2\text{SOCl}_2 = \text{AsPhCl}_2 + \text{SO}_2\text{Cl}_2 + \text{SO}_2 + \text{H}_2\text{O}$; chlorobenzene and arsenic trichloride are simultaneously produced, $\text{AsPhO}(\text{OH})_2 + 2\text{SOCl}_2 = \text{PhCl} + \text{AsCl}_3 + 2\text{SO}_2 + \text{H}_2\text{O}$. With 1-anthraquinonylarsinic acid only the second type of change is realised, the product being 1-chloroanthraquinone. 1-Anthraquinonyldichloroarsine, m. p. 237°, is prepared by reduction of the acid in the usual manner. Diphenylarsinic acid and thionyl chloride afford diphenylarsenic trichloride, m. p. 191°. Dichloroarsinoacetic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{AsCl}_2$, m. p. 123—125°, is obtained by simultaneous reduction and chlorination from phosphorus trichloride and arsinoacetic acid. The corresponding methyl ester, b. p. 78°/5 mm., is described (cf. Gibson and Johnson, this vol., 311).

H. WREN.

Organic compounds of arsenic. XII. Action of acid chlorides on diphenylarsine. W. STEINKOPF, I. SCHUBART, and S. SCHMIDT (Ber., 1928, 61, [B], 678—682; cf. Job and Reich, A., 1923, i, 873).—Diphenylarsine reacts vigorously with acetyl chloride in an atmosphere of carbon dioxide, giving diphenylacetylarsine, b. p. 167—168°, decomposed by oxygen in presence of water into diphenylarsinic and acetic acids. Under similar conditions, chloro- and bromoacetyl chloride yield, respectively, diphenylchloroarsine and diphenylbromoarsine. Carbonyl chloride, probably by elimination of carbon monoxide from the intermediate compound, $\text{AsPh}_2\cdot\text{COCl}$, affords diphenylchloroarsine, which also results when phosphorus trichloride is used. Benzoyl chloride and diphenylarsine evolve hydrogen chloride and give diphenylarsinic acid. Diphenylarsine and benzenesulphonyl chloride afford diphenylchloroarsine, diphenyl sulphide, and a compound, m. p. 106—108° to a turbid liquid, which becomes clear at 109°; since the compound is obtained more simply and in better yield from diphenylarsinic acid and benzenesulphonyl chloride, it is regarded as the mixed anhydride, $\text{AsPh}_2\text{O}\cdot\text{O}\cdot\text{SO}_2\text{Ph}$. Phenyldichloroarsine and chlorosulphonic acid afford benzenesulphonyl chloride, whereas diphenylchloroarsine with the same reagent yields benzenesulphonyl chloride and the compounds $\text{AsPh}_2\text{O}(\text{OH})\cdot\text{HCl}$ and $2\text{AsPh}_2\text{O}(\text{OH})\cdot\text{HCl}$. Fluoro-

sulphonic acid and diphenylchloroarsine yield benzene-sulphonyl fluoride and the sulphate, $2\text{AsPh}_2\text{O}(\text{OH})_2\text{H}_2\text{SO}_4$, m. p. 117° , more conveniently prepared from diphenylarsinic acid and 50% sulphuric acid. The following esters are incidentally described: *diisoamyl phenylarsinite*, b. p. $173\text{--}176^\circ/11$ mm.; *isoamyl diphenylarsinite*, b. p. $188\text{--}189^\circ/11$ mm.; *isoamyl diphenylthioarsenite*, b. p. $215\text{--}220^\circ/11$ mm.; *allyl diphenylarsinite*, b. p. $280.5\text{--}281.5^\circ/11$ mm.

H. WREN.

Synthesis of 4-amino-3-hydroxyphenylarsinic acid. I. E. BALABAN (J.C.S., 1928, 809—813).—The mixture of 4 nitro- and 6-nitro-chloroacetanilides obtained (cf. Mayes and Turner, this vol., 513) by nitration of *m*-chloroacetanilide yields, on hydrolysis with 25% sulphuric acid, the corresponding chloro-nitroanilines, readily separable by means of their difference in basicity. 3-Chloro-4-nitroaniline undergoes the Bart-Schmidt reaction, giving a 45% yield of 3-chloro-4-nitrophenylarsinic acid, decomp. 200° (barium, calcium, and magnesium salts). This acid is converted on boiling with 25% aqueous sodium hydroxide into 4-nitro-3-hydroxyphenylarsinic acid (magnesium and barium salts), reduced by dextrose to 4-amino-3-hydroxyphenylarsinic acid (I) [acetyl derivative (II) (magnesium and sodium salts)]. The following were also prepared: 2-nitro-4-acetamido-3-hydroxyphenylarsinic acid (calcium, magnesium, and barium salts); 2-nitro-4-amino-3-hydroxyphenylarsinic acid (monohydrate; magnesium salt); 2-amino-4-acetamido-3-hydroxyphenylarsinic acid (diazo-oxide; calcium and magnesium salts), and 2:4-diacetamido-3-hydroxyphenylarsinic acid. When 3-chloro-6-nitrophenylarsinic acid, m. p. 250° (magnesium salt), prepared from 3-chloro-6-nitroaniline, is treated with alkali it undergoes dearsenication, giving *p*-nitrophenol. Reduction of the acid with ferrous sulphate gives 3-chloro-6-aminophenylarsinic acid [calcium and barium salts; acetyl derivative (III) (magnesium salt)], which is converted, on heating with chloroacetamide on the water-bath, into 6-glycineamide-3-chlorophenylarsinic acid (IV), m. p. 195° (decomp.) (magnesium and calcium salts). The following are described: 4-amino-4'-acetamido-3:3'-dihydroxyarsenobenzene, 3:4'-diamino-4:3'-dihydroxyarsenobenzene, 4:4'-diacetamido-3:3'-dihydroxyarsenobenzene, and 3:4'-diacetamido-4:3'-dihydroxyarsenobenzene. The trypanocidal action on infected mice of these compounds, of 4:4'-diamino-3:3'-dihydroxyarsenobenzene, and of compounds (I), (II), (III), and (IV) is described.

M. CLARK.

Triphenylstibine sulphide. O. MAGIDSON [with B. SÜSSKIND] (Trans. sci. chem.-pharm. inst., Moscow, 1923, 6, 21—28; Chem. Zentr., 1927, ii, 2542).—Good yields of triphenylstibine sulphide are obtained by a modification of Michaelis and Reese's method, the time of reaction being shortened, and half the usual quantity of sodium employed.

A. A. ELDRIDGE.

Organic selenium compounds; derivatives of aromatic seleno-ethers. D. G. FOSTER and S. F. BROWN (J. Amer. Chem. Soc., 1928, 50, 1182—1188).—Fuming nitric acid does not nitrate the ethers of selenophenol but converts them into selenoxide nitrates which are ionogenic in aqueous solution.

The selenoxides, liberated by sodium carbonate, yield, with concentrated hydrochloric acid, dialkylselenodichlorides. These are also formed from the dialkyl selenides, (a) by oxidising them with aqueous permanganate and saturating the solution with hydrogen chloride, (b) by treatment with chlorine in ether. The following are described: *phenylmethylselenoxide nitrate*, m. p. 97° ; *phenylmethylselenodichloride*, m. p. 122° (decomp.); *phenyl ethyl selenide*, b. p. $214\text{--}216^\circ$ (dichloride, m. p. $64\text{--}65^\circ$); oily *phenylethylselenoxide nitrate*; *phenyl isoamyl selenide*, b. p. $105^\circ/3$ mm. (dichloride, m. p. 80°); oily *phenylisoamylselenoxide nitrate*, which is converted by sodium carbonate followed by hydrochloric acid into benzeneseleninic acid; *diphenylselenoxide nitrate*, m. p. 97° , and *diphenylselenodichloride*, m. p. 142° (decomp.) (cf. Krafft and Vorster, A., 1894, i, 88).

H. E. F. NOTTON.

Position occupied by acetatomercuric (Hg·OAc) groups in anilines having in the nucleus a halogen group or a hydrocarbon residue. II. L. VECCHIOTTI (Gazzetta, 1928, 58, 181—190; cf. A., 1927, 1098).—The action of mercuric acetate on *m*-bromoaniline in alcohol yields 4-acetatomercuri-3-bromoaniline, m. p. 181° (acetyl derivative, m. p. 215°); the corresponding hydroxymercuri-compound has m. p. 170° , the bromidomercuri-compound, m. p. 215° , and mercury di-*o*-bromo-*p*-aminophenyl, m. p. 185° . The constitution of the acetato-compound is determined by treating it with bromine in acetic acid, when 3:4-dibromoacetanilide, m. p. 158° , hydrolysed to 3:4-dibromoaniline, is obtained. With excess of mercuric acetate in aqueous solution, 2:4:6-tri-acetatomercuri-3-bromoaniline, m. p. 229° (acetyl derivative, m. p. 240° , decomp.), is obtained, which with bromine in acetic acid yields 2:3:4:6-tetra-bromoacetanilide, m. p. 128° , hydrolysed to 2:3:4:6-tetrabromoaniline.

E. W. WIGNALL.

Mercuration of naphthalene derivatives. J. KRYŃSKI (Rocz. Chem., 1928, 8, 71—87).—The following compounds in which mercury is substituted in the nucleus were prepared by the action of a salt of mercury on the appropriate naphthalene derivative: 2:4-diacetatomercuri- α -naphthol, $\text{C}_{10}\text{H}_5(\text{Hg}\cdot\text{OAc})_2\cdot\text{OH}$, m. p. 140° , readily changing into 2-mercuri-4-acetatomercuri-1:2-naphthaquinone, 1-acetatomercuri- β -naphthol, m. p. $168\text{--}170^\circ$, yielding on hydrolysis 1-mercuri-1:2-naphthaquinone, acetatomercuric 4-nitro- α -naphtholate, 2-acetatomercuri-4-nitro- α -naphthol, m. p. 142° , yielding on iodination 2-iodo-4-nitro- α -naphthol, m. p. 115° (decomp.), 4-acetatomercuri-2-nitro- α -naphthol, m. p. 185° (decomp.), 1-acetatomercuri-2-ethoxynaphthalene, m. p. $103\text{--}104^\circ$, 1-acetatomercuri-2-bromonaphthalene, m. p. $128\text{--}130^\circ$, N-mercuri- α -naphthylamine, $\text{C}_{10}\text{H}_7\cdot\text{N}\cdot\text{Hg}$, m. p. 203° (decomp.), 1:1'-diacetatomercuri-2:2'-dinaphthylamine, m. p. 198° , and the corresponding 1:1'-di-iodo-derivative, m. p. $165\text{--}166^\circ$ (decomp.). Mercuration of naphthols, nitronaphthols, naphthyl ethers, and amines proceeds more readily than that of chloronaphthalenes. The mercury always occupies the *ortho*- and *para*-positions, never the *meta*-position; in this way mercury behaves as a halogen. The tenacity with which mercury is retained by the nucleus depends on other

substituents already present; thus the nitro-group produces a stabilising influence as compared with the hydroxy-group.

R. TRUSZKOWSKI.

Salt formation of chromium pentaphenyl hydroxide, $\text{CrPh}_5\cdot\text{OH}$. F. HEIN [with O. SCHWARTZKOPFF, K. HOYER, H. KLAR, W. EISSNER, and W. CLAUSS] (Ber., 1928, 61 [B], 730—753).—The production of salts from chromium pentaphenyl hydroxide has been examined with numerous acids and phenols, whereby in part chromium pentaphenyl and in part chromium tetraphenyl salts are obtained. The strength of the acid has some influence on the production of the penta- or tetra-phenyl salts, but is certainly not the sole decisive factor. The fate of the phenyl group, if eliminated, has not been ascertained. *Chromium pentaphenyl hydrogen carbonate*, $\text{CrPh}_5\text{HCO}_3\cdot 3\text{H}_2\text{O}$, m. p. 120° (also *di-* and *mono-hydrate*), is prepared by saturating a methyl-alcoholic solution of the base with carbon dioxide. With acetic acid in water or chloroform the hydroxide affords *chromium pentaphenyl acetate tetrahydrate*, m. p. 118° (also *dihydrate*); an *acid acetate*, $\text{CrPh}_5\cdot\text{OAc}\cdot\text{AcOH}$, m. p. 108 — 110° , and a *basic salt*, m. p. 51 — 53° after softening at 45° , are also described. Monochloroacetic acid yields a *chromium pentaphenyl salt* (trihydrate, m. p. 103° , and anhydrous), whereas dibromomalonic acid smoothly yields *chromium tetraphenyl hydrogen dibromomalonate*, m. p. 88.5° . *Chromium tetraphenyl hydrogen oxanilate*, m. p. 141° , *acid α -chlorophenylacetate*, m. p. 118° , and *acid α -bromocinnamate*, m. p. 127° , are described. Equivalent amounts of the pentaphenyl hydroxide and benzoic acid in chloroform afford *chromium tetraphenyl benzoate trihydrate*, m. p. 99° , whilst with excess of acid the corresponding *acid benzoate dihydrate*, m. p. 84° , is obtained. Anthranilic acid, on the other hand, affords *chromium pentaphenyl acid anthranilate*, m. p. 141 — 142° . From *p-* and *m-*aminobenzoic acid the *salts* $3\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CrPh}_4\cdot 2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 141° , and $2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CrPh}_4\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 130° , are derived. *N*-Phenylanthranilic acid differs from the parent acid in giving the *chromium tetraphenyl salt*, $2\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CrPh}_4\cdot\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 105° . *Chromium tetraphenyl o-chlorobenzoate*, m. p. 107° after blackening at 104° , the *m-bromobenzoate*, $2\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\cdot\text{CrPh}_4\cdot\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, m. p. 97° , *chromium tetraphenyl m-nitrobenzoate*, m. p. 90° , and the corresponding *acid 3:5-dinitrobenzoate*, blackening above 149° , are described. *Chromium tetraphenyl acid 5-nitrosalicylate* has m. p. 132° . *Chromium pentaphenyl sulphate tetrahydrate* (also anhydrous, m. p. 130° , and $+3\text{COMe}_2$, m. p. 143 — 144°) is prepared from the reactants in alcoholic solution. On the other hand, sulphonic acids give *chromium tetraphenyl salts* of which the *1:2:3:4-tetrahydronaphthalene-2-sulphonate*, m. p. 131° (decomp.), and the *azobenzene-p-sulphonate monohydrate*, m. p. 167° (decomp.), are described. *Chromium tetraphenyl sulphanilate*, m. p. 90° , and the *compound* $\text{CrPh}_4\text{Cl}\cdot 0.5\text{CHCl}_3$, m. p. 118° , are described incidentally.

Phenol in absolute alcoholic solution gives the *compound* $\text{CrPh}_5\cdot\text{OPh}\cdot\text{PhOH}$, m. p. 127° , whereas in aqueous alcohol abnormal salt formation occurs with

production of the *substance* $\text{CrPh}_4\cdot\text{OPh}\cdot\text{PhOH}$, m. p. 145° , identical with the product of the action of an excess of phenol on chromium tetraphenyl hydroxide. *m*-Chlorophenol and chromium pentaphenyl hydroxide in absolute alcohol afford the *compound*

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{O}\cdot\text{CrPh}_5\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, m. p. 112.5 — 113° , which when crystallised from a mixture of alcohol and acetone or submitted to protracted washing with ether gives the *tetraphenyl derivative*,

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{O}\cdot\text{CrPh}_4\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, m. p. 129.5 — 131° , thus illustrating the influence of the solvent on the course of the change. *p*-Cyanophenol and *m*-nitrophenol give the *chromium pentaphenyl salts*,

$2\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CrPh}_5\cdot\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 123.5° , and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CrPh}_5\cdot\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 86° , whereas all the other phenols investigated afford chromium tetraphenyl derivatives. From *o-* and *p*-nitrophenol the *compounds* $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CrPh}_4$, m. p. 130° , and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CrPh}_4\cdot\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 134° , are obtained, whereas *p*-bromophenol affords the salt $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{CrPh}_4\cdot\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$, m. p. 121° . Pyrocatechol, resorcinol, and quinol afford sparingly soluble, well-crystallised *salts*,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CrPh}_4\cdot\text{C}_6\text{H}_4(\text{OH})_2$, m. p. 153.5° , 180 — 181° , and 206° (decomp.) after softening, respectively. 3-Nitropyrocatechol and 2-nitroquinol give *compounds*,

$\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{O}\cdot\text{CrPh}_4$, m. p. 157° and decomp. 175° , whereas 2-nitroresorcinol yields the *substance* $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{O}\cdot\text{CrPh}_2)_2\cdot 2\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, m. p. 162.5° (decomp.). *Chromium tetraphenyl o-nitro-p-tolylloxide* has m. p. 135° . 2:6-Dinitrophenol affords the normal *salt*, m. p. 160° (violent explosion), whereas dibromoquinol yields the *compound*

$\text{C}_6\text{H}_2\text{Br}_2(\text{O}\cdot\text{CrPh}_4)_2\cdot\text{C}_6\text{H}_2\text{Br}_2(\text{OH})_2$, m. p. 184 — 185° . 2:4:6-Tribromophenol and picrolonic acid give the *substances* $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{O}\cdot\text{CrPh}_4$, m. p. 153° , and $\text{C}_3\text{H}_2\text{O}_5\text{N}_4\text{Cr}$, m. p. 176° .

The chloroform layer obtained during the preparation of chromium pentaphenyl hydroxide is repeatedly shaken with water, dried over potassium carbonate, and evaporated over paraffin in a vacuum. The residue is treated with ether and extracted with alcohol. After removal of ionic halogen by silver hydroxide, stable alcoholic solutions remain which are used in the preparation of the following salts: *dibromogallates*, $(\text{OH})_3\text{C}_6\text{Br}\cdot\text{CO}_2\cdot\text{CrPh}_5$ and $(\text{OH})_3\text{C}_6\text{Br}\cdot\text{CO}_2\cdot\text{CrPh}_4$, and the *compound* $[(\text{CNS})_4\text{Cr}(\text{NH}_3)_2]\text{CrPh}_5\cdot\text{Et}_2\text{O}$. H. WREN.

Synthesis of dipeptide anhydrides containing arginine. M. BERGMANN and H. KÖSTER (Z. physiol. Chem., 1928, 173, 259—267; cf. A., 1927, 755).—*d*-Phenylalanyl-*d*-arginine anhydride has been prepared from the salicylaldehyde compound of *d*-phenylalanyl-*d*-arginine and also by the action of methyl-alcoholic ammonia on the ester hydrochloride of the dipeptide, as the *hydrochloride*, m. p. 261 — 262° , *sulphate*, m. p. 270° , and *picrate*, m. p. 246° . *d*-Phenylalanyl-*d*-arginine anhydride is readily hydrolysed by alkalis and in aqueous solution it undergoes "auto-hydrolysis" due to the alkalinity of its guanidine group; the hydrolysis can be prevented by the addition of 1 mol. of hydrochloric acid. Free arginine has a similar hydrolytic action on aqueous solutions of glycine anhydride. The possible influence of the

arginine present in proteins containing diketopiperazine structures on the hydrolysis of these proteins in aqueous solution is discussed. Inactive *phenylalanyl-arginine anhydride* has been prepared as the *hydrochloride*, m. p. 242°.

A. WORMALL.

Preparation of *l*-histidine from protein. J. KAPFFHAMMER and H. SPÖRER (Z. physiol. Chem., 1928, 173, 245—249).—The "Reineckate" method (cf. this vol., 527, 542) has been utilised for the preparation of *l*-histidine, which forms a relatively insoluble "Reineckate," the solubility of this compound being between those of the similar compounds of *l*-proline and *l*-hydroxyproline. The protein (hæmoglobin etc.) is hydrolysed by acid, the arginine precipitated as flavianate, and the filtrate treated with "Reinecke" acid, whereby the "Reinecke" compounds of *l*-histidine, *l*-proline, and *l*-hydroxyproline are precipitated. To remove the "Reinecke" acid the precipitate is treated with copper sulphate and sulphur dioxide in methyl-alcoholic solution, the filtered solution is freed from copper, sulphuric acid, and chromium, and after concentration in a vacuum, *l*-histidine is precipitated as the insoluble picrolonate, leaving *l*-hydroxyproline and *l*-proline in solution; the proline is then separated as the double salt with cadmium chloride. 12.2 g. of histidine hydrochloride, 5.9 g. of the proline-cadmium chloride compound (corresponding with 2.17 g. of proline), and 4.0 g. of hydroxyproline have been obtained from 250 g. of hydrolysed hæmoglobin. The properties of *histidine* "Reineckate," $C_6H_9N_3O_2 \cdot 2C_4H_7N_6S_4Cr \cdot 4H_2O$, decomp. 220°, are given.

A. WORMALL.

Behaviour of polypeptides and their derivatives towards alkalis and acids. V. Polypeptides built up from glycine. E. ABDERHALDEN and S. SUZUKI (Z. physiol. Chem., 1928, 173, 250—258).—Tetraglycylglycine, pentaglycylglycine, and heptaglycylglycine are hydrolysed by *N*-hydrochloric acid at 16° and more quickly at 37°, but the hydrolysis by *N*-sodium hydroxide is more marked, a result similar to that obtained previously with glycylglycine, diglycylglycine, and triglycylglycine (this vol., 81). Measurements of the rate of hydrolysis by 0.5*N*- and *N*-sodium hydroxide of these polypeptides and their benzoyl and β -naphthalenesulphonyl derivatives show that the velocity of the hydrolysis increases with the length of the chain or with the introduction of the benzoyl group; the benzoyl group has a greater accelerating effect than the addition of one glycine molecule to the chain, whilst the β -naphthalenesulphonyl group has an inhibitory effect. Tetraglycylglycine is hydrolysed at 37° in concentrations of alkali as low as p_H 9.16 and to a slight extent at p_H 8. The preparation of the benzoyl and β -naphthalenesulphonyl derivatives of triglycylglycine, tetraglycylglycine, and pentaglycylglycine is described.

A. WORMALL.

Tetrapeptide from gliadin. R. NAKASHIMA (J. Biochem. Japan, 1927, 7, 441—446).—A tetrapeptide composed of tyrosine (1 mol.) and glutamic acid (3 mols.) was completely hydrolysed by erepsin, but not by trypsin.

CHEMICAL ABSTRACTS.

Porphyryns. XIV. Addition of halogen to hæmin. W. KÜSTER and H. BOSCH. XV. Por-

phyrin formation from monoethylated hæmins. W. KÜSTER and R. FLEISCHMANN (Z. physiol. Chem., 1928, 172, 72—97, 98—125; cf. A., 1927, 980).—XIV. The action of aniline on acetic acid-hæmin differs from that of pyridine, and the solution of the hæmin in pyridine gives a hæmochromogen spectrum, whilst the aniline solution gives a hæmatin spectrum. Addition of bromine to de(hydrochloride)hæmin results in the elimination of hydrogen bromide and the formation of *dibromohæmin bromide*, $C_{34}H_{30}O_4N_4Br_3Fe$; this product by the action of hydrogen bromide and acetic acid and subsequent treatment with methyl alcohol yields the same dimethyl ether of dibromohæmatoporphyrin (no definite m. p.) as that produced from dibromodimethylhæmin bromide. Acetic acid-hæmin consists of a double molecule which is dissociated by pyridine into radical molecules and the iron tends to go to the ferrous state, as shown by the hæmochromogen spectrum, whilst there is wandering of the pyridinium structure ($C_5H_5NCl \cdot Fe <$) formed from pyridine and the chloroferri-group to the radical position. The different action of aniline is explained as the decomposition of the double molecule with the addition of a hydrogen atom to each portion; in addition, aniline has a reducing action, the aniline being thereby oxidised to dianilinoquinoneanil. Aniline subsequently attaches itself to the chloroferri-group and to the lactone group; if the aniline solution is treated with dilute acetic acid, formation of the carboxyl and free hydroxyvinyl groups occurs. The relationship between these differences in the action of aniline and pyridine and the lactone structure of hæmin is discussed.

XV. Experiments made to determine the constitution of the prosthetic group of hæmoglobin indicate that isomerides of acetic acid-hæmin, monomethylated and dimethylated hæmins exist. Three preparations of monoethylhæmin chloride obtained by different methods have been examined and compared. The first, prepared from the blood of a horse inoculated with glanders, is soluble in chloroform, is not methylated by diazomethane, and is insoluble in 5% sodium hydroxide at the ordinary temperatures, although on digestion with this alkali 71% of the chlorine is removed. In chloroform solution 2 atoms of chlorine can be added (without substitution), and this dichloroethylhæmin chloride, on decomposition with hydrogen bromide and acetic acid and treatment with methyl alcohol, yields a *dimethyl ether* of *chlorohæmatoporphyrin*, $C_{36}H_{38}O_6N_4Cl$ (complex zinc salt), which on treatment with diazomethane takes up two methyl groups. It is concluded that addition of chlorine to the vinyl group of the hæmin occurs and that the second side-chain retains its lactone structure until the treatment with hydrogen bromide. A second ethylhæmin chloride, prepared from the same blood by a modified method, is soluble in chloroform, soluble in cold sodium hydroxide, and insoluble in sodium hydrogen carbonate, whilst 64% of the chlorine is removed by treatment with the latter; on long treatment with diazomethane one methyl group is added. The porphyrin derivative prepared from it is a mixture of the dimethyl ether of chlorohæmatoporphyrin and the dimethyl ether of chlorobromomesoporphyrin, $C_{36}H_{40}O_6N_4ClBr$, these being separ-

ated as the zinc salts. A betaine structure is suggested for this second ethylhæmin chloride. From the same blood a third ethylhæmin chloride can be obtained by making the sulphuric acid-ethyl alcohol extract of the blood alkaline with alcoholic potassium hydroxide, extracting the precipitate with acidified alcohol, and precipitating from the boiling extract with hydrochloric acid. Of the crude product 75% is soluble in chloroform and this portion is soluble in sodium hydroxide, insoluble in sodium hydrogen carbonate (in which it loses 65% of its chlorine), and is slowly monomethylated by diazomethane; addition of chlorine occurs without substitution to give a crystalline dichloroethylhæmin chloride. The porphyrin preparation obtained by the method used before is the same mixture as is obtained from the second hæmin derivative, with, however, more of the dimethyl ether of chlorobromomesoporphyrin. By the action of hydrogen bromide and acetic acid on a preparation obtained by decomposition of coagulated blood-corpuscles with methyl alcohol at 180°, a mixture of a porphyrin and proline is obtained. No combination of proline and hæmochromogen occurs in an atmosphere of carbon monoxide. A. WORMALL.

Natural porphyrins. XXII. Hæmin obtained from yeast. H. FISCHER and F. SCHWERDEL (*Z. physiol. Chem.*, 1928, 175, 248—260).—The presence of hæmin, identical with that obtained from animal origin, has been demonstrated in a vegetable organism by its isolation, using special experimental precautions, from yeast. The yeast is first plasmolysed for 48 hrs. with salt solution and then extracted with a mixture of pyridine and ether until 80% of the hæmin present has been removed. The filtered solution, which exhibits an intense hæmochromogen spectrum, is extracted with water. Removal of the pyridine from the aqueous layer by extraction with ether causes the precipitation of a flocculent material. The first fraction of the precipitate is yellowish-brown and gives a negative Teichmann reaction, but the main fraction is brownish-violet and gives an intense hæmochromogen spectrum and a typical positive Teichmann reaction. This precipitate is heated with acetic acid and salt and, after 24 hrs., the separated solid is filtered and extracted with a pyridine-chloroform mixture. After repetition of this process of purification a crystalline specimen of hæmin, identical in physical and chemical properties with animal hæmin, is obtained. It is considered probable that some of the hæmin exists in the yeast in the free state, whilst a portion is combined with albumins and is liberated by the yeast enzymes during the (necessary) prolonged period of plasmolysis. In some cases a by-product is obtained which, from spectroscopic evidence, appears to be a tin salt of protoporphyrin. The proportion of coproporphyrin and protoporphyrin formed in the autolysis of yeast depends on the hydrogen-ion concentration. When alkali is used much coproporphyrin and no protoporphyrin is obtained, whilst with acids very little of the former and much of the latter is produced, the proportion of hæmin being the same in each case. J. W. BAKER.

Blood pigments. IV. W. KÜSTER and K. KIMMICH (*Z. physiol. Chem.*, 1928, 172, 199—224).—It

has been shown (*Chem. Zelle Gewebe*, 1926, 13, 66) that hæmogoblin contains a sterol as an integral constituent, the quantity of free sterol isolated together with steryl esters in the preparation of hæmin being greater from blood-corpuscles than from total blood of the same animal.

Purified, crystalline oxyhæmoglobin, freed from uncombined sterol by ether extraction at 15°, undergoes alteration when extracted for 24 hrs. with boiling, dry ether, being no longer completely soluble in water but containing, with unchanged oxyhæmoglobin, soluble methæmoglobin and insoluble cathæmoglobin; sterol is liberated during this process, and also during the subsequent separation of the methæmoglobin by coagulation at 55°, and of the oxyhæmoglobin at 70°. The crude sterol in each case contains an oxidised sterol, m. p. 240—241°. The structural relationship between hæmoglobin and methæmoglobin is discussed in the light of these facts.

The preparation of oxy- and met-hæmoglobins, the fission of crystallised hæmoglobin by diazomethane in chloroform, and by hydrochloric acid, and the fission of crystallised oxyhæmoglobin by ether and by water in a closed vessel, are detailed.

C. HOLLINS.

Blood. V. Isomeric non-alkylated hæmins. W. KÜSTER [with A. JOB and M. GREISS] (*Z. physiol. Chem.*, 1928, 172, 138—158).—Chlorohæmin has been prepared from ox-blood, horse-blood, and cow's blood by various methods. Older animals give a larger yield than young animals, possibly due to the presence in the former of more readily decomposable hæmoglobin. Acetone-chlorohæmin crystallises in two forms at least—needles and Teichmann's crystals—and from the differences in the properties of the various preparations obtained it is suggested that at least four modifications of the isomeric substances of formula $(C_{34}H_{29}O_4N_4FeCl)_2$ exist. This would be possible on the assumption of a betaine structure (cf. A., 1926, 315) or a lactone structure, whilst if hæmin exists as a double molecule (which is highly probable) the number of possible isomerides is even larger. The results of experiments with diazomethane indicate that besides methylation other changes usually occur which render the methylated hæmins non-crystallisable. Aniline has an action similar to that of pyridine on the chloroferri- and the lactone groups, but no dissociation of the double molecule occurs with the former solvent. The significance of the differences in the action of these two bases and the possible structures of the chlorohæmins are discussed. A. WORMALL.

Fluorohæmin. W. KÜSTER and O. NEUNHÖFFER (*Z. physiol. Chem.*, 1928, 172, 179—181).—Monoethyl(chloro)hæmin, prepared by the glacial acetic acid method, is suspended in acetone and boiled with excess of aqueous silver fluoride. After removal of silver chloride by filtration, *monoethyl-fluorohæmin*, $(C_{34}H_{29}O_4N_4FFe)_2$, is obtained from the acetone solution as a black, indistinctly crystalline power, showing an absorption band at 605—630 μ .

C. HOLLINS.

Bromoporphyrin I and tetramethylhæmatoporphyrin iron salt. II. H. FISCHER and G.

HUMMEL (Z. physiol. Chem., 1928, 175, 75—96; cf. A., 1927, 886).—Bromination of tetramethylhæmatoporphyrin iron salt in chloroform gives a crystalline product identical with the complex iron salt of the ester of bromoporphyrin I, which yields bromoporphyrin I on removal of iron by sulphuric acid, hydrobromic-acetic acid, or hydriodic-acetic acid, and on oxidation bromocitraconimide, m. p. 178°. The identity of the bromoporphyrin I is confirmed by preparation of the methyl ester, m. p. 277°, and its copper salt, m. p. 283° (sometimes 272°), and iron salt, m. p. 295°; oxidation of the ester gives hæmatic acid, m. p. 114°. The bromine in bromoporphyrin I is not removed by 5% potassium hydroxide at 140°, potassium methoxide at 180°, or hydrobromic-acetic acid at 180°. Bromoporphyrin I results when tetramethylhæmatoporphyrin is brominated in acetic acid.

By the action of methyl-alcoholic hydrogen chloride on hæmin, or hæmin crystallised from acetic anhydride, there are formed tetramethylhæmatoporphyrin and its iron salt, methyl alcohol being added at the side-chain double linking. Tetramethylhæmatoporphyrin iron salt is converted by hydrobromic-acetic acid at 180° into mesoporphyrin methyl ester, m. p. 204°. Protoporphyrin reacts with methyl-alcoholic hydrogen chloride more slowly than hæmin. Oxidation of protoporphyrin with permanganate yields a new porphyrin.

C. HOLLINS.

Crystallisation of casein. S. S. PEROV (Trans. Volgoda Dairy Inst., 1925, Bull. 50, 1—15).—Casein from milk (100 c.c.) and acetic acid (10%, 5 c.c.) is collected, washed with water, alcohol, and ether, and then precipitated from alkaline solution (1 g. and 8.2 c.c. of 0.1*N*-sodium hydroxide) with acetic acid (2 c.c. of 10% acid for 1 g. of soluble sodium salt), washed with alcohol, then with ether, and dried at 45°. Of this substance (equivalent weight 1220), 0.081 g. is dissolved in 0.68 c.c. of 0.1*N*-sodium hydroxide and diluted to 500 c.c., and 500 c.c. of *N*/7500 hydrochloric acid are added, with stirring. Several drops of toluene are added, and the solution is left in the dark for 9—10 days. Monoclinic and triclinic crystals are obtained.

CHEMICAL ABSTRACTS.

Products of oxidation of keratin by permanganate. II. T. LISSIZIN (Z. physiol. Chem., 1928, 173, 309—311).—Acid hydrolysis of a product formed by the oxidation of keratin (human hair) by potassium permanganate yields *dl*-cysteic acid.

A. WORMALL.

Proteins. IV. Hypobromite reaction with amino-acid derivatives. P. BRIGL, R. HELD, and K. HARTUNG (Z. physiol. Chem., 1928, 173, 129—154).—The ability of the following amino-acid derivatives to react with hypobromite has been tested: δ -benzamidovaleric acid, *dl*-ornithuric acid, δ -benzoylornithine, barium carbamylacetate, glycylglycinecarboxylic acid, barium carbamate of glycylglycine, carbonylbisglycylglycine, *N*-carbamyl-leucine, 5-*n*-butylhydantoin, creatine, creatinine, arginine, dibenzoylarginine, and ϵ -guanido-*n*-hexoic acid. The results are given in tabular form, particular attention being paid to the rapid uptake, during some 10—15 min., of hypobromite. Acylation of the amino-

group, even with carbonic acid, prevents the uptake of hypobromite, exceptions to this rule being substituted carbamides, such as carbonylbisglycylglycine and leucineuraminic acid. The guanido-group reacts with hypobromite unless acylated. The results are discussed in regard to the modes of linking of amino-acids in the protein molecule.

H. D. KAY.

Basic proteins and their development. A. KOSSEL and E. G. SCHENCK (Z. physiol. Chem., 1928, 173, 278—308).—Protamines may be classified as mono-, di-, and tri-protamines according to the nature of the hexone bases present; cyprinin which contains arginine and lysine is a diprotamine, as is percine which contains arginine and histidine. Most of the known histones contain all three hexone bases. It is suggested that a third group of basic proteins should be added, "basic peptones," which, like the protamines, are to be classified as mono-, di-, and tri-peptones according to the hexone bases present. These basic peptones contain no sulphur or phosphorus, but contain hexone bases which account for 25—65% of the total nitrogen; they differ from the protamines and histones in giving no precipitate with ammoniacal protein solution, potassium ferrocyanide, or sulphosalicylic acid. They are digested to some extent by pepsin, yielding basic peptones with a different composition from that of the original product. Carp sperm contains a protamine (cyprinin), basic di- and tri-peptones, and in one preparation a cyprohistone, all of which have been examined and analysed; on digestion with pepsin, the histone yields products intermediate between histones and basic peptones, whilst the basic dipeptones yield products (basic peptones) which are less rich in bases. Similar investigations have been carried out with herring sperm, and several clupeins, basic clupeodipeptones, and a small amount of clupeotripeptone separated. Barbel sperm, but not salmon or sturgeon sperm, yields basic peptones. Trout sperm contains a monoprotamine ("truttin") which may be identical with salmin. The sperm of the carp at different stages in ripening of the testes has been examined to determine the relationship between the different groups of basic proteins. From February to May there is a marked decrease in the basic peptones, with a decrease in the hexone base content of these proteins. The relationship between the basic proteins of carp sperm and the history of the development of these proteins are discussed.

A. WORMALL.

Scleroproteins. R. O. HERZOG (Helv. Chim. Acta, 1928, 11, 529—533).—A lecture delivered to the Swiss Chemical Society.

H. BURTON.

Physico-chemical analysis of changes in proteins by heat. Reversibility of albumin denaturation. M. SPIEGEL-ADOLF (Naturwiss., 1927, 15, 799—803; Chem. Zentr., 1927, ii, 2316).—Heat-treatment of globulin affects the terminal amino- and carboxyl groups; the peptide linkings are modified to a small extent only. The effect of heating on the solubility in alkali and reprecipitation on neutralisation of globulin, serum-albumin, and ovalbumin is discussed. Ring-closure is more probable than hydrolysis.

A. A. ELDRIDGE.

Determination of the equivalent weight of proteins. A. E. STEARN (*J. Gen. Physiol.*, 1928, 11, 377—389).—Results are given of experiments indicating that the same amount of 0.1*N*-acid is equivalent to 1 g. of gelatin whether the gelatin is titrated with acid or the acid with gelatin. In the case of gelatin and sodium hydroxide, a slightly higher equivalent weight for gelatin is obtained when titrating base with protein than when protein is added to base. From this it is concluded that in the case of gelatin, the reactions are due to chemical neutralisation, and any adsorption of acid or alkali is negligible.

E. A. LUNT.

Determination of diamino-nitrogen in the products of hydrolysis of proteins. J. C. KERNOT and J. KNAGGS (*Biochem. J.*, 1928, 22, 528—534).—The percentage of nitrogen precipitated by phosphotungstic acid from the products of hydrolysis of a protein depends on the concentration of nitrogen in the solution, the conditions of precipitation, such as temperature, the concentration of the acid used for the hydrolysis of the protein, and the period of contact of the protein with the cold acid before hydrolysis.

S. S. ZILVA.

Variation of the Carius method for sulphur determination. V. C. ROGERS and G. DOUGHERTY (*J. Amer. Chem. Soc.*, 1928, 50, 1231—1232).—The amount by which the rate of oxidation of sulphonal by nitric acid (*d* 1.60) is accelerated by the addition of equivalent amounts of bromine, barium bromide, barium nitrate, barium chloride, and sodium chloride increases in the order given. Accordingly, the use with difficultly oxidisable substances of 0.3—0.4 g. of sodium or potassium chloride and 3 c.c. of nitric acid is recommended.

H. E. F. NOTTON.

Micro-phosphorus determination. A. ELEK (*J. Amer. Chem. Soc.*, 1928, 50, 1213—1214).—A rapid and accurate modification of Lieb's method (*cf.* A., 1924, ii, 781). The substance (3—6 mg.) is oxidised to phosphate by fusion with potassium hydroxide and nitrate in a platinum crucible. Results are given for some nucleic acid derivatives.

H. E. F. NOTTON.

Unification of bromination methods of analysis as applied to phenols and aromatic amines. A. R. DAY and W. T. TAGGART (*Ind. Eng. Chem.*, 1928, 20, 545—547).—Koppeschaar's bromination method for the determination of phenols and aromatic amines, in which an excess of bromine is used and the excess determined by addition of potassium iodide and titration with sodium thiosulphate, is, when applicable, more satisfactory than direct titration with potassium bromate. A general procedure for the excess method is described and good results were obtained with phenol, *o*-, *m*-, and *p*-nitrophenols, 2:4-dinitrophenol, *p*-chlorophenol, salicylic acid, *m*-hydroxybenzoic acid, methyl salicylate, acetylsalicylic acid, phenyl salicylate, *m*- and *o*-cresols, resorcinol, β -naphthol, thymol, aniline, *p*-chloroaniline, *o*- and *m*-nitroanilines, acetanilide, sulphanilic acid, metanilic acid, anthranilic acid, *m*-aminobenzoic acid, and *o*-, *m*-, and *p*-toluidines.

E. H. SHARPLES.

Determination of tannic acid. S. KRISHNA and N. RAM (*Ber.*, 1928, 61, [B], 771—781).—Tannic acid

may be determined by adding to its aqueous solution an excess of titanium chloride, removal of the precipitated *titanium tannate*, $\text{TiO}(\text{C}_{14}\text{H}_{10}\text{O}_9)$, in an atmosphere of carbon dioxide, and titration of the excess of titanium chloride by ferric alum; precipitation is incomplete at 22°, but becomes quantitative at 40—50°. Gallic, salicylic, mandelic, and other hydroxy-acids yield precipitates with titanium chloride, but these can be retained in solution without affecting the precipitated titanium tannate if hydrochloric acid within certain limits of concentration is added. On the assumption that the mol. wts. of the technical tannins are all approximately equal, the method can be applied to the determination of tannins in extracts of *Acacia Arabica* and myrobalans if similar precautions with regard to the concentration of hydrochloric acid are taken. Comparison with the hide powder method shows that the latter indicates only 90% of the tannic acid present and is seriously affected by the simultaneous presence of gallic acid.

H. WREN.

Determination of phenylalanine by an oxidative method. G. KOLLMANN (*Biochem. Z.*, 1928, 194, 1—14).—A method is described for the determination of phenylalanine by oxidation to benzoic acid with potassium dichromate in acid solution. Using pure phenylalanine or adding it to the protein hydrolysate, the method gave a mean determination of 95.2%. The phenylalanine contents of the following proteins are: caseinogen, 3.10%; fibrin, 2.11%; edestin, 3.47%; haemoglobin, 3.57%; zein, 6.57%; legumin, 5.10%; gelatin, 0.24%. The nitrogen is almost entirely liberated as ammonia. By oxidation of caseinogen, about 17% of the carbon is left in the form of volatile acids, chiefly isovaleric acid, 7% as succinic acid, 32% as carbon dioxide; oxalic and other acids are also present. For complete oxidation, however, the amount of dichromate used only corresponds with about one third of that necessary to oxidise it completely to carbon dioxide, ammonia, and water.

P. W. CLUTTERBUCK.

Alkalimetric determination of amino-acids and peptides by the method of Willstätter and Waldschmidt-Leitz. E. TAKAMIYA (*Bull. Agric. Chem. Soc. Japan*, 1927, 3, 66—67).—Temperature and dilution are without influence. Alcoholic solutions of amino-acids do not react as acids towards either rosolic acid or *p*-nitrophenol. Acids and alkalis depress the titration values, the depression being the greater the lower is the concentration of alcohol. Manganese and magnesium salts must be absent.

CHEMICAL ABSTRACTS.

Identification of organo-magnesium halides by crystalline derivatives prepared from α -naphthylcarbimide. H. GILMAN and M. FURRY (*J. Amer. Chem. Soc.*, 1928, 50, 1214—1216).—Small quantities of Grignard reagents and similar organo-metallic derivatives may be rapidly identified by means of α -naphthylcarbimide. The resulting acyl- α -naphthylamines are usually easily separated from *s*-di- α -naphthylcarbamide. In this way *hexahydrobenzoyl*-, m. p. 188° (uncorr.); *phenylacetyl*-, m. p. 166°; *cinnamoyl*-, m. p. 217°; *p-toluoyl*-, m. p. 173°;

and α -naphthoyl-, m. p. 236°, α -naphthylamines have been prepared. H. E. F. NOTTON.

Volumetric determination of carbamide by oxidation of xanthylcarbamide. H. CORDEBARD (Bull. Soc. Chim. biol., 1928, 10, 461—471).—When xanthhydrol is added to a boiling aqueous solution of sulphuric acid and potassium dichromate, it is partly converted into xanthane, which volatilises and escapes oxidation. By preliminary treatment at the ordinary temperature with the oxidising agent only xanthone is obtained, and this, on boiling the solution, is

quantitatively oxidised to carbon dioxide and water. These facts are applied to the determination of small amounts of carbamide, which, when isolated in the form of the dixanthyl derivative by precipitation with an excess of xanthhydrol and acetic acid, may be titrated with a standard solution of potassium dichromate and sulphuric acid. Three mols. of dixanthylcarbamide require 58 mols. of potassium dichromate for complete oxidation.

G. A. C. GOUGH.

Detection of hydroxylamine. J. BLOM.—See this vol., 674.

Biochemistry.

Concentration of carbon dioxide in successive portions of an expired breath. R. S. AITKEN and A. E. CLARK-KENNEDY (J. Physiol., Proc. Physiol. Soc., 1927, 64, xvii—xviii).—An S-shaped curve is obtained. A. A. ELDRIDGE.

Identification of blood in the insoluble state. F. PISANI (Arch. Farm. sperim., 1928, 44, 260—264).—The blood spot is dissolved in potassium hydroxide solution, when globin and hæmatin are produced. The alkaline solution is shaken with saturated ammonium sulphate solution and pyridine; this precipitates the protein and the hæmatin and the latter dissolves in the pyridine, which is shaken with saturated ammonium sulphate solution. A few drops of the clear pyridine solution are evaporated at 70—80° on a microscope slide and the residue is treated with acetic acid and sodium chloride; the hæmin crystals appear as long, thin, reddish-brown prisms. The remainder of the pyridine solution is examined spectroscopically, the spectrum exhibiting a very pronounced line just beyond the *D* line and being extinguished towards the blue. Addition of a few drops of ammonium sulphide to the pyridine solution of the alkaline hæmatin converts this into hæmochromogen, which shows two absorption lines, one between *D* and *E* in the yellow and the other between *E* and *F*. T. H. POPE.

Occurrence of ergosterol in ox blood. W. KÜSTER and O. HÖRTH (Ber., 1928, 61, [B], 809—811).—Ergosterol, identified crystallographically and by Salkowski's reaction, has been isolated from the alcohol-sulphuric acid extract of ox blood obtained by treatment of the whole blood by Mörner's method. H. WREN.

Displacement of the isoelectric point of erythrocytes depending on their age. A. H. ANDRES (Zhur. exp. Biol. Med., 1927, 6, 285—299).—The isoelectric point of erythrocytes from white rats, determined in a buffered 8% sucrose solution, is at p_H 4.4—4.8. CHEMICAL ABSTRACTS.

Preparation and properties of erythrocyte-stromata. F. HAUROWITZ and J. SLÁDEK (Z. physiol. Chem., 1928, 173, 268—277).—Erythrocytes free from plasma, leucocytes, and platelets have been obtained by the following method. Fresh horse blood is mixed with an equal volume of citrate solution (0.75% sodium citrate and 0.9% sodium chloride),

kept, and the erythrocyte layer filtered through cotton wool. The filtrate is treated with citrate solution, centrifuged, and the deposit filtered, and the process repeated four times. The suspension of erythrocytes is washed repeatedly with 0.9—1.2% sodium chloride, water and toluene are added, and the mixture is shaken and kept in an ice-chest for 48 hrs. After complete hæmolysis the solution is centrifuged and yields three layers, a bottom layer of hæmoglobin solution, a colourless middle layer of stromata, and the toluene layer. The stromata have been analysed and figures are given for the total lipins (part soluble in toluene, part in ether, and part soluble in hot alcohol but insoluble in ether), phosphatide, cholesterol (which accounts for the whole of the unsaponifiable matter), and fatty acids. The distribution of phosphatide, unsaponifiable matter, and fatty acids varies considerably with different preparations. The proteins of the stromata, from which nucleoprotein and globulin are almost entirely absent, have been examined quantitatively and the nitrogen distribution has been determined. The stroma-protein powder still contains some hæmoglobin and an analysis has been made of the nitrogen distribution of that part which is digested by pepsin (hæmoglobin?) and that undigested. The latter (true stroma-protein) is not digested by pepsin or trypsin, is almost free from phosphorus, and contains small quantities only of sulphur; it is thus not of the keratin type.

A. WORMALL.

Formation of crystals within the red blood-corpusele. H. W. KRANZ (Z. Biol., 1928, 87, 258—268).—When viewed through the polarising microscope red blood-corpuseles fixed by dichromate according to a method fully described show a spherulitic appearance indicating the presence of crystals within them. The conditions of formation and properties of these crystals are described.

W. O. KERMAK.

Preparation of oxyhæmoglobin crystals from ox blood. W. MARSHALL (J. Physiol., Proc. Physiol. Soc., 1927, 64, xxv—xxvi).—The corpuscular mass is washed three times with 1% sodium chloride solution, shaken with tap-water, and the mixture shaken with ether. The bottom clear solution is separated after 12 hrs., and 0.5 vol. of a mixture of 96% alcohol (70 parts) and ether-saturated water (30 parts) is added with agitation. After 30 min. the mixture is

barium chloride (at high concentrations a slight peptising action is observed) and peptised by saponin and bile salts. The latter also peptise cholesterol. The inhibitory action of egg-protein and blood-serum on the hæmolysis of the red blood-corpuscles of sheep is due to antagonistic action of the peptising and sensitising agents. Sodium glycocholate is a much more powerful hæmolytic agent than sodium taurocholate.

G. A. C. GOUGH.

Antigenic character of albumins modified by heat and their specific differentiation by precipitant sera. E. NICOLAS and K. KATRANJIEV (Compt. rend., 1928, 186, 1068—1070).—The properties of the antisera obtained by the inoculation of rabbits with ox sera which have been coagulated at 80°, 100°, 110°, and 120° have been studied. The heat-coagulated proteins of the serum are antigens, this property being maintained even after heating at 120°. The antiserum obtained precipitates the antigen which has not been heated, and the alteration produced in the proteins by heat, treatment with sodium hydroxide, or even formaldehyde has no effect on their specificity of action. The antisera obtained will also precipitate the heated antigens and will react with an aqueous or 0.4% sodium chloride extract of the meat-muscle and blood-proteins. It is possible to prepare suitable solutions of the latter which after neutralisation and dilution react with the antisera obtained from rabbits which have been treated with the coagulated sera, but give only very feeble reactions with those obtained when a serum which has not been heated has been used. By these methods the specific differentiation of cooked meats can be achieved.

J. W. BAKER.

Acetone method applied to study of distribution of antibodies on agglutinating sera during immunisation. M. PIETRE and A. CHRÉTIEN (Compt. rend., 1928, 186, 1240—1242).—The distribution of agglutinants between the three protein fractions obtained by acetone treatment of anti-paratyphoid-B serum, from a horse injected subcutaneously with washed bacilli, is demonstrated. The agglutinating action of the above serum, and also that of the protein constituents brought to the same concentration as in the serum, was compared under the same conditions. The serum-globulin was employed in faintly alkaline solution and the "myxoprotein" in physiological saline. The serum-globulin is the most active during the first phases and the serum-albumin later. The amount of total extract and particularly that of the serum-albumin increases with agglutinating power, a fact which was noted also during immunisation against rattlesnake venom.

J. D. FULTON.

Specificity of muscle- and serum-proteins of animals. I. T. TADOKORO, M. ABE, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1927, 19, 107—115).—Differences in the isoelectric point, specific rotatory power, and amino-acid content of myosin, myogen, and serum-globulin of the ox, horse, cock, and man are recorded.

CHEMICAL ABSTRACTS.

Egg-yolk oil. K. SUZUKI (Bull. Agric. Chem. Soc. Japan, 1927, 3, 54—55).—The oil (from white leghorns

and Chinese hens) contained, as saturated fatty acids, isopalmitic and palmitic acids (2:1), and as unsaturated fatty acids, oleic with some linoleic acid. That from the former variety contained stearic acid, and from the latter a little arachidonic acid.

CHEMICAL ABSTRACTS.

Charcot-Leyden-Böttcher-Neumann crystals. A. NEUMANN (Z. physiol. Chem., 1928, 173, 69—71).—A note, with reference to the publication of Wrede, Bolt, and Buch (A., 1927, 478) on the same subject.

J. STEWART.

Oil from the abdomen of the queen ant. J. B. DA ROCHA (Bol. Soc. Chim. São Paulo, 1928, 1, 27—30).—The abdomina of queens of the leaf-cutting ant *Atta sexdens* yielded 29% of oil by expression. The oil had the following properties: yellowish-red colour, rancid odour, setting point 8°, m. p. 13.5—15°, d_{15}^{20} 0.9753, n_D^{40} 1.456, butyrefractometric index 46.0 at 40°, Reichert-Meissl value 1.43, total acid (as oleic acid) 48.5%, soluble acid (as butyric acid) 9.5%, iodine value (Hübl) 84, saponification value 187, soluble in 5 parts of boiling alcohol, in 50 parts at 25°, miscible with chloroform and ether, and, with slight deposit on keeping, with light petroleum, carbon disulphide, and benzene; ash (chiefly potassium sulphate and carbonate) 0.263%. A trace of lecithin was present. Extraction of the residue by carbon disulphide yielded 13.2% of its weight of solid, which, re-extracted and evaporated, gave a product of m. p. 46°, d_{25}^{25} 0.9196, total acid (as oleic acid) 91.9%. Subsequent extraction by alcohol removed 11.7% of reddish oil.

R. K. CALLOW.

Chemistry of the placenta; presence of choline. H. SIEVERS (Z. Biol., 1928, 87, 319—326).—From an aqueous placental extract spermine, neosine, and choline have been isolated. The presence of choline accounts for certain of the physiological properties of the extract.

W. O. KERMAK.

Presence of a lactacidogen-like substance in glands. II. F. KRAUSE (Z. physiol. Chem., 1928, 173, 235—244; cf. A., 1927, 901).—Stimulation of the salivary gland (parotid) of the dog by pilocarpine produces no increase in phosphoric acid, but the concentration of lactic acid (corrected for the increase in volume) increases slightly, the maximum increase being 20%. Muscle, liver, or pancreas pulp liberates phosphoric acid from the neutralised Schenck filtrate prepared from the resting gland (pancreas or liver). The precursor of this phosphoric acid is not nucleic acid, which was suggested as the source of the phosphoric acid liberated on incubation of pulped glands (*loc. cit.*), but is considered to be an organic phosphoric acid. No hexosemonophosphoric acid could be isolated, however, from ox pancreas or salivary glands by the method of Embden and Zimmermann (A., 1925, i, 729).

A. WORMALL.

Identity of "kanirin" with trimethylamine oxide. F. A. HOPPE-SEYLER (Z. physiol. Chem., 1928, 175, 300—303).—By a comparison of the physical constants and analytical data of the base, its hydrochloride, platinite, and picrate, "kanirin," isolated from the Japanese giant crab by Suzuki, Inouye, and Bharatkar (J. Coll. Agric. Tokyo, 1913,

5, 9), is shown to be identical with trimethylamine oxide. J. W. BAKER.

Isolation of various natural phosphoric acid compounds and their homogeneity. K. LOHMANN (Biochem. Z., 1928, 194, 306—327).—Methods for the preparation of phosphagen and lactacidogen and for the determination of inorganic-, phosphagen-, and total phosphate are described. Investigation of the kinetics of the hydrolysis of the various phosphoric esters by acid shows that Embden's and Robison's esters, which are 30% hydrolysed in 3—4 hrs., cannot be identical with Neuberg's ester, which is 75% hydrolysed. It is suggested therefore that Neuberg's ester consists chiefly of a readily hydrolysable ketose ester together with a smaller amount of a difficultly hydrolysable aldose component, the latter predominating in the other two esters. The course of reaction of creatine phosphate in acid solution is, however, that of a unimolecular reaction. P. W. CLUTTERBUCK.

Occurrence of labile phosphorus in various kinds of muscles. L. IRVING and P. H. WELLS (J. Biol. Chem., 1928, 77, 97—113).—The presence of labile phosphorus of the nature of phosphagen (cf. Eggleton and Eggleton, A., 1927, 271, 990) was demonstrated in the striated muscles of all vertebrates except fishes; it could not be detected in any muscle of invertebrates nor in plain muscle and heart muscle of vertebrates; its distribution seems, therefore, to run parallel with that of creatine.

C. R. HARRINGTON.

Extractives of muscle. XXVII. Determination of carnosine. L. BROUDE (Z. physiol. Chem., 1928, 173, 1—16).—By the action at the ordinary temperature, in an atmosphere of carbon dioxide, of an aqueous solution of sodium nitrite in presence of acetic acid, the β -alanine residue of carnosine is converted quantitatively into β -hydroxypropionic acid. Excess of nitrous acid is destroyed by treatment with aluminium in an alkaline solution, and after 22 hrs. the diluted solution is acidified with sulphuric acid and distilled (avoiding the use of rubber stoppers). Acrylic acid is determined in the distillate by its absorption of bromine. The method failed to determine more than 86.3% of the carnosine present, but is specific for this substance. J. STEWART.

New base from ox muscle, and its constitution. W. LINNEWEH (Z. physiol. Chem., 1928, 175, 91—96).—The lysine fraction of the bases precipitated by phosphotungstic acid from Liebig's meat extract which has been freed from substances precipitable by tannic acid contains *crotonbetaine* [methylbetaine of γ -dimethylaminocrotonic acid], $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2$,

which is isolated as *chloroaurate*, m. p. 215—217° (corr.). The *chloride* is converted into the *ethyl ester chloroplatinate*, m. p. 223—225° (decomp.), and is hydrogenated to γ -butyrobetaine. The easy reduction indicates the presence of an α - rather than a β -double linking. C. HOLLINS.

Determination of amino-acid-nitrogen in animal tissues. J. M. LUCK (J. Biol. Chem., 1928, 77, 1—12).—The fresh tissue is frozen in liquid air, powdered, and a sample weighed; the sample is extracted with boiling dilute acetic acid, and the

extract cleared by successive treatment with trichloroacetic acid and kieselguhr; ammonia is removed by boiling after addition of sodium hydroxide and the amino-nitrogen is then determined by the method of Van Slyke. C. R. HARRINGTON.

Determination of mineral matter in various parts of a cell by micro-incineration. A. POLICARD (Compt. rend., 1928, 186, 1066—1067).—By use of 48 hr. cultures of the cells of the spleen of the white rat in very dilute plasma, and improvement in the optical conditions of examination, it is possible to apply the author's method of micro-incineration (A., 1924, i, 119) to animal cells. It is thus found that the nucleus contains an appreciable amount of mineral matter (probably calcium and magnesium), whilst only a small amount is present in the surrounding cytoplasm. J. W. BAKER.

Phosphatides of milk. G. BISCHOFF (Z. physiol. Chem., 1928, 173, 227—232).—Repeated extraction of 10 kg. of dried milk with boiling ethyl alcohol yields a phosphatide mixture containing 15 g. of crude lecithin and 7 g. of crude cephalin; these constituents have been separated and purified. Butter yields a much smaller amount of phosphatide under these conditions, and the conclusion is reached that in the preparation of butter most of the phosphatide remains in the butter-milk. The phosphatide of milk is associated, therefore, with the water-soluble fraction rather than with the fat. A. WORMALL.

Relationship of blood-sugar content to milk production in cows. K. SCHWARZ and E. MEZLER-ANDELBERG (Biochem. Z., 1928, 194, 362—375).—The blood-sugar values of a large number of milking cows varied in 5% of the animals between 40 and 50, in 20% between 50 and 60, in 45% between 60 and 70, in 20% between 70 and 80, and in 10% was above 80 mg. per 100 g. of blood, being usually lower than in non-milking animals (82 mg. per 100 g. of blood). A direct relationship between the amount of milk and the blood-sugar content was not found nor was any sudden fall in blood-sugar after calving detected.

P. W. CLUTTERBUCK.

Nephelometric determination of peptones in sodium chloride solutions (1 in 1000). H. SURMONT and R. PROVINO (Bull. Soc. Chim. biol., 1928, 10, 406—412; cf. A., 1927, 376).—The nephelometric determination of peptones in aqueous media (0.1—0.3%; 0.5 c.c.) is best made by the use of 30% aqueous trichloroacetic acid (9.5 c.c.), which gives the maximum and most permanent precipitates at that concentration, or 3% sulphosalicylic acid at the ordinary temperature. At 80°, the nephelometric values fall rapidly with time. Since these values, even under the standard conditions, are not strictly proportional to the peptone concentration, it is essential to construct a calibration curve.

G. A. C. GOUGH.

Nephelometric determination of protein derivatives in gastric fluids. H. SURMONT and R. PROVINO (Bull. Soc. Chim. biol., 1928, 10, 413—414).—In gastric fluid containing ovalbumin, albuminoses, and peptones, the material derived from proteins may be determined by the trichloroacetic acid method (preceding abstract). The peptone content may be

found by the same method after preliminary removal of the first two components by coagulation with acetic acid.
G. A. C. GOUGH.

Buffering power of gastric fluids. M. POLO-NOVSKI and J. SWYNGEDAUF (Bull. Soc. Chim. biol., 1928, 10, 443—449).—The buffering power of gastric fluid is determined by the hydrogen electrode method and is expressed as the quantity of sodium hydroxide necessary to change the p_H by a fixed amount. Although great variations, due to pathological conditions and time of digestion, are observed, in general there is maximum buffering power at p_H 3.5 with a lower maximum at p_H 8.
G. A. C. GOUGH.

Ursodeoxycholic acid in the bile of bears, and its physiological action. M. SHODA (J. Biochem. Japan, 1927, 7, 505—517).—Ursodeoxycholic acid has m. p. 198—200°, $[\alpha]_D^{20} + 44.5^\circ$. It stimulates the action of lipase and hæmolyses red blood cells at a concentration of 1 in 320.
CHEMICAL ABSTRACTS.

Reducing substances in urine. R. D. LEAS (J. Lab. Clin. Med., 1926, 12, 15—19).—Administration of sodium salicylate, "cinchophen," or "tolysin" is followed by the appearance of lævortatory reducing (but non-fermentable) substances in the urine.
CHEMICAL ABSTRACTS.

Detection of urochromogen in urine. E. SCHUMTERMANN (Beitr. Klin. Tuberkul., 1927, 65, 773—776; Chem. Zentr., 1928, i, 99).—Concentrated sulphuric acid (1 c.c.) containing a little sodium perborate is added (cold) to 2 c.c. of the urine; the mixture is again cooled and extracted with ether (3 c.c.). Normally the ether becomes light yellow; in the presence of urochromogen it acquires an intense lemon-yellow colour.
A. A. ELDRIDGE.

Colorimetric determination of small quantities of bismuth in urine. B. GLASSMANN (Z. physiol. Chem., 1927, 172, 300—309).—If potassium iodide is added to a solution containing very small quantities of bismuth and a little free acid, a yellow colour is produced (Tresh, Z. anal. Chem., 1883, 22, 432). On the basis of this reaction, which is not affected by the presence of mercury or silver, a method is given in detail for the determination of bismuth in urine, in amounts of from 0.5 mg. to 0.005 mg. per 50 c.c.
H. D. KAY.

Phosphate content of renal capsular fluid in Necturus. F. O. SCHMITT and H. L. WHITE (Amer. J. Physiol., 1928, 84, 401—406).—In fourteen samples out of fifteen tested the "inorganic phosphate" concentration varied between 1.3 and 2.0 mg. of phosphorus per 100 c.c. The corresponding plasma values were 5.4—8.9 mg. % and the urine 1.0—8.3 mg. %. It would appear that only one third to one fourth of the plasma "inorganic phosphate" was diffusible through the glomerular membrane.
R. K. CANNAN.

Determination of stercobilin. A. BAREGGI (Folia Clin. Chim. Micro., 1926, 1, 194—197).—According to Pietra and Bozzolo (Policlinico, Med. Sect., 1924, No. 3), stercobilinogen may be determined by mixing 1 g. of the fæces with 50 c.c. of 95% alcohol, treating with an oxidising agent (5—6 drops of

nitrous-nitric acid and 11—12 drops of Obermeyer's reagent) to complete the transformation of stercobilinogen into stercobilin, and heating the liquid to b. p. for 30 min. Of the clear decanted extract 1 c.c. is employed for the determination by the fluorescence method using Nencki's reagent. The author considers that this method does not give accurate results and that it may be vitiated by the presence of bilirubin. Use of the spectroscopic method is recommended, the liquid being continuously diluted with alcohol until the characteristic absorption band of stercobilin disappears, and it is considered advisable to take 5 g. instead of 1 g. of the sample. The Riva-Zoia method, in which chloroform is used for extracting the fæces, gives results about one half of those furnished by the Pietra and Bozzolo method, but serves well for ordinary clinical purposes.
T. H. PORR.

Reaction of tissue. II. Hydrogen-ion concentration in the tissue during experimental acidosis and alkalosis. J. OGAWA (Proc. Imp. Acad. Tokyo, 1928, 4, 82—83).—When acidosis is produced in an animal, whether by nephrectomy or by the injection of acids, the intracellular p_H decreases and it increases when alkalosis is produced by the administration of sufficient alkali. Injection of insulin increases the intracellular p_H .
W. O. KERMACK.

Hæmocidal properties of blood-serum with reference to pernicious anæmia. O. H. HORRALL and T. E. BUCHMAN (Arch. Int. Med., 1928, 41, 482—498).—Hæmolytic substances are present in the serum of patients suffering from certain forms of anæmia. A test for clinical use based on this finding is described.
W. O. KERMACK.

Fate of secretin in pancreatic diabetes. T. NAKAGAWA and M. HARADA (J. Biophys., 1927, 2, xxxviii—xxxix).—The amount of secretin in the intestine of depancreatized dogs was not subnormal.
CHEMICAL ABSTRACTS.

Comparative study of the physical characters and chemical components of blood and of serous discharges. A. ORSI and L. VILLA (Folia Clin. Chim. Micro., 1926, 1, 190—193).—The density of inflammatory discharges approaches that of the plasma. The refraction and viscosity increase with exudates and, after a discharge, change in a manner depending on the rapidity with which the discharge re-forms; in the plasma these characters increase after a discharge and in the case of transudates diminish in both the liquid and the plasma. In general, the electrical conductivity varies inversely with the protein concentration, systematic variations in relation to certain salts (chlorides) being apparent. The p_H value varies greatly with liquids of either similar or different character, and the alkaline reserve in general follows the p_H value. The ratio between the amounts of chloride in the plasma and the corresponding liquid remains constant, and the proportions of total non-protein nitrogen and of carbamide vary within very narrow limits. Dextrose is always found, being usually in less amount in the liquids. Cholesterol is present in minimum amounts in the transudates, but the exudates contain it in determinable quantity, even when that present in the plasma is normal.

Bilirubin is constantly present in the liquids in smaller proportion than in the plasma. T. H. POPE.

Iodine problem and exophthalmic goitre prophylaxis from the point of view of agricultural chemistry. K. SCHARRER (Münch. med. Woch., 1927, 74, 1788—1790; Chem. Zentr., 1928, i, 218—219).—Administration of sodium iodide in the fodder of goats and cows considerably increases the iodine content of the milk and blood, and larger quantities increase the yield of milk. The milk obtained after moderate administration of iodine is readily tolerated by infants. Application of fertilisers containing iodine considerably increases the iodine in plants. A. A. ELDRIDGE.

Basal metabolism in diseases of the thyroid and the effect of certain therapeutic measures. T. KAMEI (Folia endocrinol. japon., 1927, 3, 211—265). CHEMICAL ABSTRACTS.

Pathological significance of the variations of the free and latent acid in gastric fluids. H. SURMONT and J. SWYNGEDAUF (Bull. Soc. Chim. biol., 1928, 10, 450—455).—The p_H and the latent, free, and total acid of a large variety of pathological gastric juices are given. At the higher p_H values there is little latent acidity, since protein ionisation and pepsin action are inhibited. In cases of permeability of the pyloric orifice the latent acidity almost disappears after 1 hr. of digestion, whilst in cases of stenosis the latent acidity persists since some of the partly hydrolysed protein remains in the stomach. G. A. C. GOUGH.

Inflammation. V. Acetone compounds in the blood of inflamed tissue. F. BRICKER (Arch. exp. Path. Pharm., 1928, 129, 285—287).—The venous blood from a rabbit's ear injured by immersion in hot water or hot oil contains more acetone than does the venous blood from the uninjured ear. This observation confirms the view that inflamed tissues often fail to effect complete oxidation. W. O. KERMACK.

Inflammation. D. ALPERN and L. TUTKEVICH (Zhur. exp. Biol. Med., 1927, 6, 177—186).—A study of the blood-potassium/calcium ratio in inflammation. CHEMICAL ABSTRACTS.

Cause of the delay in the Van den Bergh reaction in icteric serum. N. SOFUE (Proc. Imp. Acad. Tokyo, 1928, 4, 27—29).—Stromata of hæmolysed blood-corpuscles cause a delay in the Van den Bergh reaction whether these stromata are previously injected into the animal from which serum is obtained or whether they are added *in vitro* to the serum. The stromata react with bilirubin *in vitro*, oxidising the latter and producing colours analogous to those obtained in Gmelin's test. The biphasic and delayed reactions appear to depend on this phenomenon. W. O. KERMACK.

Parathyroidectomised dogs. Blood-mineral changes in tetany. C. I. REED, R. W. LACKEY, and J. I. PAYTE (Amer. J. Physiol., 1928, 84, 176—188).—Tetany almost always appeared in the operated animals when the ratio of calcium to phosphorus in the plasma fell to or below unity. The severity of the symptoms,

however, was not related to the value of this ratio or to the absolute concentrations of either element. R. K. CANNAN.

Serum-calcium in pulmonary tuberculosis and on intravenous injection of calcium. W. BROCKBANK (Quart. J. Med., 1927, 20, 431—448).—In pulmonary tuberculosis the serum-calcium varied from 8.6 to 12.0 mg. per 100 c.c., being decreased in the acute stage and gradually increased after healing, but the value is not a trustworthy criterion of activity. Intravenous, but not oral, administration of calcium raised the value above normal. CHEMICAL ABSTRACTS.

Causes of malignant tumours. V. Cysteine content of normal and tumour tissues. R. BIERICH and K. KALLE (Z. physiol. Chem., 1928, 175, 292—299).—Cysteine, as determined colorimetrically by the Sullivan reaction, is found to be absent from absolutely fresh tissues, with the exception of the kidney, of rats, rabbits, and pigs, but prolonged contact with air alters the tissue and a positive result is then obtained, except in the case of the suprarenal gland, in which case the reaction is probably hindered by the presence of adrenaline. The behaviour, in this respect, of malignant human tumours is similar to the normal animal tissue. Yeast gives a negative reaction for cysteine. Suprarenal extract contains, in addition to glutathione, a substance which absorbs iodine in acid solution. J. W. BAKER.

Preparation of colloidal lead. S. W. PENNYCUICK and A. E. SCOTT (Austral. J. Exp. Biol., 1928, 5, 95—99).—Details are given for the preparation of solutions of colloidal lead by sparking in presence of gelatin solution, and data are given relating to their stability. When used in cancer therapy, very pure samples, prepared in presence of nitrogen, proved less effective than those obtained by the ordinary method; the presence of hydroxide is therefore considered to be essential. E. A. LUNT.

Chlorides and nitrogenous substances in the duodenal fluid in uræmia. C. AUGUSTE (Bull. Soc. Chim. biol., 1928, 10, 386—396).—The duodenal fluid of uræmics as compared with that of normal subjects contains larger amounts of water and of chloride, the concentration of which is greater than that of the urine. In both the normal and the pathological states more nitrogen is liberated from the urine by sodium hypobromite than from the duodenal fluid; the latter values, which represent only about 40—70% of the total nitrogen, are smaller than the corresponding blood values, which represent almost the entire nitrogen content. G. A. C. COUGH.

Changes in blood during fasting and subsequent refeeding. II. S. MORGULIS (Amer. J. Physiol., 1928, 84, 350—362).—The electrolyte concentrations of the plasma of dogs were maintained remarkably constant during inanition. Striking changes occurred only in advanced starvation. There was a diminution in chlorides accompanied by a rise in hydrogen carbonate. Normal relations rapidly reappeared on renewed feeding. There was a fall in the calcium concentration during fasting which may be due to a change in the globulin-albumin ratio. R. K. CANNAN.

Growth on synthetic diet containing small amounts of sodium. J. L. ST. JOHN (J. Biol. Chem., 1928, 77, 27—32).—Normal growth in rats could not be obtained on diets containing 0.3% or less of sodium.
C. R. HARRINGTON.

Calcification *in vitro*. III. Inorganic factors determining calcification. D. H. SHELLING, B. KRAMER, and E. R. ORENT (J. Biol. Chem., 1928, 77, 157—170).—Calcification of rachitic cartilage incubated in blood-serum is favoured by a p_H similar to that of normal blood-serum, and is inhibited by increase in the ionic strength of the serum produced by excess of either sodium or potassium chloride; the inhibiting effect of such increase in ionic strength is more marked the lower the concentration of calcium and phosphorus. Calcification is also inhibited by magnesium, but this effect can be neutralised by addition of phosphate.
C. R. HARRINGTON.

Phosphorus metabolism. A. CHARIT and A. LIVSCHITZ (Arch. Sci. biol. [Moscow], 1927, 27, 89—99; Chem. Zentr., 1927, ii, 2688).—The phosphorus metabolism of dogs is discussed. The blood-serum contains $3.1\text{--}7.2 \times 10^{-5}$ g./c.c. of inorganic phosphorus, and $2.6\text{--}3.5 \times 10^{-4}$ g./c.c. of total phosphorus.
A. A. ELDRIDGE.

Behaviour of ethyl diethylacetoacetate in the organism. E. PACE (Arch. Farm. sperim., 1928, 44, 265—272).—In a dose of 0.007 g., ethyl diethylacetoacetate exerts a depressing effect on the central nervous system of a frog weighing 20 g., the general action being similar to, but more intense than, that of ethyl acetoacetate (A., 1927, 1218). When administered to the rabbit, the diethylacetoacetate is not decomposed, but is excreted in combination with glycuronic acid.
T. H. POPE.

β -Oxidation of δ -aminovaleric acid. W. KEIL (Z. physiol. Chem., 1927, 172, 310—313).—After subcutaneous administration, to a dog, of 40 g. of sodium δ -aminovalerate, 1.5 g. of the chloroaurate of methyl β -aminoethyl ketone has been isolated from the urine, and identified by analysis. At least a part, therefore, of the δ -aminovaleric acid suffers β -oxidation in the animal body.
H. D. KAY.

Action of ions on the metabolism of sugars. O. KAUFFMANN-COSLA (Bull. Soc. Chim. biol., 1928, 10, 397—405; cf. A., 1926, 1063).—The urine of normal dogs, to which increasing doses of dextrose are administered without exceeding the limit above which the sugar is only partly oxidised, shows increasingly large calcium values, whilst the faecal calcium remains almost constant. It is suggested that there is some relation between cellular oxidation and calcium metabolism. The calcium content of the urine falls slightly when the dextrose is not completely assimilated.
G. A. C. GOUGH.

Carbohydrate metabolism and ammonia formation in the blood. A. GIGON (Schweiz. med. Woch., 1927, 57, 294—296; Chem. Zentr., 1928, i, 84).—A distinct relation exists between dextrose and ammonia in blood. Ingestion of urea causes an increase in the blood-ammonia, with a parallel hyperglycaemia; injection of dextrose reduces the ammonia value.
A. A. ELDRIDGE.

Ammonia content of and ammonia formation in muscle and its relationship to function and changes of condition. V. Course of traumatic formation of lactic acid and ammonia and their dependence on inhibiting factors. S. CHRZASZCZEWSKI and W. MOZOLOWSKI (Biochem. Z., 1928, 194, 233—243).—When a muscle is macerated with sand and water, the lactic acid formed in 2 min. is ten times the resting value and the course of formation is similar to that of ammonia. The traumatic formation of lactic acid and of ammonia is inhibited by borate solution of p_H 9.3. By means of sodium fluoride solution (1%) the traumatic formation of lactic acid is entirely abolished whereas the formation of ammonia is only somewhat inhibited, the two processes being thereby separable. No direct relationship exists between the formation of ammonia and lactic acid in muscle (A., 1927, 694; this vol., 198).
P. W. CLUTTERBUCK.

Transformation of creatine into creatinine by the male and female human organism. W. C. ROSE, R. H. ELLIS, and O. C. HEMING (J. Biol. Chem., 1928, 77, 171—184).—After long continued feeding of creatine to human subjects larger amounts were excreted unchanged in the female than in the male, but, of the remainder, the same proportion (about one third) was excreted as creatinine in both sexes; the results suggest the existence of two metabolic processes concerned with creatine, one leading to creatinine and the second to some other end product; a lower efficiency of the latter process may account for creatinuria in women.
C. R. HARRINGTON.

Excretion of creatinine and the height of energy loss in man. L. GAROT (Arch. int. physiol., 1927, 29, 326—341).—During the first 15 yrs. of life the creatine:creatinine excretion ratio, at first unity, changes, the latter gradually replacing an equivalent amount of the former. The creatinine excretion per kg. diminishes with increasing age and size, and corresponds with, but is not proportional to, the change in production of heat.

CHEMICAL ABSTRACTS.

Specific dynamic action and nitrogen elimination following intravenous administration of various amino-acids. C. M. WILHELMJ and J. L. BOLLMAN (J. Biol. Chem., 1928, 77, 127—149).—Intravenous injections of glycine, alanine, and phenylalanine cause immediate increases in heat production accompanied by rise in the respiratory quotient; the specific dynamic effects of these amino-acids, expressed as calories of extra heat produced per millimol. of amino-acid, are in the ratio 1.3:1:2. Following administration of a racemic amino-acid, more than 50% of the nitrogen may be excreted as carbamide, indicating a small utilisation of the non-biological isomeride.
C. R. HARRINGTON.

Metabolism of amino-acids. J. M. LUCK (J. Biol. Chem., 1928, 77, 13—26).—After oral administration of various amino-acids to rats the ammonia content of the liver and muscles remained unchanged; the amino-acid nitrogen of the liver was increased to a variable extent; that of the muscles showed an increase only after administration of glycine, which also produced the largest rise in the amino-nitrogen

of the liver; the rise in the latter does not, apparently, depend on the concentration of amino-nitrogen attained in the blood.

C. R. HARRINGTON.

***l*-Hydroxyproline and *l*-proline as sugar formers.** Metabolic investigations with dogs dosed with phloridzin. J. KAPFFHAMMER and C. BISCHOFF (Z. physiol. Chem., 1928, 172, 251—254; cf. Dakin, A., 1913, i, 225).—The amount of extra sugar excreted in the urine of phloridzinised dogs after injection of *l*-hydroxyproline corresponds closely with the utilisation of three carbon atoms for sugar formation. Pure *l*-proline gives about the same quantity of extra sugar as the proline (66% *dl*, 34% *l*) used by Dakin.

C. HOLLINS.

Synthesis of hippuric acid in the animal organism. VII. Rate of elimination of hippuric acid after ingestion of sodium benzoate, benzyl alcohol, and benzyl succinate. S. L. DIACK and H. B. LEWIS (J. Biol. Chem., 1928, 77, 89—95).—The urinary excretion of hippuric acid after oral administration of benzyl alcohol to rabbits is almost as rapid as that resulting from ingestion of sodium benzoate; recovery of benzyl succinate as hippuric acid in the urine amounted to 61% in 24 hrs. and that of sodium benzyl succinate to 45%, although the excretion of hippuric acid in the first hour after ingestion was more rapid in the latter case.

C. R. HARRINGTON.

Regulation of the metabolism of the liver by the nervous system. I. P. ASTANIN, I. KRIWSKY, and W. RUBEL. II. Influence of the vegetative nervous system on the carbamide and sugar formation in the liver. P. ASTANIN and W. RUBEL (Biochem. Z., 1928, 194, 254—261; 262—272).—I. When the surviving liver is perfused with defibrinated blood, the carbamide content of the blood is always increased, whilst by addition of ammonium carbonate the carbamide content is considerably but not proportionately increased, the acid-base equilibrium is scarcely affected, and the amounts of sugar and residual nitrogen are increased.

II. The carbamide content of blood perfusing a surviving liver is increased by stimulating the vagus but not affected by stimulating the sympathetic, whilst the sugar content is increased by stimulating the sympathetic but is not affected or slightly decreased by stimulating the vagus.

P. W. CLUTTERBUCK.

Physiological study of glutathione by liver perfusion. R. FABRE and H. SIMONNET (J. Pharm. Chim., 1928, [viii], 7, 447—449).—See this vol., 196.

Metabolism of the bile acids. C. H. GREENE, M. ALDRICH, and L. G. ROWNTREE (J. Physiol., Proc. Physiol. Soc., 1927, 64, vii—viii).—By adaptation of Pettenkofer's reaction, glycocholic acid (0.1—0.5 mg.) is determined with an error of 5%. Intravenous injection of whole bile or bile salt markedly increases the blood bile acid, but the acids rapidly leave the blood; oral administration leads to an increase of the amount in the blood of the portal, but not of the jugular, vein.

A. A. ELDRIDGE.

Site of formation of bilirubin. K. TANIUCHI (Arch. exp. Path. Pharm., 1928, 130, 37—48).—

Although extra-hepatic formation of bilirubin does occur, the liver is the chief site of its formation. After administration of tolylenediamine or phenylhydrazine to a dog, icterus occurs only when the liver is present.

W. O. KERMAK.

Sense of taste in bees. II. K. VON FRISCH (Naturwiss., 1928, 16, 307—315; cf. *ibid.*, 1927, 15, 321—327).—Fasting bees can differentiate between *M*/4 and *M*/8 solutions of sucrose, but *M*/16 solutions are neglected. A threshold concentration for the recognition of sweetness is indicated. Without fasting, however, *M*/8 and *M*/12 solutions receive little attention, whilst *M*/2 (17%) solutions are invariably attractive. Bees will absorb solutions containing two sweet constituents when the concentrations are below the limiting values, provided the additive concentration is sufficiently high. Tasteless substances exert no such additive effect. The following compounds are sweet both to men and bees: dextrose, laevulose, α -methylglucoside, sucrose, trehalose, maltose, melibiose, whereas bees neglect galactose, mannose, sorbose, mannitol, dulcitol, sorbitol, arabinose, xylose, rhamnose, erythritol, cellobiose, and raffinose. No simple relationship between chemical constitution and sweetness emerges either from the work on the bee or on the human sense of taste.

R. A. MORTON.

Calcium and ultra-violet irradiation. Effect on serum-calcium. Effect on calcium utilisation on a calcium-poor diet. L. T. FAIRHALL (Amer. J. Physiol., 1928, 84, 378—385).—On a normal diet irradiated rats had a somewhat higher concentration of calcium in the serum than did normal rats of the same age. Irradiation increased calcification in rats both on a normal and on a calcium-poor diet; nevertheless, on the latter diet irradiated rats, although their growth appeared normal, contained only about 50% of the calcium of normal rats on a normal diet.

R. K. CANNAN.

Influence of nucleic acids of various origin on the growth and longevity of the white mouse. T. B. ROBERTSON (Austral. J. Exp. Biol., 1928, 5, 47—67).—The effect of nucleic acid of various origins on the growth and longevity of mice has been investigated. Thymus nuclei in daily doses corresponding with 0.5 g. of fresh tissue, and yeast-nucleic acid, daily dose 25 mg., have no effect on the growth curve; the former, however, results in a 12.6% increase in life-duration for the male and a 17% increase for the female; the latter results in a 16% increase for the male. Mice receiving a daily dose of 15 mg. of spleen-nucleic acid exhibit an increase of growth over the controls between the 18th and 72nd weeks of age but show no increase in life-duration.

E. A. LUNT.

Effect of mental fatigue on the excretion of organic phosphorus in the urine. L. E. TARANOWITSCH (Biochem. Z., 1928, 194, 461—465).—The organic phosphorus of the urine is not directly dependent on the phosphorus content of the food absorbed, but both the organic phosphorus and the ratio of organic to total phosphorus increase in all cases of fatigue by continuous mental work.

P. W. CLUTTERBUCK.

Constitution and [physiological] action. Aromatic fluorine compounds. F. LEHMANN (Arch. exp. Path. Pharm., 1928, 130, 250—255).—The action of the following compounds has been determined on frogs: toluene, ω -trifluorotoluene, ω -trichlorotoluene, ω -chloro- ω -difluorotoluene, ω -trifluoro-*m*-nitrotoluene, sodium ω -trifluoro-*m*-toluate, ω -trifluoro-*m*-toluidine hydrochloride, *m*-toluidine hydrochloride, and aniline hydrochloride. The toxicity of toluene is increased by the introduction of chlorine and still more by the introduction of fluorine into the side-chain, whilst the toxicity of ω -trifluorotoluene is further increased by the presence of an amino-group or to a smaller extent of a nitro- or carboxyl group in the *meta*-position.

W. O. KERMACK.

Effect of drugs on the protein content of the cerebrospinal fluid of rabbits. L. F. HEWITT and H. FLOREY (J. Physiol., Proc. Physiol. Soc., 1927, 64, xxvii—xxviii).—The protein content of the cerebrospinal fluid of rabbits is not increased by administration of hexamethylenetetramine, histamine, or pilocarpine; *p*-phenylenediamine causes a 25% increase, an increase negligible in comparison with that caused in man by tubercular meningitis.

A. A. ELDRIDGE.

Metabolic action of "synthalin" with special reference to the analysis of the organs. A. BOEDEKER and P. JUNKERSDORF (Arch. exp. Path. Pharm., 1928, 129, 354—366).—After administration of synthalin the blood-sugar usually rises and then shows a fairly marked fall. Glycogen tends to disappear from the liver and peptone appears in the urine, and it is suggested that synthalin may possess a toxic action.

W. O. KERMACK.

Guanidine derivatives which lower the blood-sugar. T. KUMAGAI, S. KAWAI, and Y. SHIKINAMI (Proc. Imp. Acad. Tokyo, 1928, 4, 23—26).—A large number of guanidine derivatives have been prepared and their blood-sugar lowering actions determined when administered to rabbits by mouth or subcutaneously. The action is exerted particularly by the polymethylenediguanidines. The following compounds have been prepared by the condensation of the corresponding polymethylenediamines with ψ -thiocarbamide in presence of hydriodic acid: agmatine sulphate, m. p. 228°, tetramethylenediguanidine sulphate (not easily obtained pure), pentamethylenediguanidine sulphate, decomp. 330°, and hexamethylenediguanidine hydrochloride, m. p. 175—176.5°.

W. O. KERMACK.

Chemical constitution and physiological action. K. KINDLER (Arch. Pharm., 1928, 266, 19—33).—A lecture.

W. A. SILVESTER.

Excretion of barbituric acid derivatives in the urine of the dog. M. REINERT (Arch. exp. Path. Pharm., 1928, 130, 49—60).—When diethylbarbituric acid, phenylethylbarbituric acid, or isopropylallylbarbituric acid is administered to dogs 70% of the first is excreted in the urine during 7—8 days and about 25—30% destroyed in the organism, 20% of the second is excreted during about 9—10 days and 80% is destroyed, whilst 20% of the third is excreted within 2 days and 80% is destroyed.

W. O. KERMACK.

Influence of convulsions on the gases and the reaction of blood: mechanism of action of strychnine. S. DIETRICH and H. EBSTER (Arch. exp. Path. Pharm., 1928, 129, 339—353).—The difference in their powers to combine with carbon dioxide between oxygenated and reduced rabbit's blood is of the same order as that between oxygenated and reduced human blood. A formula is given for the calculation of the carbon dioxide content of the plasma from that of the whole blood and the hæmoglobin content. The mechanism of the circulatory and respiratory changes in strychnine poisoning are discussed.

W. O. KERMACK.

Uptake, fixation, and decomposition of digitalis compounds and their action on the heart. H. FISCHER (Arch. exp. Path. Pharm., 1928, 130, 111—193).—A pharmacological investigation has been made of the mode of action of digitoxin and bigitaligenin and of the methods by which their activity *in vivo* is neutralised, whether by elimination from the organism, by fixation in the tissues, or by chemical decomposition.

W. O. KERMACK.

Photodynamic action of hæmatoporphyrin. E. N. RASK and W. H. HOWELL (Amer. J. Physiol., 1928, 84, 363—377).—The photodynamic action of hæmatoporphyrin is limited to those tissues directly exposed to light. From observations on frogs, mice, guinea-pigs, rabbits, and dogs sensitised with hæmatoporphyrin and on the isolated turtle's heart, it is suggested that the hæmatoporphyrin combines slowly with some constituent or constituents of the tissues. The resultant effects are attributed to the effect of light on these compounds.

R. K. CANNAN.

Antiseptic action of water-soluble dyes. C. SCHWEIZER (Mitt. Geb. Lebensm. Hyg., 1928, 19, 1—43).—Chiefly a discussion of the mechanism of the toxic action of dyes on cells and micro-organisms. Many basic triphenylmethane dyes and, to a smaller extent, the basic azo-dyes of the chrysoidine class, possess a powerful action on yeast-cells. Dyes of the acid-pyrone and eosin classes have only an inhibitive action.

G. A. C. GOUGH.

Distribution of arsenic in the tissues after serial administration of nearsphenamine. F. P. UNDERHILL and A. DEMICK (Amer. J. Physiol., 1928, 84, 56—60).—The greatest quantity of arsenic was found in the kidney, the amounts found in other tissues being in the descending order spleen, liver, adrenals, heart, muscle, reproductive organs, and brain. The amounts found did not, in general, bear any simple relation to the amount administered or to the number of injections. This distribution of arsenic is in striking contrast to that found in arsenious oxide poisoning.

R. K. CANNAN.

Concentration of enzyme solutions. B. N. SASTRI (J. Indian Inst. Sci., 1928, 11A, 14—15).—Enzyme solutions may be concentrated by freezing, the solution being stirred continuously to favour the formation of small ice crystals.

F. E. DAY.

Micro-method for the determination of enzyme activity. B. N. SASTRI and M. SREENIVASAYA (J. Indian Inst. Sci., 1928, 11A, 31—39).—The method is an adaptation of Barger's micro-method

for mol. wt. determination. Alternate drops of substrate+active enzyme and substrate+inactivated (boiled) enzyme are introduced into a narrow glass tube and the resulting short liquid columns measured microscopically. As the vapour pressure changes with the alteration of molecular concentration due to action of the enzyme in the former solution, the volume of the drops adjusts itself sufficiently rapidly to give a time-value graph agreeing in form with that determined by chemical methods. Examples are given for taka-diastrase and invertase, and sources of error and possible improvements are discussed.

F. E. DAY.

Extraction of amygdalin and emulsin from bitter almond cake. M. BRIDEL and M. DESMAREST (Bull. Soc. Chim. biol., 1928, 10, 373—380).—A more detailed account of previous work (this vol., 201).

G. A. C. GOUGH.

Hydrolysis of lichenin and cellulose by the enzymes of barley malt. H. PRINGSHEIM and K. BAUR (Z. physiol. Chem., 1928, 173, 188—210).—The hydrolysis of lichenin and cellulose, by the same enzymes yielding dextrose as the final product, occurs in three stages, the decomposition of the micelle of the polysaccharide into its structural molecules (glucose anhydrides), synthesis to cellobiose, and hydrolysis of cellobiose to dextrose. To prepare licheninase an extract of green malt is fermented by yeast to remove reducing sugars, or these may be removed by dialysis. Adsorption of the enzyme on kaolin in acid solution and elution with a phosphate buffer of p_H 6.8 yields a solution with enzymic activity 1.7 times that of the malt extract, whilst adsorption on β -alumina (Willstätter) at p_H 3 and elution in a secondary phosphate solution produces an increase of 2.3 times in the activity of the enzyme solution. The kinetics of the hydrolysis of ordinary and purified lichenin by the enzyme preparations have been studied and it has been found that the results vary with different preparations and mainly with the purity and age of the lichenin. With a pure heated lichenin the hydrolysis follows the unimolecular law up to 60% hydrolysis, the reaction velocity being approximately equal to the amount of enzyme used; similar results are obtained for the cellobiase activity of the malt extracts. The extent of hydrolysis of cellulose by the enzyme solution depends on the degree of dispersion of the cellulose; of the cellulose solutions used, cellulose dispersed by heating in a saturated calcium thiocyanate solution is most readily hydrolysed.

A. WORMALL.

Purification of the lactic acid-forming enzyme of muscle. O. MEYERHOF and K. MEYER (J. Physiol., Proc. Physiol. Soc., 1927, 64, xvi).—The extract from frog or rabbit muscle, at p_H 5 with an acetate buffer, precipitates protein and enzyme; the latter is redissolved on elution with phosphate solution at p_H 8. The process is repeated, and the activity of the preparation may be increased by adsorption on aluminium hydroxide. The co-enzyme and phosphoric esters are removed during the process.

A. A. ELDRIDGE.

Mutase. H. VON EULER and E. BRUNIUS (Z. physiol. Chem., 1928, 175, 52—67).—The dismutation

of acetaldehyde (oxido-reduction into alcohol and acetic acid) by aldehyde-mutase shows no parallelism with the decolorisation of methylene-blue by redoxase even in presence of excess of co-enzyme and donors. The experiments afford no evidence for or against the identity of aldehyde-mutase with redoxase.

C. HOLLINS.

Effect of temperature on catalase reaction.

VI. Heat-inactivation of catalase at different p_H . S. MORGULIS and M. BEBER (J. Biol. Chem., 1928, 77, 115—126).—Catalase is most stable towards heat at p_H 6.0; at more acid or alkaline reactions heat-inactivation is slow below 50°, but rapidly increases above this temperature; at 65° inactivation is instantaneous whatever be the reaction. The experiments lead to the supposition that the isoelectric point of catalase is at p_H 6.0, which involves modification of the previous view (A., 1926, 976) that the enzyme acts as a weak acid.

C. R. HARRINGTON.

Glycerophosphate fission by means of kidney phosphatase and its activation. H. ERDTMAN (Z. physiol. Chem., 1928, 172, 182—198).—Dialysis of a phosphatase preparation, obtained by extraction of pig's kidney with water and toluene and precipitation with alcohol, considerably reduces its activity. The activator thus removed appears to be an organic substance with high stability towards heat, alkalis, and acids. It is present in urine and in Liebig's meat extract, and is obtained from the latter in purified form as a colourless, amorphous mass, soluble in water and methyl alcohol, by precipitation with baryta and treatment with lead acetate.

C. HOLLINS.

Liver esterase, its purification and stability.

H. KRAUT and H. RUBENBAUER (Z. physiol. Chem., 1928, 173, 103—117).—Pig's liver is dried with acetone and ether and the dried powder extracted with 40 times the volume of 0.025*N*-ammonia. The extract is dialysed against running water for 3 days, with slight loss of enzyme. The contents of the dialyser are filtered, and certain impurities, together with some 30% of the esterase, are adsorbed from the acidified (0.01*N*-acetic acid) solution first with kaolin, and then with aluminium hydroxide. The remaining purified solution is evaporated in a vacuum to one quarter of its bulk, keeping the reaction of the fluid neutral throughout with ammonia. There is a 15—20% loss of activity during this operation. After filtering through kieselguhr, a small quantity of aluminium hydroxide is added. Further impurities together with some enzyme are removed thereby. The solution is then rendered acid (0.01*N*-acetic acid) and kaolin added. This now adsorbs 80% of the remaining enzyme. After elution with 0.25*N*-ammonia, the enzyme solution is again rendered acid and adsorbed on aluminium hydroxide, from which it is again eluted by ammonia to give an enzyme preparation which may possess 650 times the activity of the dried liver per g. of dry weight. The enzyme gives now no Millon's reaction.

In strong contrast to the esterase of the original dried tissue, which even after months retains the greater part of its activity, the purified enzyme is very unstable, losing 50% of its activity in a single

day, and becoming completely inactivated in eight weeks.

H. D. KAY.

Configurational specificity of esterases in various stages of purification. R. WILLSTÄTTER, E. BAMANN, and J. WALDSCHMIDT-GRASER (*Z. physiol. Chem.*, 1928, 173, 155—168).—Esterases derived from the pancreas, stomach, and liver of the pig have been investigated, using ethyl *r*-mandelate and *r*-phenylchloroacetate as substrates. In no case has it been found possible, by purification, to alter the original optical selective power of the enzyme for one or other of the two optical isomerides in the substrate. Configurational specificity is thus most probably an attribute of the enzyme itself, and not of associated impurities. For an equivalent total amount of hydrolysis the specific rotation of the product increases with increasing purity of gastric esterase. The esterases of corresponding organs in different animal species are not necessarily the same. Thus the gastric esterase of the dog gives the dextrorotatory acid first when acting on ethyl *r*-phenylchloroacetate, but that from the pig gives first the *l*-isomeride. Using a number of different racemic esters, the stereochemical identity of two or more esterases may be tested.

H. D. KAY.

Asparaginase. W. F. GEDDES and A. HUNTER (*J. Biol. Chem.*, 1928, 77, 197—229).—Asparaginase has been prepared from yeast and from calf liver. From the former source the enzyme is best extracted by water or 50% glycerol from the dried and powdered material, at p_{H} 7.0. Treatment of the aqueous solution with alcohol or acetone causes inactivation of the enzyme; the latter is adsorbed by ferric hydroxide and by kieselguhr, but cannot be satisfactorily recovered from the adsorbate. It is also precipitated at p_{H} 4.5. The enzyme is most conveniently concentrated by precipitation with safranin; the activity of preparations so obtained is greatest at p_{H} 7.9—8.1, and is limited to the hydrolysis of the amide-nitrogen of asparagine and of glutamine. The course of the enzymic hydrolysis is not that of a unimolecular reaction but is expressed by an equation of the same form as that given by Michaelis and Menten (*A.*, 1913, i, 540) for the action of invertase on sucrose.

C. R. HARRINGTON.

Plant proteases. R. WILLSTÄTTER. X. Mode of action of yeast polypeptidase. W. GRASSMANN and H. DYCKERHOFF (*Z. physiol. Chem.*, 1928, 175, 18—37).—By fractional adsorption of yeast proteases on alumina a dipeptidase and a polypeptidase may be completely separated. The latter is unable to attack dipeptides, but breaks down tri- and tetrapeptides. *dl*-Leucylglycylglycine is hydrolysed by yeast polypeptidase almost quantitatively into *dl*-leucine and glycylglycine; glycylglycyl-*l*-leucine similarly gives glycine and glycyl-*l*-leucine with no trace of leucine. From *dl*-leucyldiglycylglycine the polypeptidase liberates *dl*-leucine and diglycylglycine, and from triglycylglycine glycine and diglycylglycine. In the presence of leucine the tripeptide, diglycylglycine, is protected from attack. In each case the amino-acid linked through its carboxyl group is removed. Benzoylglycylglycine, benzoyldiglycyl-

glycine, and β -naphthalenesulphonylglycyl-*l*-tyrosine are unattacked by yeast polypeptidase.

C. HOLLINS.

Plant proteases. II. R. WILLSTÄTTER and co-workers. Specificity of yeast peptidases. W. GRASSMANN and H. DYCKERHOFF (*Ber.*, 1928, 61, [B], 656—670).—Observations are recorded on the action of yeast dipeptidase, polypeptidase, and protease on a number of peptides. In all the cases examined, the dipeptides behave exclusively as substrates of dipeptidase, whereas the higher peptides without exception are hydrolysed by polypeptidase. The presence of a free carboxyl group in the position characteristic for normal dipeptides appears essential for susceptibility of the substrate to yeast dipeptidase. Amides of dipeptides, including the tripeptides and higher polypeptides, decarboxylated peptides, and dipeptides such as glycyl- β -aminobutyric acid, in which the carboxy-group has an unusual position with respect to the peptide linking, are without exception resistant to homogeneous yeast dipeptidase (which thus differs from intestinal crepsin), whereas the dipeptide esters cannot be investigated owing to their instability under optimal conditions of activity of dipeptidase. The attack of yeast polypeptidase appears to occur by reason of the presence of a free amino-group in the substrate. Hydrolysis of tri- and tetra-peptides by the enzyme invariably and exclusively occurs in such a manner that the peptide linking at the amino-end of the peptide chain is ruptured. In conformation it is noted that benzoyldiglycylglycine is not hydrolysed by polypeptidase. The presence of a free carboxyl group appears unnecessary for susceptibility to yeast polypeptidase; hydrolysis of tripeptide esters takes place initially at the peptide linking and only towards the end of the change does the ester hydrolysis assume considerable proportions. Unexpectedly, esters of dipeptides are hydrolysed by yeast polypeptidase as rapidly as similarly constituted tripeptides and reaction occurs mainly (almost exclusively at its commencement) at the peptide linking. This is also true for the amides of dipeptides. Esterification, amidation, and lengthening of the peptide chain at the carboxyl group transform a dipeptide from a substrate for dipeptidase into one for polypeptidase. The proximity of a free carboxyl group to the peptide linking hinders the attack of polypeptidase.

H. WREN.

Specificity of peptidases. II. Comparison of the peptide-sugar condensation with the mode of action of erepsin. E. WALDSCHMIDT-LEITZ and G. RAUCHALLES (*Ber.*, 1928, 61, [B], 645—656).—The condensation of dextrose with peptides, which shows many points of similarity with the action between aldehydic sugars and simple amino-acids (stoichiometric course of the change, dependence on concentration of the components), differs remarkably from the latter reaction in its relationship to the hydrogen-ion concentration. This corresponds, at any rate approximately, with the difference in electrochemical character between peptides and amino-acids, since glycylglycine or leucylglycine condenses most readily with dextrose at p_{H} 8.0 and only to an inappreciable extent at p_{H} 9.0, whereas the

action between the sugar and glycine or alanine becomes appreciable only in a more alkaline medium. The p_H curve for the hydrolysis of glycyglycine by intestinal erepsin coincides within the limits of experimental error with that of the rate of condensation of glycyglycine with dextrose. It appears therefore justifiable to assume that the peptide reacts with similar groups in each case and that the union of peptide and erepsin is similar to that of peptide and aldose and hence is due to a free aldehydic group of the enzyme. In confirmation, it is observed that corresponding with the indifference of acylated peptides towards erepsin their condensation products with dextrose are not decomposed by the enzyme. No diminution of susceptibility is observed in the case of lævulose, which does not condense with peptides. Further support of the view that the power of erepsin to unite with the substrate depends on a free aldehydic group is found in the comparison of the condensibility of simple amino-acids with their restrictive capacities towards the action of erepsin; the condensibility of glycine and alanine and their restrictive action towards enzymic hydrolysis of peptides increases with increasing alkalinity of the solution. It appears that the hydrogen ions in the preceding case affect the rate of union of enzyme and substrate and not its rate of decomposition and that the velocity of erepsin action is conditioned by the rate of formation of the enzyme-substrate compound. The mechanism of the action of erepsin therefore differs fundamentally from the enzymic hydrolysis of sucrose.

H. WREN.

Specificity of animal proteases. XIII. Specificity and mode of action of erepsin, trypsin, and trypsin kinase. E. WALDSCHMIDT-LEITZ and W. KLEIN (Ber., 1928, 61, [B], 640—645; cf. this vol., 550).—The behaviour of intestinal erepsin and trypsin kinase towards β -naphthalenesulphonyl-glycyltyrosine, glycyglycinecarboxylic acid, carbethoxyglycyl-leucine, carbethoxypentaglycine, acetylglycyl-glycine, acetylphenylalanylalanine, benzoyl-di-, -tri-, -tetra-, and -penta-glycine, phthalaldiglycine, glycy-leucineamide, tetraglycineamide, and carbethoxy-tetraglycineamide has been investigated. Introduction of acyl groups into dipeptides renders the latter incapable of hydrolysis by erepsin and hydrolysable by trypsin, apparently without dependence on the nature of the amino-acid residue in the peptide. Conversion of the carboxyl group of peptides into the carbonylamido-group, like esterification, does not affect the behaviour towards erepsin, whereas simultaneous acylation again causes immunity to the hydrolysing action of the ferment. Hydrolysis of carbethoxyglycyl-leucine and acetylphenylalanylalanine by trypsin is not accelerated by activation of the latter with enterokinase, whereas this is notably the case with β -naphthalenesulphonyl-glycyltyrosine. H. WREN.

Inactivation of trypsin by Röntgen rays of different hardness. K. ROTHSTEIN (Amer. J. Roentgenol. Rad. Therapy, 1927, 18, 528—536).—The effect on buffered trypsin solutions, p_H 5.42, is an exponential function of the ionisation dose, and is independent of the wave-length between 0.18 and 0.72 Å.

CHEMICAL ABSTRACTS.

Invertase. I. Preparation and purification of the enzyme. B. N. SASTRI and R. V. NORRIS (J. Indian Inst. Sci., 1928, 11A, 1—13).—Washed brewer's yeast (10 lb.) was allowed to autolyse with twice its weight of water at the ordinary temperature in presence of toluene. The filtered autolysate is stable if kept under toluene. After concentrating by freezing out about half the water, 5 litres of the liquid were treated with 500 g. of purified kaolin, which selectively adsorbs impurities. To each 640 c.c. of the cleared liquid, 400 g. of ammonium sulphate were added, the whole was shaken for 30 min., and kept at 0° for 30 hrs. The precipitate was centrifuged, washed twice with saturated ammonium sulphate solution, and extracted with successive small quantities of water, totalling about 560 c.c. This solution was dialysed in collodion bags in distilled water for 3 days at 0°, the solution diluted to 1 litre, and the enzyme was adsorbed on alumina cream equivalent to 1 g. of Al_2O_3 . The alumina after two washings with distilled water was shaken with 180 c.c. of 1% disodium phosphate solution in 1% aqueous glycerol for 30 min., the liquid filtered through kieselguhr, and again dialysed for 72 hrs. Three preparations yielded products giving Willstätter's "time values" of 0.91, 0.80, and 1.10 min., respectively. F. E. DAY.

Cell-free fermentation. A. LEBEDEV (Z. physiol. Chem., 1928, 173, 89—102).—Partly polemical. The claim of Kostytschev, Medvedev, and Sysojeva (A., 1927, 902) that cell-free fermentation does not exist is criticised. Different samples of the same dried yeast yield on maceration extracts of approximately the same fermentative power, whether few or many cells pass through the filter-paper. The fermentative power of such extracts depends to a large extent on the conditions under which the yeast is dried, and is usually less in extracts made from dried yeast which contains a relatively large number of living cells. The evidence against Kostytschev's view is overwhelming.

H. D. KAY.

Comparison of the fermentability of the zymohexoses. Glycogen and starch. J. LEBOVITZ (Z. physiol. Chem., 1928, 173, 84—88).—The fermentation of the polysaccharides is much slower and less complete than that of dextrose and sucrose. It is unlikely, either in fermentation by yeast or in glycolysis by muscle, that a direct degradation of the polysaccharides occurs.

J. STEWART.

Alcoholic fermentation. XIV. Fermentation of polyhydric alcohols by yeast. S. KOSTYTSCHEV and V. FAERMANN (Z. physiol. Chem., 1928, 173, 72—79).—Mannitol and glycerol are disrupted to carbon dioxide and alcohol by yeast only when abundant oxygen is available. This indicates that yeast is able to activate the hydrogen of a hydroxyl group.

J. STEWART.

Alleged co-enzyme for oxidoreductase of yeast. A. LEBEDEV (Z. physiol. Chem., 1927, 172, 255—276).—Neither the reducing enzyme of yeast, prepared by the author's method (A., 1926, 1061), nor the reducing enzyme of milk, prepared by the method of Sbarski and Michlin (A., 1926, 977), is dependent for its activity on the presence of a

co-enzyme. What has hitherto been regarded as a co-enzyme is, in fact, a mixture of oxidisable materials which can be separated from boiled yeast extract by precipitation with alcohol. On dialysis the enzyme loses part of its activity which cannot be restored by addition of boiled yeast extract. After long-continued dialysis the activity of the oxidoreductase solution may slightly increase, possibly owing to the removal of inhibitory substances. Yeast oxidoreductase is probably protein in nature, or associated with a protein carrier. H. D. KAY.

Co-enzyme requirement of yeast in the fermentation of hexosemonophosphate and hexosediphosphate. A. GOTTSCHALK (Z. physiol. Chem., 1928, 173, 184—187).—The fermentation of hexosemonophosphate (Robison) by dried bottom yeast requires larger amounts of co-enzyme than does the fermentation of hexosediphosphate (Harden and Young), but not as much as an equivalent amount of dextrose. It is concluded therefore that this hexosemonophosphate is not an intermediate product formed from the hexosediphosphate, and it is suggested that from the latter a labile hexosemonophosphate (fructosemonophosphate?) is first formed. A. WORMALL.

Production of a yeast-growth stimulant by heating media under pressure. E. I. FULMER and B. HUESSELMANN (Iowa State Coll. J. Sci., 1927, 1, 411—417).—Sterilisation of media *C* and *D* (cf. A., 1921, i, 292) produces a stimulant for the growth of *Saccharomyces cerevisiae*; the stimulation is not due to change of p_{H} . CHEMICAL ABSTRACTS.

Intracellular hydrogen-ion concentration. I. Method. II. *Entamoeba histolytica* and *E. coli*. J. OGAWA (Proc. Imp. Acad. Tokyo, 1928, 4, 76—78, 79—81).—I. The intracellular hydrogen-ion concentration is determined by a slight modification of Schmidtman's method (injection of indicator into the cell) and the results are compared with those obtained by Gräff's method. The intracellular p_{H} of animal tissues decreases fairly rapidly after they have been removed from the body.

II. The p_{H} of the protoplasm of *E. histolytica* and of *E. coli* usually lies between 6.0 and 7.0.

W. O. KERMACK.

Detection of hydroxylamine. J. BLOM (Biochem. Z., 1928, 194, 385—391).—Hydroxylamine (down to 0.0001 g. litre) may be detected colorimetrically by means of *p*-bromonitrosobenzene and α -naphthol. P. W. CLUTTERBUCK.

Formation of hydroxylamine by the reduction of nitrates by micro-organisms. J. BLOM (Biochem. Z., 1928, 194, 392—409).—The formation of hydroxylamine in culture media is detected by the author's method (see preceding abstract) and in presence also of acetone, the amount of acetoxime is greatly increased. The mechanism of the reaction is discussed. P. W. CLUTTERBUCK.

Quantitative metabolism of paratyphoid-*B* bacillus, *B. coli*, and *B. pyocyaneus*. F. FRIEDLEIN (Biochem. Z., 1928, 194, 273—291).—The smallest amounts of a number of substances necessary to produce luxuriant growth of the three bacteria in

24 hrs. on a lactic acid-ammonia medium are determined and the quantities of these substances required for an optimal synthetic nutritive medium are tabulated. Potassium, sodium, and chlorine are unnecessary to maintain life when omitted singly from media containing the other two, whilst magnesium and sulphur, although unnecessary, stimulate growth. Carbon, nitrogen, and phosphorus are necessary for life. Sodium lactate is as good a source of carbon and energy as dextrose or succinate. Ammonium chloride is as good a source of nitrogen as the sodium salt of asparagine. P. W. CLUTTERBUCK.

Physical chemistry of d'Herelle's phenomenon. K. VON ANGERER (Zentr. Bakt. Par., 1927, I, 104, 261—262; Chem. Zentr., 1927, ii, 2685).—The association of the bacteriophage and bacteria accords with the adsorption laws. The exponent $1/n$ of the adsorption isothermal is 0.75—0.80. Only at a certain large concentration of the bacteria in the course of growth is the lysin, at first free, combined.

A. A. ELDRIDGE.

Behaviour of d'Herelle's lytic principle (bacteriophage) towards collodion membranes and in distilled water. L. VILLA (Folia clin. chim. microscop., 1926, 1, 52—57; Chem. Zentr., 1927, ii, 2685).—The lytic principle behaves like a colloid with large micelles. It does not pass a collodion filter. In distilled water the active bacteriophage can be isolated, and is apparently visible with an ultramicroscope. A. A. ELDRIDGE.

Antigenic properties of the distillates of certain bacterial cultures. Z. JERMOLJEWA (Z. Immunitätsforsch. exp. Ther., 1927, 53, 101—111; Chem. Zentr., 1927, ii, 2684).—Cultures of cholera and other vibrios were distilled with magnesium oxide, and the ability of the distillate to produce bacteriolytic and complement-binding antibodies in the serum was investigated. Diphtheria toxin was similarly studied. A. A. ELDRIDGE.

Antigenic properties of anatoxin. M. ISABOLINSKI and V. GITOVITCH (Zhur. exp. Biol. Med., 1927, 4, 844—849).—The combining power of anatoxin is of greater importance in determining its immunising effect than its precipitability. Addition of neutralised formaldehyde to the toxin diminishes the antigenic activity of the anatoxin.

CHEMICAL ABSTRACTS.

Physico-chemical nature of diphtheria toxin and anatoxin. V. KULIKOV and N. SMIRNOV (Zhur. exp. Biol. Med., 1927, 4, 833—841).—Diphtheria toxin shows a wide precipitation zone with increasing acidity, and a narrow zone of maximum toxicity of the precipitate. Factors influencing the toxicity are discussed. It is possible to prevent the heat inactivation of the toxin by means of substances which interfere with the coagulation and adsorption on the protein particles. CHEMICAL ABSTRACTS.

Non-colloidal cryptotoxic substances. H. VINCENT (Compt. rend., 1928, 186, 1175—1177).—The addition of sodium salts of mono- or di-carboxylic acids of the benzene series, non-colloidal in character, even in small quantities, to lethal doses of tetanus toxin renders the latter inactive, especially after 2

or 3 days' contact at 39°. Sodium salicylate is especially active in this respect. An amount of toxin corresponding with 200—400 lethal doses may be injected into a guinea-pig after addition of sodium salicylate, and the injections repeated with larger doses so that the animal becomes accustomed to the poison. The effect of adding varying amounts of the salt to the toxin is described. Successive doses render the blood of a rabbit antitoxic. Sodium salicylate likewise destroys the lethal powers of malignant oedema toxin injected into the blood-stream of a rabbit. Sodium benzoate, hippurate, butyrate, pyruvate, and mucate possess the properties of sodium salicylate to a lesser degree.

J. D. FULTON.

Prolonged storage of bacteriological nutrient media. W. PLAHL (Z. Unters. Lebensm., 1927, 54, 371—373).—In order to prevent the drying of the medium during prolonged storage, the test-tube containing it is inserted plug first into a larger test-tube, 5 cm. longer. A plug 1 cm. thick is inserted into the larger test-tube against the end of the inner tube, then a suitable disc of writing paper, followed by another plug of cotton wool similar to the first. During sterilisation the outer tube has its mouth downwards. When the medium has cooled, the mouth of the outer tube is turned upwards, and the outer plug is soaked through to the paper disc with a gelatin-salicylic acid solution (containing 1% of salicylic acid). The inner surface of the glass, in contact with the plug, is thoroughly moistened with the solution. A cork, previously dipped in the same solution, is inserted in the mouth of the test-tube. For long storage periods, the projecting part of the cork, and the adjacent glass, may be coated with paraffin. The same process may be applied in the incubation of inoculated tubes under constant moisture conditions. A simple device allows the application of the method to tubes containing a liquid medium.

W. J. BOYD.

Destruction of chloroform by animal putrefaction. G. SENSI and D. SIRI (Annali Chim. Appl., 1928, 18, 78—86).—By means of Lallemand and Duroy's method it is shown that chloroform does not prevent animal putrefaction. Chloroform was gradually destroyed as a result of the putrefaction of flesh and was not detectable after the lapse of 52 days.

T. H. POPE.

Absorption and disinfection. I. G. LOCKEMANN and H. PICHER (Z. Hyg. Infect.-Krankh., 1927, 108, 125—145; Chem. Zentr., 1928, i, 223).—A comparative study of the absorption of silver and mercury salts on textile fibres and their disinfecting power.

A. A. ELDRIDGE.

Toxic effect of some metals and alloys on bacteria. G. TAMMANN and W. RIENÄCKER (Z. anorg. Chem., 1928, 170, 288—300).—The poisonous action of various metals when immersed in nutrient media inoculated with *B. coli communis*, *B. brassicæ*, *B. gossypii*, *Sarcina agilis*, or *Penicillium glaucum* has been investigated by observing the size of the organism-free areas round the metals after incubation. The action of some salts has also been examined. Of the metals used, mercury, copper, nickel, cobalt, and antimony have the greatest effect, zinc and cadmium are less toxic, and aluminium, chromium, manganese,

iron, bismuth, gold, and platinum have little or no action. Silver ions first begin to exert a poisonous effect at concentrations of 1×10^{-5} — 1×10^{-8} , but even over this range the action is extremely variable, and the sensitivity of the organisms also varies from time to time. Copper salts, on the other hand, display a fairly sharp limit of toxicity at about 5×10^{-3} g.-atom/litre. Observations have also been made with alloys of copper or silver with varying amounts of gold, the results indicating that the present method is not suited for the investigation of the small amounts of metals given off by alloys. The size of the sterile areas round the metals is, in fact, too much influenced by purely secondary factors.

R. CUTHILL.

Photo-biological action of light. J. RISLER, A. PHILIBERT, and J. COURTIER (Compt. rend., 1928, 186, 1152—1154).—No bacteriophage is obtained by the addition of the filtrate of a culture of organisms, previously killed by the action of light in the presence of fluorescent dyes, to a similar living culture. *B. tuberculosis* is partly destroyed by the light of the neon lamp in the presence of many dyes (especially those of the pinacyanol class). The great bactericidal action of the light produced by the electrical volatilisation of aluminium wire is described.

G. A. C. GOUGH.

Analysis of an insulin preparation containing 40 units per mg. A. BOIVIN and R. GUILLEMET (Bull. Soc. Chim. biol., 1928, 10, 415—421).—The activity of insulin from ox pancreas could not be raised above 20 units per mg. by the picrate method (A., 1923, i, 967) owing probably to the continuous contamination by extraneous proteins. By repeated precipitation at p_H 5 with hydrochloric acid and sodium acetate, a non-crystalline sample (40 units of activity; maximum) was obtained which gave the following values: C, 51.8; H, 5.8; O, 25.4; N, 14.0; S, 2.96; ash, 0% (microanalysis).

G. A. C. GOUGH.

Acetylation of insulin. K. FREUDENBERG and W. DIRSCHERL (Naturwiss., 1927, 15, 832; Chem. Zentr., 1928, i, 211).

A. A. ELDRIDGE.

Insulin. II. Acetylation of insulin. K. FREUDENBERG and W. DIRSCHERL (Z. physiol. Chem., 1928, 175, 1—17).—When insulin, precipitated from methyl alcohol by benzene, is treated with pyridine and acetic anhydride at 0° for 3 hrs., it yields an acetyl derivative (3—4% Ac) which is almost inactive. By the action of 0.03N-alkali at 1—3° for 24 hrs. (conditions under which insulin is unattacked) acetylinsulin is converted into a "regenerated" substance (0.8% Ac) three to five times as weak as insulin, which, however, loses only 20% of its activity by a second acetylation and hydrolysis. If insulin is assumed to be a single individual, acetylation in the first place probably attacks hydroxyl, amino-, and imino-groups, and only acetoxy-groups are hydrolysed by the dilute alkali; the N-acetyl present constitutes less than 1% of the acetylinsulin. The "regenerated" substance is much more stable to alkali than is insulin.

C. HOLLINS.

Action of insulin on the utilisation of carbohydrate by the starving animal. B. FÖRSTNER (Biochem. Z., 1928, 194, 422—440).—Injection of

insulin into starving, curarised, artificially respiring dogs is accompanied by a moderate increase in oxygen utilisation, but change of respiratory quotient, indicating increased utilisation of carbohydrate, does not occur.
P. W. CLUTTERBUCK.

Effect of insulin on amino-acid content of blood. J. M. LUCK, G. MORRISON, and L. F. WILBUR (J. Biol. Chem., 1928, 77, 151—156).—Administration of insulin lowers the amino-acid nitrogen of the blood, the molecular decrease of the amino-acids being almost as great as that of the sugar; the decrease in the amino-acids appears not to be a secondary effect of the hypoglycaemia.

C. R. HARRINGTON.

Distribution of lipins in normal and abnormal liver tissue. II. Effect of insulin on lipins of rabbit liver. E. R. THEIS (J. Biol. Chem., 1928, 77, 75—80).—Prolonged administration of insulin to rabbits causes a decrease in the total lipins of the liver; the livers of animals killed shortly after injection of insulin show a relatively greater decrease in the phospholipin fraction. C. R. HARRINGTON.

Action of pepsin and trypsin-kinase on insulin. A. HARTENECK and W. SCHULER (Z. physiol. Chem., 1927, 172, 289—299).—Both pepsin and trypsin (the latter purified by adsorption on alumina, and activated by enterokinase) inactivate insulin when the mixtures are allowed to digest at suitable hydrogenation concentrations. The enzymic inactivation of insulin is irreversible. Its rate depends on the amount of enzyme used. An increase in amino-nitrogen (formol titration) indicates that the insulin (or the accompanying protein) suffers hydrolysis.

H. D. KAY.

Recovery of a pancreatic secretory excitant by vivi-dialysis of the circulating blood. H. NECHELES and R. K. S. LIM (J. Physiol., Proc. Physiol. Soc., 1927, 64, xxviii—xxix).—The presence of a pancreatic excitant in the circulating blood is proved, and preliminary experiments on its separation by vivi-dialysis have been performed.

A. A. ELDRIDGE.

Influence of thyroid alone and of thyroid administered together with nucleic acids on the growth and longevity of the white mouse. T. B. ROBERTSON (Austral. J. Exp. Biol., 1928, 5, 69—88).—The daily administration of 1.5 mg. of desiccated thyroid tissue to white mice accelerates early growth and diminishes the life-duration period by 17%. The combined effect of the administration of thyroid and either thymus- or spleen-nucleic acid appears to be approximately additive.

E. A. LUNT.

"Antithyroidin (moebius)." A. GÜRBER and O. GESSNER (Arch. exp. Path. Pharm., 1928, 129, 370—379).—The active principle of "Antithyroidin-moebius" is insoluble in alcohol and ether, stable when illuminated or heated to 56°, non-dialysable, and is precipitated practically entirely with the euglobulin fraction of the protein, from which it cannot be separated. Further, normal sheep serum contains a substance inhibiting the metamorphosis of tadpoles, but it is less active than "Antithyroidin-moebius." Phenol 1 : 20,000 to 1 : 40,000 accelerates

the metamorphosis of tadpoles under the influence of thyroid.

W. O. KERMAK.

Insects as test animals in vitamin research. I. Vitamin requirements of the flour beetle, *Tribolium confusum*, Duval. M. D. SWEETMAN and L. S. PALMER (J. Biol. Chem., 1928, 77, 33—52).—The above insect could be reared on a diet lacking fat and fat-soluble vitamins and vitamin-C; vitamin-B was, however, necessary to growth, and was present in considerable amount in the bodies of the larvæ.

C. R. HARRINGTON.

Hydrogenation of sterol-free unsaponifiable matter of cod-liver oil. I. Z. NAKAMIYA and K. KAWAKAMI (Bull. Agric. Chem. Soc. Japan, 1927, 3, 62—66).—Hydrogenation of bioosterin (vitamin-A) yielded nonacosane, batyl alcohol, octadecyl alcohol, palmitic ester, myricyl alcohol, and an unidentified saturated alcohol.

CHEMICAL ABSTRACTS.

Mode of action of vitamin-B. H. BIERRY and M. KOLLMANN (Compt. rend., 1928, 186, 1062—1064).—When the external secretion of the pancreas is suppressed the islet tissue hypertrophies. A similar phenomenon is observed in pigeons suffering from beriberi, but ingestion of small quantities of vitamin-B in such cases maintains the normal balance of the functions of the pancreas. Similarly a condition of hyperglycaemia is developed in pigeons which have been deprived of the vitamin, but is removed by subsequent injection of the vitamin. It is concluded that vitamin-B exerts a stimulating action on the glands both of internal and external secretion.

J. W. BAKER.

Differentiation between vitamins-B₁ and -B₂. H. M. EVANS and G. O. BURR (J. Biol. Chem., 1928, 77, 231—240).—The concentrate tikitiki prepared from an alcoholic extract of rice polishings (Wells, B., 1922, 77A) contains almost exclusively vitamin-B₁; it is also found that commercial maize-starch and commercial caseinogen both contain appreciable amounts of vitamin-B₂.

C. R. HARRINGTON.

Avitaminosis. Behaviour of some blood ferments in avitaminosis. Antitryptic action of serum in experimental avitaminosis. F. GENTILE (Arch. fisiol., 1927, 25, 21—32, 33—42; Chem. Zentr., 1928, i, 87).—In pigeons (with experimental beriberi diet) and guinea-pigs (with diet free from vitamin-C) the glycolytic power of the blood is decreased; in hunger the blood glycolysis is greatly increased. The catalase value for guinea-pigs (on a scorbutic diet) sinks at first, and then gradually rises to and above the normal. With pigeons fed with polished rice there is a considerable rise in the antitryptic ferment content, with a fall on the appearance of symptoms. With guinea-pigs there is an increase of tryptic ferment on a scorbutic diet, and a diminution in hunger.

A. A. ELDRIDGE.

Avitaminosis and autoclave-sterilised food. G. GUERRINI (Biochim. terap. sperim., 1927, 14, 22—35; Chem. Zentr., 1928, i, 87).—Sterilisation of food in an autoclave effects changes, additional to the destruction of vitamins, which cause disease in pigeons.

A. A. ELDRIDGE.