BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1927.

General, Physical, and Inorganic Chemistry.

Measurement of absorption over a wide spectral range, including its application to glasses. K. Schachtschabel (Ann. Physik, 1926, [iv], **81**, 929—951).—Hansen's step-aperture arrangement (Z. Physik, 1924, **29**, 356) has been used in conjunction with the measurement of photographic negatives by a photo-electric registering photometer. Transparency factors for seventeen types of glass and two platinum films have been determined.

R. A. Morton.

Vacuum spectroscopy. I. S. Bowen (J. Opt. Soc. Amer., 1926, **13**, 89—93).—A discussion of technique.

L. F. Gilbert.

Measurement of the intensity of spectrum lines. T. R. Merton (Proc. Roy. Soc., 1927, A, **113**, 697—703).—The disadvantages of the neutral wedge method for the determination of the relative intensities of spectral lines (cf. Merton and Nicholson, A., 1916, ii, 461; 1917, ii, 433; 1920, ii, 69), and of the method involving the measurement of the densities of the photographic images of the lines, are discussed. A new method is described, by which the relative intensity of a line is determined directly in terms of a standard continuous source of radiation, *e.g.*, the positive crater of a carbon arc. The spectrum under investigation is photographed without the interposition of a wedge, whilst the standard continuous spectrum is photographed on the same plate through a wedge system, which consists of a glass plate coated with "Cellire (Black)" varnish, ruled, and cemented on to a Goldberg gelatin neutral wedge with the ruled surface in contact with the gelatin. When the wedge is mounted, the rulings are perpendicular to the slit. Two methods may be used to determine the intensities of the lines, one involving the use of a magnifying glass only, whilst for more complex spectra a comparator is used, by means of which identification and intensity measurement can be made simultaneously. The method is specially adapted to the measurement of the relative intensities of lines in the spectra of gases in vacuum tubes, where the physical width of the lines is very small.

L. L. Bircumshaw.

Singlet and triplet systems with their inter-combinations forming one unit. L. S. Ornstein and H. C. Burger (Z. Physik, 1926, **40**, 403—413).—The whole of the singlet and triplet lines together with their inter-combination lines having the same n and k values are regarded as an "extended multiplet." For singlets and triplets without inter-combination lines, the summation rule for intensities holds for lines not far apart. When inter-combination lines have to be taken into account, the problem is more complex. The decrease of intensity along a series is discussed.

E. B. Ludlam.

Specific oscillations characteristic of continuous spectra. A. Wintner (Ann. Physik, 1926, [iv], **81**, 846—854).—Mathematical.

Fine structure and wave-lengths of the Balmer lines. W. V. Houston (Astrophys. J., 1926, **64**, 81—92).—Each of the first three lines of the Balmer series in hydrogen (studied at the temperature of liquid air) is a doublet with wave-number differences H_α 0·315, H_β 0·331, H_γ 0·353, and absolute wave-lengths H_α 6562·852, 6562·716; H_β 4861·362, 4861·284; H_γ 4340·497, 4340·429, giving 109677·70±0·04 as the value of Rydberg's constant. The apparent doublet separation decreases with an increase in current density, whilst the component of short wave-length increases in relative intensity. At a sufficiently high current density, the light polarised with its electric vector perpendicular to the tube shows a wider doublet separation than the light with the electric vector parallel to the tube. It is assumed that those forbidden components for which $\Delta k=0$ are present are polarised with the electric vector parallel to the tube and increase in intensity with increase of current.

A. A. Eldridge.

Continuous spectrum of hydrogen. I. M. Freeman (Astrophys. J., 1926, **64**, 122—127).—The excitation of the continuous spectrum of hydrogen in tubes employing hot, activated filaments is trustworthy and reproducible. The spectral energy is maximal between 4800 and 5100 Å.

A. A. Eldridge.

Hydrogen spectrum in the new quantum theory. C. Eckart (Physical Rev., 1926, [ii], **28**, 927—935).—Mathematical. The Born and Jordan matrices are calculated. Computed intensity ratios for the two brighter components of H_α and H_β are not in agreement with observed values, the discrepancy being too great to be ascribed to the incompleteness of the model.

A. A. Eldridge.

Continuous spectrum of hydrogen. W. H. Crew and E. O. Hulburt (Physical Rev., 1926, [ii], **28**, 936—946).—The character of the continuous spectrum of hydrogen is similar, but the intensity differs, when arising from various sources. The intensity is appreciable near H_α, rises slowly to a maximum in the near ultra-violet, and falls slowly from 300 to 220 μμ. A formula for the distribution of energy across the continuous spectrum, involving an unknown probability that the atom exists through the *n*th orbit, the region beyond being unquantised, is in qualitative agreement with observation.

A. A. Eldridge.

Certain regions in the helium spectrum. W. Leo (Ann. Physik, 1926, [iv], 81, 757—799).—The intensities and frequencies of the fine lines composing the line groups 4686 and 3203 of the helium spectrum when excited by direct current and by damped wave-train oscillations have been examined by means of a Rowland grating having a photographic dispersion of 0·97 Å. per mm. The results are held to be in agreement with the theory of Sommerfeld rather than with that of Bohr and Kramers. The value deduced for $\Delta\nu_H$ is 0·3459 cm.$^{-1}$ R. W. Lunt.

Effects of changes in potential and frequency on the line spectrum of certain gases. J. A. Swindler (Physical Rev., 1926, [ii], 28, 1136—1146).—The spectra of hydrogen, helium, neon, krypton, xenon, nitrogen, mercury, and chlorine exhibit no differences for changes in frequency between 2 and 0·4 × 10^6 alternations per sec. when the potential is constant; the high-frequency and 60-cycle spectra are identical for pressures between 1 and 6 mm., but not for low pressures. The lines of mercury in a helium tube were strong when stimulated with Tesla frequencies, and the bands of nitrogen in chlorine tubes with 60-cycle currents. The differences are due to a trigger action on the part of the high-frequency waves, making possible the release in the atom of a greater variety of quanta. A. A. Eldridge.

Regularities in the arc spectra of fluorine and chlorine. T. L. de Bruin (Z. Physik, 1926, 39, 869—876).—The experimental data for fluorine and chlorine have been examined. Fluorine has fewer lines in the visible region than other halogens; they are grouped into quadruplet and doublet systems; the results so far obtained for the Zeeman effect are in good agreement with the interval rule. Difference curves for chlorine are drawn, but their interpretation is difficult in the absence of data for the Zeeman effect. E. B. Ludlam.

Double normal state of the arc spectrum of fluorine. T. L. de Bruin (Nature, 1926, 118, 804).—The line 606·9 is identified as a ^4P-P' combination, and the lines 657·69, 658·31 as a ^2P combination. One of the ^2P term differences 145·5 (0·02 volt) or 325·6 (0·04 volt) is assigned to the double normal state (“ Grundterm ”) of the fluorine atom.

A. A. Eldridge.

Double normal state of the arc spectrum of fluorine. H. Dingle (Nature, 1927, 119, 86).—De Bruin's assignation of Millikan's complex hot spark lines of fluorine at 607, 657, to F I is criticised (cf. preceding abstract). It is probable that the extreme ultra-violet lines are emitted by a fluorine atom which has been ionised one or more times.

A. A. Eldridge.

***M*-Doublet of argon.** W. Grotrian (Z. Physik, 1926, 40, 10—11).—Calculating from the results of Meissner (A., 1926, 766), the value for the screening constant for the *M* ring of argon is 7·3, in agreement with the figure 7·5 obtained by Turner (*ibid.*, 550) for chlorine. This value is about one unit less than for elements of high atomic number.

E. B. Ludlam.

Electrical discharge in mixed gases. F. R. Terroux (Physical Rev., 1926, [ii], 28, 1242—1249).—The principal lines and relative intensities of spectra of argon, hydrogen, and oxygen in the negative glow and positive column of a discharge tube containing argon–hydrogen (10 : 90, 50 : 50) and argon–oxygen (10 : 90; 50 : 50) mixtures are tabulated. Whereas in hydrogen and helium the Balmer lines are more strongly developed in the striation than in the negative glow, the reverse is the case in hydrogen and argon. Striæ were always produced. A. A. Eldridge.

Intensities of multiplets. R. Frerichs (Ann. Physik, 1926, [iv], 81, 807—845).—The relative intensities of the multiplets of a large number of lines in the arc spectra of iron, chromium, manganese, titanium, and vanadium have been examined by an improved photometric method. The results are held to sustain the relation advanced by Burger and Dorgelo (Physikal. Z., 1925, 26, 756) between the sum of the intensities of a group of lines and their corresponding quantum number. R. W. Lunt.

New terms in the spectra of zinc and mercury. R. A. Sawyer and N. C. Beese (Science, 1926, 64, 44—46).—The four-line *pp'* group in the arc spectrum of zinc, re-examined by Zumstein, shows fine sharp reversals, whereas the diffuse pair, 2086·72 and 2070·11 Å., shows broad diffuse reversals, and hence arises from deep-lying terms, being classified as $2p_2$—$2D''$ and $2p_1$—$2D''$. The mercury spectrum has been photographed from 2100 to 1500 Å., and a group 2002·7, 1900·1, 1832·6, 1774·9 is classified as the *pp'* group of Hg I. The lines 1987·2 and 1662·6 Å. are classified as the first pair of the sharp series of Hg II. The terms 1*s*, $2p_1$, and $2p_2$ in the Hg II spectrum are computed as 156,300, 106,000, and 96,200, respectively. A. A. Eldridge.

Stripped yttrium (Y III) and zirconium (Zr IV) I. S. Bowen and R. A. Millikan (Physical Rev., 1926, [ii], 28, 923—926).—The hot spark spectra of Y III and Zr IV have been identified and series relationships and term values are tabulated. In yttrium and zirconium, the normal position of the electron is in a 4*d* orbit rather than in a 5*s* orbit.

A. A. Eldridge.

Interpretation of spectra, especially of the second long period. O. Laporte (J. Opt. Soc. Amer., 1926, 13, 1—24).—The three prevailing systems of atomic quantum nomenclature are mentioned, and the interpretation of spectra of atoms with several valency electrons is discussed.

S. Barratt.

New lines in the arc spectrum of europium at normal pressure between 3500 and 3100 Å. S. Piña de Rubies (Anal. Fís. Quím., 1926, 24, 524—527).—A number of new lines in the arc spectrum of europium at normal pressure between the above limits are described. G. W. Robinson.

Continuous spectrum of mercury. (Lord) Rayleigh (Nature, 1926, 118, 767).—The effect of heat on a stream of mercury vapour, showing the continuous spectrum as it distilled away from the electric discharge in which it originated, is to cause the disappearance of the visual glow, but the resonance line 2537 Å. survives, together with a continuous spectrum in the region 3300 Å. A. A. Eldridge.

Spark spectra of mercury in the ultra-violet region. G. Déjardin (Compt. rend., 1926, **183**, 1340—1342).—Lists of lines, many of which are new, with their intensities, are given for the three successive groups of spark spectra Hg II, Hg III, and Hg IV resulting from the emission of the ions Hg^+, Hg_2^+, Hg_3^+, respectively. The corresponding extreme wavelengths are 1860·10—2296·12, 1894·06—2301·22, and 1881·31—2277·46 Å. They extend into the ultraviolet as far as the Schumann region, and thus link up the ordinary and extreme ultra-violet.

J. Grant.

Effect of helium on the intensity of the mercury spectrum. W. G. Nash (Science, 1926, **64**, 190).—A study of the influence of inert and radiating helium on the spectrum of mercury. The intensities of the mercury lines increase on the admission of helium; with radiating helium, helium lines appear. Up to a helium pressure of 0·03 mm., the intensity increase is greater for inert helium, but above 0·06 mm. the effect is the same for inert and radiating helium.

A. A. Eldridge.

Time intervals between the appearance of certain spectrum lines of helium and of mercury. J. W. Beams and P. N. Rhodes (Physical Rev., 1926, [ii], 28, 1147—1150).—Values are tabulated of the times ($0·07—5·06 \pm 0·3 \times 10^{-8}$ sec.) between the appearance of various lines in the visible region of the spectra of helium and mercury. The time intervals are practically independent of the conditions of excitation, and are believed to be of the same order of magnitude as the differences in the total times between excitation and emission.

A. A. Eldridge.

Spectrographic junction between the *X*-ray region and the extreme ultra-violet. R. Thoræus (Nature, 1926, **118**, 771).—A criticism of the interpretation of Dauvillier's results (A., 1926, 1072).

A. A. Eldridge.

Effects of temperature on *X*-ray absorption. H. S. Read (Physical Rev., 1926, [ii], 28, 898—906).—It is confirmed that with silver and nickel, rise of temperature (to 700—1000°) decreases the average transmission (1·3—1·7%). The effect varies with the wave-length, particularly near the *K* absorption limit of silver. A. A. Eldridge.

Direct measurement of *X*-ray mass scattering coefficient. P. Mertz (Physical Rev., 1926, [ii], 28, 891—897).—Values of σ/ρ in cm.²/g. were obtained as follows for wave-lengths of 0·32, 0·43, 0·54, 0·66, and 0·79 Å., respectively: lithium, 0·133, 0·165, 0·157, 0·169, 0·200; boron, 0·154, 0·162, 0·169, 0·165, 0·179; carbon, 0·166, 0·182, 0·194, 0·214, 0·234; water, 0·198, 0·206, 0·210, 0·216, 0·228; sodium, 0·173, 0·191, 0·248, —, —. A. A. Eldridge.

Absorption of *X*-rays from 0·08 to 4·0 Å. S. J. M. Allen (Physical Rev., 1926, [ii], 28, 907—922).—The fluorescence absorption coefficients cannot always be represented by a formula of the type $\tau/\rho = C\lambda^n$, but each element must be considered by itself. Aluminium is suitable as a standard of reference. In several cases, the absorption of a low series of an element of high atomic weight is the same as that of the next higher series of some element of lower atomic weight. A. A. Eldridge.

Precision measurements in the *L*-series of the elements tungsten to uranium. E. Friman (Z. Physik, 1926, **39**, 813—827).—A new tubular spectrometer is described and the method of making exact measurements is given in some detail. The wave-lengths of the α_1, α_2, β_1, β_2, and γ lines of the nine elements are given and a table of frequency differences for $L\beta_1 - L\alpha_2$ and $L_2 - L_1$.

E. B. Ludlam.

Theory of dispersion of *X*-rays. R. de L. Kronig (J. Opt. Soc. Amer., 1926, **12**, 547—557).—The quantum theory of dispersion is applied to the refraction of *X*-rays. A general formula is given for the index of refraction in terms of the atomic absorption coefficient and the critical frequencies, and other results are obtained. S. Barratt.

Quantum theory and intensity distribution in continuous spectra. J. R. Oppenheimer (Nature, 1926, **118**, 771).—Estimates of the intensity distribution in continuous *X*-ray absorption spectra based on the quantum theory of aperiodic phenomena support the theory (cf. Proc. Camb. Phil. Soc., 1926, **23**, 422). A. A. Eldridge.

Zeeman effect and the structure of the arc spectrum of copper. L. A. Sommer (Z. Physik, 1926, **39**, 711—750).—In addition to the well-known alkali-like doublet system in the arc spectrum of copper, a second system has been established by measurements of the Zeeman effect, consisting of doublet and quadruplet terms. The alkali-like series is emitted by an electron revolving round a core containing ten 3_3 electrons; the new system is emitted by an electron revolving round a core of nine 3_3 electrons and one 4_1 electron. A combination relationship is deduced and represented graphically in the form of a cycle of electron jumps to which the appropriate energy changes are assigned.

E. B. Ludlam.

Intensities of the Zeeman components in the partial Paschen-Back effect. W. C. van Geel (Z. Physik, 1926, **39**, 877—878).—The intensities of the components in the magnesium triplet, 3838·29, 3832·30, 3829·36, were found to be in good agreement with the values predicted by quantum mechanics.

E. B. Ludlam.

New quantum theory and the Zeeman effect. P. S. Epstein (Proc. Nat. Acad. Sci., 1926, **12**, 634—638).—Mathematical. The difficulties encountered in the treatment of the Zeeman effect by means of Schrödinger's theory are avoided by a new derivation of the fundamental equation for the behaviour of a hydrogen atom in a uniform magnetic field. It is claimed that this treatment is more rigorous, since the terms of the second order are not neglected, as in the older theory. R. W. Lunt.

Graphical constructions for movements in the Stark effect. E. Buchwald (Ann. Physik, 1926, [iv], **81**, 958—973).

Compton effect according to Schrödinger's theory. W. Gordon (Z. Physik, 1926, 40, 117—133).—The quantum frequency and intensity of the Compton effect are found to be equal to the geometric mean of the corresponding classical magnitudes for the initial and final states in the process.

E. B. Ludlam.

Directional distribution of electrons set free by polarised *X*-rays. F. Kirchner (Ann. Physik, 1926, [iv], 81, 1113—1128).—An extended account of work published earlier (A., 1926, 768).

R. A. Morton.

β-Rays associated with scattered *X*-rays. J. M. Nuttall and E. J. Williams (Mem. Manchester Phil. Soc., 1925—1926, 70, 1—15).—The Wilson cloud method has been used to investigate short β-ray tracks produced in a gas traversed by homogeneous *X*-rays which have been identified with recoil electrons associated with the scattering of the *X*-rays. Data have been obtained in oxygen and in nitrogen for 0·614 Å., and in air for 0·57, 0·35 Å. According to the theory of quantum scattering, the ratio of the number of short tracks to the number of long tracks should be equal to the ratio of the scattering coefficient to the absorption coefficient multiplied by the fraction of scattered quanta which give sufficient energy to the scattering electrons to enable them to leave their parent atoms. This fraction has been calculated on theoretical grounds, and the data now cited give values agreeing within 15% with those calculated. R. W. Lunt.

Source for resonance radiation. M. A. Tuve (Nature, 1927, 119, 85).

Polarisation by electron impact. J. A. Eldridge and H. F. Olson (Physical Rev., 1926, [ii], 28, 1151—1156).—The spectrum of mercury vapour, excited by low-velocity electrons, shows polarisation of the lines of the first subordinate series in directions in accord with theory. Results for the second subordinate series are not in agreement with theory. A. A. Eldridge.

Lattice energy and the work of escape of electrons from calcium. J. J. Weigle (Z. Physik, 1926, 40, 539—544).—The lattice energy of calcium is calculated on the assumption that the electrons in the metal are arranged in a lattice similar to that of the fluorine in fluorite. The work of escape is calculated as 2·17 volts, in satisfactory agreement with values found by others. The inner configuration of the metallic crystal is discussed.

E. B. Ludlam.

Coupling of the quantum vectors for neon, argon, and some hydrocarbon groups. S. Goudsmit and E. Back (Z. Physik, 1926, 40, 530—538).—The possibilities of coupling are applied to the case of the interaction of two electrons. The spectroscopic evidence, particularly that furnished by the Zeeman effect, shows that the scheme due to Russell and Saunders is applicable for silicon and the ground terms of neon and argon, but in all other cases another scheme must be adopted which is in better agreement with observation as one passes from neon and silicon to tin and lead. E. B. Ludlam.

Voltage–intensity relations of mercury lines below ionisation. D. R. White (Physical Rev., 1926, [ii], 28, 1125—1135).—Accelerating voltage–intensity curves were obtained for 28 mercury lines between 5500 and 2500 Å., and the photographic densities of the lines at 10·2 volts are tabulated. The extrapolated minimum accelerating potentials for excitation of the lines agree with the theoretical values, except for the line 4078 Å. Where two or more lines had the same outer orbit, the curves were identical when the intensity scales were so chosen that the curves coincided at one point.

A. A. Eldridge.

Electron affinity of hydrogen. G. Joos and G. F. Hüttig (Z. Physik, 1926, 40, 331—332; cf. A., 1926, 1189).—A new determination of the lattice constant of sodium hydride leads to the value 0·927 for the density, and this gives, by different methods of calculation, values for the electron affinity of hydrogen between +15 and +35 kg.-cal.

E. B. Ludlam.

Critical potentials and *X*-ray term values. (Miss) A. C. Davies and F. Horton (Phil. Mag., 1926, [vii], 2, 1253—1263).—A general discussion on the measurement of critical potentials, the interpretation of the results, and their relationships with *X*-ray spectral determinations. A. E. Mitchell.

Ferromagnetism of nickel and the quantum state of the atom. D. Rožansky (Physikal. Z., 1926, 27, 779—787).—An attempt has been made to determine the quantum states of the nickel atom from the ferromagnetic behaviour of nickel in the neighbourhood of the Curie point. Two states, corresponding with *s* and d_2 terms, suggest themselves. A new hypothesis concerning the number of ferromagnetic atoms has been introduced. At the lowest temperatures, this number corresponds with 25% of the nickel atoms, whilst at the Curie point it has increased to 40%. A decrease in the concentration of ferromagnetic atoms occurs at higher temperatures. The temperature variations follow linear relations outside the region 610—680° Abs. (Curie point 631·8° Abs.). These ideas provide a satisfactory account of the magnetic behaviour of nickel.

R. A. Morton.

Thermionic properties of the rare-earth elements. E. E. Schumacher and J. E. Harris (J. Amer. Chem. Soc., 1926, 48, 3108—3114).—The thermionic emission of the rare-earth metals (those of the cerium group in powder form and those of the yttrium group alloyed with aluminium) was investigated by two simple methods. The electron emission of these metals is about 10^6 times that of tungsten; it is hindered when the metal is alloyed with aluminium. S. K. Tweedy.

Photo-electric properties of thin films of alkali metal. II. Phenomena at high temperatures. H. E. Ives (Astrophys. J., 1926, 64, 128—135; cf. A., 1925, ii, 344).—Thermionic currents and, on illumination, photo-electric currents, obtained when a platinum ribbon is electrically heated in cæsium vapour at low pressure, increase with the temperature to a sharp maximum, and then decrease to negligible values. Thermionically emitted electrons cannot be due to an internal photo-electric excitation. A. A. Eldridge.

Active nitrogen. R. C. Johnson (Nature, 1927, **119**, 9—10).—The view of Willey and Rideal (A., 1926, 893, 1213) that active nitrogen consists of metastable molecules having an energy of about 42,500 g.-cal. per g.-mol. is not readily reconciled with spectroscopic data. The formation and decomposition of a quasi-stable molecule, *e.g.*, N_2I_2, can scarcely account for the excitation of the iodine line 2061 Å., and activated nitric oxide molecules cannot account for all the spectra which active nitrogen is capable of exciting. The theory that active nitrogen is atomic nitrogen is preferred. A. A. Eldridge.

Directional distribution of electrons liberated by *X*-rays. F. Kirchner (Physikal. Z., 1926, 27, 799—801; cf. A., 1926, 768).—The electrons can be liberated by either a photo-effect or a Compton effect. Experiments on the former, using carbon dioxide and argon, show that over the range investigated the distribution curve is independent of wave-length and the work necessary for electron liberation; the distribution curve follows approximately a third-power sine function. For the Compton effect, there is an accumulation in a direction perpendicular to the electric vector. R. A. Morton.

Significance of certain critical potentials of mercury in terms of metastable atoms and radiation. H. A. Messenger (Physical Rev., 1926, [ii], 28, 962—975).—When the critical potentials of mercury are examined by a method distinguishing between effects due to metastable atoms and those due to true radiation, all the breaks found by Franck and Einsporn (Z. Physik, 1920, **2**, 18) except those at 5·76, 6·73, and 8·35 volts are shown to be associated with increased production of metastable atoms, and breaks at 6·04, 6·30, 7·12, 7·46, and 8·09 volts are shown to be due mainly to the formation of metastable atoms. Breaks at 6·7 and 8·35 volts are due to radiation of wave-length 1849 Å.

A. A. Eldridge.

Kinematics of an electron with an axis. L. H. Thomas (Phil. Mag., 1927, [vii], 3, 1—22).—Mathematical.

Configuration of a Lorentz electron moving arbitrarily along a straight line. S. C. Wang (Physical Rev., 1926, [ii], 28, 1309—1314).—A differential equation is obtained which is invariant under a Lorentz transformation. The exact solution of the equation is obtained. A. A. Eldridge.

Value of the potential in the interior of a moving group of electrons. P. Bricout (Compt. rend., 1926, **183**, 1269—1271).—Poisson's equation for the determination of the distribution of the potential between two electrodes is applied to plane electrodes, and to coaxial cylindrical electrodes. It is concluded that in the determination of the resonance potential of a gas by the method of electronic shock the electrodes should be placed so that the electronic current is sufficiently feeble to maintain a constant potential at different points in the gas.

J. Grant.

Velocity filter for electrons and ions. W. R. Smythe (Physical Rev., 1926, [ii], 28, 1275—1286).—As a substitute for magnetic analysis, particularly in positive-ray work, a method employing two identical alternating electric fields is proposed, and theoretically worked out. A. A. Eldridge.

Effect of light on the electron emission from hot filaments. W. H. Crew (Physical Rev., 1926, [ii], 28, 1265—1274).—Hot, oxide-coated platinum filaments show increased electron emission when exposed to the light from a quartz mercury arc. The results suggest that the action of the light is to free electrons from a thin film of metal of which the work-function varies with the temperature of the filament. A. A. Eldridge.

Determination of electronic charge from measurements of shot-effect in aperiodic circuits. N. H. Williams and H. B. Vincent (Physical Rev., 1926, [ii], 28, 1250—1264).—The mean value $4·774 \times 10^{-10}$ e.s.u. is obtained. A. A. Eldridge.

Experiments with high-voltage cathode rays outside of the generating tube. W. D. Coolidge and C. N. Moore (J. Franklin Inst., 1926, 202, 722—735).—The effect of cathode-ray bombardment on a variety of substances, including quartz, diamond, halite, rosin, shellac, milk, bacteria, fruit, flies, plant and animal tissues, is described in a general manner. The cathode-ray tube was operated with potentials in the range 100—200 kilovolts. R. W. Lunt.

Ionisation by electrons in a homogeneous electric field. F. M. Penning (Z. Physik, 1926, 40, 4—9).—The number of collisions, the loss of energy on elastic collision, and the number of ionisations per unit length are calculated. For neon more than 10% of the electrons leaving the cathode produce excitation and rather less than 90% produce ionisation. E. B. Ludlam.

Ionisation of atoms by electron impact. E. O. Lawrence (Physical Rev., 1926, [ii], 28, 947—961).—By the use of electron beams having sharp upper limits of velocity distribution, critical potentials in mercury vapour were determined as follows: 10·40, 10·60, 11·29 (all ±0·2%), 11·70 (±0·3%), 12·06 volts. The relative maximum probabilities of the several types of inelastic impacts are calculated. It is suggested that light quanta and electrons obey the same general laws in processes involving ionisation of atoms and molecules. In particular, the probability of atomic ionisation of a certain type by a light quantum is the same function of its energy, except as regards constants, as that of the corresponding electron inelastic impact.

A. A. Eldridge.

Collisions of the second kind between ions and atoms or molecules. H. D. Smyth, G. P. Harnwell, T. R. Hogness, and E. G. Lunn (Nature, 1927, **119**, 85—86).—Mixtures of two gases, in equal amounts, were ionised by electron impact, the impact electrons having velocities well above the ionisation potentials. The relative amount of that ion corresponding with the higher ionisation potential decreased regularly with increase of pressure, indicating collision between ions and atoms or molecules. The cases studied were: $He^+ + Ne = Ne^+ + He$; $Ne^+ + A = A^+ + Ne$; $A^+ + NO = NO^+ + A$; $He^+ + NO = NO^+ + He$. The ionisation potentials of helium, neon, argon, and nitric oxide are 24·5, 21·5, 15·4, and 9 volts, respectively. Computed relative probabilities of ionisation accord with the results of Compton and Van Voorhis (A., 1926, 769). A. A. Eldridge.

Electrification of dust clouds. V. E. Whitman (Physical Rev., 1926, [ii], 28, 1287—1301).—All dust clouds contain positive, negative, and neutral particles. The sign does not depend on the size; the large particles carry most of the charge. A. A. Eldridge.

Gas ion mobilities in ether–hydrogen mixtures. L. B. Loeb (Proc. Nat. Acad. Sci., 1926, 12, 617—621).—Measurements, by the Franck modification of the Rutherford alternating-current method, have been made of the mobilities of the ions in mixtures of pure ethyl ether and dry hydrogen in fields of the order of 25—50 volts $cm.^{-1}$, and in the pressure range 600—760 mm., at 21—23°. The results are in agreement with the law of mixtures proposed by Blanc (J. Physique, 1908, [iv], 7, 825) for concentrations of ether greater than 30%. At lower ether concentration, abnormally low values are obtained for the positive ions, which are held to sustain the view that these are to be associated with selective changes in concentration of one of the gases about an ion in a cluster. R. W. Lunt.

Spectroscopic interpretation of magneton numbers in the iron group. O. Laporte and A. Sommerfeld (Z. Physik, 1926, 40, 333—343).—A theoretical paper in which, by developing the work of Hund (A., 1925, ii, 912) on the spectroscopic determination of the magneton numbers of the rare earths, the author proceeds to a discussion of the magneton numbers of the metals of the iron group, with particular reference to the anomalies shown by copper and nickel, and of the temperature variation of their susceptibilities. R. W. Lunt.

Magnetic displacement of spectral lines. W. Wien (Ann. Physik, 1926, [iv], 81, 994—998; cf. A., 1923, ii, 349).—The nature of the carriers in the emission of spectral lines can be ascertained by experiments on electrical deflexion. Magnetic deflexion is now shown to extend and confirm the earlier work. R. A. Morton.

Susceptibility of gases, Curie's law, and diamagnetism of flame gases. W. Gerlach and E. Lehrer (Ann. Physik, 1926, [iv], 81, 1129—1134).—Two simple experiments in demonstration of Curie's law for paramagnetic gases are described. The well-known experiment in demonstration of the diamagnetism of flame gases is not unequivocal. R. A. Morton.

Revision of the atomic weight of titanium. Analysis of titanium tetrachloride. II. G. P. Baxter and A. Q. Butler (J. Amer. Chem. Soc., 1926, 48, 3117—3121; cf. A., 1923, ii, 498).—The atomic weight previously found for titanium, viz., 47·90 ($Cl = 35·458$), is confirmed by the use of more refined analytical methods. S. K. Tweedy.

Existence and half[-value] period of radium-*C′*. A. W. Barton (Phil. Mag., 1926, [vii], 2, 1273—1282).—The previous work of Fajans (A., 1911, ii, 569; 1912, ii, 824) and of Jacobsen (*ibid.*, 1924, ii, 142) on the existence and half-value period of radium-*C′* is discussed and the experiments of Jacobsen have been repeated. These experiments confirm the results of Jacobsen in showing that radium-*C′* does exist and that its half-value period is of the order of 10^{-6} sec. A. E. Mitchell.

Separation of radium and of mesothorium-1 from barium by the ionic migration method. J. Kendall, E. R. Jette, and W. West (J. Amer. Chem. Soc., 1926, 48, 3114—3117).—Migration experiments by the moving boundary method indicate that the isotopic radium and mesothorium-1 ions have greater mobilities than the barium ion and a separation of the latter from the former by this method is practicable. The ionic mobility increases with atomic weight throughout the alkaline-earth group. S. K. Tweedy.

Influence of the nature of the source on the liberation of radon. G. Vaugeois (Compt. rend., 1926, 183, 1277—1279).—Sources of radon for therapeutic purposes have been prepared from radioactive salts, the liberation of the emanation being assisted by moistening them with aqueous glycerol, which absorbs very little of the emanation. Pure carbon, quartz, or silica was used as an inert base for the source. When the source had assumed a state of radioactive equilibrium, the emanation was allowed to accumulate, and was determined daily by aspirating the air charged with emanation into a gas condenser. After a year, the activities of the sources were constant. In 24 hrs., 44·5, 55, and 58% of the accumulated emanation was obtained from radioactive iron hydroxide, iron chromate, and a radioactive solution absorbed on pure charcoal, respectively. J. Grant.

Radioactivity of rubidium extracted from lepidolite and zinnwaldite of Japan. S. Iimori and J. Yoshimura (Bull. Chem. Soc. Japan, 1926, 1, 215—219).—Rubidium was separated from some Japanese lithia micas by a method involving its precipitation as rubidium chlorostannate. The β-ray activity of preparations of rubidium sulphate from Tanokami zinnwaldite and Nagatori lepidolite and of a Kahlbaum's specimen was found to be nearly constant, and hence it is concluded that the activity of rubidium bears no relation to its mineral source (cf. Campbell, A., 1909, ii, 288). A. S. Corbet.

Radioactivity of potassium and its geological significance. A. Holmes and R. W. Lawson (Phil. Mag., 1926, [vii], 2, 1218—1233).—It has been shown that in the earth's crust the rate of production of heat from the radioactive disintegration of rubidium must be insignificant in comparison with that produced by potassium, which latter is of the same order as that developed by uranium and thorium, and must have exerted an important, if not a controlling, influence on the igneous history of the earth. The yearly production of heat from the disintegration of uranium, thorium, and potassium has been estimated to be, in an average igneous rock, $11·4 \times 10^{-6}$; in an average granite, $15\cdot9\times10^{-6}$; and in an average plateau basalt, $3\cdot9\times10^{-6}$ g.-cal./g. It is concluded that not more than 1% of the radioactive rays can be expended in any other way than by conversion into heat. When a geothermal gradient of 35°/km. and an average thermal conductivity of 0·006 c.g.s.u. are assumed for the earth's crust, the above figures lead to the result that the thickness of the continental crust must be less than 30, and probably does not exceed 20 km., on the average, a result which is in fair agreement with recent seismic observations. For reconciliation with isostatic data, this thickness of crust requires that the substratum must have a density of 3·4—3·5, and it is concluded that it is most probably composed of eclogite.

A. E. MITCHELL.

Radioactivity of certain Czechoslovakian rocks. J. SEBOR (Chem. Listy, 1926, 20, 511—516).

Absorption of β-rays by matter. H. BRENNEN (Compt. rend., 1926, 183, 1342—1344).—A generalised form of Fournier's formula (A., 1926, 880) for the coefficient of mass absorption of β-rays (μ/ρ) by compound bodies is deduced. The formulæ, however, give different values of μ/ρ for molecules which contain different isotopes of the same element. This is improbable, since μ/ρ depends on the atomic number, and not on the atomic weight. If Fournier's atomic masses are replaced by atomic numbers, an expression is obtained which may be simplified in cases where the atomic numbers of the components are approximately equal. The two last expressions then give values of μ/ρ in better agreement with the experimental values than do Fournier's equations.

J. GRANT.

Temperature coefficient of γ-ray absorption. L. BASTINGS (Nature, 1927, 119, 51).—The coefficient of γ-ray absorption of lead over a range of 250° is shown to increase by about 0·2% per 100° rise of temperature (cf. Read, A., 1926, 551).

A. A. ELDRIDGE.

Properties of high-frequency radiations. J. A. GRAY (Nature, 1926, 118, 801—802).

Natural ionisation in spherical containers. Theoretical. J. W. BROXON (Physical Rev., 1926, [ii], 28, 1071—1085).

Artificial disintegration of the lead atom. A. SMITS and A. KARSSEN (Z. Elektrochem., 1926, 32, 577—586).—Details are given of experiments previously reported (A., 1926, 106) on the production of traces of mercury (1) during the operation of a silica–lead lamp with high currents at low voltages and (2) during the dispersion of lead electrodes by a high-voltage discharge under carbon disulphide. Although by the former method strong mercury spectra were obtained (photographs given) and in one case 5 mg. of mercury were isolated from 850 g. of lead which had been used in the lamp for 188 hrs., conditions favourable to transmutation were difficult to reproduce; the latter method is better in this respect. With a frequently interrupted current of 10 milliamp. at 160,000 volts for 1 hr., 30 g. of dispersed lead yielded 0·1—0·2 mg. of mercuric iodide. The former method is now being modified to permit the use of high voltages and currents as high as possible in an atmosphere of nitrogen.

H. J. T. ELLINGHAM.

Synthesis of elements. F. H. LORING (Chem. News, 1926, 133, 356—358).—A continuation of previous attempts (A., 1926, 656) to synthesise elements in the *X*-ray tube. Although the results are not always reproducible, some spectroscopic evidence has been obtained which suggests that under appropriate conditions atoms condense to form elements not present in the original mixture. It is suggested that the masses of the atoms which condense are additive, and also their atomic numbers, but from the latter sum 4 must be subtracted.

J. S. CARTER.

Synthesis and disintegration of atoms as revealed by the photography of Wilson cloud tracks. W. D. HARKINS and H. A. SHADDUCK (Nature, 1926, 118, 875—876).—An examination of 34,000 photographs, showing about 270,000 α-particle tracks of 8·6 cm. range, revealed two cases in which an α-particle attached itself to a nitrogen nucleus (cf. Blackett, A., 1925, ii, 256). Values for one case are given; 11% of the kinetic energy is stored in the atom, presumably oxygen of mass 17, which is synthesised. The smallest velocity of the α-particle which has so far been sufficient to disintegrate a nitrogen atom corresponds with a remaining range at 15° of 6·2 cm.; thus positive results would not have been obtained with α-particles from polonium, which have been stated to liberate hydrogen particles from aluminium.

A. A. ELDRIDGE.

Existence of the sub-electron. J. MATTAUCH (Z. Physik, 1926, 40, 551—556).—Polemical. Ehrenhaft's criticisms of the author's work are controverted (cf. A., 1926, 880).

E. B. LUDLAM.

Structure of sodium. H. COLLINS (Chem. News, 1926, 133, 501—405).—Speculative.

Atomic structure and the quantum theory. I. H. MARK (Z. angew. Chem., 1927, 40, 16—20).—A review of modern atomic theories showing how they have developed from the older theories and discussing the principles on which they are based.

A. R. POWELL.

Quantum theory of the specific heat of hydrogen. I. Relation to the new mechanics, band spectra, and chemical constants. J. H. VAN VLECK (Physical Rev., 1926, [ii], 28, 980—1021).—Satisfactory specific heat curves are obtained when whole quanta are used, or when the state $m=\frac{1}{2}$ is excluded. Recent theories of the secondary spectrum of hydrogen give moments of inertia more easily reconciled than older values with the specific heats. According to the correspondence principle, the angular momentum, even in a non-polar molecule, can change by zero or $h/2\pi$, provided there are simultaneous electron jumps, thus causing difficulty in Ehrenfest and Tolman's theory. Croze and Dufour's peculiar Zeeman doublets may be due to loose coupling of the spin axis of the valency electron in either the initial or final state, but not in both. The Stern–Tetrode formula for chemical constants requires modification. The moment of inertia, 10^{-41}

g. cm.^{2}, often deduced for the hydrogen molecule from chemical constants, is erroneous.
A. A. Eldridge.

Quantum theory of the specific heat of hydrogen. II. Comparison of various theories with experiment. E. Hutchisson (Physical Rev., 1926, [ii], 28, 1022—1029).—A review. Average values for temperatures up to 1000° are tabulated. A satisfactory temperature-specific heat curve for both high and low temperatures, based on an elastic model, is obtained with (*a*) the *a priori* probability $p=2m$ for whole quanta, and (*b*) $p=2m$, $m=\frac{1}{2}$ excluded, for half quanta. Half integral vibrational quantum numbers do not appreciably affect the specific heat except to change an arbitrary constant (cf. preceding abstract). A. A. Eldridge.

Principle of correspondence. E. O. Lawrence (Science, 1926, 64, 142).—When mercury vapour is bombarded by electrons of homogeneous velocities, critical potentials are observed at 10·6, 11·2, 11·6, and 11·9 volts, the minimum ionising potential being 10·4 volts. The probability of ionisation is finite when the electron has just enough energy to ionise the mercury atom, decreasing with increasing electron energy to the next critical potential, thereafter rising and falling alternately. It is suggested that electrons and radiation quanta obey the same general laws, expressed as functions of their energy, concerned with ionisation of atoms. In particular, the probability that an electron will produce a given type of ionisation expressed as a function of its energy is of the same form as the corresponding probability function for radiation quanta. A. A. Eldridge.

Grouping of electrons in the atom. H. Lessheim and R. Samuel (Z. Physik, 1926, 40, 220—236; cf. Samuel and Markowicz, A., 1926, 881).—The electrons in the elements in the short periods are divided into sub-groups from a consideration of the spectroscopic evidence for the normal state. The term with the smallest inner quantum number is taken as that of the normal state, both for regular and irregular terms. The elements nitrogen and phosphorus differ from the rest, the three outer electrons being symmetrical. The same principle of grouping is extended to the elements from scandium to copper and discussed in connexion with the chemical evidence, variable valency, and stability of compounds. E. B. Ludlam.

Electronic structure of the atom and the quantum theory. A. Sommerfeld (Mem. Manchester Phil. Soc., 1925—1926, 70, 141—151).

Undulatory theory of the mechanics of atoms and molecules. E. Schrödinger (Physical Rev., 1926, [ii], 28, 1049—1070).—Theoretical. In the new theory, the existing discrepancy between the frequency of motion and the frequency of emission disappears in so far as the latter frequencies coincide with the differences of the former. A definite localisation of the electric charge in space and time can be associated with the wave-system, and this with the aid of ordinary electrodynamics accounts for the frequencies, intensities, and polarisations of the emitted light and makes superfluous all kinds of correspondence and selection principles. In several cases, where the new theory is at variance with the old, the former is the better supported by experiment.
A. A. Eldridge.

Quantum mechanics and the magnetic moment of atoms. E. Fermi (Nature, 1926, 118, 876).—Mathematical. Schrödinger's hypothesis (Ann. Physik, 1926, [iv], 81, 109) connecting the field scalar of his undulatory mechanics with the electric density of current leads to the right expression for the magnetic moment of a hydrogen-like atom.
A. A. Eldridge.

Screening constants of relativistic or magnetic *X*-ray doublets. L. Pauling (Z. Physik, 1926, 40, 344—350).—Mathematical. It is shown that the theory of circular electron orbits may be used to calculate values of the screening constants in good agreement with those observed experimentally.
R. W. Lunt.

Possible significance of the tetrahedral numbers in the natural system for the arrangement of protons and electrons in the atom. H. Stintzing (Z. Physik, 1926, 40, 92—106; cf. A., 1926, 7; Reinicke, *ibid.*, 773).—The author extends his hypothesis that the configuration of the protons in the nucleus of all elements follows a scheme of tetrahedra. His new postulate is that the configuration of the electrons in the atoms of all elements follows a tetrahedral scheme and assumes the symmetry of the tetrahedral type in alternating relation to that of the protons. E. B. Ludlam.

Conservation of photons. G. N. Lewis (Nature, 1926, 118, 874—875).—The objections to the hypothesis of the existence of a new kind of atom, the "photon," which acts as the carrier of radiant energy and persists after absorption as an essential constituent of the absorbing atom until again sent out bearing a new amount of energy, are not insuperable. Photons are postulated to be intrinsically identical, to carry all radiant energy, and to be present in constant number in any isolated system; the energy of an isolated photon, divided by the Planck constant, gives its frequency; all photons are alike in one property which has the dimensions of action or of angular momentum, and is invariant to a relativity transformation; the condition that the frequency of a photon emitted by a certain system be equal to some physical frequency existing within that system is not in general fulfilled, but comes the nearer to fulfilment the lower is the frequency. The thermodynamics of Wien and Planck is criticised, and a new thermodynamics, a fuller account of which is promised, adds the number of photons to the variables previously deemed sufficient to define the state of a system. The new theory does not conflict with spectroscopic observations if the existence of a number of atomic states with nearly the same energy but different numbers of photons is assumed. The rigorous rule that only one photon is lost in each elementary radiation process forbids the majority of processes which are now supposed to occur; hence it must be assumed that atoms frequently change their photon number by the exchange of photons of very small energy. The theory predicts that many atomic processes will be inhibited at very low temperatures.

A. A. Eldridge.

Maxwell's equations and atomic dynamics. A. Bramley (J. Franklin Inst., 1926, **202**, 775—808).—Mathematical.

Apparatus for producing spark spectra of solutions. B. A. Lomakin (Z. Physik, 1926, **40**, 548—550).—A simple method of producing a spark between drops of the solution is described.

E. B. Ludlam.

Spectroscopic examination of light emitted during reaction. K. Ljalikov and A. Terenin (Z. Physik, 1926, **40**, 107—116).—The action of iodine vapour on the vapours of sodium, potassium, rubidium, and lithium has been studied. The lines observed were those of the principal series of the alkali metals; in addition, faint bands were observed which appeared to be continuous and are ascribed to the alkali molecule. No emission peculiar to the reaction was observable, but the *D*-lines were broader and more diffuse than would be expected for the temperature and pressure of the vapour.

E. B. Ludlam.

Absorption spectrum of hydrogen and the analysis of its ultra-violet band spectrum. G. H. Dieke and J. J. Hopfield (Z. Physik, 1926, **40**, 299—308; cf. A., 1926, 1078).—The absorption spectrum was obtained by photographing the light from a condensed discharge through a capillary tube in a vacuum spectrograph containing hydrogen at reduced pressure. The bands between 1000 and 1650 Å. could be grouped in two systems having a common final state. The resonance potential of the molecule is 11·1 volts. The absorption bands get closer together towards the extreme ultra-violet, and, when the limit value for the oscillatory energy is exceeded, pass into continuous absorption with the dissociation of the molecule. This limit is clearly marked at 849·4 Å. (=14·53 volts). A normal atom results, together with an excited atom, in the second quantum state, with 10·15 volts energy. The difference, 4·38 volts, represents the energy of dissociation. The continuous emission spectrum from the visible far into the ultra-violet is regarded as a dissociation spectrum.

E. B. Ludlam.

"H and K" bands of carbon. A. S. Ganesan (Nature, 1926, **118**, 842).—During experiments, using an uncondensed discharge, on the spectrum of neon at low pressure, carbon and oxygen being present as impurity, the "H and K" bands of carbon were observed to consist each of a central sharp line bounded on each side by a diffuse line, the less refrangible diffuse towards the red, and the more refrangible diffuse towards the violet, the wave-lengths being 2897·23, 2896·25, 2895·35, and 2883·74, 2882·84, 2881·97 I.Å., respectively.

A. A. Eldridge.

Impact-broadening of spectral lines and the sharpness of quantum states. G. Hettner (Physikal. Z., 1926, **27**, 787—789).—Theoretical. The sharpness of a quantum state depends strictly on its duration period. Whether a quantum theoretically equivalent to the collisional damping of Lorentz can be found is discussed. It has been shown that addition of foreign gases can in fact bring about a broadening of lines by collisions. The breadth and broadening of lines in the ultra-red rotation and rotation–vibration spectra of gases with pressure increases are regarded as essentially due to impact-damping.

R. A. Morton.

Line-spectrum for wave-lengths of a few decimetres. G. Mie (Physikal. Z., 1926, **27**, 792—795).—Weichmann (A., 1922, ii, 5, 331) has measured the refractive index of water for wave-lengths from 27 to 65 cm., and has found several sharply-defined regions of anomalous dispersion. The water he employed had a conductivity varying from 20×10^{-6} to 40×10^{-6}. When specially purified water of conductivity 2×10^{-6} is used, no trace of anomalous dispersion is now found, and the refractive index of water is 8·975 approx. over the range 52—58 cm.

Weichmann's results can be reproduced by adding a trace of a solution made up from chemically pure sodium hydrogen silicate ($NaHSiO_3$). The curve, refractive index–wave-length, shows three maxima between 54 and 57 cm. The curve for clean solutions of sodium hydrogen silicate can now be expressed by the ordinary dispersion formula, the resonance wave-lengths being 54·49, 55·55, and 56·29 cm. The physical interpretation of the curve is discussed.

R. A. Morton.

Influence of foreign gases on the infra-red absorption band at $4\cdot2\,\mu$ of carbon dioxide. Application to analysis. M. Wimmer (Ann. Physik, 1926, [iv], **81**, 1091—1112).—The infra-red absorption band at $4\cdot27\,\mu$ of carbon dioxide increases in intensity and is shifted in the direction of longer wave-length as the pressure of gas is increased. The addition of an indifferent gas causes the absorption to increase as the partial pressure of the foreign gas is increased. With a constant partial pressure of carbon dioxide in the presence of foreign gases at equal partial pressures the absorption of the mixed gases decreases in the order: hydrogen, nitrogen, air, argon (partial pressure of carbon dioxide, 1·62 mm., of indifferent gas, 198·38 mm.). The increased absorption is due to line broadening within the unresolved band.

These results have been utilised for a method of determining the partial pressure of carbon dioxide in mixed gases. The area of the absorption curve is a measure of the carbon dioxide present in a mixture in which the nature of the indifferent gas and the total pressure are known. A series of curves is given, in each of which the area of the absorption curve is plotted against partial pressure of carbon dioxide at a constant total pressure. The method is accurate to 2% in the region of 0·02—1·0 mm. partial pressure, but to only 10% at higher pressures.

R. A. Morton.

Theory of intensity distribution in band systems. E. Condon (Physical Rev., 1926, [ii], **28**, 1182—1201).—A theory of the relative intensities of the bands in an electronic system predicts the existence of two especially favoured values of the change in the vibrational quantum numbers. A means of calculating the intensity distribution from the known constants of the molecule is roughly in agreement with experiment for SiN, AlO, CO (fourth positive group of carbon), O_2 (Schumann–Runge system), CN (violet system), CO (first negative group of carbon), N_2 (second positive group of nitrogen), and N_2 (first negative group of nitrogen).

A. A. Eldridge.

Production of selective emission by flames. D. A. Kreider (J. Opt. Soc. Amer., 1926, 13, 83—86).—An apparatus is described by means of which illuminating gas discharging through a type of Bunsen burner may be loaded with salts producing notable selective emission. The flames produced are about 1 cm. in diameter and 20 cm. high, and have an exceptionally rich and constant colour.

L. F. Gilbert.

Absorption spectra of nitrates in the region 300 $\mu\mu$. R. A. Morton and R. W. Riding (Proc. Roy. Soc., 1927, A, **113**, 717—731).—The effects of varying the positive ion, the concentration, and the solvent have been investigated. Metallic nitrates and nitric acid in dilute solution (0·025—0·0025*N*) show a band at 300 $\mu\mu$, $e_{max.}$ 7·2, which is due to the nitrate ion. A region of continuous end absorption extends from about 270 $\mu\mu$ towards the ultra-violet. This is regarded as due to inter-ionic attractions, which result in the formation of activated quasi-molecules. Beer's law is valid over the range 0·025—0·0025*N*, but breaks down at higher concentrations owing to the shifting of the band in the direction of higher extinction coefficients. By subtracting the 0·025*N*-curve from the *N*-curve, a superimposed band of selective absorption is disclosed, which is approximately reproduced when very concentrated solutions are examined. Concentrated nitric acid and the alkyl nitrates show no selective absorption. A detailed study of the absorption of calcium nitrate shows that a shift in the head of the band and an increase in $e_{max.}$ can be brought about by addition of, or solution in, a non-ionising solvent, by a greatly increased concentration in water, or by addition of a salt likely to throw back dissociation. The superimposed selective absorption is therefore thought to be due to undissociated molecules. Since all the absorbing entities considered contain the nitrate group, possible correlation of the characteristic frequencies has been considered by the methods underlying Baly's absorption theory. It is shown that the frequencies of the three bands deduced in the ultra-violet are integral multiples of a band in the short-wave infra-red due to the nitrate grouping. An explanation, based on the views of Born and Franck, is offered for the fact that von Halban, in his work with photo-electric cells, did not observe a region of general absorption with the metallic nitrates (cf. A., 1925, ii, 1083).

L. L. Bircumshaw.

Penetrability of various rays through glasses. I. Ultra-violet ray penetration through alkali-lime glasses, and the method of manufacture of glass transparent to ultra-violet rays. II. Ultra-violet ray penetration through alkali-barium glass and alkali-zinc glass. III. Glasses non-transparent to visible, but transparent to ultra-violet rays. S. Sugie (Rep. Osaka Ind. Res. Lab., 1924, 5, No. 11, 1—26; No. 15, 1—19; 6, No. 4, 1—26).—I. An examination of glasses of the composition 0·7—1·6Na_2O (part or all substituted by potassium oxide), 0·9—1·5CaO,6SiO_2. No systematic relation was found between the absorption of ultra-violet rays and the composition of the glass. Glass of the composition 1·0Na_2O,1·4CaO,6SiO_2 transmits down to 2370 Å., for thickness 1·5 mm., whereas one of composition 1·0Na_2O,1·5CaO,6SiO_2 transmits only to 2790 Å. Antimony, titanium, ferric, magnesium, and aluminium oxides decrease the penetration, whilst phosphoric oxide has no effect.

II. Barium oxide tends to decrease, and zinc oxide to increase, penetrability to ultra-violet rays. Substitution of sodium in soda–zinc glass by potassium has the unusual effect of decreasing the penetrability.

III. In potash glass containing nickel, the shortest transmitted visible ray has a greater wave-length than in similar soda glass; the transparency to ultra-violet rays is not affected by the kind of alkali used. Cobalt behaves like nickel in increasing transparency to ultra-violet rays, but when employed together they absorb both red and ultra-violet rays.

Chemical Abstracts.

Absorption spectrum of solid benzene at —180°. A. Kronenberger and P. Pringsheim (Z. Physik, 1926, 40, 75—91).—A thin wedge of benzene between quartz plates was frozen in a silica Dewar flask constructed so that a beam of light could be passed through four plane parallel plates of silica and focussed on the slit of a spectrograph. The bands beyond 270 $\mu\mu$, which at the ordinary temperature are diffuse, form a series of narrow bands at —180°, closely resembling the absorption spectrum of the vapour. The bands are grouped in series and energy levels suggested, but no entirely satisfactory scheme is obtained; it is evident that the characteristic vibrations of the atoms in the benzene vapour remain with little change when the molecule is in the crystalline state at a temperature sufficiently low to avoid disturbance by neighbouring molecules. Experiments using liquid hydrogen have been begun.

E. B. Ludlam.

Absorption spectra of pyrone derivatives in the near infra-red. A. Ross (Proc. Roy. Soc., 1926, A, 113, 208—220).—The infra-red absorption spectra of pyrone derivatives and their solutions have been investigated. Liquid films of pyrone show absorption maxima at 2·95, 3·2, 5·9, 6·22, 7, 7·6, 8·3, and 9·8 μ. Of these, the 2·95 and 5·9 are due to hydroxyl, the 3·2 and 9·8 to the benzene nucleus, and the 6·22 possibly to carbonyl oxygen. The weaker bands, with one exception, agree well with the equation of Henri ("Structure des Molecules") for infra-red bands of benzene, $1/\lambda=921{\cdot}7n-162p$, where *n* and *p* are integers signifying quantisation. Solutions of pyrone and dimethylpyrone in chloroform with and without hydrochloric acid were examined, and also similar solutions of pyridine, and a solution of pyridine methiodide in pyridine. The solution spectra of dimethylpyrone show bands at 3 μ due to hydroxyl, 3·43 μ due to methyl, and 6·15 μ due possibly to the carbonyl group. The results indicate the presence of a benzene nucleus and a hydroxyl group in the pyrone molecule, both in the free state and in solution. The solution spectra agree with the structure proposed by Hantzsch (A., 1920, i, 72), but for the films of liquid pyrone a multimolecular complex is suggested.

W. Hume-Rothery.

Absorption of ultra-violet light by alkaloids and glucosides. V. Brustier (Bull. Soc. chim., 1926, [iv], 39, 1527—1543).—The curves of absorption of ultra-violet light of numerous alkaloids and glucosides were determined spectrographically. All the substances exhibiting band spectra have similar absorption curves exhibiting one or more points of inflexion at positions depending on the wave-length of the light, and on the nature of the substance. Some alkaloids containing common nuclei or groups exhibit identical points of inflexion (*e.g.*, cocaine and aconitine). Alkaloids of the cocaine group are more absorbent than those of the atropine group, and their spectra are shifted more towards the red region. Spectrographic methods of identifying and determining approximately certain alkaloids or glucosides in a mixture are described. S. K. Tweedy.

Resonance absorption and yield of fluorescence in the *X*-ray region. V. Posejpal (Compt. rend., 1926, 183, 1097—1099).—A general expression for the yield of fluorescence R at the K- and L-levels has been deduced from the probability that resonance absorption will occur in the X-ray region. Thus an atom ionised at its K-level will emit radiation as fluorescence, and consequently become ionised at its L-level; this ionisation will then immediately be absorbed by resonance at the K-level. The probability is governed by the coefficient of absorption of the fluorescence, and by the probability that the quantum producing ionisation, and consequently radiation of the frequency concerned, will penetrate below the level under consideration. The calculated values agree completely with those obtained experimentally by Auger (A., 1926, 551, 659). J. Grant.

Fluorescence of superheated mercury vapour. H. Niewodniczański (Nature, 1926, 118, 877).—The fluorescence of mercury, just sufficient to fill a quartz tube with saturated vapour at 240°, is practically unchanged when the vessel is heated at 300—355°. The fluorescence changes, however, on variation of the temperature of the saturated vapour. Hence for a given exciting light the fluorescence of the mercury vapour depends mainly on the density of the vapour, its age being unimportant.

A. A. Eldridge.

Relation between intensity of fluorescence and concentration in solid solutions. E. Merritt (J. Opt. Soc. Amer., 1926, 12, 613—622).—Perrin's second suggestion as to the cause of the decrease in luminescence of solid solutions when the active material is increased beyond a few per cent. (A., 1919, ii, 177) is applied to fluorescence in solid solutions and is developed quantitatively. The results of Nichols and Slattery (*ibid.*, 1926, 659) for uranium phosphors are in approximate agreement with the theory. L. F. Gilbert.

Links connecting fluorescence and the luminescence of incandescent solids. E. L. Nichols (J. Opt. Soc. Amer., 1926, 13, 661—677).—Evidence connecting the luminescence of incandescent bodies with the fluorescence of solids at the ordinary temperature is collected and reviewed. It is concluded that the luminescence superposed on the incandescence of the various solids is to be regarded as essentially identical with ordinary fluorescence.

C. J. Smithells.

Luminescence from solid nitrogen, and the auroral spectrum. L. Vegard (Nature, 1926, 118, 801).—Polemical against McLennan and others (A., 1926, 985, 1081). Present knowledge of the auroral line 5230 Å., and of the experimental conditions for obtaining the N_2-band, do not permit a comparison of their structures. The identification of the auroral line with an oxygen line seems to be in contradiction to observed facts; solid nitrogen gives the whole typical auroral spectrum from red to ultra-violet. The position of the N_1-band for small concentrations of nitrogen c is given by the expression $\lambda = 5577{\cdot}56 - 0{\cdot}8754c$. A. A. Eldridge.

Alkali halide phosphors. R. Pohl and E. Rupp (Ann. Physik, 1926, [iv], 81, 1161—1166).—Pure sodium chloride crystals are practically transparent down to 186 $\mu\mu$, and do not show phosphorescence. The yellow or brown crystals formed in various ways and showing a broad absorption band in the visible are only weakly phosphorescent. These crystals are described as coloured in the first way: by amicrons with a very simple absorption spectrum; crystals may be coloured in a second way: by the presence of ultramicrons of a foreign metal. Blue sodium chloride appears to be of this type, which is characterised by narrow absorption bands in the ultra-violet and strong phosphorescence. A spark provides sufficient light to excite phosphorescence visible in an undarkened room. Whilst sodium chloride coloured in the first way has a very poor optical efficiency, a very high value is found for the salt coloured in the second way. A close resemblance thus exists between these phosphors and the sulphide phosphors, and the relationship between photoelectric conduction and absorption is common to both.

R. A. Morton.

Measurements of the thermo-phosphorescence of glass produced by radium radiation. R. E. Nyswander and S. C. Lind (J. Opt. Soc. Amer., 1926, 13, 651—660).—The intensity of the light emitted by glass, previously exposed to radium, when heated at temperatures at which thermo-phosphorescence takes place was measured. The total quantity of light emitted by equal areas of similarly irradiated glass of the same thickness was found to be constant, independent of temperature or rate of light emission. The rate of decay at constant temperature approximately fits the equation $dx/dt = k(a-x)^2$ for a second order chemical reaction. The values of k increase with temperature, in accordance with van 't Hoff's equation $\log k = C - a/T$. Measurements with a silver–bismuth thermopile failed to reveal any increased heat radiation accompanying the luminescence. C. J. Smithells.

Critical potentials of the vapours of mercuric halides. V. I. Pavlov and A. I. Leipunsky (Nature, 1926, 118, 843).—The following values were obtained : mercuric chloride, 1·6, 2·7, 3·9, 6·6 volts; mercuric bromide, 1·5, 2·9, 6·6, 8·9 volts; mercuric iodide, 1·4, 2·7, 6·2, 7·8 volts; iodine, 1·2, 2·3, 3·8, 5·1, 7·5 volts. A. A. Eldridge.

Optical excitation of the vapours of mercuric halides. A. Terenin (Nature, 1926, **118**, 843).—When the vapours, of low density, are illuminated by the spark, bright, visible fluorescence is observed as follows : mercuric chloride, green; mercuric bromide, blue; mercuric iodide, violet, with abrupt intensity maxima at 5600, 5000, and 4400 Å., respectively. The lines stimulating the bands are confined to the limits 1900—1850, 2100—1900, and 2200—2100, respectively. A. A. Eldridge.

Photo-electric polarimetry. H. von Halban (Nature, 1927, **119**, 86).

Method of molecular rays. O. Stern (Z. Physik, 1926, **39**, 751—763; cf. following abstracts).—The method of producing and utilising streams of molecules is discussed in general and its unique value for a number of problems is considered, *e.g.*, (*a*) measurement of magnetic moments of molecules : electron moments of the magnitude of one Bohr magneton, moments of a nucleus of the order 1/2000 of a Bohr magneton, induced moments; (*b*) measurement of the electric moment of molecules; natural dipole moments, quadrupol moments; (*c*) investigation of the field of force of a molecule; (*d*) testing fundamental ideas : whether an atom on emitting a light-quantum is subject to a corresponding recoil (and a similar effect for absorption), the real existence of De Broglie waves. E. B. Ludlam.

Method of molecular rays. F. Knauer and O Stern (Z. Physik, 1926, **39**, 764—779; cf. preceding and following abstracts).—The experimental difficulties are fully discussed and apparatus is described. It is possible to obtain a stream of molecules 20 cm. long and 0·01 mm. thick which will produce a visible deposit in about 10 sec. E. B. Ludlam.

Determination of small magnetic moments of molecules. F. Knauer and O. Stern (Z. Physik, 1926, **39**, 780—786; cf. preceding abstracts).—The apparatus is described by means of which the magnetic moment of the water molecule was determined and a value of the order of one nuclear magneton was obtained. For mercury a negative result was obtained, and this is discussed. E. B. Ludlam.

Variation of the dielectric constant of liquids with pressure up to 3000 kg./cm.^{2} S. Kyropoulos (Z. Physik, 1926, **40**, 507—520).—The dielectric constants were determined for undamped waves of 350 metres at 20° for ether, methyl alcohol, carbon disulphide, chloroform, light petroleum, ethyl alcohol, acetone, water, and pyridine up to 3300 kg./cm.^{2}; for carbon tetrachloride up to 1000, and for benzene up to 390 kg./cm.^{2}, as these begin to solidify at these pressures. The experimental values are compared with the Lorenz–Lorentz equation $(\varepsilon-1)/d(\varepsilon+2)=f_{(p)}$. E. B. Ludlam.

Dielectric constant of "rod-like-particle" sols. J. J. Bikerman (Physikal. Z., 1926, **27**, 769—771).—A statistical computation of the orientation of ellipsoids in a homogeneous electric field has been made, and the conclusions have been applied to the behaviour of vanadium pentoxide sols with rod-like particles (cf. A., 1924, ii, 835). R. A. Morton.

Lack of effect of a magnetic field on the dielectric constant of hydrogen chloride and nitric oxide. L. M. Mott-Smith and C. R. Daily (Physical Rev., 1926, [ii], 28, 976—979).—A field of 4800 gauss produced no detectable change. A. A. Eldridge.

Electrical anisotropy of crystalline liquids. M. Jezevski (Z. Physik, 1926, **40**, 153—160).—The dielectric constants of *p*-azoxyphenetole and *p*-azoxyanisole were determined by a resonance method, using an oil thermostat to obtain the requisite temperature. Measurements were made from the m. p. up to and beyond the clearing point, (1) with no magnetic field, (2) with a magnetic field of 5000 gauss parallel to the lines of electric force in the condenser, (3) varying the angle between the electric and magnetic fields. Tables and curves of the results are given. A magnetic field perpendicular to the electric field produces no effect on the dielectric constant. The magnetic moment for *p*-azoxyphenetole at 143° is $1{\cdot}23\times10^{-15}$, and at 154° $0{\cdot}82\times10^{-15}$, for *p*-azoxyanisole the value at 122° is $1{\cdot}1\times10^{-15}$. E. B. Ludlam.

Molecular and atomic volumes. XI. Volumes of chloro- and aquo-cobaltammines. E. Birk (Z. anorg. Chem., 1926, **158**, 111—116; cf. Ephraim and Schütz, A., 1926, 785).—The molecular volume of trichlorotriamminecobalt is additively constituted of the molecular volumes at 0° Abs. of its constituents. If the chlorine atoms pass outside the nucleus and their places are taken by fresh ammonia molecules, their volume gradually diminishes, until in hexamminecobaltic chloride it is only two thirds of the volume at 0° Abs. (cf. A., 1923, ii, 768). Replacement of a molecule of ammonia by a molecule of water lowers the molecular volume by about 2·5, whereas the difference in the volumes of ammonia and water at 0° Abs. is 5·0. It therefore seems that the volume of the cation is primarily determined by its volume in the hexammine. R. Cuthill.

Physico-chemical properties of cæsium eosinate. R. Delaplace and N. Marinesco (Compt. rend., 1926, **183**, 1106—1107).—Eosin and cæsium eosinate prepared by the method of Delaplace (A., 1926, 949) contain 4 atoms of bromine. Measurements of the volumes in various solvents of the calcium and cæsium eosinate molecules by the method of Marinesco (*ibid.*, 673) confirm the validity of the formula proposed by the latter. Values of the ratio c/S of $7{\cdot}5\times10^{14}$ and $4{\cdot}8\times10^{14}$ were obtained for the cæsium and sodium salts, respectively, where c is the number of dipoles of solvent attached to the molecule and S the surface of the large molecule. Solutions in pure water of the cæsium salt have p_H values corresponding with neutrality, and for a molecular concentration of $2{\cdot}\times10^{-4}$, Λ is 700 times less than for a potassium chloride solution of the same concentration. Mol. wt. determinations by the method of Marinesco (this vol., 17) gave a value of 892 in place of 911. J. Grant.

Magnetic double-refraction in liquids. I. Benzene and its derivatives. C. V. Raman and

K. S. Krishnan (Proc. Roy. Soc., 1927, **A**, **113**, 511—519).—The magnetic double-refraction of liquids is discussed from the point of view of Langevin's theory, which explains this phenomenon as being due to the orientation of the molecules in the magnetic field, and connects the absolute value of the Cotton–Mouton constant with the optical refractivity and the magnetic susceptibility of the molecules along three mutually perpendicular axes. The light scattered by the ideal, spherically symmetrical molecule in a direction transverse to the incident beam would be completely polarised, and the optical anisotropy of the molecule may be calculated from the degree of polarisation of the scattered light. The optical anisotropy of the paraffins is less than that of the aromatic hydrocarbons. The Cotton–Mouton constant is calculated from the polarisation data, the magnetic susceptibility, and the refractive indices. With benzene, assuming an axis of optical symmetry, it is shown that the observed value of the constant can be explained only on the assumption that the molecule exhibits a very pronounced magnetic anisotropy, the susceptibility in the direction of the axis being about twice as large as in the perpendicular direction. On the basis of these results, it is suggested that at least twelve of the electron orbits binding the atoms in the molecules must be oriented in a plane parallel to the ring. In the case of some simple benzene derivatives, where it can be assumed that the optical ellipsoid is still a spheroid of revolution (as in benzene), and that the group which replaces the hydrogen atom is magnetically isotropic, the Cotton–Mouton constant has been calculated and the values have been found to be in fair agreement with the observed values. L. L. Bircumshaw.

Dispersion of atomic hydrogen. I. and II. R. M. Langer (Proc. Nat. Acad. Sci., 1926, **12**, 639—644, 644—648).—I. The dispersion of hydrogen when subjected to ionisation by collision excited by damped wave-trains of high voltage and unspecified current or frequency has been determined for 6000 μμ, and in the pressure range 1·0—20·0 mm., by an interferometer method. The correction for the partial pressure of monatomic hydrogen has been evaluated on the basis of Bonhoeffer's work on the rate of recombination of monatomic hydrogen (A., 1925, ii, 52). On the assumption of an extreme estimate for this correction, the results lead to the value $(\mu_H^2-1)=(1{\cdot}36\pm0{\cdot}34)\times10^{-4}$ (μ_H=refractive index of monatomic hydrogen).

II. Mathematical. It is shown that the values calculated for μ_H^2-1 (cf. above) on the basis of the dispersion theory of Kramers and Heisenberg (Physikal. Z., 1925, **31**, 693) and of the empirical data of Ladenburg (Ann. Phys., 1912, [iv], **38**, 249) are two to three times greater than the values obtained experimentally above This discrepancy is held to question the validity of the correspondence principle. R. W. Lunt.

Anomalous dispersion in electrically excited hydrogen, helium, neon, and mercury. R. Ladenburg (Physikal. Z., 1926, **27**, 789—790).—See A., 1926, 994.

Optical rotation and atomic dimension. VI. D. H. Brauns (J. Amer. Chem. Soc., 1926, **48**, 2776—2788; cf. A., 1925, ii, 633).—The specific rotations, $[\alpha]_D^{20}$, of the following sugars are recorded: halogenated cellobiose hepta-acetates: fluoro-compound, +30·62°; chloro-compound, +71·70°; bromo-compound, +95·76°; iodo-compound, +125·70°; cellobiose β-octa-acetate, −14·11°; *fluoro-4-glucosidomannose hexa-acetate*, m. p. about 145°, +20·75°; 4-glucosidomannose octa-acetate, +36·20°; 4-glucosidomannose, +5·8° (after 24 hrs.); halogen 4-glucosidomannose hepta-acetates: *fluoro*-compound, m. p. 155—156°, +13·60°; *chloro*-compound, m. p. 172°, +51·20°; *bromo*-compound, m. p. 168—169°, +77·90°; *iodo*-compound, m. p. (decomp.?) 140°, +111·50°. The methods of preparation are given in detail. The rotations for the two sets of biose derivatives deviate from the regular relationship observed for the corresponding derivatives of the monose sugars, although an agreement is obtained if the fluoro-compounds are ignored.

S. K. Tweedy.

Scattering of light by gaseous mixtures at high pressures. L. A. Ramdas (Physical Rev., 1926, [ii], **28**, 1030—1033).—Experiments with oxygen and carbon dioxide are described.

A. A. Eldridge.

Scattering and polarisation of light in disperse carbon. G. I. Pokrovski (Z. Physik, 1926, **40**, 278—282; cf. A., 1926, 779).—The scattering and polarisation of light by carbon from flames, from dilute Indian ink, and reflexion from soot are calculated and compared with experiment, with fairly good agreement. E. B. Ludlam.

Crystallised nitrogen. D. Vorländer and W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 1069—1074).—See A., 1926, 1082.

Vibrational energy of the molecules CO and CO_2. F. Matossi (Z. Physik, 1926, **40**, 1—3).—For CO, the coefficient of deformation, calculated from the electric moment of the molecule, is $1{\cdot}10\times10^{-21}$; for CO_2, the value is $4{\cdot}58\times10^{-25}$; the corresponding figures obtained from the molecular refraction are 1·73 and $1{\cdot}43\times10^{-21}$, respectively. E. B. Ludlam.

Molecular constitution of water. G. Tammann (Z. anorg. Chem., 1926, **158**, 1—16).—Examination of the specific volume–temperature and compressibility–temperature curves of water indicates that the difference between these curves and those for normal liquids is due to the presence in the water of relatively large molecules of "water-I," having the space-lattice of ice-I. These molecules diminish in concentration with rise of temperature or pressure, and are incapable of existence above 50°, or under more than 2500 kg./cm.² pressure. The other types of molecules present probably differ so little in volume that variation in their concentrations does not appreciably influence the specific volume or compressibility. From existing compressibility data, it seems likely that water-I has the formula $(H_2O)_6$, and that the other molecular species are isomerides, with the formula $(H_2O)_3$. The effect of water-I on the surface tension and refractivity is proportional to its concentration. R. Cuthill.

***cis-trans*-Isomerism in the case of metallic salts of the type R_2MX_2.** A. Hantzsch (Ber., 1926, 59, [*B*], 2761—2765).—The two forms of the salt $[Cl_2Pt(C_5H_5N)_2]$ are unimolecular in molten phenol, thus establishing the possibility of *cis–trans*-isomerism with this type of substance (cf. Reihlen, A., 1926, 888). The explanation of the plane configuration of molecules R_2EX_2 (in which R and X are positive and negative groups, respectively), whereas molecules of the type ER_4 (in which the substituents are four similar positive or negative groups) are tetrahedral is found in the mutual attraction of the groups R and X, which causes them to be brought into closer proximity with one another than is possible with a tetrahedral configuration. The plane configuration is always possible when the substituents are unsaturated, and is independent of the nature of the central atom. H. Wren.

Electrical polarisation of some carbon compounds. Geometrical and position isomerism. J. Errera (Physikal. Z., 1926, 27, 764—769).—Electrical polarity has been investigated by direct experiment. The total polarisation suffered by a substance in an electric field is approximately equal to the sum of the effects due to electronic, atomic, and molecular polarisations. The latter is a measure of the polarity of a molecule with a permanent dipole. Measurement of dielectric constants under various conditions permit of an analysis of the gross polarisation into the three effects enumerated. Near the m. p., the dielectric constant increases with decreasing frequency for solids which possess permanent dipoles in the liquid state, whereas at a temperature a few tenths of a degree below the m. p. the true dielectric constant characteristic of the solid state is obtained, and is independent of frequency and much less in magnitude than the value for the liquid state. On the other hand, those liquids which have no permanent dipole possess no dispersion on solidification, and at once attain a steady value for the dielectric constant in which the value for the solid is somewhat greater than that for the liquid. These considerations have been applied to dihalogen isomerides of the *cis–trans* and *o*-, *m*-, *p*-types. *Trans*- and *p*-isomerides have no detectable electric moment, whilst *cis*- and *o*-isomerides show a relatively large polarisation; *m*-isomerides show an intermediate effect. Asymmetric ethylene derivatives (two chlorine atoms attached to the same carbon atom) have a weaker moment than the corresponding *cis*-form. In both isomeric series the electric moment increases in the order chlorine, bromine, iodine; the moment for an *o*-substitution product of benzene is greater than that for the corresponding *cis*-derivative of ethylene. Association does not appear to occur in *trans*- and *p*-derivatives. Evidence is given that the deformation of the benzene ring which results from substitution is greater for substituents of greater atomic weight.

The electronic polarisation, molecular refraction, and absorption spectra in the ultra-violet all exhibit higher values for *trans*- than for *cis*-derivatives and for *p*- than for *o*-derivatives. Certain aspects of "polarity" theories do not receive experimental support from the work. It is concluded that the dielectric constant of an organic substance depends less on the nature of the constituent atoms than on their relative positions (cf. A., 1924, ii, 810; 1925, ii, 362, 738). R. A. Morton.

Valency theory and the electrical resistance of metals. H. Burgarth (Z. Elektrochem., 1926, 32, 552—553).—According to the author's valency theory (A., 1926, 560), a point in the outer shell of an atom where an A- and a B-valency neutralise one another (neutralisation point) is a place where a free electron may easily be loosely attached. The electrical conductivity of a metal should thus be determined by the number of these neutralisation points, viz., $\kappa=k(d/A)N.f(M)$, where d=density, A=atomic weight, N=number of neutralisation points on each atom, k=a constant, and $f(M)$ is an undetermined factor to allow for any effect of the relative positions or movement of neutralisation points. Neglecting $f(M)$, the relation for two different metals is $\kappa_1/\kappa_2=d_1N_1A_2/d_2N_2A_1$. It is shown that there is a parallelism between relative values calculated from this relation and the observed values for metals of groups 1, 2, and 3 of the periodic classification. The greatest discrepancy is with mercury, but $f(M)$ may be an important factor here. H. J. T. Ellingham.

Law of homopolar combination of atoms. Co-ordination compounds of platinum metals. H. Remy (J. pr. Chem., 1926, [ii], 114, 337—347).—The law of homopolar combination of atoms, which was formulated in connexion with the oxy-acids (A., 1921, ii, 501), may also be applied to metallic co-ordination compounds in general, and particularly to the new compounds of ferric iron of co-ordination number 5 and 7 (see Remy and Rothe, J. pr. Chem., 1926, [ii], 114, 137). The co-ordination number of a metallic ion represents the number of electrons which must be added to the outer sphere to bring the total up to a value which represents a stable electronic configuration. a is independent of valency, but may have more than one value for the same element. Values of a for a number of elements are tabulated. H. E. F. Notton.

Colour and magnetism of ions. G. Joos (Ann. Physik, 1926, [iv], 81, 1076—1085).—Spectroscopic, chemical, and magnetic evidence shows that the colour and magnetism of the transition elements are due to complexes rather than to simple ions; the complexes are formed by assemblage of electrons into definite entities, and not merely by electrostatic attractions. Between the absorption spectra of salts and their solutions and the spectra of free ions of equal charge no relationship exists, and absorption in the visible region is conditioned by large units which owe their existence to the peculiar configuration of electronic shells in the transition elements which favours complex formation. The paramagnetism is likewise not consistent with simple ions as the effective unit. Magnetic susceptibility affords a means of investigating the structure of the complexes. The method of interpretation is illustrated with reference to cobalt compounds (cf. A., 1920, ii, 301, 366; 1923, ii, 750; 1924, ii, 372). R. A. Morton.

Born's dipole theory of anisotropic liquids. G. Szivessy (Z. Physik, 1926, 40, 477—478).—Polemical (cf. Kast, A., 1926, 1194). E. B. Ludlam.

Molecular diameters at the b. p. P. Walden (Z. anorg. Chem., 1926, 157, 41—44).—The value $0{\cdot}885\times10^{-8}\times V^{1/3}$ cm. (V=mol. vol. at the b. p.) has been derived for the diameter of molecules at the b. p. This is in much better agreement with the values deduced by means of the kinetic theory than is Mokruschin's expression (A., 1926, 780).

R. Cuthill.

Size of the iodine molecule. B. Topley (Nature, 1926, 118, 802—803).—The agreement between Mack's value for the cross-section of the iodine molecule (A., 1925, ii, 1124) with that of Rankine is fortuitous; Mack's value for the diffusion coefficient is too large, and the method of calculation is invalid. The mean value of the diffusion coefficient of iodine vapour in air at 25° and 760 mm. is 0·0815(±1%), whence the effective radius of the average iodine molecule, $\sigma_{I_2}=2{\cdot}923\times10^{-8}$ at 25°, Rankine's value being $3{\cdot}656\times10^{-8}$. A. A. Eldridge.

Changes in the surface of freshly-pulverised crystalline salts [on keeping]. D. Balarev (Z. anorg. Chem., 1926, 158, 103—104).—If powdered crystalline neutral salts such as potassium chloride are heated at 300—400° in a vacuum, they acquire an alkaline reaction, presumably because the free acid formed by hydrolysis by the surface layer of water has been volatilised. This alkaline reaction is more pronounced if the salt has been powdered immediately before heating than if it has been kept for some time before heating. This is taken to mean that the surface of a freshly-powdered crystalline solid rapidly becomes less, *i.e.*, smoother, on being kept in air.

R. Cuthill.

Search for the sixth alkali [metal]. E. Murmann (Oesterr. Chem.-Ztg., 1926, 29, 226—227).—In the course of the unsuccessful search for a sixth alkali metal, the cæsium line 3861·5 was detected in cigar ash, North Sea water, commercial magnesium chloride, rubidium alum, hay ash, and fungi, but not in cæsium alum, potash from beet molasses, and the mother-liquors from oxalic acid and lithium salt preparations. J. W. Baker.

Laue-photograph taken with a long slit. U. Yoshida and K. Tanaka (Nature, 1926, 118, 912—913).—Divergent *X*-rays starting from the focus on the molybdenum target of a Coolidge tube are passed through a long, narrow slit, and then illuminate a long, thin crystal. The Laue spots thus become an assemblage of lines, each point on any one of which corresponds with a certain part of the specimen. Such correspondence may be observed by the shadows cast by thin lead wires across the slit very near to the specimen. The orientation of the atomic plane of the crystal which causes a diffraction line, and the glancing angle of the beam of *X*-rays to the atomic plane can then be calculated at each corresponding point on the specimen, and the indices of an atomic plane responsible for a diffraction line can readily be found. Measurements with single-crystal aluminium wires are recorded; the angles between the axis of the wire and the three edges of the elementary cubic lattice of the crystal are nearly the same for six specimens, and one of the (100) planes of the crystal is situated nearly parallel to the axis of the wire. A. A. Eldridge.

***X*-Ray method of determining coefficient of expansion at high temperatures.** K. Becker (Z. Physik, 1926, 40, 37—41).—The Debye-Scherrer method was used and the preparation was heated by means of an electric current through a tungsten wire. For tungsten, the linear coefficient from 18° to 2200°=$7{\cdot}5\times10^{-6}$, from 18° to 1750°=$6{\cdot}6\times10^{-6}$, from 18° to 1380°=$5{\cdot}8\times10^{-6}$. For zircon, silicon, silicon carbide, and the Nernst filament the values are 4·5, 3·55, 6·25, and $10{\cdot}7\times10^{-6}$, respectively, to the temperatures 1300°, 950°, 1200°, and 2000°. E. B. Ludlam.

Intensity of reflexion of *X*-rays by powdered crystals. I. Sodium chloride, and sodium, lithium, and calcium fluorides. II. Effect of crystal size. R. J. Havighurst (Physical Rev., 1926, [ii], 28, 869—881; 882—890).—I. Structure factor curves for fluorine in the three fluorides are almost identical, but for sodium in the fluoride and chloride there is a difference.

II. An examination of the necessity for extinction corrections in single crystal measurements.

A. A. Eldridge.

Atomic radii. II. M. L. Huggins (Physical Rev., 1926, [ii], 28, 1086—1107).—The atomic radius is defined as the distance between the nucleus and a point midway between the "positions" of the single electrons constituting a valency electron pair. The interatomic distance is then equal to the sum of the two atomic radii only when there is a valency pair on the straight line joining their centres. Further, the radii of the same element in different crystals are the same only when the atoms of the element are structurally similar and are similarly surrounded in the two crystals. Hence many crystal structure determinations are valueless for the calculation of accurate atomic dimensions; new values which the author obtains depend on certain approximations and assumptions. Comparable values of atomic radii have been calculated for a number of elements, and approximate values have been obtained for others. Diameters of the hydrogen atom vary from 1·02 Å. in potassium hydrogen fluoride to 1·7 Å. in ammonium bromide. A. A. Eldridge.

Relation between lattice constants and densities in nickel steels. A. Ôsawa (Sci. Rep. Tôhoku Imp. Univ., 1926, 15, 619—630).—See A., 1926, 564.

Recrystallisation of copper wire. E. Schmid and C. Wassermann (Z. Physik, 1926, 40, 451—455).—Copper wire hard drawn shows no change in *X*-ray photographs until heated at about 100°, when recrystallisation begins, a simple thread-like structure being formed with the (112) direction parallel to the axis of the wire. Such wire possesses no elastic recoil. E. B. Ludlam.

Arrangement of micro-crystals in silver deposited by electrolysis. H. Irata and H. Komatsubara (Mem. Coll. Sci. Kyōtō, 1926, 10, 95—109, and Z. anorg. Chem., 1926, 158, 136—152).—Silver was deposited electrolytically on rolled silver plates from solutions of the nitrate containing free nitric acid. The crystals tend to take up a fibrous arrangement, in which the axis of the fibre is parallel to the diagonal of a cube face in the cubic lattice, but in which the orientation about this axis is haphazard. *X*-Ray photographs taken before and after treating the deposit with nitric acid showed that the above structure exists through the whole fibre, and not merely on the surface. Some specimens showed grains oriented at random as well as those in the fibrous arrangement. W. Hume-Rothery.

Atomic structure of AgMg and AuZn. E. A. Owen and G. D. Preston (Phil. Mag., 1926, [vii], 2, 1266—1270).—The crystal structure of the compound AgMg has been determined both by means of an *X*-ray spectrometer and by the powder method, using a Müller camera. Both methods show a simple cubic structure for the compound, the parameters being 3·28 and 3·27 Å., respectively, by the two methods. The density of the material was determined as 6·2, which leads to the result that one atom of silver and one of magnesium are associated in the unit cell. When the material was etched before examination with the spectrometer, a spectrum was obtained corresponding with a face-centred cube of side 4·076 Å. This is in fair agreement with the value obtained by McKeehan (A., 1923, ii, 428) for the parameter of the silver lattice, and indicates that the etching medium dissolved out the magnesium from the body-centred lattice and that the silver atoms recrystallised at the ordinary temperature on a face-centred lattice. The compound AuZn shows a simple cubic structure of parameter 3·19 Å., there being one atom each of gold and zinc in the unit. Both structures are therefore of the cæsium chloride type.
A. E. Mitchell.

Crystal structure of beryllium, zinc, cadmium, and mercury tellurides. W. Zachariasen (Z. physikal. Chem., 1926, **124**, 277—284).—The crystal structure of these substances was investigated by means of the powder method. All four tellurides crystallise regularly, with the zinc-blende structure. The lengths (in Å.) of the sides of the unit cells, as determined by precision measurements, and the densities are as follows: BeTe, 5·615$\pm$0·006, 5·090; ZnTe, 6·089$\pm$0·002, 5·639; CdTe, 6·464$\pm$0·002, 5·866; HgTe, 6·434$\pm$0·003, 8·123 (cf. Hartwig, A., 1926, 664; de Jong, *ibid.*, 996). L. F. Gilbert.

Form and energy of crystalline sodium nitrate. J. Topping and S. Chapman (Proc. Roy. Soc., 1927, **A**, **113**, 658—673; cf. A., 1926, 664).—Calculations of the kind made by Lennard-Jones and Dent (following abstract), of the energy in various configurations corresponding with the "intrinsic" repulsive forces between the atoms of a crystal of the calcite type have been used, in conjunction with the values of the electrostatic energy given previously (*loc. cit.*), to determine the total energy of the sodium nitrate crystal in various possible configurations, this total energy being reckoned from a state of infinite dispersion of the sodium ions and nitrate ionic groups. If a slight change in the repulsive force data given by Lennard-Jones and Dent is made, the series of possible stable configurations is found to pass through the actual measured configuration. The corresponding value of b (the distance between the nitrogen ion and the force-centres of the asymmetric oxygen ions of a nitrate group) is 0·96 Å. The source of discrepancy between this value and the value 0·72 Å. given previously (*loc. cit.*) is probably due to a slight variation, during the special type of virtual displacement of the crystal in which the size of the nitrate group is assumed fixed, in the energy of the repulsive forces between oxygen atoms not of the same nitrate group. Similar considerations explain the discrepancy found by Lennard-Jones and Dent with calcium and magnesium carbonate crystals.
L. L. Bircumshaw.

Theoretical determinations of the structure of carbonate crystals. I and II. J. E. Lennard-Jones and (Miss) B. M. Dent (Proc. Roy. Soc., 1927, **A**, **113**, 673—689, 690—696).—I. From a knowledge of the intrinsic repulsive forces between all the constituent ions, the potential energies of calcium and magnesium carbonate crystals are calculated for all possible configurations. The function passes through a minimum, which corresponds with the most stable arrangement. For a carbonate group of given size, this direct method determines the size and angle of the rhombohedral cell, and also furnishes an absolute value for the crystal energy, a quantity not yet determined by any other method. The potential energy per mol. of the crystal is given by $W=W^{(e)}+W^{(n)}$, where $W^{(e)}$ is the energy due to the electrostatic forces (cf. Chapman, Topping, and Morrall, A., 1926, 664), and $W^{(n)}$ the contribution of the repulsive forces. A detailed description is given of the method of calculation. The distance b between a carbon ion and the force centre of an oxygen ion in the same carbonate group is regarded as an adjustable parameter to be determined theoretically. The value 1·08 Å. gives the best agreement between theory and experiment, for both calcium and magnesium carbonate. The values of the crystal parameters, corresponding with this value of b, are: for magnesium carbonate, rhombohedral angle 102° 24′ (calc.), 103° 21·5′ (obs.); distance between carbon ions 4·66 (calc.), 4·61 Å. (obs.); crystal energy per g.-mol. 771 kg.-cal.; and for calcium carbonate, rhombohedral angle 102° 18′ (calc.), 101° 55′ (obs.); distance between carbon ions 4·96 (calc.), 4·96 Å. (obs.); crystal energy per g.-mol. 701 kg.-cal. It is found that no improvement is obtained in the agreement between the theoretical and experimental values on the assumption that the centre of the repulsive forces of the oxygen ion does not coincide with that of the electrostatic forces.

II. On the assumption that $b=1·08$ Å. for the crystals of calamine, chalybite, rhodochrosite, and cadmium carbonate, and that the repulsive forces operating between the ions of these crystals are represented by inverse power laws, the numerical values of the force constants may be calculated, provided that the indices of repulsion are known. A formula is given for calculating the work required to separate one g.-mol. of a crystal of the calcite type into its metallic ions and carbonate groups (U), which is a function of two unknowns only, μ_{12} and n_{12}, the force constant and index, respectively, which determine the repulsive forces between the metallic ions and the carbonate groups. For calamine and chalybite, two sets of values are given for U, corresponding with the two alternative cases $n_{12}=10$ and $n_{12}=11$.

Thus, for calamine, if $n_{1\,2}=10$, $U=772$ g.-cal./g.-mol., if $n_{1\,2}=11$, $U=777$ g.-cal./g.-mol.; for chalybite, if $n_{1\,2}=10$, $U=759$ g.-cal./g.-mol., if $n_{1\,2}=10$, $U=765$ g.-cal./g.-mol. For manganous and cadmium carbonates, $n_{1\,2}=11$, and $U=750$ and 719 g.-cal./g.-mol., respectively. L. L. Bircumshaw.

Crystal structure of ammonium hexachloroplumbate, $(NH_4)_2PbCl_6$. R. W. G. Wyckoff and L. M. Dennis (Amer. J. Sci., 1926, [v], 12, 503—509).—*X*-Ray powder photographs of ammonium chloroplumbate indicate that it forms a face-centred cubic lattice with odd order reflexions only from planes with all odd indices. The length of the edge of the unit cube containing four molecules is 10·14 Å. The experimental value for the density obtained by using benzene as the wetting liquid is 2·6; $d_{\text{calc.}}$ is 2·89. The structure is similar to that of the platinum, tin, and silicon analogues. M. S. Burr.

Crystallographic investigations on certain heteropoly-compounds. F. Rodolico (Atti R. Accad. Lincei, 1926, [vi], 4, 471—475).—Compounds of the series $(NH_4)_6H[X(W_2O_7)_x(V_2O_6)_y],nH_2O$, in which X is either P or As and *x* and *y* are variable but have the sum 6 for any one compound, crystallise in the tetragonal system. For the one limiting (α) compound of the phosphorus series, containing 40·06% WO_3 and 32·86% V_2O_5, the axial ratio is $a:c=1:0{\cdot}9932$, and for the other (ω), containing 64·22% WO_3 and 12·09% V_2O_5, $a:c=1:1{\cdot}0011$. The corresponding values for the arsenic series are, for the α-compound, with 40·26% WO_3 and 31·60% V_2O_5, 1 : 0·9994, and for the ω-compound, with 63·28% WO_3 and 13·06% V_2O_5, 1 : 1·0011. Hence, geometrically these crystals may be regarded, within the limits of experimental error, as possessed of monometric symmetry. The two series of crystals are isomorphous, and as, moreover, the radical W_2O_7 may be partly replaced by Mo_2O_7, arsenophosphomolybdotungstovanadates, containing five acid radicals, are obtainable; these compounds exhibit almost unchanged the crystalline characters of the simpler ones.

The crystals of the silicotungstates, studied by Wyrouboff (A., 1897, ii, 173), exhibit marked morphological analogy with those described above. T. H. Pope.

Symmetry of sylvine and the nature of its etching figures. K. F. Herzfeld and A. Hettich (Z. Physik, 1926, 40, 327—330; cf. A., 1926, 889; Valeton, *ibid.*, 1085).—The right and left groups of the six-faced octahedron are stereochemically different and would behave differently towards optically active impurities. It is claimed that the plagihedry of potassium chloride has not been proved. E. B. Ludlam.

Structure of phenacite, Be_2SiO_4. W. L. Bragg (Proc. Roy. Soc., 1927, A, 113, 642—657).—Twenty-one parameters are required to define the structure of phenacite. An attempt has been made to measure the fifteen parameters determining the positions of the silicon and oxygen atoms. Knowledge of other structures is used to suggest a series of possible configurations of the crystal, the SiO_4-group being assumed to be distinct, and to have the same form as in other orthosilicates. These configurations are tested by their capacity to explain the reflecting powers of the crystal planes. All experimental observations of reflecting power are expressed as absolute values, and interpreted by means of Darwin's formula for reflexion by an imperfect crystal, which for phenacite is $F=11{\cdot}65\sqrt{\{\sin 2\theta/(1+\cos^2 2\theta)\}}(\rho\times10^6)$, ρ being the integrated reflexion $E\omega/I$, measured by rotating the crystal at constant angular velocity, ω. It is believed that the method of using absolute measurements leads directly to a close approximation of the structure. The following measurements were made on the crystal: (*a*) a rotation photograph with the trigonal axis vertical; (*b*) an absolute determination of intensity of reflexion by the planes (111), $(1\bar{1}0)$, $(11\bar{2})$, (110), (100) for a number of orders; and (*c*) a relative determination of intensity for about fifty planes round the trigonal axis. The crystal belongs to the space-group C_{3i}^2; the space lattice is rhombohedral, with $a=7{\cdot}17_8$, $b=7{\cdot}66_4$, $c=8{\cdot}22_6$ Å.; the unit cell contains six molecules, each occupying a volume of 61 Å.^{3} The proposed structure is built up as follows: four parallel rows of oxygen atoms at intervals of 2·74 Å. are placed together so that a column of Y-shaped section results; two sets of these composite columns are packed together, one set being displaced 1·37 Å. parallel to its length relatively to the other; the silicon atoms lie at the centres of tetrahedral groups of oxygen atoms, similar positions being probably occupied by the beryllium atoms. L. L. Bircumshaw.

Formation of mixed crystals by precipitation. G. Lunde (Ber., 1926, 59, [*B*], 2784—2786; cf. Barth and Lunde, A., 1926, 895).—Addition of potassium iodide to a cold solution of silver nitrate and copper sulphate causes the precipitation of homogeneous mixed crystals of silver and cuprous iodides. With potassium bromide and iodide, silver nitrate gives mixed crystals of the silver bromide type if 50% or less of silver iodide is present, whereas if the proportion of silver iodide exceeds this amount, two forms of mixed crystals (silver bromide and zinc sulphide types) are simultaneously produced. The mixed crystals obtained by addition of thallium carbonate to potassium iodide and bromide are of the cubic or rhombic type, according to the relative proportion of thallous bromide and iodide. The double *salt*, 2AgCl,3TlCl, is described. H. Wren.

***X*-Ray analysis of crystal structures and its relation with chemical constitution.** W. L. Bragg (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 44—65). Chemical Abstracts.

Organic crystals. W. H. Bragg (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 21—27). **Tables [of cleavage spacings] relating to long-carbon-chain derivatives.** A. Muller (*ibid.*, 27—29). G. Shearer (*ibid.*, 29—38). **Succinic acid etc.** (Miss) K. Yardley (*ibid.*, 38—41). **General list of organic crystals.** W. T. Astbury (*ibid.*, 41—43). Chemical Abstracts.

Orientation in solids. G. Shearer (Trans. Faraday Soc., 1926, 22, 465—468).—See A., 1926, 1195.

X-Ray evidence for the existence of different modifications of fatty acids. G. M. de Boer (Nature, 1927, **119**, 50).—Stearic acid, obtained by slow crystallisation from acetone, alcohol, or petroleum, shows a long spacing of 43·95 Å., whilst a thin layer obtained by fusion or by the evaporation of an alcoholic solution gives a spacing of 39·75 Å. Thus the existence of different modifications of stearic acid is indicated. The long spacing of undecoic acid is 25·4 Å. at 20°, and 30·1 Å. at 12·5°, supporting the results of Garner and Randall (A., 1924, ii, 385) and Garner and Ryder (*ibid.*, 1925, ii, 355). A. A. Eldridge.

Various crystalline forms of long-chain organic compounds. Difficulties in the interpretation of their X-ray spectra. J. Thibaud (Compt. rend., 1927, **184**, 24—26).—Measurements of the X-ray spectra of pure stearic acid indicate that it can crystallise in various forms having carbon chains of different lengths (cf. Piper, Malkin, and Austin, A., 1926, 1083). Similar measurements with mixed fatty substances (such as butters), with the mixed fatty acids obtained by hydrolysing them, and with their lead soaps, indicate that the method may be used to distinguish between the various types of butter. The analytical interpretation of the results is complicated by the variation of the value of the crystal spacing according to the origin, method of preparation, and purity of the substance. This is especially true for mixtures, particularly of substances of similar nature and having the same number of carbon atoms in the molecule. When heavy atoms are introduced into the chain (as in the case of lead soaps), the variations are less. J. Grant.

X-Ray examination of the crystal structure of certain compounds. A. N. Sarkar (Phil. Mag., 1926, [vii], **2**, 1153—1165).—Examination of the crystal structure of pyrocatechol by the powder method indicates that the basic lattice is Γm, there being 2 molecules per unit cell. The space-group is C_{2h}^{4}. The molecules should thus possess an element of symmetry which can be either a centre of symmetry or an axis of binary symmetry; the data are not sufficient to differentiate between the alternatives. The translation of the glide plane parallel to itself is $c/2$, so that the molecules are most densely packed in the (100) plane, thus accounting for the fact that the direction of cleavage is parallel to the (100) plane. Examination of a crystal of potassium ferricyanide by Laue's method shows that the basic lattice is Γm, that the molecules are asymmetric, and that the space-group is either C_{2h}^{4} or C_{2h}^{5}, according as the axis of symmetry is a simple or a screw axis. The Laue photograph of aluminium acetylacetonate, together with some measurements of Astbury, shows that the space-group is C_{2}^{2}, with a screw-axis of symmetry and 4 molecules per unit cell. A. E. Mitchell.

X-Ray study of isomorphism in simple organometallic series. I. Tetraphenyls. W. H. George (Proc. Roy. Soc., 1927, *A*, **113**, 585—593).—Crystals of carbon, silicon, germanium, tin, and lead tetraphenyl, examined by the rotating and oscillating single-crystal methods, using the $K\alpha$ radiation from a copper anticathode, and employing Bernal's method of interpretation (this vol., 9), yield X-ray photographs which are identical, except for intensity and small dimensional variations. The unit cell contains 2 molecules, having a tetrad alternating axis of symmetry parallel to the c axis of the crystals. The dimensions of the unit cell are: for the carbon compound, a=10·86, c=7·26 Å.; for the silicon compound, a=11·32, c=7·03 Å.; for the germanium compound, a=11·60, c=6·85 Å.; for the tin compound, a=11·83, c=6·42 Å.; and for the lead compound, a=12·06, c=6·50 Å. Thus the size of the square base of the cell increases with increase of atomic number of the grouping element, whilst the height of the cell decreases. The molecules lie very nearly in the (110) planes, consistent with the marked development of the (110) faces, and although the space-group is D_{2d}^{1}, the structure approximates very closely to that of the space-group D_{4h}^{15}, which has a plane of symmetry parallel to the (110) plane. The grouping atoms of the molecules lie at the corners and at the centre of the cell, and the phenyl groups are very nearly bisected by the (110) planes, and probably lie near the direction of the shortest distance between the metallic atoms. L. L. Bircumshaw.

Space-group and molecular symmetry of β-benzene hexabromide and hexachloride. S. B. Hendricks and C. Bilicke (J. Amer. Chem. Soc., 1926, **48**, 3007—3015).—X-Ray examination of the cubic β-(or *cis*-)modifications of the hexachloride or hexabromide of benzene showed them to have the atomic arrangement of the space-group T_{h}^{6}, the molecular symmetry being that of the point-group C_{3i}. The unit cubes contain 4 molecules, the edge being 10·07 for the chloride and 10·42 Å. for the bromide. These structures do not eliminate the possibility that the carbon or the halogen atoms are coplanar, but, neglecting this specialisation, the arrangement of 4, 5, or 6 atoms on the same side of the plane of the molecule would not give the correct symmetry. The structures given by Friedel (A., 1891, 1196) are considered to be incorrect. The conclusions are not in agreement with Mohr's theory of strainless rings as applied to *cyclo*hexane and its derivatives (*ibid.*, 1919, ii, 229). S. K. Tweedy.

Crystalline forms of 5-nitrosalicylic acid and of related compounds. F. D. Chattaway and W. R. C. Curjel (J.C.S., 1926, 3210—3215).—By cooling slowly, to the ordinary temperature, a hot, saturated, aqueous solution of 5-nitrosalicylic acid, a hitherto unrecognised *monohydrate* has been separated as very slender, strongly doubly-refracting, elongated, and almost colourless prisms, which readily lose water on exposure to air. Dilatometric and solubility measurements indicate that the transition point is in the neighbourhood of 42·5°. Details of the crystalline structure of the anhydrous form are given, but do not agree with those observed by Fels (Z. Krist., 1903, **37**, 486). No measurable crystals of the hydrated form have been obtained, but they are probably orthorhombic. Crystallographic details are also given for ethyl 5-nitrosalicylate, m. p. 96°, d^{19} 1·429, and for the stable modification of 5-nitro-2-ethoxybenzaldehydesemicarbazone. The crystals of the labile form, which are unsuitable for measurement, are slender, strongly doubly-refracting prisms. M. S. Burr.

The crystal as a homogeneous polyhedron and the relations between the physical properties of crystals and the various groups of geometrical crystallography. J. Beckenkamp (Z. Physik, 1926, 40, 237—254).—Crystal nomenclature, types of symmetry, electrical polarity, enantiomorphy, transmission of light, and elastic deformation are discussed from the point of view of the space lattice. E. B. Ludlam.

Magneto-spectroscopic investigations on nickel wires with short Hertzian waves. H. Israël (Z. Physik, 1926, 39, 841—857).—Waves from 30 cm. to 2 metres in length were produced by means of a quenched spark and measured by means of Lecher wires. By a comparison of the decrement of the oscillations in nickel wire, magnetised and unmagnetised, with that of copper, the permeability of the nickel wires could be calculated for the different wave-lengths; these are given in tables and the curves are plotted; they are complicated, but less so for the thinner of the two wires used than for the thicker. E. B. Ludlam.

Apparent doubling of the optic axis of calcite by means of Federov's plate. (Miss) M. Philibert (Atti R. Accad. Lincei, 1926, [vi], 4, 376—381).—This phenomenon (cf. this vol., 10) is shown to be due to the anisotropy of the spherical segments of Federov's plate, which behave like a biaxial doubly-refracting substance. Far from being negligible, this double refraction of the segments gives axial angles of 11° and 14° in the two cases considered. T. H. Pope.

Increase of tensile strength of single crystals by plastic deformation. E. Schmid (Z. Physik, 1926, 40, 54—74).—The increase of strength of the main faces of slip in zinc crystals caused by plastic extension has been investigated; after passing the elastic limit, the strength increases linearly with the extension. The shape of the extension curve for single crystals depends on the angle between the slip and the direction of the applied force. The group of curves relating the force in the main plane of slip to the extension can be represented by a single line, almost straight. A comparison is obtained for the increase in strength along the actual planes of slip and the latent planes (which cut the former) for crystals of zinc and tin; if the two planes are crystallographically identical, the increase of strength is less in the actual than in the latent planes; for zinc, in which the planes are not the same, the increase is greater in the main actual plane of slip. E. B. Ludlam.

Variation of mol. wt. of lead with temperature. A Jouniaux (Bull. Soc. chim., 1926, [iv], 39, 1680—1686).—It is shown that, above 450°, the molecule of lead is monatomic, and that below it is associated somewhat. The mol. wt. was determined cryoscopically at a number of temperatures between 450° and 1850° by using various metals as solvents, and the values are distributed irregularly about the atomic weight of lead, the anomalies being explained by the formation of mixed crystals. The mol. wt. at the b. p. deduced from latent heat data, and also the vapour-density values, indicate a monatomic molecule above 450°. The mol. wt. below 450° was obtained both ebullioscopically, using mercury as solvent, and also from surface-tension data, using the Eötvös–Ramsay equation. Thence, on the assumption that lead is monatomic at high temperatures, its critical temperature is calculated to be approximately 2200°; by inserting this value in the equation, the mol. wt. is calculated at lower temperatures, and is found to increase from 207·2 at 500° to 285·7 at 327°. S. J. Gregg.

Mol. wt. of egg-albumin. I. In electrolyte-free condition. T. Svedberg and J. B. Nichols (J. Amer. Chem. Soc., 1926, 48, 3081—3092).—The method of determining atomic weights by the ultracentrifuge (A., 1926, 340, 677) is adapted so as to be applicable to colourless proteins. By this modified method, the mol. wt. of egg-albumin, purified by electro-dialysis, is found to be 34,500±1000 in electrolyte-free solutions. Moderately pure egg-albumin contains a small amount of a substance of mol. wt. 170,000, probably unprecipitated globulins. S. K. Tweedy.

Influence of pressure on electrical conductivity of platinum. A. Michels and P. Geels (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1106—1112).—A platinum-resistance thermometer was used and its resistance determined at 15·57°, 21·95°, and 34·75° at pressure intervals up to 251·5 kg./cm.^{2} The results differ from previously published data in that the pressure coefficients vary more considerably with the pressure, and at lower pressures the coefficient varies to a greater extent with the temperature. The importance of this for the measurement of temperature by means of the platinum-resistance thermometer is pointed out. E. S. Hedges.

Hall effect in bismuth sputtered films. T. F. Hargitt (Physical Rev., 1926, [ii], 28, 1034—1037).

Determination of optical constants of metals in the visible and ultra-violet. G. Pfestorf (Ann. Physik, 1926, [iv], 81, 906—928).—A method of examining the light polarised by reflexion from metallic surfaces has been described which enables the refractive index and absorption coefficient to be evaluated. These constants have been determined over the range 250—600 μμ for copper, gold, zinc, silicon, manganese, nickel, and a steel. Considerable discrepancies found between the results of earlier workers are traced to variations in the degree of polishing and alterations in the chemical condition of the metallic surface. Adsorption of liquid films has been investigated in relation to the reflexion of light by nickel and copper mirrors. The high polish necessary for trustworthy results was obtained by a process, not disclosed, due to the firm of Zeiss. The effect of high polish is much greater than that due to adsorption. R. A. Morton.

Applicability of discharge tubes containing noble gases as photometers. H. Kniepkamp (Z. Physik, 1926, 40, 12—36).—The method consists in counting the number of flashes per sec. produced when the light to be measured falls on the discharge tube. The mean number of flashes is proportional to the intensity of the light. A dark effect was traced to impurities, probably remains of water vapour or air in the bulb. The method is described in detail. Comparison showed that the method of counting flashes was several thousand times more sensitive than using the bulb as a photo-electric cell in the ordinary way, *e.g.*, a normal candle produced one flash per sec. at a distance of 5 metres; a mercury vapour lamp would produce one per sec. at about 150 metres distance. E. B. Ludlam.

Deviation from Lambert's law and polarisation of light emitted by incandescent tungsten, tantalum, and molybdenum, and changes in the optical constants of tungsten with temperature. A. G. Worthing (J. Opt. Soc. Amer., 1926, **13**, 635—649).—The deviations from Lambert's cosine law for the light emitted by tungsten, molybdenum, and tantalum are of the same order. The brightness increases from the normal value at normal emergence gradually with increase in emergence angle to about 75° by 20%, and then decreases rapidly to 0 at grazing emergence. Straight filaments of circular cross-section have average brightnesses, viewed normal to their axes, which are greater than the normal brightness by 2·8% for tungsten, 3·6% for molybdenum, 2·7% for tantalum. The average brightness of a filament considering all directions is about 5% greater than the normal brightness. The polarisation of the light emitted, which is zero for normal emergence, increases with angle of emergence to about 95% at grazing emergence, and, for straight circular filaments viewed normal to their axes, is about 20%. The values of the optical constants n and k for tungsten were found to be 3·86 and 0·81 at 300° Abs., and 3·85 and 0·89 at 1900° Abs. C. J. Smithells.

Polishing of surfaces. F. W. Preston (Nature, 1927, **119**, 13).—In the polishing of glass, the amount of material removed corresponds with a solid layer of the order of ten wave-lengths in thickness. The efficiency of the operation, on the assumption that the energy is required for liquefying a thin surface layer, is not more than about 0·5%. The process is regarded as primarily one of abrasion (cf. Macaulay, A., 1926, 998). A. A. Eldridge.

High-temperature thermometer. [Properties of gallium.] S. Boyer (J. Opt. Soc. Amer., 1926, **13**, 117—122).—Details are given for constructing a thermometer in which the glass and mercury of the ordinary type are replaced by fused quartz and gallium, respectively. Temperatures up to 1000° may be measured; the position of the lower limit depends on the fact that liquid gallium is easily undercooled below the m. p. (29·7°); undercooling to —20° was often observed. The removal of gas from liquid gallium and the effect of impurities on the amount of undercooling and on the tendency to wet quartz have been investigated. The ease of surface oxidation of gallium is greater than is reported in the literature. L. F. Gilbert.

Determination of high temperature by the effusion and transpiration of gas. Y. Yamaguchi (Bull. Chem. Soc. Japan, 1926, **1**, 209—215).—For the measurement of high temperature, three methods are given, depending on the rate of flow of gases. The first requires the measurement of t, the time of effusion of a given volume of gas through a quartz tube, and from the relation $t=a+b\sqrt{T}$ (where a and b are constants) temperatures up to 1000° can be determined. In the second method, also applicable up to 1000°, the temperature is found from the expression $\log T=a+b\log t+c(\log t)^2$, where t is the rate of transpiration of gas through a quartz capillary tube and a, b, and c are constants. The temperature of the transpiring gas may also be determined by observation of the increase of pressure p required to maintain a constant rate of flow with elevated temperature. In this case, the relation $\log p=a\log T+b$ (where a and b are constants) obtains up to 1200°. A. S. Corbet.

Method for obtaining very low temperatures. F. Simon (Physikal. Z., 1926, **27**, 790—792).—The liquefaction of gases would be easy if the less volatile gas (*e.g.*, hydrogen) could be so far removed by pumping that the temperature would fall below the critical point of the more volatile gas (*e.g.*, helium). The lowest point attained by pumping off hydrogen (9°) is still well above the critical temperature (5·2°) of helium. This and similar gaps can be bridged by a new device. A vessel containing gas-free carbon is connected to a vessel containing helium. The preliminary cooling is carried out by means of liquid hydrogen and the temperature reduced as far as possible by pumping off hydrogen. Helium is then passed into the cold charcoal under a few atm. pressure. The considerable heat of adsorption is taken up by the hydrogen in the surrounding Dewar flask. On bringing the vessel into thermal isolation and pumping off the adsorbed helium, the temperature of the charcoal falls. Using 17 litres of helium, 15 g. of charcoal, 8 litres of helium were adsorbed, and in a few seconds after beginning to pump off the gas the temperature fell to 7° Abs. and in a few minutes to below 4° Abs. The high degree of cold can be maintained for a few hours. There are serious difficulties in the way of making a continuous process employing the new principle. R. A. Morton.

Measurement of true specific heats at high temperatures. H. Klinkhardt (Z. Elektrochem., 1926, **32**, 534—535).—The substance, preferably in the form of a short cylinder, is made the anode in an evacuated glass vessel and subjected to bombardment by electrons from a neighbouring cathode consisting of platinum foil coated with an alkaline-earth oxide or a tungsten wire coated with thoria. A cage around the electrode system minimises energy losses due to reflexion of the electrons. The current may be a few milliamps. at 100—200 volts, but it is important that the pressure should be at least as low as 10^{-4} mm. Under these conditions, the kinetic energy of the electrons is converted almost entirely into heat in the anode. The rise in temperature of the latter due to the transfer of a measured amount of energy during a short period of bombardment is measured by a thermocouple in contact with the anode. Data obtained for nickel over the range 100—450° are recorded on a graph; the accuracy is about 0·5%. Materials which are insulators or have high vapour pressures can be dealt with if sealed in a metal container, but the accuracy is less than with metals. Values for the specific heat and the heat of transition of ammonium chloride are recorded.

H. J. T. Ellingham.

Specific heats of a highly cooled, non-condensed phase. N. Perrakis (Compt. rend., 1927, **184**, 28—30).—Starting from the revised form of Trouton's rule, the author has confirmed, by means of simple thermodynamical considerations, Perrin's conclusion that all gases cooled sufficiently have molecular heats equal to those of monatomic gases.

J. Grant.

Six-place tables of the Debye energy and specific heat functions. J. A. Beattie (J. Math. Phys. Mass. Inst. Tech., 1926, 6, 1—32).—The values of $\frac{1}{3}UR^{-1}T^{-1}$ and of $\frac{1}{3}C_vR^{-1}$ have been computed as functions of the argument x ($=h\nu_mk^{-1}T^{-1}$, where v_m is a frequency characteristic of the substance) in the range 0—24 in increments of 0·1. For values of x greater than 24, an error of less than one in the sixth significant figure is introduced by using $\frac{1}{3}UR^{-1}T^{-1}=19{\cdot}481818x^{-3}$, and $\frac{1}{3}C_vR^{-1}=77{\cdot}92727x^{-3}$.

R. W. Lunt.

Latent heat of fusion. N. von Raschevsky (Z. Physik, 1926, 40, 214—219).—Proceeding from the assumption that the liquid state is reached when the distance between the atoms becomes so great that the elastic modulus becomes zero, the second differential of the lattice energy in respect to lattice constant becoming zero, the value of the latent heat of seven metals is calculated and is in satisfactory agreement with experiment.

E. B. Ludlam.

Determination of the latent heat of vaporisation of liquid helium. L. I. Dana and H. K. Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1051—1060).—A simple method is described by means of which the latent heat of vaporisation of liquid helium has been measured for pressures at and below 1 atm. The results show that the curve representing the heat of vaporisation as a function of temperature shows a maximum near 3° Abs. and descends again at lower temperatures. This agrees with the values of latent heat derived by application of the Clapeyron–Clausius formula to the data of other workers. The behaviour of the saturated vapour deviates appreciably from the ideal gas laws. An anomaly was noticed at the temperature of maximum density.

E. S. Hedges.

Determination of the specific heat of liquid helium. L. I. Dana and H. K. Onnes (Proc. K. Acad. Wetensch. Amsterdam, 1926, 29, 1060—1068).—An apparatus is described for measuring with an accuracy of about 3% the specific heat of liquid helium and its variation with temperature for saturation pressures at and below 1 atm. The method of following the rise in the temperature of the liquid on heating was to determine the rise in vapour pressure. A table is given showing the specific heats at different temperatures; these values, when plotted, tend to lie on a straight line.

E. S. Hedges.

Heats of vaporisation of condensed gases at low pressures. A. Eucken and E. Donath (Z. physikal. Chem., 1926, **124**, 181—203).—A method of determining heats of vaporisation or sublimation is described which depends on the measurement of heats of condensation and is applicable at pressures as low as 1 mm. Liquid and solid ammonia, solid carbon dioxide, nitrous oxide, and hydrochloric acid were investigated. Giacomini's value for the heat of vaporisation of ammonia (A., 1925, ii, 757) was not confirmed. The heats of vaporisation of carbon dioxide and nitrous oxide accord with the hypothesis that the molecules of these gases have open structures (cf., for carbon dioxide, A., 1922, ii, 349, 805). The data obtained for ammonia and carbon dioxide allow the integration constant i in the vapour-pressure formula to be directly calculated (cf. *ibid.*, 1925, ii, 98); for carbon dioxide, the value is the same as previously obtained (*loc. cit.*), but for ammonia it is somewhat less.

L. F. Gilbert.

Degree of polymerisation of vapours at the b. p. V. Kirejev (Z. anorg. Chem., 1926, **157**, 138—140; cf. A., 1926, 1088).—Reasons are given for supposing that the molecular heat of vaporisation in the usual expression for Trouton's constant K is that of the vapour, not that of the liquid. Hence by comparing the observed values with those calculated by means of the equation $K=f(T_s)$, where T_s is the b. p., the mol. wt. of the vapour can be calculated. For a number of liquids, the results are in good agreement with the values obtained from the ebullioscopic constant and vapour pressure. In some instances, the opposing effects of association of the liquid and polymerisation of the vapour may cause Trouton's constant to have its theoretical value. R. Cuthill.

Heat of formation of cementite. G. H. Brodie, W. H. Jennings, and A. Hayes.—See B., 1927, 14.

Influence of pressure on the crystallisation temperature of *p*-azoxyanisole and α-naphthylamine. N. A. Pushin and I. W. Grebenschtschikov (Z. physikal. Chem., 1926, **124**, 270—276; cf. Hulett, A., 1899, ii, 468).—The influence of pressure on the m. p. and transition point (temperature of change from liquid-crystalline to isotropic state) of *p*-azoxyanisole and on the m. p. of α-naphthylamine has been investigated; the maximum pressures employed were 1088, 2645, and 2995 kg./cm.^{2}, respectively. In each case, pressure is an approximately linear function of temperature. Ostwald's opinion that with increase of pressure the range of existence of liquid crystals decreases, *i.e.*, that the critical point isotropic liquid–solid may be realised experimentally, is contradicted by the data obtained for *p*-azoxyanisole.

L. F. Gilbert.

Trouton's quotients. W. Herz (Z. anorg. Chem., 1926, **157**, 382—384).—There appears to be no corresponding temperature above the b. p. at which the ratio of the molecular heat of vaporisation of liquids to their b. p. (Abs.) is any more nearly constant than it is at the b. p.

R. Cuthill.

Rule of the three temperatures. E. van Aubel (J. Chim. phys., 1926, **23**, 823).—A correction of Prud'homme's paper (A., 1921, ii, 376).

R. Cuthill.

Relation between temperature of incipient increase in size of granules and m. p. of metals. A. A. Botschwar (Z. anorg. Chem., 1926, **157**, 319—

320).—For a number of metals the ratio of the temperature (Abs.) at which new granules commence to be formed in the metal, worked as far as possible in the cold, to the m. p. (Abs.) tends to increase with decrease in the latter temperature, but usually lies between 0·35 and 0·45. R. CUTHILL.

Temperature of commencement of internal diffusion in crystals. G. TAMMANN (Z. anorg. Chem., 1926, **157**, 321—325).—The sintering together of powders on heating is most probably due to the molecules commencing to change their places. If T is the m. p. (Abs.), the average temperature at which this change commences is for metals $0{\cdot}33T$, for salts $0{\cdot}57T$, and for organic compounds $0{\cdot}90T$. The more complicated the molecule is, the nearer does this temperature approach the m. p. R. CUTHILL.

[Temperatures of] equal internal pressure. W. HERZ (Z. anorg. Chem., 1926, **157**, 326—328).—The temperatures at which the internal pressure is 800 and 1500 atm., respectively, have been calculated for a number of liquids. The quotient of these temperatures and also that of the corresponding densities are roughly the same for all the liquids. With substances of a similar structure, the difference of the two temperatures tends to rise with rise in mol. wt. R. CUTHILL.

Transformation of the theoretical chemical constants. E. WERTHEIMER (Physikal. Z., 1926, **27**, 771—773).—Theoretical. R. A. MORTON.

Absolute density and coefficient of expansion of silicon tetrachloride. P. L. ROBINSON and H. C. SMITH (J.C.S., 1926, 3152—3153).—After the application of a correction for the coefficient of cubical expansion of the glass floats employed in determinations of the relative densities and coefficients of thermal expansion of silicon tetrachloride, prepared from siliceous material from different sources (A., 1926, 771), the absolute density of this liquid is found to be $1{\cdot}481475\pm0{\cdot}0_568$ and the absolute coefficient of thermal expansion $0{\cdot}0014044\pm0{\cdot}0_687$. The results do not affect the previous conclusion that silicon, in the samples obtained, shows no greater variation in atomic weight than 0·005 unit.

M. S. BURR.

Gaseous methyl chloride. T. BATUECAS (Anal. Fís. Quím., 1926, **24**, 528—551; cf. A., 1925, ii, 753).—The mean value of twenty-three determinations of the weight of a normal litre of methyl chloride, obtained by the thermal decomposition of tetramethylammonium chloride, is 2·3075, compared with 2·3084 previously given by the author and 2·3045 given by Baume. The weight of the normal litre is a linear function of the pressure, and the value obtained by extrapolation to zero pressure is 2·2527. The deviation from Avogadro's law is therefore 1·0243. The author discusses the divergence between the relationships obtained from measurements of compressibility and those obtained from measurements of density at low pressures. G. W. ROBINSON.

Determination of gas density with the gas-density balance. II. Ethylene as a comparison gas. A. STOCK and G. RITTER (Z. physikal. Chem., 1926, **124**, 204—216; cf. A., 1926, 669).—Ethylene is a convenient comparison gas for density determinations, as it is easily prepared in the pure state and is almost quantitatively condensed by liquid air, a necessary property during the manipulation. Its density at 0° and 760 mm., and the necessary data concerning its deviations from Boyle's law, have been determined by means of type IV of the gas-density apparatus previously described, using oxygen as the comparison gas. The preparation of pure oxygen is discussed. L. F. GILBERT.

Dependence of density on temperature. A. PREDVODITELEV (Z. Physik, 1926, **40**, 474—476).—Polemical (cf. A., 1926, 669, 999). E. B. LUDLAM.

Recording small pressure differences. I. B. SMITH (J. Opt. Soc. Amer., 1926, **12**, 655—657).—A pair of parallel wires constituting, together with parts of the slide-wire, one arm of a Wheatstone bridge was placed in each limb of a U-tube containing a solution of an electrolyte. A difference of level of 0·00003 inch of the liquid in the limbs of the U-tube could be detected by the disturbance of the bridge equilibrium. It is suggested that the principle be applied to the recording of small pressure differences.

L. F. GILBERT.

High-temperature investigations. O. RUFF and M. KONSCHAK (Z. Elektrochem., 1926, **32**, 515—525).—The previously described method for the measurement of vapour pressures at high temperatures (A., 1919, ii, 265; 1925, ii, 579) has been further tested by new measurements on copper and gold. A slight modification in the method of obtaining b. p. from the graphs of experimental data produces almost no change from previously recorded values for these metals. In an atmosphere of pure argon, trustworthy vapour-pressure data have now been obtained for alumina and silicon, crucibles of tantalum and carborundum, respectively, being used; values for silica in an iridium crucible are regarded as less accurate. The factors governing the choice of crucible materials are discussed. The following b. p. at 760 mm. are recorded: copper, 2360°; gold, 2677°; alumina, 2980°±60°; silicon, 2392°±50°; silica, 2590° (estimated minimum). Plotting $\log p$ against $1/T$ gives straight lines. The latent heats of vaporisation of alumina and silicon are estimated from the data obtained. The behaviour of carborundum was investigated in a graphite crucible glazed externally with a mixture of vanadium carbide and oxide. Examination of the residue left in the crucible showed that the vapour from carborundum contains free silicon. The total vapour pressure was measured at various temperatures and the corresponding partial pressures of silicon were calculated from analytical data. On a $\log p-1/T$ graph, two parallel straight lines are thus obtained. At 2717°, the total vapour pressure is 764 mm. and the partial pressure of silicon 193 mm. By the aid of the van 't Hoff reaction isochore, the heat of dissociation is calculated: $SiC=C+Si(vapour)-106{\cdot}6$ kg.-cal. whence $SiC=C+Si(solid)-25$ kg.-cal. No carbide other than SiC was recognised (between 2400° and 2700°). From the calculations of Pollitzer on the basis of the Nernst theorem, the equilibrium temperature of the system $SiO_2+3C=SiC+2CO(1\text{ atm.})$ is

1462°, whereas the experimental result obtained by heating silica and lampblack in a carbon crucible is 1635° when the carbon monoxide pressure is 1 atm. It is concluded that $SiO_2+2C=Si+2CO$ is the primary process in the formation of carborundum, for, on this basis, the equilibrium temperature is calculated to be 1612°. The formation and decomposition of carborundum in technical furnaces and the significance of data recorded in the literature for the operation of these furnaces are discussed.

H. J. T. Ellingham.

Vapour pressures and m. p. of sodium and potassium. W. Edmondson and A. C. G. Egerton (Proc. Roy. Soc., 1927, **A**, **113**, 520—533; cf. A., 1923, ii, 491).—The vapour pressures of potassium between 100° and 200° and of sodium between 220° and 300° have been measured by the effusion method previously used (*loc. cit.*). Pyrex glass vessels were used, and the action of sodium on these was found to be mainly due to metal absorbed by the glass at the temperatures of the experiments. The effect on the results was negligible. A new type of air regulator is described, involving the use of a wireless valve. The results are compared with those of previous investigators, and it is found that the equation $\log p$ (mm.)$=-4507{\cdot}0/T+7{\cdot}3447$ represents the results for potassium with sufficient accuracy, whilst the equation $\log p=-5573{\cdot}2_7/T+9{\cdot}7255-0{\cdot}6794\log T$ is in close accord with the results for sodium obtained by the authors and by previous workers. The purity of the sodium and potassium used was tested by measurements of the m. p.; for sodium, the m. p. is 97·7°, for potassium, $63{\cdot}6_5° \pm 0{\cdot}05°$.

L. L. Bircumshaw.

Chemical and other thermal constants of sodium and potassium. W. Edmondson and A. C. G. Egerton (Proc. Roy. Soc., 1927, **A**, **113**, 533—541).—The chemical constant of potassium was calculated from the vapour pressure and specific heat data by three slightly different methods: (1) from the $\log p$–$1/T$ curves (cf. preceding abstract); (2) from the equation $\log p=-4607{\cdot}2/T-0{\cdot}68\log T+9{\cdot}3678$; and (3) from data given by Ladenburg and Minkovski (Z. Physik, 1922, 8, 137). The values obtained by the three methods were 0·918, 1·008, and 0·970, respectively. The value for sodium was calculated from the equation $\log p=-5573{\cdot}2_7/T+9{\cdot}7255-0{\cdot}6794\log T$. The values finally given are $C_K=0{\cdot}92\pm0{\cdot}04$ and $C_{Na}=0{\cdot}63\pm0{\cdot}03$, which are higher than the values on the basis of the Sackur theory by an amount greater than the probable error, and less by an amount greater than the probable error than the theoretical value of the constant $+\log 2$. They are, however, within the possible error. The latent heats of vaporisation at 0° Abs. are computed to be 21,460 g.-cal. for potassium and 25,800 g.-cal. for sodium.

L. L. Bircumshaw.

Vapour-pressure equation at low temperatures. V. Fischer (Z. Physik, 1926, **39**, 879—882).—The vapour-pressure equation is obtained without neglecting the change in space content for the liquid or solid.

E. B. Ludlam.

Vapour-pressure curves. F. Schuster (Monatsh., 1926, **47**, 341—351).—A discussion of the variations, with varying values of $T_r=T/T_c$ for a number of substances, of the "constant" f of the relation $\log p_c/p=f(T_c/T-1)$ due to van der Waals. Except for hydrogen and helium, the value of f passes through a minimum at the reduced temperature B, and the variation of f is given by the expression: $f=a-(T_r+B)^2(2B-T_r)$.

G. M. Bennett.

Equilibrium pressure of certain hydrated salts. F. J. Norton and J. Johnston (Amer. J. Sci., 1926, [v], **12**, 467—476).—The equilibrium vapour pressure of the system S_2–S_1–V, at different temperatures, where S_2 and S_1 are a pair of adjacent hydrates, can be determined by measuring the equilibrium pressure of the system S_2–S_1–L'–V, where L' is a solution saturated with both S_2 and S_1, and contains sufficient of a third solute to lower the transition temperature to the temperature required. Some of the technical difficulties of the ordinary method are thus overcome. This method has been found to be satisfactory for the system $Na_2SO_4,10H_2O$–Na_2SO_4–water vapour, using sodium chloride, sodium nitrate, and sulphuric acid, respectively, as the third solute. The vapour-pressure measurements were made by both a static (cf. Johnston, A., 1908, ii, 358) and a dynamic method (cf. Schumb, *ibid.*, 1923, ii, 219). At temperatures down to 0°, the equilibrium pressure is represented by the equation $\log p=-2710/T+10{\cdot}370$, where p is expressed in mm. Values for the vapour pressure of saturated solutions of sodium chloride, at temperatures from 20·4° to 50·4°, are also given.

M. S. Burr.

Magnitude of internal pressures, especially that of mercury. T. W. Richards (J. Amer. Chem. Soc., 1926, **48**, 3063—3080).—A more satisfactory mathematical treatment of internal pressures is given. The rate of increase of intrinsic cohesive pressure with decreasing volume for mercury is 1·98; some of the derived equations are verified for this element. Very great internal pressures must be supposed in order to account for the observed coefficients of expansion and compressibility. The approximate behaviour of these coefficients under pressure is calculated to within the limit of experimental error.

S. K. Tweedy.

Relation between coefficients of expansion and compressibility of liquids. V. S. Vrkljan (Z. Physik, 1926, **40**, 270—277; cf. A., 1926, 786).—A continuation of the former work. The experimental values for water, alcohol, acetone, and ether are in good agreement with the formula.

E. B. Ludlam.

Theory of state of matter. VII. Molecular volume at the b. p. F. Schuster (Z. Elektrochem., 1926, **32**, 550—552).—It has previously been shown (A., 1926, 670) that for normal organic substances, $V_b=0{\cdot}79b$, where V_b is the mol. vol. at the b. p. and b van der Waals' constant. Van Laar has shown ("Die Zustandsgleichung," 1924) that the value of b for a substance is made up of definite contributions by each of the constituent atoms, although the mode of combination has an effect with some atoms. From these atomic contributions, values of the atomic volumes at the b. p. have been obtained from the above relation and are tabulated beside those of Kopp.

Tabulation of values of molecular volume for various organic substances obtained (1) by direct measurement, (2) from Kopp's atomic volumes, and (3) from van Laar's atomic volumes, shows better agreement between (1) and (3) than between (1) and (2). The ratio v_c/V_b, where v_c is the critical volume, is not a general constant, but increases with increasing critical temperature. The increment of molecular volume between successive members of a homologous series increases on ascending the series and, in general. the difference of molecular volume between two substances of high b. p. is greater than between two similarly constituted substances of lower b. p.

H. J. T. Ellingham.

Correction to the equation of state for nitrogen. L. B. Smith and R. S. Taylor (J. Amer. Chem. Soc., 1926, **48**, 3122—3123).—The correction of a small error in the measurements recorded previously (A., 1923, ii, 755) gives the following revised equation of state for nitrogen: $p=[2\cdot9286/(v-\delta)]T-1650\cdot5/(v+0\cdot313)^2$, where $\log_{10}\delta=0\cdot2174-(0\cdot4307/v)$. Verschoyle's inference that impure gas was used is shown to be unfounded (A., 1926, 894).

S. K. Tweedy.

Surface tension of insulating liquids in an electric field. G. Bruhat and M. Pauthenier (Compt. rend., 1926, **183**, 1272—1274).—It is shown theoretically by two independent methods, involving the application of thermodynamics and mechanics, respectively, that the surface tension of an insulating liquid in an electric field is independent of the strength of the field. This is in agreement with most experimental results.

J. Grant.

Occurrence of helium and neon in vacuum tubes. R. W. Lawson (Nature, 1926, **118**, 838—839).—A consideration of the conditions leading to diffusion of helium and neon into vacuum tubes. The precautions taken by Baly and Riding (A., 1926, 1191) appear insufficient to exclude the possibility that the helium and neon obtained were of atmospheric origin.

A. A. Eldridge.

Experimental contributions to the theory of [liquid] diffusion. E. Wilke and W. Strathmeyer (Z. Physik, 1926, **40**, 309—321).—Glass capillary floats of exactly the desired specific gravity were obtained by making a very large number (5000) and picking out those which floated horizontally and had a specific gravity inside the desired range. The behaviour of these indicated change of concentration with an accuracy of 0·1%. It was found that the influence of vibration from machinery etc. had been much exaggerated, but the effect of temperature changes was very great. The diffusion coefficient for concentrated solutions of the halogen acids rises and sinks periodically with the increase of concentration.

E. B. Ludlam.

Densities and vapour pressures of aqueous solutions of ammonia and of liquid nitrogen tetroxide for the temperature interval 0—60°. A. Mittasch, E. Kuss, and H. Schlueter (Z. anorg. Chem., 1926, **159**, 1—36).—A method has been devised for the simultaneous determination of densities and vapour pressures. Two types of tension pyknometers, (i) with mercury manometer, (ii) with a glass spring manometer, and also a compression pyknometer for the measurement of higher pressures, are described. The densities and vapour pressures of 20, 30, 40, and 50% solutions of ammonia and of liquid nitrogen tetroxide were determined between 0° and 60° and the results represented graphically.

For ammonia solutions up to 35% at 0—50°, the vapour density results agree with those of Mollier (Forsch-Arb. Ing., 1909, Heft 63/64); above 50° and with ammonia concentrations up to 50%, there is a maximum deviation of about +7·5%. For nitrogen tetroxide, the results agree with the values of Scheffer and Treub (Z. physikal. Chem., 1913, **81**, 300) between 0° and 40°; above this to 60°, the maximum deviation is +1·5%.

M. Carlton.

Composition of hydrochloric acid of constant b. p. W. D. Bonner and B. F. Branting (J. Amer. Chem Soc., 1926, **48**, 3093—3095).—The compositions of hydrochloric acid solutions of constant b. p. are recorded between 620 and 660 mm. Under a pressure of 640 mm., the constant-boiling acid has b. p. 104·1°, *d* 1·0983, and contains 20·504% of hydrogen chloride. The composition of the acid solution is not a linear function of pressure.

S. K. Tweedy.

Determination of the b. p. and condensation curves of mixtures of hydriodic acid and water under a pressure of 746 mm. of mercury. E. Carrière and Ducasse (Compt. rend., 1926, **183**, 1281—1282).—The hydriodic acid was purified by distillation over calcium iodide and collected in hydriodic acid which had been similarly treated. This then contained 70% of the acid. The b. p. of mixtures containing from 15·1 to 64·9% of the acid were determined with the thermometer immersed in the liquid, a maximum value (126·5°) being obtained for 56·7% of acid. Two cases are distinguished in the determination of points on the condensation curve, according as the hydriodic acid–water mixture contains more or less than 56·7% of the former. The curves conform to the Gibbs–Konovalov rule. Both the mixture distilled and the distillate contained traces of iodine.

J. Grant.

Electrical properties of copper–nickel resistance alloys. S. Kimura and Z. Isawa (Res. Electrotechn. Lab. Japan, 1926, **171**, 1—10).—The resistivity–temperature curve (from −200° to 800°) for a certain range of nickel content has one maximum and one minimum, and thus corresponds with certain nickel–chromium and copper–manganese alloys. The negative character of the temperature coefficient of copper–nickel alloys is believed to be closely related to the A2 transformation of nickel. For alloys poor in nickel there is, however, a considerable discrepancy between the temperature at which the lowering of the temperature coefficient becomes conspicuous and the Curie point. The question whether copper–nickel alloys form a series of continuous solid solutions is discussed.

Chemical Abstracts.

Properties of saturated salt solutions at 100°. M. Prudhomme (Bull. Soc. chim., 1926, [iv], **39**, 1703—1708).—The depression *d* of the vapour pressure at 100° of a saturated solution is a function of the molecular fraction of the solute, the generalised form of the relationship being $M(760-d).g/d(100-g)$, where g is the solubility in g. referred to 100 g. of solution and M is the mol. wt. of the solute. In any individual case, however, one or more of the factors of the formula may be suppressed or inverted.

S. J. Gregg.

Diffusion of zinc in the α-series of solid solutions in copper. J. S. Dunn (J.C.S., 1926, 2973—2979).—The measurement of the rate of evaporation of zinc from a brass surface forms a simple method of measuring the diffusion of zinc through copper. The sample of brass was heated under vacuum in a silica tube, and weighed after a definite time, and the rate of zinc loss was found to vary with the square root of time, as demanded by the equation used in calculating the diffusion coefficient. This calculation is analogous to that used by Rayleigh in his estimation of the age of the earth from the temperature gradient at the surface. The loss of zinc per sq. cm. in a given time and the diffusion coefficient increase approximately exponentially with zinc content; their variation with the temperature is also exponential, as demanded by Hevesey's view that diffusion is due to loosened patches in the crystal lattice. The temperature coefficient of diffusion is in fair agreement with the Rideal–Dushman equation for a unimolecular reaction.

S. J. Gregg.

Solubility rule. F. Crotogino (Z. Elektrochem., 1926, 32, 558—561).—An attempt to find a rule stating the way in which the solubility of various salts of the alkali metals changes in passing along the series, sodium, potassium, rubidium, cæsium.

H. J. T. Ellingham.

Effect of addition of less volatile substances on the solubility of non-electrolytes. G. Tammann (Z. anorg. Chem., 1926, 158, 25—32).—Addition of a less volatile substance to water affects its physical properties in much the same way as does an increase in external pressure, *e.g.*, the temperature of maximum density is depressed. It seems likely that this effect is due to a change in the molecular constitution of the water, resulting from an increase in the internal pressure. If, with increase in the concentration of water-I molecules (this vol., 93), the solvent power of water for non-electrolytes increases proportionately, then neglecting the solvent power of the other water molecules and assuming that the volume change in the transformation of water-I into the other kinds of water molecules is independent of the pressure, Setschenov's formula, $s=s_0e^{-kc}$, follows. Here s_0 is the solubility of a non-electrolyte in pure water, s the solubility in water containing a concentration c of an added substance, and k is a constant. This formula is not valid for high concentrations of foreign substance, on account of the approximations used in deducing it. If the added substance lowers the solubility of the non-electrolyte by increasing the internal pressure, then the value of k should be proportional to the increase in internal pressure per g.-mol. of added substance. Data for the solubility of gases in solutions of salts approximately confirm this deduction. Since the concentration of water-I diminishes with rise in temperature, and water-I increases the solubility of non-electrolytes, the solubility depression produced by the foreign substance must decrease with rising temperature, until at 50° it corresponds with the effect of the foreign substance alone.

R. Cuthill.

Influence of temperature on solubility of gases. G. Tammann (Z. anorg. Chem., 1926, 158, 17—24).—If the heat of solution of a gas in its saturated solution corresponds with the work done against the osmotic pressure, the solubility, s, will be related to the temperature (Abs.), T, by the equation $1/\log_e s \,.\, d\log_e s/dT=\mp 1/T$, according as s is greater or less than 1. Many solutions of gases in liquids fulfil this equation, but in other cases deviations occur on account of thermal effects accompanying the formation of new molecular species, such as compounds of solvent and solute. Thus with aqueous solutions of gases, except those of helium and neon, the solubility first decreases with rise of temperature, even when s is less than 1, and afterwards increases again. This abnormal behaviour is probably due to hydrate formation (cf. this vol., 93), and as the concentration of these molecules diminishes with rise in temperature, the relation between the temperature and the solubility ultimately becomes normal.

R. Cuthill.

Adsorption. XI. Kinetic theory of gas adsorption. A. Magnus (Z. anorg. Chem., 1926, 158, 67—83; cf. A., 1926, 1001).—Lorenz and Landé's derivation of an equation for the amount of gas adsorbed by a surface (A., 1923, ii, 13) is corrected. A value is deduced for the "critical adsorption temperature," this being the temperature at which the heat of adsorption is zero and above which adsorption cannot occur. For adsorbed carbon dioxide at high concentrations, an equation of state analogous to that of van der Waals is deduced. This is supported by new experimental data, which do not accord with Langmuir's equation (*ibid.*, 1918, ii, 430). The results also show that adsorbed gases cannot be in the liquefied state unless the external pressure is such that the gas would be liquefied in absence of the adsorbent. If the dipole theory of adsorption is correct, the experimental evidence makes it necessary to assume that the dipoles are not rigid. This removes certain difficulties in Eucken's theory of the configuration of the carbon dioxide molecule (*ibid.*, 1926, 882).

R. Cuthill.

Adsorption of nitrogen at low pressures by activated charcoal. R. Chaplin (Phil. Mag., 1926, [vii], 2, 1198—1207).—The adsorption isotherm for nitrogen and charcoal at 25° has been determined between the pressures 2×10^{-4} and $1{\cdot}3\times10^{-2}$ mm. Under these conditions, the quantity of nitrogen adsorbed is a linear function of the pressure, being given by the expression $q=0{\cdot}023p$, where q is in mg. of nitrogen per g. of charcoal and p is in mm. Thus for this region the value of n in Freundlich's adsorption formula is 1. Provided that pure nitrogen is employed, equilibrium is rapidly attained and the adsorption is completely reversible. A modified form of McLeod gauge for use in this type of investigation is described.

A. E. Mitchell.

Vanadium, titanium, and hydrogen. H. Huber, L. Kirschfeld, and A. Sieverts (Ber., 1926, 59, [*B*], 2891—2896).—Vanadium which has been heated in a vacuum at 1100° readily absorbs hydrogen, and equilibrium is rapidly and certainly attained from either side. The pressure–volume curves are recorded at 300°, 400°, 600°, and 800°. There is no evidence of ageing in the behaviour of the metal. Titanium, after being pre-heated at 800—1100° in a vacuum, absorbs hydrogen with noticeable rapidity at 375°. At higher temperatures, equilibrium is attained with speed and certainty, but with repeated use the absorptive capacity of the element decreases. The pressure–volume curves are recorded at 500°, 600°, 800°, and 1000°. For the metals of the fourth and fifth groups of the periodic system, the following regularities are observed. The form of the isobars is similar for all elements; the rapid decline in the isobars is displaced towards higher temperatures as the absorptive capacity of the metal for hydrogen increases; the power of absorbing hydrogen increases with increasing atomic weight of the metal in each group; of two neighbouring elements that with the lower atomic number has the greater absorptive power. H. Wren.

Adsorption on solids. W. E. Garner (Trans. Faraday Soc., 1926, 22, 459—464).—See A., 1926, 1091.

Hydrolytic adsorption on platinum-black. A. Frumkin and A. Obrutscheva (Z. anorg. Chem., 1926, 158, 84—86).—If a hydrogen electrode is immersed in a solution of a neutral salt, *e.g.*, sodium sulphate, in which the osmotic pressure of the hydrogen ions is less than the electrolytic solution tension of the electrode, a small amount of hydrogen ions will pass into solution, and the resulting negative charge on the surface of the electrode will attract sodium ions from the solution, which will therefore become acid. This has been confirmed by experiment. The alkali can be removed from the electrode by destroying its charge of hydrogen with a current of air.

R. Cuthill.

Adsorption of metal complexes on charcoal. B. V. Nekrasov (J. Russ. Phys. Chem. Soc., 1926, 58, 207—214).—The hitherto uninvestigated phenomenon of adsorption of complex metallic salts on active charcoal was studied with double salts, metal ammines, and stable complexes (cobalt). Solutions of these salts were treated with highly purified active charcoal and analysed. Eight double sulphates of the type $M^{\cdot\cdot}(NH_4)_2SO_4,6H_2O$ gave a constant adsorption for the ammonium salt, but an increasing value for the metal according to the series Ni, Zn, Mg, Mn, Cd, Co, Fe, Cu, which is in the reverse order of the decrease in solubility of their sulphates due to complex formation, thus showing that selective adsorption of the complex-forming metal had taken place.

The metal ammines gave results completely analogous to the series of tervalent cobalt compounds, from $[Co(NH_3)_6]Cl_3$ to $Na_3[Co(NO_2)_6]$. It is concluded that during adsorption the complexes are destroyed, and tervalent cobalt is reduced to the bivalent state. Groups containing NH_3 are adsorbed in the form $M(NH_3)_2$, any excess of ammonia remaining in solution. Of the anions, chlorine is not at all, nitrite slightly adsorbed. Un-ionised complexes are more adsorbed than ionised, and, in the case of isomerides, the asymmetrical *cis*-isomerides more than the symmetrical. Other metal complexes are being studied, to determine whether the same regularities persist. M. Zvegintzov.

Adsorption of hydrogen and hydroxyl ions by animal charcoal. I. Isoelectric point of animal charcoal. H. Bohn (Biochem. Z., 1926, 178, 119—138).—Phosphate buffer solutions treated with animal charcoal undergo an alteration in hydrogen-ion concentration, the magnitude of which varies with the p_H of the buffer present and with the isoelectric point of the charcoal (cf. Silberstein, A., 1922, ii, 452). This observation is made the basis of determinations of the isoelectric points of various charcoals. Conductivity measurements of pure water after treatment with charcoal show that the impurities present influence the value of the isoelectric point. The adsorption of hydrogen and hydroxyl ions by charcoal follows a typical adsorption isotherm.

J. Pryde.

Adsorption of solids by fibres from aqueous suspensions. M. A. Iljinski, A. A. Balandin, M. V. Gaverdovskaja, and B. Tourova Poliak (J. Russ. Phys. Chem. Soc., 1926, 58, 241—248).—The kinetics of adsorption by cotton, wool, and silk fibres from aqueous suspensions were studied. Clean, dry fibres were immersed for a definite time in suspensions of ferric hydroxide, barium chromate, manganese dioxide, lead carbonate, lead sulphate, nickel carbonate, copper ferrocyanide, indigo, and ultramarine (which had been washed free from electrolytes), pressed out, and the solid adsorbed determined gravimetrically. The amount adsorbed was in all cases a linear function of the initial concentration, suggesting a distribution of the solid between the liquid and the fibre according to the partition law. The process, however, was irreversible, as treated fibres, when immersed in pure water, did not obey the law. Microscopical observation showed the existence of a dynamic equilibrium of the solid particles between the fibre and the suspension.

M. Zvegintzov.

Adsorption of sols and ions by precipitates and its influence on the formation of periodic precipitates. A. C. Chatterji and N. R. Dhar (Z. anorg. Chem., 1927, 159, 186—196; cf. A., 1924, ii, 158; 1925, ii, 865).—Quantitative measurements of the adsorption of various sols by the corresponding freshly-precipitated substance show that sols of lead chromate, silver chromate, ferric hydroxide, and arsenious sulphide are strongly adsorbed, the percentage adsorption increasing with increasing values of the ratio of precipitate to sol. Sols of cadmium sulphide, antimony trisulphide, and manganese dioxide are not adsorbed under these conditions, and in fact the precipitated substance has a marked tendency to pass into the colloidal state. Substances which adsorb their sols give Liesegang rings in which consecutive rings are separated by a clear space. Those substances which do not adsorb the corresponding sols form periodic precipitates consisting of alternate layers of precipitated substance and the sol. Only small amounts of silver ion are adsorbed by silver chromate, whilst the adsorption of chromate ion by silver chromate and lead chromate is practically zero. J. S. Carter.

Adsorption of dyes on silver halides. S. E. Sheppard (Nature, 1926, 118, 913—914).—Experimental curves indicate that the dye is first adsorbed until the surface is saturated. The dye disperses in water to form colloidal as well as true solution, and the last ascending portion of the curve corresponds with mechanical adsorption. A modification of Langmuir's formula for the unimolecular adsorption of gas molecules on a plane surface is in good agreement with the data. At p_H 5·5, 1 mol. of dye is computed to be adsorbed for 20 ions of the lattice surface. Possible explanations of the low adsorption density of the dye are considered. The solubility of the dye in water is greatly diminished in the presence of small amounts of soluble halides. A. A. Eldridge.

Mists from chemical reactions. IV. Absorption of mists by liquids and solids. H. Remy and H. Finnern (Z. anorg. Chem., 1927, 159, 241—255; cf. A., 1925, ii, 107).—When mists of ammonium chloride or sulphur dioxide are passed through water or aqueous solutions of alkalis or through tubes packed with coarse pumice, gas-mask charcoal, etc., relatively little absorption occurs. Absorption is, however, almost complete on passing the mists through tubes packed with fibrous material such as glass wool, filter-paper, etc. As an example of the orders of magnitude encountered, the following numbers give the mean percentage absorption for moist mists under the author's experimental conditions by water (Winkler absorption coil), 10 cm. of tube containing gas-mask charcoal, and 10 cm. of tube packed with glass wool, respectively, the figures in parentheses are the corresponding numbers for the dry mists: ammonium chloride: 58 (39); 27 (93); 99 (98); sulphur trioxide: 37 (7); 30 (82); 99 (90). The behaviour of an absorbent towards a mist depends primarily on the size and mobilities of the suspended particles. With decreasing size and increasing mobility (*e.g.*, on drying or filtering) the mists more closely resemble gases; the efficiency of purely filtrational absorbents diminishes, whilst that of absorbents for gases, *e.g.*, charcoal, increases. Water, however, absorbs moist mists more readily than dry, since the dry mists take up water to form particles larger than those existing in moist mists. A dried, filtered mist of ammonium chloride consisting of very fine particles was, however, almost completely freed from the salt on passing through a Winkler coil containing water. Experiments in which a moist mist of sulphur trioxide was passed through solutions of gelatin of concentrations ranging up to *N* show that the percentage absorption decreases with increasing gelatin content (*i.e.*, increasing viscosity). Mists of sulphur trioxide are more completely absorbed by water at low temperatures than at high temperatures. J. S. Carter.

Stabilising ions and their adsorption. G. Rossi and V. Osti (Gazzetta, 1926, 56, 811—816).—The conductivity of solutions of tetramercuriacetanilide acetate containing various proportions of acetic acid shows that, for constant concentration of the acetic acid, the adsorption of this increases with the concentration of the colloid, and that, when the concentration of the colloid is kept constant, the adsorption of the acetic acid by the disperse particles increases to a maximum and then diminishes as the concentration of the acid rises continuously. These results are discussed in relation to the authors' views (A., 1924, ii, 330, 459). T. H. Pope.

Action of silica on electrolytes. A. F. Joseph (Nature, 1926, 118, 878).—Polemical against Mukherjee (A., 1925, i, 488, ii, 383; 1926, 1112). The author holds that silica does not adsorb acids. A. A. Eldridge.

Interaction between hydrated silica and neutral electrolytes in its relation to the nature of hydrolytic adsorption. J. N. Mukherjee, B. C. Ghosh, K. Krishnamurti, G. N. Ghosh, S. K. Mitra, and B. C. Roy (J.C.S., 1926, 3023—3033).—The usual conceptions of chemical equilibrium fail to explain the reaction between silica and solutions of neutral electrolytes. By treating hydrated silica with saturated potassium chloride solution, 50 c.c. of the solution being removed daily and replaced by fresh, the hydrogen-ion concentration gradually diminished to a definite limit, leaving a residue which was inactive to potassium chloride. According to the ordinary equation, however, $2n\text{KCl}+\text{H}_{2n}\text{SiO}_{n+2}=2n\text{HCl}+\text{K}_{2n}\text{SiO}_{n+2}$, the hydrogen-ion concentration should remain constant and then suddenly fall when no more silica remains. Also, a solid residue remains which contains much hydrogen partly replaceable by washing with solutions of certain other neutral electrolytes. From *E.M.F.* measurements, the hydrogen-ion concentration for solutions in contact with silica was found to be greater for barium chloride than for calcium chloride; whereas since the silicate of calcium is less soluble than that of barium, the opposite order would be predicted from ordinary chemical theory. Further, the hydrogen-ion concentration of potassium chloride solution in contact with silica depended on the relative weights of silica and potassium chloride present. The above facts can be explained by Mukherjee's theory of ionic adsorption (A., 1922, ii, 689). Adsorption was confirmed by electro-osmotic measurements, and the adsorption of acids by silica was directly demonstrated by determining the concentration of an acid solution (by *E.M.F.* measurements) before and after contact with silica. S. J. Gregg.

Adsorption in its relation to catalysis and enzyme actions. J. Duclaux (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 630—645).—The hypothesis that molecules and atoms exist either completely independently or in chemical combination is extended to all liquid, gaseous, and solid systems. Adsorption is but a particular case of the formation of additive compounds, which proceeds spontaneously, either without activation or by autoactivation. These compounds are considered to be capable of spontaneous internal transposition, followed by dissociation. Catalysis is defined in these terms. Chemical Abstracts.

Physical phenomena at interfaces. E. K. Rideal (Trans. Faraday Soc., 1926, 22, 434—439).—See A., 1926, 1093.

Arrangement of molecules on the surface of pure liquids. S. Sugden (Trans. Faraday Soc., 1926, 22, 486—490).—See A., 1926, 1094.

Physical properties of composite surfaces. W. Ramsden (Trans. Faraday Soc., 1926, 22, 484—485).—See A., 1926, 1094.

Electrification at interfaces. H. Freundlich (Trans. Faraday Soc., 1926, 22, 440—451). R. K. Schofield (*ibid.*, 452—458).—See A., 1926, 1094.

Insoluble films on liquid surfaces. N. K. Adam and G. Jessop (Trans. Faraday Soc., 1926, 22, 472—476).—See A., 1926, 1093.

Spreading of proteins. E. Gorter and F. Grendel (Trans. Faraday Soc., 1926, 22, 477—483).—See A., 1926, 1094.

Ring method for the determination of surface tension. W. D. Harkins, T. F. Young, and L. H. Cheng (Science, 1926, 64, 333—336).—The ring method for the determination of surface tension may yield results in error by 25% or more, unless the ring is large. A correction factor has been introduced into the equation employed, and preliminary values for the factor have been obtained by a comparison of the surface tension of various liquids by the ring, capillary height, and drop-weight methods. Certain essential experimental precautions are enumerated.

A. A. Eldridge.

Absolute measurement of the average size of droplets of the disperse phase of an emulsion. W. P. Davey (Science, 1926, 64, 252—253).—If one drop of a permanent oil-in-water emulsion is deposited on the surface of clean water so as not to break the surface film, it spreads on the water like an oil. Assuming that the layer is one particle deep, and that the droplets are small enough to retain their shape, the average diameter of the particles can be measured by Langmuir's method for measuring the cross-section of oil molecules. This involves a knowledge of the total volume of the droplets of the disperse phase as they exist in the emulsion; so far, this volume has been found to be the same as that of the same mass of undispersed material.

A. A. Eldridge.

Surface tension and heat of vaporisation. J. E. Verschaffelt and F. de Block (Z. anorg. Chem., 1927, 159, 265—268).—The relation, $\log L = a + b \log \gamma$, where L is the heat of vaporisation, γ the surface tension, and a and b are constants, put forward by Herz (A., 1926, 1008), is discussed, and it is shown that a relation of this type will hold between any two magnitudes which become zero at the critical point. The relation $L/a^2=18$, where a^2 is the capillary constant, deduced by de Kolossovski (*ibid.*), is valid only for normal liquids at the b. p. and is not independent of temperature. J. S. Carter.

Preparation of colloidal manganese dioxide. II. A. Steopoe (Bul. Soc. Româna Stiinte, 1926, 29, 11—15; cf. A., 1926, 676).—Colloidal manganese dioxide is prepared by reducing a neutral solution of potassium permanganate with acetylene in presence of colloidal silica. The stability increases with rising concentration of the silica; it is decreased in presence of sodium hydroxide. The precipitation by electrolytes of a manganese dioxide sol (prepared with ethylene as a reducing agent) does not proceed in accordance with the Hardy–Schulze law; immediate precipitation occurs, except in the case of cobalt and silver nitrates, when the precipitation is preceded by coagulation. The presence of electrolytes does not modify the true colours of colloid particles (Dhar, A., 1926, 24). The latter are covered with a thin layer of metal hydroxide, produced by interaction of the added electrolyte with the potassium hydroxide adsorbed on the particles. The true colours are thus masked. S. K. Tweedy.

Synthesis of colloidal tungstic acid. A. B. Dumanski and A. P. Buntin (J. Russ. Phys. Chem. Soc., 1926, 58, 107—112).—The problem whether colloidal tungstic acid is formed directly or is built up in successive stages from complexes, as is the case with vanadium pentoxide (A., 1923, ii, 771), was investigated.

The electrical properties of the solutions indicate that the reaction takes place in stages: $Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl$ and $H_2WO_4 + Na_2WO_4 = Na_2O,2WO_3 + H_2O$. This process is repeated, until a colloidal particle of the composition Na_2O,nWO_3 or $H_2[WO_4,nWO_3]$ is obtained. Numerous complexes of tungstic acid are known which confirm this view. One of these, $Na_2O,4WO_3$, was prepared, and gave results in agreement with the theory. Experiments on the viscosity of the tungstic acid sols were also carried out. M. Zvegintzov.

Thermal colloid syntheses. III. Colloidal mercury. A. Gutbier [with R. Köhler and W. Schieber] (Z. anorg. Chem., 1926, 158, 99—102; cf. A., 1926, 1003).—Nordlund's work on the preparation of mercury sols by thermal dispersion (A., 1920, ii, 376) has been confirmed, using the apparatus previously described (*ibid.*, 1926, 574). The sols so obtained contain negatively-charged particles, and up to 2·5% of mercury; they are very unstable, decomposition commencing within 24 hrs. after preparation, and being much accelerated by electrolytes or changes in temperature. Addition of the usual protective colloids to the freshly-prepared sols does not increase their stability, but the products obtained by using a 1% solution of gum arabic instead of pure water as the dispersive medium can be kept, with care, for more than a week. The residue obtained by evaporating such sols over sulphuric acid gives, on treatment with water, a secondary sol, which coagulates within 24 hrs. R. Cuthill.

Dispersion in sulphur suspensions. G. I. Pokrowski (Z. Physik, 1926, 40, 368—377).—The dispersion of sulphur particles produced by the action of sulphuric acid on aqueous solutions of sodium thiosulphate is shown to be in agreement with Rayleigh's theory. The variation of the diameter of particles, η, as a function of the time, t, and the thiosulphate concentration c is given by an empirical equation $\eta=\eta_0(1-e^{-\alpha ct})$, where α and η_0 are constants. R. W. Lunt.

State and stability of colloid solutions. K. Linderstrøm-Lang (Compt. rend. trav. Lab. Carlsberg, 1926, 16, [6], 1—47).—Theoretical. Solutions of colloid electrolytes, regarded as one-phase systems in internal equilibrium, are discussed from the point of view of the thermodynamic principles developed by Lewis, Bjerrum, and Brønsted. On the basis of Gibbs' conditional equation for stability of a phase, it is shown that the behaviour of the so-called osmotically abnormal colloid electrolytes must be explained on the assumption that the activity of the large ion is a diminishing function of the concentration. This can be due only to the presence of strong van der Waals cohesive forces between the large ions, which may or may not result in micelle formation. The bearing of these views on the interpretation of the experimental data of Hammersten (A., 1924, i, 456, 1139; ii, 386) and of McBain and Salmon (*ibid.*, 1920, ii, 234; J.C.S., 1920, **117**, 530) is discussed. M. S. Burr.

Charge on the particles in colloids. R. Wintgen (Kolloid-Z., 1926, 40, 300—302).—The amount of colloidal substance deposited by one Faraday of electricity may be regarded as the electrochemical equivalent of the colloid, and colloids may therefore be expressed in terms of normality, according to the number of electrochemical equivalents of colloid per litre. This value may be determined by measuring the electrical conductivity of the system before and after ultrafiltration, the difference representing the conductivity due to the charged colloid particles. Results are given for sols of ferric oxide and for dialysed and undialysed gold sols. E. S. Hedges.

Emulsions. II, III. H. Limburg (Rec. trav. chim., 1926, 45, 854—874, 875—880).—II. The influence of potassium, barium, and aluminium chlorides, hydrochloric acid, potassium carbonate, and thallium nitrate on the rate of cataphoresis of the particles in paraffin oil emulsions has been examined. Measurements of the interfacial tension oil–water in presence of potassium chloride, hydrochloric acid, and potassium carbonate were made by the drop-weight method and the stability of the emulsions was examined in presence of potassium, barium, and aluminium chlorides, hydrochloric acid, potassium carbonate, and thallium nitrate, sedimentation of the emulsion being prevented by means of slow rotation. With univalent cations, the rate of cataphoresis increases to a maximum with increasing electrolyte concentration, and then decreases. Barium chloride in moderate concentration is without effect on the cataphoresis. With tervalent cations, the velocity decreases to zero and changes its direction. This reversal of charge is ascribed to the products of hydrolysis of the salts. From a consideration of the effects of electrolyte addition on the stability of the emulsions, it is shown that, in addition to such factors as the charge on the particles, the interfacial tension, and the presence of protective films, the stability is largely determined by the electrical conductivity of the continuous phase. A theoretical explanation is given.

III. Using emulsions of paraffin oil containing 0·5 and 5% of oleic acid, in water, a study has been made of the influence of electrolytes (potassium chloride, hydrochloric acid, and potassium carbonate) on the velocity of cataphoresis of the particles, the stability of the emulsion, and the interfacial tension, oil–water. The fact that the rate of cataphoresis is practically the same as in the absence of oleic acid is explained on the basis of the Langmuir–Harkins orientation theory. From the course of the curves showing the influence of electrolytes on the stability of the emulsions, it is seen that, whilst the stability is greater in presence of oleic acid, the general character of the curves remains unaltered. The increased stability is ascribed to a lowering of surface tension caused by a film of oriented oleic acid molecules, which opposes the combination of the particles. Similar measurements have been made on oil–water emulsions containing 0·089 g. of saponin per litre, in presence of potassium chloride, hydrochloric acid, potassium carbonate, and aluminium chloride. The stability is greatly increased by saponin, which is assumed to form a highly resistant film round the particles. On the other hand, the relation between the charge on the particles and the electrolyte concentration is the same as if no saponin were present. The surface tension appears to be only slightly lowered by saponin, but it is suggested that this may be due to difficulties in the exact measurement of the property. The addition of gelatin to oil–water emulsions has a marked effect on the rate of cataphoresis, dependent on the degree of acidity of the emulsion. The curves showing the influence of gelatin on the stability of emulsions of varying p_H (2·8—9·6) all have a minimum, which is the more pronounced the greater is the acidity. L. L. Bircumshaw.

Polarised fluorescence of dyes in colloidal solutions. W. L. Levschin (J. Russ. Phys. Chem. Soc., 1926, 58, 177—183).—See A., 1925, ii, 13, 629, 1117.

Relation between viscosity and molecular complexity of cellulose nitrate. N. Yamaga (Cellulose Ind., Tokyo, 1926, 2, 357—362).—Decrease in viscosity of cellulose nitrate is brought about by the action of heat; light also has a similar action. Change of viscosity does not depend on the decomposition of the cellulose nitrate, but accompanies decrease of molecular complexity. This has been measured by determining the coefficient of diffusion by Schaffer's method. The coefficient of diffusion in acetone solution for a heated sample was found to be 0·8070 cm. per day, as against 0·5962 cm. per day for the original sample. Thus the sample with lower viscosity has also the smaller molecular diameter. Calculations from the experimental data gave for the molecular radii (P) $9{\cdot}838\times10^{-8}$ cm. for the original and $9{\cdot}148\times10^{-8}$ cm. for the heated cellulose nitrate. Assuming the molecular formula $[C_{24}H_{29}O_9(NO_3)_{11}]_n$ for a cellulose nitrate containing 13·32% N, the molecular volume can be calculated by Traube's method from the sum of the atomic weights, $V=n\times 2{\cdot}6\Sigma\sqrt{A}=M/d$ and from the molecular radii $V=\frac{4}{3}P^3\times6{\cdot}5\times10^{23}$. From these two equations the real mol. wt. M may be calculated, taking the density of cellulose nitrate as 1·655. These calculations gave mean values for M of the original guncotton 8751;

n=about 8, and for the heated sample M=3329, n=about 3. J. F. Briggs.

Optical properties of sols and gels containing cellulose. O. Faust (Ber., 1926, 59, [*B*], 2919—2920).—The double refraction of artificial silk threads and films is due to tension or pressure during production, and disappears when they are nitrated unless the tension has been very great. Threads prepared in the absence of pressure do not exhibit double refraction. H. Wren.

Effect of anions on the physical, chemical, and colloidal properties of aluminium hydroxides. L. B. Miller (Third Colloid Symposium Monograph, 1925, 206—215).—The "floc" obtained with sulphate settles rapidly and is compact, thus being suitable for water clarification. The effective p_H range for aluminium sulphate is 5·3—8·7 (max. 5·5), and for chloride 7·8—8·6. The precipitate from a dilute solution (except perhaps at high p_H values) is not aluminium hydroxide, but a complex substance containing varying proportions of the anions. Chemical Abstracts.

Behaviour of silicic acid gel during the drying-up process. J. B. Firth and H. A. Fells (Nature, 1927, 119, 84—85).—A question of priority (cf. Krishnamurti, this vol., 19). A. A. Eldridge.

Effect of acids on hydrophobic colloids, particularly gold. W. Prosch (Kolloid-Z., 1926, 40, 318—321).—A lecture on the influence of hydrogen-ion concentration on the precipitation of colloidal gold and on the inhibitive effect of protective colloids. E. S. Hedges.

Deformation of titration curves of proteins in presence of strong electrolytes. L. Reiner (Kolloid-Z., 1926, 40, 327—332).—A discussion of the effect of strong electrolytes on the acid- and alkali-fixing power of proteins. The high valency of the protein ions strongly influences the activity of the other ions present. E. S. Hedges.

Structure of organic acids and protein coagulation. I. N. A. Isgarishev and M. I. Bogomolova (J. Russ. Phys. Chem. Soc., 1926, 58, 156—163).—The coagulation of casein and edestin by different organic acids was investigated in order to determine the physical or chemical nature of the mechanism. Alkaline solutions of the proteins were titrated with the acids, the amount in excess of neutralisation needed to cause precipitation being an inverse measure of the activity of the acid. The results with casein were accurate and reproducible.

No direct connexion was found between the dissociation constant of the acids or the Lorenz ionic volume of the anions and the activities of the acids. Differences of chemical structure, however, were important. Increase of CH_2 groups in the fatty series slightly increased the activity. Hydroxyl groups increased it in aliphatic, but decreased it in aromatic series. A second carboxyl group was ambiguous, whilst halogens when present singly were highly active.

From these results a possible chemical mechanism is suggested. The alkaline proteins are capable of combining with salts of the acids to form complexes analogous to the known silver complexes, which have different solubilities; in consequence the excess of common ion required for precipitation varies considerably. M. Zvegintzov.

Effect of organic acids on the imbibition of gels. II. N. A. Isgarishev and A. L. Pomeranzeva (J. Russ. Phys. Chem. Soc., 1926, 58, 164—169; cf. preceding abstract).—The effect of the structure of organic acids on the imbibition of gels was determined by the increase in volume of pure, dry casein, when treated with dilute solutions of the acids. It was found that the dissociation constant has no direct effect, and, consequently, the main factor was the nature of the anion. The presence of hydroxyl or a second carboxyl group, especially in close juxtaposition, enhances the activity up to a point, but such acids as citric and tartaric acids show a reverse effect. Chlorine is very active, and the amino-group acts as an inhibitor, whilst double linkings give ambiguous results. The adsorption of active acids by the casein, the formation of ion complexes, and the possible specific effects of ions are also discussed. M. Zvegintzov.

Electrical endosmose with sulphur. A. F. Guerasimov (J. Russ. Phys. Chem. Soc., 1926, 58, 201—206).—The phenomena of electrical endosmose have been examined to ascertain whether octahedral sulphur, like colloidal, adsorbs anions in suspensions in hydrochloric acid (cf. Perrin, A., 1905, ii, 138). The formula employed was Smoluchowski's: $P_1-P_2=CE(\varphi_l-\varphi_s)/4\pi w$, where P_1, P_2 are the pressures at the two ends of the tube, φ_l, φ_s the potentials of the liquid and the diaphragm, and C and w are constants depending on the nature of the latter. An apparatus was devised in which powdered sulphur acted as a diaphragm and P_1, P_2 were measured by changes of level of the liquid.

The results are affected by electrolysis of the chloride and the changes in the condition of the diaphragm, for which a correction must be applied. In all cases, and at all concentrations, the negative charge of the sulphur decreases, *i.e.*, there is no preferential adsorption of anions. M. Zvegintzov.

Rapid dialysis of solutions of sodium silicate. A. Gutbier and H. Brintzinger (Z. anorg. Chem., 1927, 159, 231—240).—The results of experiments on the dialysis of solutions of sodium silicates of varying composition and concentration show that, although the major portion of the silica present passes through the membrane, considerable quantities are retained, together with a little sodium. For example, a solution originally containing 0·3224 g. Na_2O and 0·7160 g. SiO_2 per 100 c.c. contained after dialysis 0·0006 g. Na_2O and 0·2320 g. SiO_2 per 100 c.c., the p_H value falling from 12·47 to 10·20. Solutions of sodium silicate contain ions of the type SiO_3'', Si_2O_5'', etc., which are readily diffusible if the concentration of hydroxyl ions is sufficiently high. As the concentration of sodium and hydroxyl ions decreases, hydrolysis occurs according to the schemes: $SiO_3''+nH_2O \rightleftharpoons SiO_2,(n-1)H_2O+2OH'$; $Si_2O_5''+nH_2O \rightleftharpoons 2SiO,_2(n-1)H_2O+2OH'$. The silicic acids are initially present in a highly dispersed state, but they immediately commence to form large aggregates incapable of diffusion, especially when the concentration of hydroxyl ion further diminishes.

J. S. Carter.

Rapid dialysis of solutions of silicic acid. H. Brintzinger (Z. anorg. Chem., 1927, **159**, 256—264; cf. Mylius and Groschuff, A., 1906, ii, 160; Willstätter, Kraut, and Lobinger, *ibid.*, 1926, 36; Gutbier and Brintzinger, preceding abstract).—Since aqueous solutions of sodium silicate contain colloidal silicic acids produced as a result of hydrolysis, in addition to the ions, SiO_3'', Si_2O_5'', etc., the relative quantities of which depend on the ratio $[Na_2O]:[SiO_2]$, a rather complex mixture of silicic acids results on acidification. On dialysis, the molecularly dispersed silicic acid will pass through the membrane, whilst the colloidal acid originally present, and that resulting from the agglomeration of the molecularly dispersed particles, remain behind. Hence if the solution obtained on acidification is kept for some days before dialysis, there is a considerable decrease in the percentage of diffusible silica as a result of this aggregation. It is probable that the rate of agglomeration is proportional to the number of collisions between particles, and hence dependent on concentration and temperature. There should therefore be a greater proportion of diffusible silica in dilute solutions, and at low temperatures, provided that the ratio $[Na_2O]:[SiO_2]$ of the solution of sodium silicate acidified is maintained constant. The results of experiments in which solutions of a sodium silicate of the composition, $Na_2O,2{\cdot}3SiO_2$, of varying concentration, were acidified at various temperatures with a slight excess of hydrochloric acid and dialysed, either at once or after some days, are in entire agreement. In all cases, the p_H value of the resulting solution was about 4·6. J. S. Carter.

Ionic volume and hydration. N. R. Dhar (Z. Elektrochem., 1926, **32**, 596—598).—Theoretical. The view has been put forward (A., 1913, ii, 916) that the ions of an electrolyte occupy a smaller volume than the corresponding undissociated molecule. Also Eddington has expressed the view that when an atom loses an electron, the positive ion remaining may be much denser than the original atom. This explains the marked decrease in molecular volume accompanying the dissolution of electrolytes such as sodium or potassium chlorides in water. But with lithium chloride this decrease in molecular volume is very small; this is ascribed to the considerable hydration of the lithium ion. Hence, degree of hydration might be deduced from molecular volume data. The conclusion that strongly hydrated ions have a smaller charge per unit surface than weakly hydrated ions is applied to the explanation of certain properties of colloidal solutions. H. J. T. Ellingham.

Nature of the solution of strong acids from the point of view of the salt effect. System: nitric acid–sodium nitrate. L. H. Angus and H. M. Dawson (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 104—107).—According to previous work (Carter, A., 1926, 236), the solubility of iodine in water is depressed by salts, such as sodium nitrate and sodium sulphate, with which it does not form a complex ion, and the salting-out effect may be expressed by the formula $s=s_0e^{-kc}$, where s_0 is the solubility of iodine in pure water, s the solubility in the same quantity of water containing c g.-mol. of salt, and k a constant depending on the nature of the salt. The behaviour of free acid varies, *e.g.*, nitric acid raises, whilst sulphuric acid lowers the solubility. To determine whether or not the behaviour of nitric acid is due to incomplete ionisation, the solubility of iodine in $1{\cdot}3N$ and $2{\cdot}7N$ solutions of nitric acid in the presence of varying quantities of sodium nitrate has been examined. The behaviour is similar to that with water and sodium nitrate alone, the value of k in the formula increasing very slightly from 0·0533 for water to 0·0577 for the weaker acid and 0·0593 for the stronger. The results suggest that the condition of the acid is not much affected by the addition of the salt, and therefore that the proportion of non-ionised acid is probably very small. M. S. Burr.

Determination of vapour pressures of aqueous solutions. R. Whytlaw-Gray and H. Whitaker (Proc. Leeds Phil. Lit. Soc., 1926, **1**, 97—103).—The rate of evaporation of a droplet of a solution can be followed by attaching to a silica spring, suspended on a micro-balance, and following the change in weight. The diffusion gradient round the droplet can be fixed by surrounding it by a hollow vessel the inside of which is covered with a suitable absorbent material. If s is the surface at any time t, vapour pressures may be calculated from the ds/dt values for different concentrations by Langmuir's method (Physical Rev., 1918, **12**, 368). By a second comparative method, a solution of known vapour pressure may be used to wet the inside of the vessel surrounding the droplet, which is then allowed to evaporate until equilibrium is reached, when its vapour pressure will be the same as that of the surrounding liquid. The composition of the droplet can then be calculated by weight. By the second method, the vapour pressures of about 65% and 19% sulphuric acid solutions have been determined, using in the first case a mixture of oxalic acid and its dihydrate to cover the inside of the surrounding vessel, and in the second a solution of sucrose of known vapour pressure. The values obtained for the lower concentrations are in good agreement with those of Grollman and Frazer (A., 1925, ii, 398), and for the higher with those of Daudt (Z. physikal. Chem., 1923, **106**, 255). M. S. Burr.

Binary liquid mixtures. XXIV. G. Weissenberger and R. Henke (J. pr. Chem., 1927, [ii], **115**, 75—77).—The fact that the partial pressures of methyl alcohol in many binary mixtures (cf. Weissenberger, Henke, and Sperling, A., 1926, 787) calculated on the van Laar formula are greater than those of methyl alcohol alone led the authors to redetermine the values of the van der Waals constants for a number of substances, and so to detect many inaccuracies in the recorded data. The new values, determined between 20° and 30°, for a (litre-atm.) and b (litre), respectively, are as follows: tetrahydronaphthalene, 20·9 and 0·1147; *cyclo*hexanone, 15·7 and 0·0873; anethole, 8·5 and 0·0825; *cyclo*hexanol, 14·4 and 0·0869; methyl alcohol, 7·4 and 0·0349; monochloroacetic acid, 5·9 and 0·0462; dichloroacetic acid, 14·3 and 0·0709; trichloroacetic acid, 31·8 and 0·0985; pentachloroethane, 16·3 and 0·0992; benzaldehyde, 16·4 and

0·0864; phenetole, 18·1 and 0·1051; phenyl acetate, 32·4 and 0·1138. When these values are employed, the deviations from the calculated curve vanish.

J. W. Baker.

Binary liquid mixtures. XXV. G. Weissenberger (J. pr. Chem., 1927, **115**, 78—80).—A summary of conclusions concerning the nature of residual fields which have resulted from the study of binary mixtures (cf. A., 1926, 787). All organic compounds possess a residual field which is polar in character and depends on the constitution of the compound, the formation of molecular compounds being only an extreme case.

J. W. Baker.

Phase-rule study of the zinci-, cadmi-, mercuri-, and nickelo-cyanides of potassium. A. S. Corbet (J.C.S., 1926, 3190—3202).—Potassium cyanide forms compounds of the type $K_2M(CN)_4$ with the cyanides of zinc, cadmium, and mercury, respectively. Aqueous solutions of the double compound dissolve increasing amounts of the heavy metal cyanide on passing from zinc to mercury. Hence, in the cyanometric determination of zinc, the potassium cyanide solution must not be too strong, about $0{\cdot}2N$ being suitable. With nickel cyanide, a compound, $K_2Ni(CN)_4,H_2O$, is formed, and solutions which are in equilibrium with solid nickel cyanide contain the simple cyanides in the stoicheiometric ratio required for the double salt. S. J. Gregg.

Stability of iron carbide at high pressures. E. Scheil (Z. anorg. Chem., 1926, **158**, 175—180).—From the data of Sauerwald for the changes in volume of white and grey cast iron on solidifying (B., 1926, 131) it is deduced that at high pressures iron carbide probably possesses a region of stability, and the *p–t–x* diagram is discussed. R. Cuthill.

Double sulphates of rare-earth and alkali metals. VII. Lanthanum ammonium sulphates. F. Zambonini and (Miss) A. Stolfi (Atti R. Accad. Lincei, 1926, [vi], **4**, 424—429; cf. A., 1926, 1113).—The isotherms for the system $La_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 25° reveal the existence of the compounds 1 : 1 : 2, 1 : 3 : 0, 1 : 5 : 0, and 1 : 6 : 0 (cf. Marignac, "Oeuvres," I, 393; Cleve, A., 1875, 337; Kraus, *ibid.*, 1901, ii, 453, and Barre, *ibid.*, 1911, ii, 42). T. H. Pope.

Thermal analysis of binary systems of anhydrous beryllium chloride with various metallic chlorides. J. M. Schmidt (Bull. Soc. chim., 1926, [iv], **39**, 1686—1703).—The beryllium chloride was prepared by passing carbonyl chloride over beryllium oxide at 750—800°; it contained 98·5% $BeCl_2$, the remainder being water. The binary mixture was prepared in each case by fusing the two substances together and allowing to cool with constant stirring. The f.-p. diagrams so obtained showed that the chlorides of silver, lead, and cadmium give no compounds with beryllium chloride; those of sodium, lithium, and thallium give compounds of the type $BeCl_2,2MCl$, whilst thallium chloride gives in addition $2BeCl_2,TlCl$ and barium chloride gives $BeCl_2,BaCl_2$. In no case were mixed crystals obtained. S. J. Gregg.

Double decomposition in absence of solvents. VI. Irreversible salt pair $HgCl_2+Ag_2I_2 \longrightarrow Ag_2Cl_2+HgI_2$. A. G. Bergman and T. A. Henke (J. Russ. Phys. Chem. Soc., 1926, **58**, 80—112; cf. A., 1923, ii, 568, 636, 764, 1761; 1924, ii, 178).—The several binary systems involved were studied by the synthetic method and both liquidus and solidus curves were traced. The system Ag_2Cl_2–Ag_2I_2 has eutectic m. p. 264°, 46·5% AgI, polymorphic, transition point AgI 129—130°; $HgCl_2$–HgI_2 has eutectic m. p. 145°, 47% HgI_2, transition point 73°; Ag_2Cl_2–$HgCl_2$ has eutectic m. p. 272°, 16·5% AgCl, no solid solutions; HgI_2–Ag_2I_2 both solid solutions and compound formation ($2AgI,HgI_2$, incongruent), eutectic m. p. 245°, 5·5% Ag_2I_2. Steger's work (A., 1903, ii, 482) is criticised. Ag_2Cl_2–HgI_2 has eutectic m. p. 137°, 32·5% Ag_2Cl_2.

The salt pair, $HgCl_2+Ag_2I_2 \longrightarrow Ag_2Cl_2+HgI_2$, is shown in a three-dimensional diagram. One diagonal (Ag_2Cl_2–HgI_2) cuts it into two ternary systems, the other is a section through them. Diagrams for both are given. The ternary system Ag_2Cl_2–HgI_2–$HgCl_2$ has eutectic m. p. 121°, 14% Ag_2Cl_2, 56·5% HgI_2, 29·5% $HgCl_2$, HgI_2 transition point 80—82°. The system Ag_2Cl_2–HgI_2–Ag_2I_2 has eutectic m. p. 136°, 31% Ag_2Cl_2, 68% HgI_2, 1% Ag_2I_2. The diagrams are complicated by the compound $2AgI,HgI_2$.

M. Zvegintzov.

Independent components and univariant systems. R. Wegscheider (Z. anorg. Chem., 1927, **159**, 161—185; cf. A., 1904, ii, 17).—Theoretical.

J. S. Carter.

Reaction regions. XII. Reaction space Fe–Mg–Al–S. W. P. Jorissen and B. L. Ongkiehong (Rec. trav. chim., 1926, **45**, 849—853; cf. A., 1926, 246, 690).—The upper limit of the reaction region iron–aluminium–sulphur lies approximately at a mixture of 43% Fe and 57% of a mixture of 62·5% Al and 39·5% S. For the region magnesium–aluminium–sulphur, the top of the curve lies at approximately 80% Al, 20% S, and 25% Mg. The space models are discussed.

L. L. Bircumshaw.

Equilibrium of heterogeneous systems including electrolytes. II. Equilibrium at interfaces and the theory of electrocapillarity. J. A. V. Butler (Proc. Roy. Soc., 1927, A, **113**, 594—604; cf. A., 1926, 908).—The conditions of equilibrium at the interfaces in a heterogeneous system including electrolytes may be obtained by the general method of Gibbs. A critical survey is made of previous theories held with regard to the mechanism of the changes produced by electrolytic polarisation at the interface between mercury and solutions of electrolytes. On the basis of the equilibrium equations, a theory of electrocapillarity is developed, including the effect of capillary-active substances. The integration of the equations requires the introduction of kinetic considerations, and a kinetic theory is developed for the adsorption of ions and the effect on the electrocapillary curves. The equations are in good agreement with the data given by Smith (Phil. Trans., 1899, A, **193**, 48) for potassium iodide solutions. L. L. Bircumshaw.

Activity coefficients of sodium and potassium bromides and iodides in concentrated aqueous solutions. H. S. Harned and S. M. Douglas (J. Amer. Chem. Soc., 1926, **48**, 3095—3101).—From

E.M.F. measurements at 25° of cells of the type $Ag|AgX|MX(m_1)|M_xHg(0{\cdot}01\%)|MX(m_2)|AgX|Ag$, where X=Br or I, and M=Na or K, the above activity coefficients are calculated. For each metal the iodide has a higher coefficient than the bromide at a given concentration. The activity coefficients of the alkali metals decrease and those of the halide ions increase with the number of electron layers in their structure, from which it is deduced that the specific action of the ions in deforming the water molecules plays an important rôle in determining the free energy of an ion in concentrated solution.

S. K. Tweedy.

Calculation of activities from f. p. C. R. Bury (J. Amer. Chem. Soc., 1926, 48, 3123—3124).—The plot of j/m against m (cf. A., 1926, 1207) can be regarded as having zero slope at $m=0$ only in the case of aqueous solutions of non-electrolytes. A deduction of the limiting value of j/m from the graph of θ/m (which is less susceptible to experimental error than j/m) against θ, the f.-p. depression, is of more general applicability. If θ/m can be written $\lambda+\alpha\theta+\beta\theta^2+\ldots$, then $j/m=-\delta(\theta/m)/\delta\theta$. The curve can be extrapolated readily and, for those cases in which the method is applicable (aqueous solutions of non-electrolytes; nitrobenzene solutions of alcohols and phenols) is almost a straight line in dilute solution. S. K. Tweedy.

Specific heats of the systems sulphuric acid–water, ferrous sulphate–water, and sulphuric acid–ferrous sulphate–water. G. Agde and H. Holtmann (Z. anorg. Chem., 1926, 158, 316—320).—The specific heats of the above systems determined at 25—45° show some deviation from those calculated on an additive basis. A. S. Corbet.

Electrical resistance of concentrated sulphuric acid and theory of hydration. M. H. Fischer and M. O. Hooker (Kolloid-Z., 1926, 40, 305—307).—The electrical resistance of sulphuric acid–water mixtures decreases with rise of temperature. For a given temperature the resistance decreases with increasing concentration of sulphuric acid, there being a minimum when the mixture contains 50 c.c. of concentrated sulphuric acid (*d* 1·84) and 200 c.c. of water. Above this concentration, the resistance increases rapidly, a second inflexion indicating the presence of excess of sulphuric anhydride. The mode of variation of properties with composition indicates a change from a solution of sulphuric acid in water to a solution of water in sulphuric acid, and the analogy with solvated colloids is discussed. E. S. Hedges.

Conductivity of phosphoric acid solutions at 0°. A. N. Campbell (J.C.S., 1926, 3021—3022).—The specific conductivity κ_0 of phosphoric acid solutions at 0° was determined for a number of dilutions, the maximum value being 1408×10^{-4} mho. The values of $1/\kappa_0\,.\,(d\kappa/dT)_9$ were calculated by using Kohlrausch's data for 18°, and since these are larger than Kohlrausch's values for $1/\kappa_{18}\,.\,/(d\kappa/dT)_{22}$, it is inferred that the temperature coefficient will eventually become negative. S. J. Gregg.

Conductivity of acetic acid in acetone. N. Sata (Bull. Chem. Soc. Japan, 1926, 1, 245—247).—The variation of conductivity with dilution has been investigated, and the results fit an equation of the Ostwald form. Since the constants of the equation give the high value 0·77 for the degree of dissociation at 500 litres dilution, it is suggested that the undissociated molecules also transport electricity. Great difficulties were experienced in purifying the materials.

S. J. Gregg.

Hydration of ions and variation in equivalent conductivity of salts on dilution. N. R. Dhar (Z. anorg. Chem., 1926, 159, 57—64).—The equivalent conductivity of a salt solution on dilution increases with the degree of ionic hydration. The order of degree of hydration is Li>Na>K>Rb,Cs and Mg>Ca>Sr>Ba.

Under similar conditions, the higher the degree of hydration, the higher is the viscosity and the smaller the electric charge on the substance. M. Carlton.

Polished platinum electrodes in conductivity work. A. F. Guerasimov (J. Russ. Phys. Chem. Soc., 1926, 58, 197—200).—The catalytic action of platinum-black on organic substances, when the latter are employed as solvents, has necessitated the use of the hitherto imperfectly investigated polished platinum electrodes. Kohlrausch has dealt with the subject theoretically, but the specific influence of a solution at different dilutions on the cell constant can be determined only by experiment. From experiments with potassium chloride and magnesium sulphate at different dilutions, it is found that the relation between W, the cell-constant, and R, the resistance, is given by: $W=a+b/R$. Within certain limits, the linear relation $W=c-dR$ holds.

M. Zvegintzov.

Conductivity of organic compounds and certain elements in the solid and liquid state. M. A. Rabinovitch (J. Russ. Phys. Chem. Soc., 1926, 58, 229—239).—The conductivity of organic compounds and halogens was investigated under a constant *E.M.F.* of 125 volts to determine the coefficient of loosening (α) of the crystal lattice, *i.e.*, the ratio of the conductivities of the solid and liquid at the m. p., with the view of elucidating the mechanism of electrical dissociation. The individual conductivities of the halogen-substituted acetic acids and the nitroparaffins are not in the same order as their conductivities in aqueous solution. The results show that symmetrical molecules with small dipole moments have little tendency to dissociate. This is confirmed by the values of α for the chloromethanes. The values of α for benzene, naphthalene, anthracene, and substituted hydrocarbons are in the order of their polarity. The behaviour of such substances in a non-polar solvent, such as ether, is analogous to the behaviour in it of acids (palmitic, stearic) of the same individual solid and liquid conductivity. Finally, the halogens were investigated by themselves and in solution, and a dynamic theory of the internal ionisation of the halogen molecule is discussed. M. Zvegintzov.

Electrolytic conductivity of solids. E. Friederich (Z. Elektrochem., 1926, 32, 576—577).—In a solid electrolyte, the ion which migrates under a potential gradient is the one carrying the smaller charge; when both ions have the same charge, the ionic diameter seems to be a determining factor (under these conditions it is generally the metallic ion which moves). This rule covers all cases which have been investigated, but they are too few to ensure generality. H. J. T. Ellingham.

Electronic conductivity of solid halides. E. Friederich and W. Meyer (Z. Elektrochem., 1926, **32**, 566—576).—The type of electrical conductivity exhibited by solids can be determined from the form of the current–voltage curves obtained from measurements of the direct current flowing through a rod of the substance when various voltages are applied. For electronic conductors, the current–voltage curve is a straight line through the origin, and at given voltage the current does not change with time. For electrolytic conductors with increasing voltage, the current remains practically zero until a definite decomposition voltage is exceeded, when it increases rapidly; at given voltage, the current changes with time. Substances showing mixed electronic and electrolytic conductivities give curves of composite character. A substance to be examined was prepared as a pure, dry powder, compressed into a rod, and then caused to sinter by heating in an indifferent gas. Silver bromide and iodide showed simple electrolytic conductivity, the decomposition voltages being 0·55 volt at 270° for the bromide, 0·507 at 110°, and 0·373 volt at 230° for the iodide. Silver chloride gave a more complex curve, but this was due to the presence of traces of finely-divided silver depolarising anodic deposition of chlorine. After prolonged electrolysis at high voltage, a simple curve with decomposition voltage at 0·733 at 230° was obtained. Cuprous iodide exhibits simple electronic conductivity at the ordinary temperature, and the statement by previous workers that this is true only when excess of iodine is present is definitely refuted. Cuprous bromide behaves like the iodide at the ordinary temperature. Cuprous chloride at 120° gives a complicated current–voltage curve, the conductivity being essentially electronic at low voltages, whilst above 0·1 volt cuprous chloride begins to depolarise anodic chlorine deposition (electrolytic conductivity). The true decomposition voltage lies at 0·466 volt, but can be obtained only by decreasing the voltage after electrolysis at above 1 volt. No other halides have been reported to show electronic conductivity. Those of univalent gold, mercury, and thallium might be expected to do so, but thallous iodide at 270° showed simple electrolytic conductivity (decomposition voltage 0·6), whilst results obtained with mercurous iodide were inconclusive. Reasons for the electronic conductivity of cuprous halides are discussed. The phenomenon may be connected with the facility with which the copper atom loses two valency electrons, although it is in group 1 of the periodic classification. H. J. T. Ellingham.

Electrical transport in solutions in fused aluminium bromide. W. Isbekov (Z. anorg. Chem., 1926, **158**, 87—93).—The following values have been obtained for the transport number of the cation in solutions of bromides in fused aluminium bromide: 11·97% solution of potassium bromide at 110°, 1·14; 14·33% solution of silver bromide at 130°, 0·837; 31·09% solution of antimonious bromide at 130°, 0·953. The results are ascribed to the presence and ionisation in solution of polymerised solute molecules and solute-solvent complexes, and to solvation of the bromide ion. R. Cuthill.

Contact *E.M.F.* between any two solutions. I. Simpler derivation of Planck's and Johnson's formulæ for solutions with equivalent cations and anions. Some considerations and formulæ for more complex cases. E. Denina (Gazzetta, 1926, **56**, 798—810).—A mathematical paper in which Johnson's expression (Ann. Phys., 1904, **14**, 995) is obtained by a new method of integrating the differential equations of Nernst and of Planck as applied to the contact of two solutions having equivalent ions. The more general case of ions of any valency is discussed, and a formula is derived for the contact *E.M.F.* in a case involving three ions of any valency, provided that the total ionic concentration is equal for the two solutions. This formula includes as a special case the expression deduced by Guyot (A., 1908, ii, 656). G. M. Bennett.

Rate of maximum activation by collision for complex molecules with applications to velocities of gas reactions. R. H. Fowler and E. K. Rideal (Proc. Roy. Soc., 1927, **A**, **113**, 570—584).—Theoretical. Homogeneous unimolecular reactions are considered from Arrhenius' point of view, *i.e.*, an equilibrium between active and inactive molecules, where the active molecules are all those which contain internal energy greater than ε_0. The rate of decomposition is then proportional to the total molecular concentration as long as the rate of activation and deactivation is large compared with the rate of decomposition. If x and y are the concentrations of active and inactive molecules at any time, then from the two equations $dx/dt=Z'y-(Z+B)x$, and $dy/dt=-Z'y+Zx$, where $Z'ydt$ is the total number of activations in time dt, and $Zxdt$ the total number of deactivations, it is shown that $x=X_0e^{-BZ't/(Z+Z')}$, $y=Y_0e^{-BZ't/(Z+Z')}$, which is of the unimolecular form. The value of ε_0 is known from Arrhenius' equation and from observations on the effect of temperature, and from ε_0 x can be calculated from statistical theory, and B is then determined from observations of the absolute rate of decomposition. The fraction of molecules with energy greater than ε, and the total number of collisions with available energy greater than ε_0 are calculated, and on the basis of these results the decomposition of nitrogen pentoxide and the dissociation of bromine are discussed. The calculation on the above basis for the decomposition of the former leads to a rate which is more than twenty times as large as the observed reaction rate at low pressures, and it is considered that the possible rate of activation may still be several hundred times the rate of decomposition at the lowest pressures, and that the real rate of activation by collision can be easily great enough to account for the observed unimolecular rate and law. Similar results are obtained in the case of bromine.

L. L. Bircumshaw.

Thermal reactivity of ozone in presence of hydrogen. J. W. Belton, R. O. Griffith, and A. McKeown (J.C.S., 1926, 3153—3166).—Reaction velocity measurements have been made in mixtures of ozone, oxygen, and hydrogen at 78° and 100°. The deozonisation process $2O_3 \longrightarrow 3O_2$, and a water-forming reaction (probably $H_2+O_3 \longrightarrow H_2O+O_2$) occur. The values of k_2 and k_1, the respective bimolecular velocity coefficients, both increase markedly with increasing partial pressure of hydrogen, but decrease with increasing partial pressure of oxygen. The catalytic effect of hydrogen is very much stronger than that of the inert gases helium and argon (A., 1925, ii, 1168). The ratio k_2/k_1 varies relatively slightly with the composition of the gas mixture, lying between 22 and 17 at both temperatures. Conditions which favour an increase in k_2 have a similar effect on k_1, and the two reactions are probably coupled in some way. The temperature coefficient of k_2 in the absence of hydrogen is 2·9; in the presence of excess of hydrogen, it is 2·4. The average value of E from the Arrhenius equation is 27,700 g.-cal. The mechanism of the reactions is discussed. W. THOMAS.

Ignition point of gases at different pressures. H. B. DIXON and W. F. HIGGINS (Mem. Manchester Phil. Soc., 1925—1926, **70**, 29—36).—A preliminary account of experiments on the ignition points of hydrogen and of methane in air and in oxygen at various pressures from 100 mm. to 7 atm. The gases were brought into contact in an improved form of concentric cylinder device, and the time elapsing, or lag, between the moment of mingling of the combustible gas with air or oxygen and that of the appearance of the flame has been observed as a function of the temperature of the mingling gases and of their pressure. The differences between the values obtained for the ignition temperatures, corresponding with experiments using an open-ended, and (the same) closed ignition tube (in which the preheating was more uniform), as a function of the lag show a maximum for hydrogen and an increase for methane as the lag is increased from 0·5 to 15 sec. The effect of increasing pressure for mixtures of hydrogen and air for values of the lag from 0·5 to 3·0 sec. show a maximum for the ignition point at 1000 mm. in the range 75—1520 mm. In the range 100—5320 mm., methane–air mixtures show a progressive diminution; methane–oxygen mixtures, however, reach a maximum at 200 mm. The existence of these maxima is held to be a general property of combustible gases. R. W. LUNT.

Supposed law of flame speeds. A. G. WHITE (Nature, 1927, **119**, 51).—Wheeler and Payman's speed generalisation must obviously break down when one of the combustible gases in a complex mixture interferes with the burning of another, as is the case with carbon monoxide–hydrogen–air mixtures (cf. Bone, this vol., 26). By mixing suitable carbon disulphide–air and ether–air mixtures having the same flame speed, mixtures can be obtained which do not propagate flame. A. A. ELDRIDGE.

Ignition of gases by an explosion-wave. I. Carbon monoxide and hydrogen mixtures. C. CAMPBELL and D. W. WOODHEAD (J.C.S., 1926, 3010—3021).—A photographic investigation has been made of the behaviour of the flame in certain gaseous mixtures ignited by the explosion-wave in a hydrogen–oxygen mixture. An apparatus is described allowing of the photographing of a flame as it travels from one explosive mixture into another. When the igniting and ignited gases are mixtures of hydrogen and oxygen in different proportions, the flame travels in both mixtures at the normal explosion-wave rates, the velocity in the second mixture becoming adjusted after travelling a few cm. in it. When the mixture $2CO+O_2$ is ignited by electrolytic gas, the flame velocity falls rapidly to less than half the normal rate, and detonation is re-established only after the flame has travelled several metres. A fairly complete drying of the carbon monoxide mixture does not appear to lower the flame speed below a certain limit, although it lengthens the period before detonation. The addition of more than 1% of hydrogen to the carbon monoxide mixture allows the flame to proceed immediately at its full rate; hydrogen is thus more efficient than water vapour in allowing the explosion wave to develop. A flame just previous to the setting up of the explosion-wave in these mixtures tends to show marked discontinuities. The reasons for the temporary damping down of the explosion wave in passing from the hydrogen–oxygen to the carbon monoxide–oxygen mixture have been suggested by Dixon and Walls (J.C.S., 1923, **123**, 1025) and Crussard (Bull. Soc. Ind. Min., 1907, 6, 257). W. THOMAS.

Pressure wave sent out by an explosive. II. W. PAYMAN and W. C. F. SHEPHERD.—See B., 1927, 30.

Influence of the reaction on the decomposition of sulphuretted waters by a current of inert gas; hydrological applications. A. DESGREZ, L. LESCŒUR, and (MLLE.) S. MANJEAN (Compt. rend., 1926, **183**, 1244—1247).—The rate of removal of hydrogen sulphide from solutions by a stream of inert gas is modified by the addition of certain salts. In the case of Challes water, 5% of sodium hydrogen carbonate and of potassium monophosphate accelerated the removal of the gas, the latter to the greater extent. Sodium borate (1%) had less influence, a curve being obtained from which the angular point previously found for sulphuretted waters (A., 1926, 1113) was absent. Experiments in which borate and phosphate buffer solutions were added to the sample showed that it is the p_H value which influences the rate of removal of hydrogen sulphide. The curve showed the instability of the gas in an acid medium and its stability in an alkaline medium, a rapid transition taking place at p_H 8—9. Since the mean p_H of the urine is 6·5, the absence from it of hydrogen sulphide, even after considerable quantities of sulphuretted waters have been drunk, is explained. J. GRANT.

Law of hydrolysis of sucrose by acids. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1926, **183**, 1285—1286).—The ratio of the velocity of hydrolysis to the weight of crystallisable sugar in the liquor, $1/t \,.\, \log a/(a-x)$, has been determined for the hydrolysis of 10% solutions of sucrose by 0·1N-nitric and oxalic acids; it increases with the time. This indicates that the reaction is neither simply unimolecular nor the resultant of two reactions, one of which is instantaneous. Such reactions would be produced respectively by the hydrogen ions and by the formation of an unstable complex compound between the sucrose and the elements of water, with subsequent decomposition into dextrose and lævulose. In the latter case, the cations and anions of the acid respectively assist in the formation and decomposition of the complex. J. GRANT.

Hydrolysis of α- and β-glycerophosphoric acids by chemical reagents and by enzymes. P. FLEURY and Z. SUTU (Bull. Soc. chim., 1926, [iv], 39, 1716—1718).—No difference in the rate of hydrolysis of α- and β-glycerophosphoric acids was found with hydrochloric acid, sodium hydroxide, or the enzyme from white mustard as hydrolysing agent. S. J. GREGG.

Irreversible oxidation of organic compounds. I. Oxidation of aminophenols by reagents of definite potential. II. Apparent oxidation potentials of certain phenols and enols. J. B. CONANT and M. F. PRATT (J. Amer. Chem. Soc., 1926, 48, 3178—3192, 3220—3232).—I. The rates of irreversible oxidation of *o*- and *p*-aminophenol and of 1 : 2- and 1 : 4-aminonaphthols by reversible oxidising agents have been studied in a manner analogous to that previously applied to irreversible reduction processes (cf. A., 1926, 1134). These rates are independent of the dilution, and are related to the oxidation-reduction potential of the reagent employed. By measuring the rate of oxidation of each of the above substances by a series of reagents of graded potentials, the potential of the (hypothetical) reagent which just causes "appreciable oxidation" can be determined, and this potential is called the "apparent oxidation potential" of the substance under examination. These relationships suggest that the rate of the total oxidation process is governed by that of the stage which is itself reversible, a condition which would be fulfilled if the first stage of the oxidation of the aminophenols to the corresponding quinones is a reversible oxidation to the quinoneimine, the subsequent hydrolysis of which is irreversible and relatively slow (cf. Wieland, A., 1910, i, 243). Evidence of the reversibility of the oxidation of *p*-aminophenol to benzoquinoneimine was obtained by the titration method and the method of mixtures in alkaline solutions (p_H 7·8—11·3), in which the quinoneimine is relatively stable. Certain electrochemical equations are developed, and the relative rates of oxidation of each amino-compound with several reagents of different potentials are shown to be of the order of magnitude predicted from these.

II. The rate of oxidation of α-naphthol in acid solution (p_H 2·6—6·9) at 60° by reversible reagents of known potential has been determined, and the rate of oxidation shown to be related to the potential of the reagent employed. The rates of oxidation of phenol, resorcinol, α- and β-naphthols, quinol monomethyl ether, ethyl malonate, and ethyl acetoacetate are practically independent of dilution. It is suggested that the first stage in the oxidation is the reversible formation of a free radical (cf. Goldschmidt, A., 1924, i, 1062), which then undergoes unimolecular isomerisation and polymerisation. Certain electrochemical equations are developed on this assumption, and the above relative rates of oxidation of α-naphthol are of the order of magnitude predicted from these equations. The apparent oxidation potentials of a number of phenolic and enolic substances have been determined in buffer solutions of varying acidity at 25° and 60°. F. G. WILLSON.

Velocities of esterification. P. PETRENKO-KRITSCHENKO, V. BOGATSKY, and N. LOUBMAN, (J. Russ. Phys. Chem. Soc., 1926, 58, 215—218).—A summary of work already published (A., 1925, ii, 556) on velocities of esterification of primary, secondary, and tertiary alcohols under different conditions with the view of elucidating the mechanism. The theories of Menschutkin and of Michael (*ibid.*, 1909, ii, 219) are only partly true; there is a lack of uniformity in the results, and the variations of rate depend more on the nature of the acid than on the groups attached to the α-carbon atom of the alcohols. M. ZVEGINTZOV.

Decomposition of diacetone alcohol [*iso*hexan-δ-ol-β-one] in alkali hydroxide-alkali salt solutions. G. ÅKERLÖF (J. Amer. Chem. Soc., 1926, 48, 3046—3063).—The velocity of decomposition of *iso*hexan-δ-ol-β-one dissolved in some alkali salt solutions (up to 6*N*) of constant alkali concentration was investigated at 25°. The results obtained were always the opposite to those obtained in an acid-salt solution of corresponding concentration. The velocity-salt concentration curves have the same general form, independent of the nature of the anion of the salt; the curves for salts with a common cation never intersect. Potassium cyanide has a higher activity coefficient than the sodium salt at the same concentration; similar behaviour is shown by the alkali hydroxides (Harned and Åkerlöf, A., 1926, 796). The rate of decomposition of a compound by hydrogen and hydroxyl ions in a salt solution is always directly related to the activity coefficients of these ions, an increase in the coefficient increasing the velocity, and *vice versa*. S. K. TWEEDY.

Rate of dissolution of copper in aqueous ferric chloride solutions. E. BEKIER and S. TRZECIAK (Rocz. Chem., 1926, 6. 483—496).—See A., 1926, 482.

[Oxidising action of iodic acid and its restriction.] O. WARBURG (Ber., 1926, 59, [*B*], 2705; cf. A., 1926, 1011).—A claim for priority against Fischer and Wagner (*ibid.*, 1215). H. WREN.

Relation between the order of a reaction and its temperature coefficient for reactions of certain organic acids with chromic acid or potassium permanganate. A. N. DEY and N. R. DHAR (Z. Elektrochem., 1926, 32, 586—596).—Velocity constants of the following reactions have been measured in the dark, at various temperatures, with various concentrations of reactants, and with or without the presence of manganous sulphate as catalyst. From the results are obtained the number of molecules of organic acid (n_1) and of oxidising agent (n_2) participating in the reaction, and the temperature coefficient ($c = k_{T+10}/k_T$) of the reaction. Tartaric acid, $n_1 = 2$, $n_2 = 0$, $c = 2·4$ (25—35°); with addition of manganous sulphate, $n_1 =$ about

1·5, $n_2 = 0$, c = about 5. Lactic acid and chromic acid, $n_1 = 2$, $n_2 = 1$, $c = 2·16$ (25—35°); with addition of manganous sulphate, $n_1 = 2$, $n_2 = 0$, $c = 2·5$ (25—35°). Maleic acid and chromic acid, n_1 = about 2, $n_2 = 1$, $c = 1·96$ (25—35°); with addition of manganous sulphate, $n_1 = 1·5$, $n_2 = 0$, $c = 3·9$ (25—35°). The reactions of tartaric, citric, and lactic acids with potassium permanganate are all unimolecular with respect to the permanganate, and the temperature coefficients are, respectively, 2·55, 1·8, and 3·2 (10—20°); they are retarded by increasing concentration of manganous salt, but accelerated by sulphuric acid. An increase in the concentration of tartaric acid or of lactic acid causes a slight decrease in the corresponding velocity constant, but change in the concentration of citric acid is practically without influence. The results are claimed to support the "von Halban–Dhar" rule that the lower is the order of a reaction (true, not "apparent" order), the higher is the temperature coefficient. The life-period of activated molecules in three of these reactions is calculated by the Turner equation.

H. J. T. Ellingham.

Acid and salt effects in catalysed reactions. III. Dependence of the characteristics of the minimum-velocity mixture on the concentration of the acid and the application of minimum velocity to the determination of catalytic and ionisation constants. H. M. Dawson and C. R. Hoskins (J.C.S., 1926, 3166—3173).—The reaction velocities (v_i) and hydrogen-ion concentration $[H]_i^+$ characteristic of the minimum-velocity mixture for the catalysis of the acetone–iodine reaction by acetic acid and sodium acetate have been determined for acid concentrations ranging from 0·01*N* to *N*. The variations of v_i and of $[H]_i^+$ with the concentration of the acid between 0·01*N* and 0·50*N* are in accordance with theoretical predictions. The ratio of the minimum velocity to the corresponding hydrogen-ion concentration is independent of the concentration of the acid. The data for *N*-acetic acid are not in agreement; this may be connected with a decrease in the ionisation constant of the acid in more concentrated solutions. Minimum velocities may be used for the determination of the catalytic coefficient characteristic of the undissociated acid. A kinetic method for the determination of the dissociation constants of weak acids is described and applied to the experimental data for acetic acid.

W. Thomas.

[Acid and salt effects in catalysed reactions. V.] Isohydric solutions and the velocity of chemical change. H. M. Dawson and C. R. Hoskins (Proc. Leeds Phil. Lit. Soc., 1926, 1, 108—112).—When the reaction between iodine and acetone is catalysed by a solution containing equimolecular quantities of acetic acid and sodium acetate, and therefore of approximately constant p_H value 4·73, the velocity is not the same for all the solutions, as might be expected by the hydrogen-ion theory of catalysis, but for a *N* solution is about 160 times as great as for a 0·005*N* solution. It is shown, however, that these results may be accounted for quantitatively on the assumption that the total catalytic effect produced by an acid, or by a mixture of this with the corresponding sodium salt, represents the sum of effects which are separately produced by the hydrogen ion, the acid anion, the hydroxyl ion, and the undissociated acid.

M. S. Burr.

Catalysis [of decomposition of ethyl alcohol]. D. Balarev [with N. Kolev] (Z. anorg. Chem., 1926, **158**, 105—110; cf. A., 1923, i, 287).—When ethyl alcohol and phosphoric acid are heated together, the reaction with rise of temperature successively assumes the following forms: (*a*) formation of phosphates, (*b*) formation of phosphates and simultaneous partial decomposition with production of ethylene, (*c*) partial adsorption of alcohol on surface of phosphoric acid, and partial combination, and (*d*) adsorption of alcohol, but no combination. In all stages except the first, ethylene is formed.

R. Cuthill.

Heterogeneous catalysis and electrochemical polarisation. E. Spitalsky and M. Kagan (Ber., 1926, 59, [*B*], 2900—2907).—The catalytic decomposition of hydrogen peroxide in neutral solution at 25° in the presence of smooth and platinised platinum and of platinum foil has been investigated. The activity of the metal depends largely on its previous electrochemical treatment, being greatly increased by cathodic polarisation, but decreased by anodic polarisation. Platinised platinum which has been exclusively treated cathodically exhibits an unusually high catalytic activity, and the reaction, under otherwise identical conditions, follows an unusual course, since the constants, calculated for a reaction of the first order, diminish rapidly during the change. The effect is not due to a metastable condition of the metal, since the original activity of the fatigued metal is restored when the concentration of the hydrogen peroxide is increased. Feeble anodic polarisation destroys this enhanced activity, and the electrode then behaves normally, causing decomposition with smaller and tolerably uniform constants of the first order. Sufficiently drastic anodic polarisation almost destroys the catalytic activity of the metal, which, however, can be restored by cathodic treatment, so that, by alternate use as anode or cathode, the activity of the metal can be varied at will. Electrodes, passive because of anodic treatment, can be activated by treatment in concentrated sulphuric acid or glycerol at 150—165°, or, to a less extent, in boiling water (cf. Teletoff, A., 1908, ii, 95); the effect is due to the temperature used.

H. Wren.

[Catalytic hydrogenation.] W. Traube and W. Lange (Ber., 1926, 59, [*B*], 2860—2863; cf. Wieland and Fischer, A., 1926, 806).—The application of the dehydrogenation theory to the decomposition of water by chromous salts (cf. Traube and Lange, A., 1926, 257) and to the action of carbon dioxide on water in the presence of palladium, necessitates the adoption of arbitrary subsidiary hypotheses without experimental foundation. The conversion of chromous to chromic salts is accelerated by substances which cannot be regarded as hydrogen acceptors. The production of sodium formate cannot be established when carbon monoxide and water interact at a palladium surface in the presence of alcoholic sodium hydroxide.

H. Wren.

Low-temperature oxidation at charcoal surfaces. III. Behaviour of blood charcoal and the influence of temperature on the reaction rate. E. K. Rideal and W. M. Wright (J.C.S., 1926, 3182—3190).—The area of carbon surface active for the oxidation of oxalic acid varies within the limits 30—55% of the total, depending on the method of preparation of the charcoal. The range of promoter action of one iron atom extends to not more than six carbon atoms, and an analogy is sought in the complex iron cyanides. The variation in adsorption of oxalic acid with the temperature is small; the temperature coefficient of oxidation increases with increasing concentration of oxalic acid. From the temperature coefficients, the following critical energy increments are calculated; for autoxidation 11,000 g.-cal. per g.-mol.; for oxidation of oxalic acid on the C–C complex 14,020 g.-cal.; on the –Fe–C– complex 13,030 g.-cal.; and on the Fe–C–N complex 12,290 g.-cal. The nature of the surface adsorption of the oxygen is more important than the surface concentration of the oxalic acid. Sugar and blood charcoals differ in the amount of oxalic acid adsorbed, but are identical in respect of the rates of oxidation of oxalic acid and the temperature coefficients of the rates (cf. A., 1926, 919). W. Thomas.

Catalytic synthesis of water vapour in contact with metallic silver. A. F. Benton and J. C. Elgin (J. Amer. Chem. Soc., 1926, 48, 3027—3046).—The above synthesis was investigated at 50—100° by the method of Pease and Taylor (cf. A., 1922, ii, 701), the results being treated by a new quantitative method. When hydrogen is in excess, the rate of water formation rapidly attains a maximum, and then falls slightly and reaches a steady state after about 40 min.; it rapidly becomes zero on cutting off the oxygen, so that the latter is not continuously taken up and retained by the catalyst, although small quantities are absorbed at the start of a run. With oxygen in excess, the steady state is attained more rapidly, no hydrogen being taken up by the catalyst. No hydrogen peroxide could be detected in the reaction products. The rate of the reaction is proportional to the pressure of hydrogen, and is independent of the oxygen pressure; the reaction is anti-catalysed by the water vapour formed, due to absorption of the latter by the silver, and is retarded by a preliminary heating of the catalyst in oxygen, when large quantities of this gas are adsorbed independently of the temperature (26—110°) and pressure. The reaction depends on collisions of gaseous hydrogen molecules with those adsorbed oxygen atoms which are free from adsorbed water, although possibly the oxygen atoms must be adjacent to bare spaces on the catalyst surface in order to react readily. S. K. Tweedy.

Catalytic decomposition of ammonia. E. Elöd and W. Banholzer (Z. Elektrochem., 1926, 32, 555—558).—The percentage decomposition of ammonia caused by passage through a heated tube containing a catalyst (iron, copper, or alumina) was measured for various rates of flow of the gas. Determinations were made at 700° and 600°. For a mixture of ammonia and nitrogen or argon, the extent of decomposition was simply that corresponding with the rate of flow of ammonia through the tube under the given conditions, but for mixtures of ammonia and hydrogen, the percentage decomposition was notably less than that corresponding with the rate of passage of the ammonia. Hydrogen causes this retardation in the velocity of decomposition of ammonia when other catalysts, such as cerium oxide, are used. With a 50% mixture of ammonia and hydrogen, increasing the rate of flow reduces the extent of decomposition of the ammonia more considerably and relatively more sharply than in the corresponding experiments with ammonia alone. Rise of temperature increases the percentage decomposition in all cases, but the magnitude of this effect depends greatly on the catalyst used and on whether the gas is mixed with nitrogen or hydrogen. H. J. T. Ellingham.

Effect of formaldehyde on the dissolution of iron in acids. G. Batta (Bull. Soc. chim. Belg., 1926, 35, 393—411).—The presence of formaldehyde greatly reduces the rate of dissolution of powdered cast iron in hydrochloric acid; the extent of the reduction is not proportional to the amount added, but addition of 0·25 c.c. of a 40% solution to 100 c.c. of 17% acid reduces the rate to 0·25 of the normal. The rate varies with the time, about half the metal added being left after 19 hrs. in presence of 0·25 c.c. of the formaldehyde solution, but all being dissolved after that time if none is present. The retardation is less pronounced at higher temperatures. Even 1 mg. of formaldehyde exercises a marked effect, using 100 c.c. of acid. No loss of formaldehyde from the solution occurs in laboratory tests. Similar results were obtained with steel and wrought-iron plates; the addition of 2% by volume of commercial formaldehyde solution to the acid reduced the loss in weight under comparable conditions to one fiftieth. The effects of acetaldehyde and propaldehyde are very similar in nature and extent. S. I. Levy.

Cathodic sputtering. II. Variations in experimental conditions. E. Blechschmidt (Ann. Physik, 1926, [iv], 81, 999—1042). **III. Theory of cathode sputtering.** A. von Hippel (*ibid.*, 1043—1075; cf. A., 1926, 1013).—A systematic study has been made of the effect of variations in experimental conditions—dimensions, materials, temperature, etc.; and a general theory of cathodic sputtering has been based on the conception of local vaporisation of the electrode metal under bombardment. The impact-velocity of the cations has been measured directly. The implications of local vaporisation are developed thermodynamically and subjected to experimental test. An expression which gives a complete qualitative formulation of the sputtering phenomena is advanced. The relationships existing between the following variables are discussed: area and thickness of sputtered film, time of sputtering, number of atoms released from electrode. The order of ease with which metals are sputtered is that of decreasing heat of sublimation. The influence of secondary factors and the elimination of some such effects are further discussed. R. A. Morton.

Use of auxiliary washing electrodes in the preparation of pure hydrogen by electrolysis.

A. Müller (Physikal. Z., 1926, 27, 778—779).—The claim that oxygen-free hydrogen can be prepared by the use of an auxiliary cathode to generate hydrogen for hindering the diffusion of oxygen through the electrolyte (Niese, A., 1923, ii, 314) is contested, and Gaede's method (Ann. Physik, 1913, [iv], 41, 302) is preferred.

R. A. Morton.

Electrolytic preparation and electromotive behaviour of complex cyanides of univalent nickel and cobalt. G. Grube [with H. Lieder and P. Schächterle] (Z. Elektrochem., 1926, 32, 561—566).—Solutions containing the complex cyanide, $K_2Ni(CN)_3$, in which nickel is univalent (cf. Bellucci and Corelli, A., 1914, i, 260), are produced by electrolytic reduction of a cold alkaline solution of potassium nickelocyanide, $K_2Ni(CN)_4$, using a nickel cathode in a diaphragm cell from which air is excluded; the anolyte is a dilute potassium hydroxide solution. Cathode materials of higher hydrogen overvoltage have no advantage, since they soon become coated with nickel. The resulting blood-red solution may have 60—70% of its nickel content in the univalent form. It oxidises in the air and evolves hydrogen on warming. Electrolytic reduction of alkaline solutions of potassium cobalticyanide under similar conditions at cathodes of platinum, cobalt, nickel, or tin produces first an olive-green solution of potassium cobaltocyanide and then a brownish-green solution containing a complex cyanide of univalent cobalt. The latter could not be isolated from the solution, which decomposes with vigorous evolution of hydrogen at the ordinary temperature. Solutions of this substance are also obtained by treating solutions of potassium cobalticyanide or cobaltocyanide with potassium amalgam. It can be determined by measuring the hydrogen evolved on boiling the solution or by titration with permanganate. Potentials of electrodes of the type Pt(platinised)|$K_4Co(CN)_6$,$K_3Co(CN)_6$ in 0·77*N*-KOH were measured and ${}_0\varepsilon_h$ was calculated to be —0·814 at 2°. Similar measurements were made on solutions containing the complex cyanides of univalent nickel and cobalt, *e.g.*, Pt(platinised)|$K_2Ni(CN)_4$ (0·057 g.-mol./litre), $K_2Ni(CN)_3$(0·049 g.-mol./litre) in *N*-KOH, $\varepsilon_h =$ —0·880 at 2°; Pt(platinised)|$K_4Co(CN)_6$ (0·057 g.-mol./litre), $K_xCo(CN)_{x+1}$ (0·043 g.-mol./litre), $\varepsilon_h = -0{\cdot}846$ at 2°. Hydrogen is evolved at the platinum in all cases, and the results may thus be low. Cobaltocyanide can be determined in the presence of cobalticyanide by oxidising with alkaline potassium ferricyanide, acidifying, and titrating electrometrically with permanganate the ferrocyanide produced.

H. J. T. Ellingham.

Mechanism of Kolbe's electrosynthesis. D. A. Fairweather and O. J. Walker (J.C.S., 1926, 3111—3121).—Solutions of acetates and propionates have been electrolysed under various conditions, and it is shown that synthesis is not due to the partial oxidation of the acid formed by the action of the discharged ions on water, but to the direct interaction of the discharged ions themselves. The effect on yield of the concentration, temperature, current density, and anode material has been studied. A certain minimum concentration of discharged ions is necessary before synthesis can commence. The yield is increased in non-aqueous solvents where reaction between the discharged ions and the solvent cannot take place, and where, therefore, the oxidation theory is not applicable. The electrolytic oxidation of acetic acid is complete to carbon dioxide and water, and not partial under ordinary conditions.

W. Thomas.

Anodic oxidation of aluminium and its alloys as a protection against corrosion. G. D. Bengough and J. M. Stuart.—See B., 1927, 16.

Decomposition of nitrogen pentoxide. R. G. W. Norrish (Nature, 1927, 119, 123).—As an alternative to the hypothesis of Fazel and Karrer (this vol., 29) decomposition of nitrogen pentoxide is regarded as taking place as follows: (*a*) $2NO_2$(in light) $\longrightarrow 2NO+O_2$; (*b*) $NO+N_2O_5=3NO_2$. Hence the decomposition of nitrogen pentoxide is not a true photosensitised reaction, but a secondary dark reaction.

A. A. Eldridge.

Quanta measurements of the decomposition of lactic acid in the presence of uranyl sulphate. R. H. Müller (Biochem. Z., 1926, 178, 77—81).—The photochemical conversion of lactic acid into acetaldehyde and carbon dioxide in the presence of uranyl sulphate gives an energy absorption of 1·05 quanta per mol., the average wave-length of the irradiation being 4025 Å. Using an oxalic acid–uranyl sulphate solution as an actinometer system, 0·99 quantum is absorbed per mol., so that the Einstein equation holds. Oxalic acid–uranyl sulphate solution is well suited to act as an actinometer in systems in which uranyl salts play a catalytic or oxidative part.

J. Pryde.

Light-distribution between two absorbing media, and the conception of intensity in photochemistry. J. Plotnikov (Z. wiss. Phot., 1926, 24, 305—308).—It is shown that, instead of the usual expression, it is preferable to regard the total absorption of light by a mixture of two absorbing media as the sum of the absorptions of the two components. The question of light intensity, in particular the bearing of the experiments of Lasarev (Ann. Physik, 1907, 24, 661) on the problem, is considered.

W. Clark.

Panchromatisation of photographic plates for use in the ordinary spectrum. E. Viterbi.—See B., 1927, 61.

Active hydrogen. M. Scanavy-Grigorieva (Z. anorg. Chem., 1926, 159, 55—56).—Formation of hydrogen sulphide by hydrogenation of sulphur at the ordinary temperature is no longer sufficient evidence that hydrogen is activated by passing it over glowing metals such as platinum, palladium, etc. In experiments on the activation of hydrogen by this method, the presence of hydrogen sulphide was always observed, whether the hydrogen on its emergence from the tube of hot metal was led through sulphur or not. This is due to the tendency of substances, especially when finely divided, to absorb sulphur compounds from the atmosphere.

All the substances examined, amongst which were platinum, palladium, copper, and glazed porcelain, gave up the absorbed sulphur as hydrogen sulphide

at 600—700°. The reduction of nitrates or of tungsten or molybdenum trioxide by this method of activation has not been confirmed, and under the conditions described no activation of hydrogen in the direction of increasing its reducing powers occurs.
M. Carlton.

Preparation of hydrogen peroxide. M. L. Kilpatrick, O. M. Reiff, and F. O. Rice (J. Amer. Chem. Soc., 1926, 48, 3019—3021).—Pure sodium peroxide is added in small portions to 20% sulphuric acid solution (which is preferable to phosphoric acid), the temperature being kept below 20°, until 95% of the acid is neutralised. The sodium sulphate decahydrate crystals are filtered off after 1 hr., washed with cold water, and the mother-liquor and washings distilled in a vacuum at 60—65° in 100 c.c. portions, the final solid residue being heated at 85°. In the first of two cooled receivers, 20—23% hydrogen peroxide solution collects (yield 96%), and in the second, colder, receiver, a 2—2½% solution. A second distillation of the concentrated peroxide solution over excess of pure silver sulphate yields pure peroxide solution, which may be concentrated to 88%, with a loss of 12% on yield, by storing in a vacuum over concentrated sulphuric acid for 3 days at the ordinary temperature.
S. K. Tweedy.

Reduction of sodium sulphate to sodium sulphide. P. P. Budnikov.—See B., 1927, 10.

Stability of alkaline solutions of potassium ferricyanide used for etching in microscopy. T. Murakami and K. Someya (Z. anorg. Chem., 1926, **158**, 117—135).—An alkaline solution of potassium ferricyanide may be used for etching steel previously to microscopical examination. Increase in the concentration of either the alkali or the salt accelerates the etching process, but the most suitable concentrations for use depend on the nature of the steel under examination. The effectiveness of the solution gradually increases for some time after it has been made up, then slowly decreases. The ferricyanide, however, decomposes in an approximately linear manner from the time of preparation, whilst the rate of disappearance of the alkali is at first rapid, but later falls off, and tends to zero. Decomposition is promoted by sunlight. The ferricyanide first forms the aquoferricyanide, which is then reduced to the aquoferrocyanide, and so to ferrocyanide. It is probable that the initial increase in the etching power of the solution with its age is due to some very active intermediate product.
R. Cuthill.

Higher oxides of silver. II. Ag_2O_2. F. Jirsa [with J. Jelinek and J. Srbek] (Z. anorg. Chem., 1926, **158**, 33—60; cf. A., 1925, ii, 1182).—Largely details of work of which the chief results have already been published (*ibid.*, 1162). The active oxygen in the oxide, Ag_2O_2, can be accurately determined by Topf and Diehl's method modified as follows. The peroxide is treated with a 57% solution of potassium iodide, and after 3 min. sulphuric acid is added and the free iodine titrated. When the oxide is boiled with water, the amount of decomposition increases in an approximately linear manner with the relative amount of water, the reaction $Ag_2O_2+H_2O=2Ag^{\cdot}+2OH'+\frac{1}{2}O_2$ apparently ceasing when the solution is saturated with silver hydroxide.
R. Cuthill.

Higher oxides of silver. III. Oxidation of silver by ozone. F. Jirsa and J. Jelinek (Z. anorg. Chem., 1926, **158**, 61—66; cf. preceding abstract).—Silver in the form of a rod is oxidised by ozone to Ag_2O, but with the finely-divided metal ternary solid solutions of Ag_2O, Ag_2O_2, and Ag_2O_3 result. Water converts the Ag_2O_3 in these into Ag_2O_2, with liberation of a corresponding amount of oxygen. Pure Ag_2O_2 is not oxidised by ozone, and solid solutions of Ag_2O_3 in Ag_2O_2 seem incapable of existence.
R. Cuthill.

Dehydration of gypsum. J. T. McCormack (J. Geol., 1926, 34, 429—433).—At the ordinary temperature, and pressures of 600—316,000 lb. per in.^{2}, gypsum is not dehydrated within short periods (0·5 hr.—5 days). Temperature is far more important than pressure in the dehydration of gypsum.
Chemical Abstracts.

Preparation of calcium cyanide. H. H. Franck and C. Freitag.—See B., 1927, 42.

Method of producing molecular mixtures. S. von Bogdandy, J. Boehm, and M. Polányi (Z. Physik, 1926, 40, 211—213).—The method consists in depositing at very low pressures on a cooled rotating drum layers of metals etc. together with naphthalene. The metals showed no *X*-ray interference lines; the colour exhibited depended on the proportion of metal to naphthalene; on dissolving out the naphthalene from the metallic deposit and warming, interference lines were obtained. A mixture of cadmium and sulphur was black; when warmed to about 50°, it turned red (cf. Semenov and Schalnikov, A., 1926, 1107). A mixture of zinc with naphthalene exploded violently after several days.
E. B. Ludlam.

Barium sulphate-potassium permanganate mixed crystals. W. Geilmann and E. Wünnenberg (Z. anorg. Chem., 1927, **159**, 271—272).—Although Balarev (A., 1926, 1195) has shown that the violet mixed crystals of barium sulphate and potassium permanganate obtained by a diffusion process were decolorised by a mixed solution of sulphuric and oxalic acids, large violet crystals containing about 5% of potassium permanganate, which are not decolorised by sulphuric and oxalic acids or by sulphurous acid, are obtained by allowing 2*N*-solutions of sulphuric acid and barium chloride to diffuse slowly into a 10% solution of potassium permanganate.
J. S. Carter.

Fluoborates. E. Wilke-Dörfurt and G. Balz (Z. anorg. Chem., 1927, **159**, 197—225; cf. Funk and Binder, A., 1926, 1015; Lange, *ibid.*, 1112).—The following fluoborates are described: sodium, $NaBF_4$; *thallous*, $TlBF_4$; calcium, $Ca(BF_4)_2,2H_2O$; *silver*, $Ag(H_2O)BF_4$; strontium, $[Sr(H_2O)_4](BF_4)_2$; magnesium, lead, cupric, *manganous*, cadmium, ferrous, nickelous, and cobaltous, $[M(H_2O)_6](BF_4)_2$; *silver-diammine*, $[Ag(NH_3)_2]BF_4$; *zinctetrammine*, $[Zn(NH_3)_4](BF_4)_2$; *nickelous-*, *cobaltous-*, *manganous-*, and *cadmium-hexammine*, $[M(NH_3)_6](BF_4)_2$; *cobaltic-* and *chromium-hexammine*, $[M(NH_3)_6](BF_4)_3$; *chrom-*

ium-hexacarbamide, $[Cr(CN_2H_4O)_6](BF_4)_3$; *magnesium-*, *manganous-*, *nickelous-*, and *cobaltous-hexa-aquohexamethylenetetramine*, $[M(H_2O)_6](BF_4,C_6H_{12}N_4,H_2O)_2$; *silverdipyridine*, $[Ag(C_5H_5N)_2]BF_4$; *silvertetrapyridine*, $[Ag(C_5H_5N)_4]BF_4$; *cuprictetrapyridine*, $[Cu(C_5H_5N)_4](BF_4)_2$; *nitrosyl*, BF_4NO; nitron, $C_{20}H_{16}N_4,HBF_4$, m. p. 227° (uncorr.). J. S. Carter.

Construction of neutralisation curves. B. Englund (Z. anorg. Chem., 1926, **158**, 359—369).—The subject is discussed theoretically with reference to the neutralisation curves of mono-, di-, and tribasic acids, carbonates, and ampholytes.
A. S. Corbet.

Reactivity of silicon. F. Roll (Z. anorg. Chem., 1926, **158**, 343—348).—When kept under oxygen-free and oxygen-saturated water for a year, crystalline silicon showed a maximum increase of 2% and 10%, respectively, in the silica content, whilst under similar conditions the amorphous form gave 5—8·2% and 12—20·5%, respectively. Increased silica formation occurred in presence of added impurities and when the two forms remained under boiling water for a month.

Oxidation experiments carried out by heating crystalline silicon in a stream of oxygen showed that no action occurs below 250°, but above this temperature oxidation increases with increased temperature and time of heating and decreased size of grain. Crystalline silicon with a high silica content does not behave very differently. A. S. Corbet.

Acidic properties of silicic acid and certain silicates. H. Kappen and J. Breidenfeld.—See B., 1927, 9.

Preparation of metallic germanium and volatility of the metal in hydrogen and in a vacuum. J. H. Müller, E. F. Pike, and A. K. Graham (Proc. Amer. Phil. Soc., 1926, **65**, 15—32).—The purest germanium is prepared by the reduction of specially purified germanium dioxide with hydrogen and graphite; the metal has m. p. 959° in hydrogen, 958° in carbon dioxide, 975° in a vacuum; it is volatile in hydrogen at atmospheric pressure below 800°, and in a vacuum below 760°. Molten germanium (1 g.) absorbs hydrogen (0·183 g.) on cooling. When heated with germanium in a vacuum, germanium dioxide is reduced to the monoxide.
Chemical Abstracts.

Germanium. XVII. Fused germanium dioxide and some germanium glasses. L. M. Dennis and A. W. Laubengayer.—See B., 1927, 42.

Hydrolysis of zirconium chromate. P. Krishnamurti and B. B. Dey (Z. anorg. Chem., 1926, **158**, 94—98).—Addition of a large excess of a saturated solution of potassium dichromate to a concentrated solution of zirconium oxychloride precipitates a *basic zirconium chromate*, $Zr(OH)_4,2Zr(OH)_2CrO_4$. Using a dilute solution of the zirconium salt, the product has approximately the formula $Zr(OH)_4,Zr(OH)_2CrO_4$. With very dilute boiling solutions of the oxychloride and only a slight excess of dichromate, the composition of the product, after washing with boiling water, corresponds with the formula $2Zr(OH)_4,Zr(OH)_2CrO_4$. R. Cuthill.

Ammoniates of compounds of the rare earths. I. Contraction during the formation of compounds. F. Ephraim and R. Bloch (Ber., 1926, 59, [*B*], 2692—2705).—Contraction in volume during the formation of compounds is ascribed mainly to the union of the electron sheaths of several atoms to a homogeneous formation and to the deflexion of outer electrons with markedly excentric path. Any deformation of the outer sheath must be followed by a similar change in the inner ring. The vibrations of the electrons must therefore become shorter, and the spectrum must consequently be expected to be displaced towards the violet. This expectation is to some extent realised with the ammines of praseodymium chloride, since the reflexion spectrum of the octammine is sharply displaced towards the region of shorter wave-length in comparison with the anhydrous chloride with respect to all the bands. With the pentammine, however, a non-uniform displacement of the position of the bands is observed. The spectrum of the diammine generally resembles that of the pentammine, but the displacement of the band of greatest wave-length is more marked. In the monammine, fission of two of the bands occurs, probably denoting the presence of two differently placed praseodymium atoms, as indicated by the formula, $[Pr(NH_3)_2]PrCl_6$. The spectrum of the chloride left after complete expulsion of ammonia from the ammines is not completely identical with that of the original chloride.

The sensitiveness of the ammonates to atmospheric air renders it necessary to prepare the anhydrous chlorides, add ammonia, decompose the ammonates thermally, measure the approximate volume of the powder, and observe the reflexion spectrum in the same apparatus, which is figured and described. The following ammines are described, the temperatures of decomposition to the next lower member being placed within parentheses: *lanthanum chloride octammine* (71°), *pentammine* (86°), *triammine* (145°), *diammine* (181°), *monammine* (265°); *cerium chloride octammine* (70°), *pentammine* (115°), *diammine* (198°), *monammine* (281°); *praseodymium chloride octammine* (71°), d^{25} 1·67, *pentammine* (115°), d^{25} 2·18, *diammine* (218°), d^{25} 2·81, *monammine* (290°), d^{25} 3·28; *neodymium chloride octammine* (70°), *pentammine* (114°), *diammine* (219°), *monammine* (293°). For the determination of density, the ammines are prepared in the pyknometer itself, pentane being used as filling liquid. H. Wren.

Oxidations and reductions of ammonium salts, nitrites, and nitrates by iron compounds, insoluble in water. K. Boresch.—See B., 1927, 10.

Formation of nitric oxide at high temperatures. E. Briner, J. Boner, and A. Rothen (J. Chim. phys., 1926, 9, 788—807).—See A., 1926, 916. The equilibrium concentration of nitric oxide in air is now given as 0·79±0·06% at 1600±10°.

Allotropic modifications of phosphorus. V. Ipatiev and W. Nikolajev (Chem.-Ztg., 1926, 50. 989—990; cf. A., 1926, 487).—A more detailed account. It is concluded that red phosphorus is probably a mixture of the black and purple varieties.
E. H. Sharples.

Oxidation of phosphorus vapour at low pressures. J. Chariton and Z. Walta (Z. Physik, 1926, 39, 547—556).—The reaction between oxygen and phosphorus vapour has been studied at pressures of the order 10 mm. If the oxygen pressure is below a critical pressure, no rapid reaction takes place; the value of the critical pressure is greater the greater the pressure of the phosphorus vapour. Above the critical pressure, the reaction is extremely rapid. If oxygen is admitted until its critical pressure is nearly reached, and then argon is allowed to enter, the luminescence appears; the effect is as though the pressure of the phosphorus had diminished, but the intensity of the light is less. With argon almost at atmospheric pressure, the glow made its appearance immediately oxygen was allowed to enter, but its intensity was very feeble. It is suggested that the reacting molecule is P_2; when this is oxidised, more molecules are formed from P_4 with absorption of heat; this, together with the fact that some of the heat of oxidation is lost as radiation, prevents the rapid action. The higher is the pressure of the phosphorus vapour the greater is the proportion of P_4 molecules and the higher is the critical pressure of the oxygen. The argon diminishes the loss by radiation, receiving energy by collision, which is then communicated to the phosphorus by further collisions and the critical pressure is reduced. E. B. Ludlam.

Quadrivalent vanadium. E. Parisi (Gazzetta, 1926, 56, 843—847).—The transformation of the pink vanadyl hydroxide into the olive-green modification (cf. Gain, A., 1908, ii, 284) is a consequence of conversion of part of the vanadium from the quadrivalent to the quinquevalent condition. The pink compound remains unchanged as regards both colour and power to reduce permanganate if kept in a tightly-stoppered vessel filled with water previously boiled and saturated with carbon dioxide (cf. Crow, J.C.S., 1876, 30, 453). T. H. Pope.

Amphoteric hydroxides, their aqueous solutions and crystalline salts. IV. Antimonic acid and the alkali antimonates. G. Jander and W. Brüll (Z. anorg. Chem., 1926, 158, 321—342; cf. A., 1925, ii, 988).—Potassium and sodium antimonates contain their component oxides in the ratio 1 : 1 and are probably derived from an orthoantimonic acid. The solubility in water, at 20°, of sodium antimonate, $NaSbO_3,3H_2O$ (the so-called "pyroantimonate"), is $2{\cdot}52—2{\cdot}55\times10^{-3}$ mol. per litre, and this value is almost equally depressed by the presence of potassium antimonate or sodium chloride in equivalent concentrations. When a cold 5% solution of potassium antimonate is saturated with carbon dioxide, a white precipitate of the triantimonate, $K_2H_3Sb_3O_{10},5H_2O$, results, and thus freshly-prepared solutions of potassium antimonate should be used when testing for sodium. At 20°, the solubilities in water of sodium and potassium triantimonates are $1{\cdot}3\times10^{-5}$ and $0{\cdot}9\times10^{-3}$ mol. per litre, respectively.

Increasing hydrogen-ion concentration in aqueous solutions of antimonate ions leads to decrease of the diffusion coefficient and increased tendency towards formation of tri- and tetra-antimonates. Antimony cations do not appear to exist in appreciable amount in *N*-hydrochloric acid, and no formation of antimonate from triantimonate appears to occur in dilute alkaline solution. A. S. Corbet.

Sulphurous acid and its salts. V. Behaviour of pyrosulphites when heated. F. Foerster and G. Hamprecht (Z. anorg. Chem., 1926, 158, 277—315).—The very complicated course of the decomposition of pyrosulphites when heated is due to the occurrence of several simultaneous reactions, and is affected by the cation combined with S_2O_5'', the nature and velocities of the principal reactions, and the temperature and partial pressure of sulphur dioxide during the experiment. The decomposition of crystalline potassium pyrosulphite has been followed from 150° upwards and three principal reactions are found to occur: $2S_2O_5''\longrightarrow S_3O_6''+SO_4''$ (i); $3S_2O_5''\longrightarrow S_2O_3''+2SO_4''+2SO_2$ (ii); $S_2O_5''\rightleftharpoons SO_3''+SO_2$ (iii). At the commencement (i) is the main reaction and yields a yellow product which dissolves very readily in water to give a trithionate. Above 250° (ii) is exclusively the main reaction, whilst (iii) commences above 200°, but only when the partial pressure of the sulphur dioxide generated by (ii) is kept low. Passage of nitrogen over the heated mixture favours (iii), which is retarded, however, when sulphur dioxide remains over the salt.

In addition, the following side reactions occur: $S_3O_6''\longrightarrow SO_4''+SO_2+S$ (iv); $2S_2O_3''+SO_2\longrightarrow 2SO_4''+3S$ (v); $4S_2O_3''\longrightarrow 3SO_4''+S_{1+4}$ (vi); $4SO_3''\longrightarrow 3SO_4''+S''$ (vii). Accompanying (i), (iv) commences when the trithionate concentration has reached a definite amount and effects its initial decomposition. Reaction (v) depends on (ii) and at 220°, in closed apparatus, (ii) and (v) dominate the decomposition. Provided all thiosulphate has not been eliminated by (v), (vi) first becomes evident above 400°. The reaction velocity of (vii) first becomes noticeable at 550°.

Combination of (i) and (iv) and of (ii) and (v) gives $2S_2O_5''\longrightarrow 2SO_4''+SO_2+S$, which completely represents the decomposition after the disappearance of thiosulphate.

Although qualitatively similar, the quantitative decomposition of sodium pyrosulphite is very different, for in this case the heat of dissociation for (iii) is much smaller and, at 150°, (iii) is the principal reaction. A. S. Corbet.

Laboratory preparation of sulphuryl chloride. H. Danneel (Z. angew. Chem., 1926, 39, 1553—1554).—Sulphuryl chloride is easily prepared by the interaction of sulphur dioxide and chlorine in presence of activated carbon if provision is made for removing the heat of reaction, *e.g.*, by allowing the catalyst tube to fill with liquid sulphuryl chloride and cooling externally. The sulphuryl chloride overflows as it is formed through a side tube into a collecting vessel, a yield of 100% being readily obtained. Sulphuryl bromide, if it exists, decomposes at 18° with evolution of sulphur dioxide. The properties of solutions of paraldehyde and metaldehyde in sulphuryl chloride are described. C. Irwin.

Molybdic acid and molybdates. A. Travers and Malaprade (Bull. Soc. chim., 1926, [iv], 39, 1543—1573).—A more detailed account of work already published (A., 1926, 1114).

Ferric and manganese dichromates. S. Husain and J. R. Partington (Chem. News, 1926, **133**, 386—387).—The prolonged action of chromic acid solution on excess of precipitated ferric hydroxide at 80—90° yielded a solution which, on evaporation at 90°, gave a residue corresponding with the composition $Fe_2O_3,6CrO_3$, or $Fe_2(Cr_2O_7)_3$, after drying in a vacuum. *Ferric dichromate* is a hygroscopic, brown solid, hydrolysing in aqueous solution on extensive dilution. It decomposes somewhat at 100°; contrary to the results of Calcagni (A., 1925, ii, 891), at 140° the chromate radical is decomposed, a black residue remaining which slowly dissolves to a green solution in boiling concentrated hydrochloric acid. The action of chromic acid solution on excess of solid manganous carbonate yielded a dark red solution probably containing manganese dichromate, $MnCr_2O_7$. Only partly decomposed solid products could be obtained from this solution. Attempts to prepare double salts of this dichromate with potassium chromate failed: the latter was oxidised to dichromate with precipitation of manganese dioxide.

S. K. Tweedy.

Chemical changes in magnetite when heated in air. E. Greulich (Z. anorg. Chem., 1926, **159**, 65—77).—For the reaction $4Fe_3O_4+O_2\longrightarrow 6Fe_2O_3$, a temperature of 1385° is necessary. Above this temperature, the reaction is one of dissociation. Magnetite, which was fractionated by a magnetic process and contained about 65% of iron, was heated in a current of air in a special furnace at known temperatures up to 1400° for periods of 0·5, 1, 2 . . . 100 hrs.

Between 400° and 1200°, the magnetite is converted into ferric oxide, the velocity of the reaction being small below 1000° (*e.g.*, in 100 hrs. at 400°, 5·4% was changed; at 900°, 95·9%). For complete oxidation at 900°, 40 hrs.' heating was required; at 1000° 10 hrs., and at 1100° only 2 hrs.; at 1200° less than 1 hr.

Magnetite is no longer oxidised in air above 1380°. Above 1450°, the ferrous oxide content of the roasted product is almost that of the original substance, but measurements of the magnetisability of this product show that a portion of the ferrous oxide is not present as ferrosoferric oxide, but as ferrous oxide. The amount of this is about 2% at 1500° and 3% at 1550°, in agreement with the values obtained by Ruer and Nakamoto (A., 1923, ii, 643).

These results are confirmed by microscopical examination. The oxidation of the magnetite at 1200° is exponential in character, and the kinetics of this reaction are compared with those of other heterogeneous systems. M. Carlton.

Mechanism of oxidation of iron with steam, air, and carbon dioxide at high temperatures. P. P. Fedotéeff [with T. N. Petrenko].—See B., 1927, 15.

Oxidations with fluorine. VI. Preparation of cobaltic sulphate. F. Fichter and H. Wolfmann (Helv. Chim. Acta, 1926, **9**, 1093—1096).—Passage of fluorine into a solution of cobaltous sulphate in sulphuric acid (24 g. of $CoSO_4,7H_2O$ in 125—150 c.c. of 8*N*-sulphuric acid) at 0° yields cobaltic sulphate which is extremely unstable, the analytical data for which do not agree, in confirmation of the observations of Marshall (J.C.S., 1891, **59**, 302), exactly with the formula $CO_2(SO_4)_3,18H_2O$. The action of fluorine on a 1·15*N*-solution of cobaltous carbonate in sulphuric acid yields the cobaltic salt only with difficulty. Increase in the concentration of the solvent acid causes the compound $CoF_2,5HF,6H_2O$ to separate, and in one case a 60% yield of cobaltic fluoride was obtained.

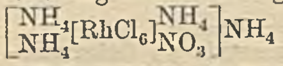
J. W. Baker.

Preparation of salts of bivalent ruthenium. H. Gall and G. Lehmann (Ber., 1926, **59**, [*B*], 2856—2860).—Ruthenium trichloride is reduced by hydrogen in alcoholic solution in the presence of spongy platinum to *ruthenium dichloride* mixed with metallic ruthenium. The production of the latter is obviated by addition of hydrochloric acid, preferably derived from chloroform, added to the alcoholic solution. The dichloride behaves as a reducing agent. In solution, it does not absorb carbon monoxide at the atmospheric temperature; at 210°, it is converted by dry carbon monoxide into the compound, $RuCl_2,2CO$ (cf. Manchot and König, A., 1925, ii, 149). *Ruthenium dibromide* is prepared by reduction of the tribromide in absolute-alcoholic solution in the presence of bromoform. Indications of the production of ruthenium di-iodide are obtained by reduction of ruthenium tri-iodide dissolved in alcohol saturated with dry ammonia. H. Wren.

Rôle of carbon monoxide in the preparation of ruthenium trichloride. W. Manchot and J. König (Z. anorg. Chem., 1927, **159**, 269—270).—The statement of Remy (this vol., 34) that Joly (A., 1892, 658) isolated a carbonyl derivative of ruthenium dichloride is erroneous. J. S. Carter.

Ternary salts of rhodium [Wilm's chloronitrate]. O. E. Zwiagincev (J. Russ. Phys. Chem. Soc., 1926, **58**, 170—176).—The history and properties of Wilm's rhodium chloronitrate, $Rh_2Cl_6,6NH_4Cl,2NH_4NO_3$ (A., 1884, 660; 1893, ii, 213) are discussed, and its structure is investigated in the light of Werner's theory. An aqueous solution of the pale lilac salt becomes blood-red. Silver nitrate precipitates an amorphous, pale-rose *compound* containing all the rhodium, and hence is formulated $[RhCl_6]Ag_3,NH_4NO_3$. The complex is soluble in ammonia and is slightly decomposed on warming. The *mercury* and *lead* salts are described.

The position of the ammonium nitrate in the molecule was determined by thermal decomposition experiments with Kurnakov's pyrometer and found to be analogous to "water of co-ordination." Such a structure explains the behaviour in solution. The following formula is suggested:



$$\left[{}^{NH_4}_{NH_4}[RhCl_6]^{NH_4}_{NO_3}\right]NH_4$$

M. Zvegintzov.

Calculation of the limiting composition of mixed crystals resistant to chemical action. G. Masing (Wiss. Veröff. Siemens-Konz., 1926, **5**, 156—169).—A theoretical and mathematical paper in which a correction is introduced into the equations of Masing (A., 1922, ii, 37) and of Borelius (Ann. Physik, 1924, [iv], 74, 216) so as to make them agree more fully with the theory of probability in expressing the limiting composition which resists attack of mixed crystals of a metal highly resistant to chemical attack and a less noble metal. The resistance limit of a plane model according to this calculation occurs when two thirds of the atoms in the plane consist of the less noble metal.

A. R. Powell.

Dehydration of salt hydrates by means of acetic anhydride. N. Schoorl (Chem. Weekblad, 1927, **24**, 13).—The method of Menke (this vol., 27) may yield only a lower hydrate in place of the anhydrous salt. S. I. Levy.

Spectrographic identification of certain elements and the possibility of quantitative determination by means of the arc spectrum. I. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, **16**, 519—555).—Omitting the rare gases, experimental spectral data are lacking for dysprosium, gadolinium, holmium, osmium, praseodymium, samarium, terbium, and thulium. For 62 elements, the spectra at relatively high dilutions are known, at least partly. In spectral analysis, knowledge of the lines of an element of great sensitiveness is of importance, which is, however, not absolute, but relative, since the experimental conditions, particularly the character of the diluent, affect the results.

As regards the possibility of determining elements spectrographically, it is pointed out that the diminution in the intensity of all lines as the concentration of an element diminishes is not uniform for the different lines composing the spectrum, and that quantitative spectral analysis on the basis of the data given in published tables is not possible unless preliminary auxiliary investigations on the relations between spectral variations and concentration are made. Details of the experimental results are to be published later. T. H. Pope.

Improving detections. M. de Jong (Pharm. Weekblad, 1926, **63**, 1428).—Very slight precipitates may be detected more readily by localising the solid formed in a ring between the water of the solution and added chloroform or petroleum. S. I. Levy.

Temperature corrections in volumetric analysis. N. Schoorl (Chem. Weekblad, 1926, **23**, 581—582; cf. Couvée, this vol., 34).—A further table of expansion coefficients for some fifteen common titration solutions in glass vessels is given. S. I. Levy.

Use of nomograms in analysis. S. Reiner (Z. anal. Chem., 1926, **69**, 377—382).—Examples are given of the application of nomograms to the calculation of analytical results. R. Cuthill.

Potentiometric determination of hydrogen-ion concentration at higher temperatures. I. M. Kolthoff and F. Tekelenburg (Rec. trav. chim., 1927, **46**, 18—27).—See A., 1926, 1220.

Simplification of electrometric p_H determinations. W. U. Behrens (Biochem. Z., 1926, **178**, 181—183).—A sliding bridge is described, adapted for use with the hydrogen and quinhydrone electrodes, which gives direct readings in terms of p_H.

J. Pryde.

Buffer solutions with p_H value between 2·0 and 6·6. I. M. Kolthoff and J. J. Vleeschhouwer (Biochem. Z., 1926, **179**, 410—413).—See A., 1926, 1220.

Separation of chlorate from perchlorate. K. Scharrer (Ber., 1926, **59**, [*B*], 2746—2749).—Chlorate may be determined in the presence of perchlorate (and nitrate) by reduction to chloride by magnesium powder in hot, dilute nitric acid solution and determination as silver chloride. If perchlorate is also to be determined in similar mixtures, reduction of it and the chlorate to chloride is effected by cautious addition of copper powder to the molten mixture; chloride is determined in the usual manner.

H. Wren.

Separation of hydrochloric from hydrobromic and hydriodic acids. G. G. Longinescu and (Miss) M. N. Bădescu (Bul. Soc. Româna Stiinte, 1926, **29**, 17—21).—The solid is boiled with concentrated sodium carbonate solution to remove certain heavy metals and the filtrate is acidified with sulphuric acid; two or three drops of "perhydrol" are added and then pure petroleum oil. The mixture is warmed until the aqueous layer is colourless, and the layers are then separated by filtration. Hydrochloric acid is then detected in the aqueous filtrate in the usual way. In the quantitative procedure, the layers are separated in a funnel, the petroleum layer being thoroughly washed with water and the washings added to the aqueous layer. S. K. Tweedy.

Determination of iodide in presence of chloride or bromide, and determination of each halide in a mixture of the three. R. Berg (Z. anal. Chem., 1926, **69**, 369—374).—In presence of acetone, hydriodic acid is decomposed by iodic acid according to the equation $2HI+HIO_3+3C_3H_6O=3C_3H_5IO+3H_2O$, whilst hydrobromic acid and hydrochloric acid are attacked only slowly or not at all. To 50—60 c.c. of the solution, which must not contain more than 2% of potassium bromide, are added 20—30 c.c. of acetone and sufficient dilute sulphuric acid to make the total volume 100 c.c. and the acid concentration 2·0—2·5*N*. Starch is then added and standard potassium iodate solution run in until the solution is colourless. The chloride or bromide is then determined with silver nitrate. In a mixture of the three halides, iodide is determined as above, chloride by Volhard's method, after destroying the bromide with bromic acid (this vol., 35), and bromide by difference.

R. Cuthill.

Potentiometric titrations. I. Determination of the end-point and potential change. II. Titration of iodide with permanganate. F. L. Hahn and G. Weiler (Z. anal. Chem., 1926, **69**, 417—449).—Two methods of determining the end-point of a potentiometric titration are available, the graphical and the differential; the former yields more accurate results when the reacting substances are not in equimolecular ratio, as is the case in the titration of iodides with permanganate (Hahn and Wolf, A., 1926, 1220). This titration gives better results potentiometrically when carbon tetrachloride is added to the solution to remove the iodine from the aqueous layer as fast as it forms; in this way, accurate results are obtained for iodide when 50 mols. of bromide and 600 mols. of chloride are present for every mol. of iodide. Fuller details are given of the direct titration with permanganate, using ethyl acetate to absorb the iodine; this method is more rapid than the potentiometric method, but does not give such good results in presence of chlorides and bromides. A. R. Powell.

Micro-titration of iodides with iodate and determination of the iodide and ferrous iron content of syrup of ferrous iodide. I. M. Kolthoff (J. Amer. Pharm. Assoc., 1926, **15**, 164—166).—To 10 c.c. of 0·1*M*-potassium iodide solution are added 80 c.c. of water, 20 c.c. of 25% hydrochloric acid, and 4—5 c.c. of 10% potassium cyanide solution. The titration is completed with *M*/60-potassium iodate solution, using carbon tetrachloride or chloroform as indicator. The method is accurate to 1% in solutions containing 0·127 mg. of iodine in 100 c.c. The reversed method, in which the iodine is oxidised to iodate by hypochlorous acid and the iodine titrated with potassium iodide, is used for mixtures containing other substances oxidised by iodate; the accuracy is then 1% for solutions containing 0·1 mg. per 100 c.c. For syrup of ferrous iodide, 10 c.c. are diluted with 80 c.c. of water, 10 c.c. of 25% phosphoric acid, and 5 c.c. of 10% potassium cyanide solution. 0·1*N*-Potassium permanganate solution is added in slight excess, then an excess of potassium iodide, and the iodine titrated with thiosulphate. Chemical Abstracts.

Determination of soluble fluorides. F. L. Hahn (Z. anal. Chem., 1926, **69**, 385—386).—The concentrated solution of the fluoride is made alkaline with sodium hydroxide, and then neutralised with acetic acid, and so much sodium sulphate added that there is at least 0·2 g. or, for large amounts of fluoride, still more of sulphate ion in 100 c.c. Excess of calcium chloride solution is then added, and the precipitate ignited and weighed. Finally, the precipitate is moistened with concentrated sulphuric acid and again ignited and weighed, the increase in weight corresponding with the conversion of calcium fluoride into calcium sulphate. R. Cuthill.

[Volumetric] determination of sulphates. H. Roth (Z. angew. Chem., 1926, **39**, 1599—1601).—The sulphate is precipitated by barium chloride and the excess of the latter titrated with excess of potassium dichromate, using as indicator *pp'*-diaminodiphenylamine (0·1 g.) dissolved in a mixture of 0·4 g. of pure tartaric acid, 0·1 g. of salicylic acid, and 20 c.c. of water. It is used on filter-paper, which must be kept in the dark. The slightest trace of chromate gives a blue colour. The back titration is performed in dilute ammonia solution free from carbonate, and the end-point is very precise. The barium sulphate need not be removed. Alkaline sulphate solutions such as are encountered in the analysis of pyrites etc. must be freed from any phosphoric and arsenic acids by precipitation with ammoniacal magnesium chloride. The accuracy is comparable with that of the gravimetric method. C. Irwin.

Decomposition of thiosulphate solutions. F. L. Hahn (Z. anal. Chem., 1926, **69**, 386—389).—Schulek's tests for sulphide and tetrathionate in thiosulphate solutions (A., 1926, 1017) were inconclusive, since they may have been given by free sulphur. It is suggested that the increase in strength of thiosulphate solutions on keeping, which is occasionally observed, is due to the transformation of some impurity in the thiosulphate into thiosulphate, and, to a small extent, to the conversion of thiosulphate into sulphide by bacteria (cf. Mayr, A., 1926, 814). R. Cuthill.

Comparison of boric and hydrochloric acids in the determination of nitrogen in leather. R. W. Frey and R. M. Hann.—See B., 1927, 54.

Spectrophotometric determination of nitrites and nitrates by means of diphenylamine sulphate. E. Tassilly and R. Savoire (Bull. Soc. chim., 1926, [iv], 39, 1755—1759).—See this vol., 35.

Microchemical determination of nitrates. F. Rogozinski (Rocz. Chem., 1926, **6**, 497—500).—See A., 1926, 813.

Detection of nitrite, nitrate, and sulphite ions. E. Eegriwe (Z. anal. Chem., 1926, **69**, 382—385).—One part of nitrite in 5,000,000 parts of water can be detected by the reddish-violet colour, due to the formation of a diazo-compound, produced when a mineral acid and a 0·03% solution of safranine-*T* are added to the solution. With larger amounts of nitrite, a blue colour results. Nitrates are detected by first reducing to nitrite with magnesium powder and dilute sulphuric acid. If to a solution containing a sulphite there is added a 0·01% solution of fast-blue-*R* crystals drop by drop, shaking after each addition until the violet colour disappears, a yellow coloration is produced, the sensitivity of the test being about 1 in 175,000. Thiosulphates and thionates do not give this reaction. Sulphides, polysulphides, and hydroxides interfere. R. Cuthill.

Application of hydrolysis to the study of differential analytical reactions. L. Rossi (Anal. Asoc. Quím. Argentina, 1926, **14**, 239—242).—By the use of a 5% solution of sodium or potassium nitroprusside in the presence of hydrogen sulphide, it is possible to distinguish between normal, monohydrogen, and dihydrogen salts of orthophosphoric acid. In the case of normal salts, the alkalinity produced by hydrolysis is so great that a considerable concentration of sulphide ions results, and a deep red coloration is formed. In the case of the monohydrogen phosphate, a less intense violet coloration is produced, whilst in the case of the dihydrogen phosphate there is no coloration. G. W. Robinson.

Titrations with arsenious acid. O. Cantoni.—See B., 1927, 10.

Analysis of volatile liquids and gases. Determination of arsenic in volatile liquids. O. Faust and E. Fischer (Z. anorg. Chem., 1926, **158**, 181—184).—Arsenic in carbon disulphide cannot be determined by the Gutzeit method because some hydrogen sulphide is formed by reduction of the carbon disulphide and blackens the silver nitrate.

The following method of determination, which is applicable to other volatile liquids, has been devised. The carbon disulphide is poured into a Marsh's apparatus, and burnt at the jet, partly as vapour and partly as reduction products, the products of combustion being aspirated through a solution of sodium hydroxide. This is then oxidised with hydrogen peroxide, acidified with sulphuric acid, and examined for arsenic with Lockemann's modification of Marsh's apparatus. R. CUTHILL.

Assay of solution of arsenious and mercuric iodide. W. H. SCHULZE (J. Amer. Pharm. Assoc., 1926, **15**, 464—465).—On keeping the solution the arsenious iodide content rapidly changes, particularly on exposure to light. The assay should consist of a determination of the total arsenic present. CHEMICAL ABSTRACTS.

Determination of carbon dioxide in carbonates. J. R. I. HEPBURN.—See B., 1927, 42.

Alkalimetric determination of the hardness of industrial waters. C. BELCOT.—See B., 1927, 62.

Volumetric determination of magnesium in industrial waters. C. BELCOT.—See B., 1927, 10.

Separation of magnesium from the alkali metals. C. OTTO (J. Amer. Chem. Soc., 1926, **48**, 3016—3018).—An almost quantitative separation of magnesium from sodium and potassium is obtained by igniting the mixed nitrates and extracting the alkali nitrates and nitrites from the residue with cold dilute ammonium hydroxide solution. Magnesium oxide is left, and may be confirmed in the usual way after dissolution in acid. Repeated ignition with nitric acid will not convert sulphates into nitrates, and when the sulphate radical is present, the modified procedure of Precht and Wittjen (Z. anal. Chem., 1883, **22**, 81) is suggested. This method was not tested experimentally, however. S. K. TWEEDY.

Determination of zinc by conductivity titration. G. SANDER and O. PFUNDT (Z. angew. Chem., 1926, **39**, 1557—1558).—The use of a membrane filter solves the difficulty of filtering and washing a precipitate of zinc sulphide, but the determination of the zinc in the precipitate by boiling with a known quantity of hydrochloric acid and titrating the residual acid requires care. An easy alternative is given by determination of the conductivity of the acid solution while adding standard sodium hydroxide solution. During neutralisation, the conductivity falls; it remains stationary during precipitation of zinc, and then rises again. The two discontinuities in the conductivity curve give a measure of the zinc content of the solution, which can be determined with an accuracy of 0·3—0·5%. The acidity of the zinc solution used must be limited if the beginning- and end-points are to be sharp. C. IRWIN.

Determination of zinc by electrometric titration. G. G. REISSAUS (Z. anal. Chem., 1926, **69**, 450—455).—The electrometric determination of zinc by titration with ferrocyanide is conveniently carried out in a 600-c.c. beaker provided with a motor-driven stirrer; one electrode consists of a platinum gauze cylinder, and is connected directly to the milliammeter; the other electrode is a narrow-bore tube filled with saturated potassium chloride solution and closed at each end with a wad of filter-paper. This tube makes connexion between the zinc solution and a saturated potassium chloride solution contained in a small flask; the latter solution is connected by a similar tube to a dilute solution of potassium ferrocyanide acidified with sulphuric acid in which is placed a platinum spiral connected through a variable resistance to the other terminal of the ammeter. The zinc solution, prepared from the ore or other material in the usual way, is acidified with sulphuric acid, treated with 5 c.c. of saturated potassium ferricyanide solution, heated to boiling, and titrated with standard ferrocyanide solution until the maximum deflexion of the ammeter for an addition of 0·1 c.c. is obtained. The normal potassium chloride electrode will last for upwards of 50 titrations without requiring renewal. A. R. POWELL.

Stabilisation of the inflexion-point in potentiometric precipitation reactions. I. ATANASIU (Bul. Soc. Română Stiinte, 1926, **29**, 7—9).—The irregularities observed in the potentiometric curves obtained in the determination of lead, barium, and mercury with potassium chromate, and of cerium, lead, and zinc with potassium ferrocyanide (cf. A., 1926, 929), are probably due to dissolution and ionisation of the precipitate, and may be eliminated by the addition of 30% ethyl alcohol solution. The titration may still be carried out at 65—70°. The addition of alcohol, besides enabling very dilute solutions to be titrated, also enables the position of the inflexion-point to be readily determined from the readings. S. K. TWEEDY.

Volumetric determination of copper in insecticides containing iron, arsenic, and mercury. J. BODNAR and A. TERÉNYI.—See B., 1927, 30.

Precipitation of aluminium hydroxide by ammonia, and determination of alumina. L. MURAVLEV and O. KRASSNOVSKI (Z. anal. Chem., 1926, **69**, 389—394).—Blum's method of precipitating aluminium hydroxide (A., 1916, ii, 493), in which precipitation is completed at p_H 7, using methyl-red as indicator, gives better results than the ordinary method in the determination of aluminium. The precipitate is washed with a hot 2% solution of ammonium nitrate, which must be adjusted to p_H 7 with ammonia, as it otherwise exerts a slight solvent action. Addition of filter-paper pulp to the solution before precipitation causes the precipitate to settle better, and, contrary to the statements of Wilke-Dörfurt and Locher (A., 1924, ii, 775), does not introduce error. The alumina so obtained is not appreciably hygroscopic. R. CUTHILL.

Determination of manganese as permanganate. R. LANG (Z. anorg. Chem., 1926, **158**, 370—376; cf. A., 1926, 581).—The quantitative oxidation of manganese to permanganate is effected by nickel dioxide, and is carried out in two stages. The chloride-free solution containing 0·015 g. of manganese and 0·25 g. of nickel as sulphate or nitrate is treated with sodium carbonate until a permanent turbidity results, and the salts are oxidised to dioxides by addition of potassium persulphate. After 3—5 min., the solution is slowly acidified with 30—50 c.c. of 5*N*-sulphuric or nitric acid, when quantitative oxidation to permanganate occurs. 0·1*N*-Arsenious acid is then added until a sap-green colour is obtained. At this point, 20 c.c. of 1 : 1 hydrochloric acid and a drop of potassium iodide or iodate are added, and titration with arsenious acid is continued to a bright green colour; the solution is then titrated back with 0·1*N*-potassium permanganate.

The procedure is not affected by non-oxidisable bivalent metals, such as calcium, copper, and zinc, provided sufficient alkali be present in the initial stage for their complete precipitation, but in presence of ferric, chromium, and lead salts, and more than 0·005 g. of cobalt, a modification in the procedure is necessary. A. S. Corbet.

Organic phosphoric acid compounds. VI. Determination of iron. III. F. Zetzsche and M. Nachmann (Helv. Chim. Acta, 1926, 9, 979—980).—Small quantities of iron ($>$0·04 g.) may be directly determined as the bis-*p*-chlorophenylphosphate (A., 1926, 705) if the precipitate is washed with 55 c.c. of *N*-hydrochloric acid, 70—100 c.c. of water, and 60—100 c.c. of 40% alcohol, and dried at 105°. Excess of water readily hydrolyses the precipitate, and more concentrated alcohol causes the precipitate to pass through the filter-paper. J. W. Baker.

Potentiometric determination of ferrous and ferrocyanide [ions] with potassium bromate. I. M. Kolthoff and J. J. Vleeschhouwer (Rec. trav. chim., 1926, 45, 923—927; cf. A., 1919, ii, 352; Collenberg and Sandved, A., 1926, 140).—Using a bright platinum gauze electrode, rolled into a cylinder, and in presence of hydrochloric acid (3—8%), ferrous solutions can be accurately determined by titration with potassium bromate. Even at the ordinary temperature, and without the addition of a catalyst, the determination may be carried out in about 15 min., and is accurate to 0·2%. The presence of cobalt chloride has scarcely any effect on the rise of potential, but mercuric chloride causes a distinct, although small, increase in the rise. Ferrocyanide solutions may also be determined accurately in this way (hydrochloric acid, 3—5%, potassium bromate, 0·01*N*), provided the concentration of the ferrocyanide does not exceed 0·01*N*. In the titration of 0·1*N*-solutions, about 1% too much bromate is required. The addition of catalysts offers no advantage. L. L. Bircumshaw.

Oxidation–reduction potentials. I. M. Kolthoff (Z. anal. Chem., 1926, 69, 374—377).—It is asserted that for the determination of ferrous and ferric salts in a mixture of the two, electrometric titration gives much more accurate results than do measurements of the oxidation potential (Hirsch and Rüter, A., 1926, 930). R. Cuthill.

Colorimetric determination of minute amounts of nickel. L. T. Fairhall (J. Ind. Hygiene, 1926, 8, 528—533).—Armit and Harden's colorimetric determination of traces of nickel with the aid of dimethylglyoxime (A., 1906, ii, 397) gives erroneous results, since the solution has no true colour, the pink tint being due to crystalline particles of the nickel oxime. A sensitive colorimetric method is described involving the use of potassium dithiooxalate, which imparts an intense magenta colour to acid or neutral solutions of nickel salts. Iron and cobalt must be absent (methods of removal are described), but calcium, magnesium, phosphates, and small amounts of manganese may be present. One mg. of nickel may be determined with an accuracy of 0·02 mg. A modified method of preparing potassium dithio-oxalate is described (Jones and Tasker, J.C.S., 1909, 95, 1904). S. K. Tweedy.

Potentiometric titration of tin with potassium bromate. K. Sandved (Analyst, 1927, 52, 2—14)—Bivalent tin is first oxidised with tervalent iron and the resulting ferrous iron titrated with potassium bromate. A boiling solution of ferric chloride in hydrochloric acid is added in quantities 2—2·5 times the stoicheiometrically calculated amount to the boiling solution of the stannous salt, and the mixture diluted and titrated at 50°, as described by Collenberg and Sandved (A., 1926, 140) with potassium bromate. The ordinary monometallic electrode system is used, and a little 0·25 molar solution of cobaltous chloride added as catalyst. An application of the method to antimony and tin alloys is described, whereby the metallic antimony which is precipitated is removed. The method was not found applicable in the presence of quinquevalent arsenic, and in the case of quinquevalent antimony the reaction between it and bivalent tin is so slow that a sharp break of the curve by potentiometric titration of a mixture of stannous and antimonous salts with potassium bromate cannot be obtained. The use of different electrode systems for the titration of the ferrous iron with potassium bromate is discussed. D. G. Hewer.

Molybdenum thiocyanate and the qualitative detection of molybdenum. F. C. Krauskopf and C. E. Swartz (J. Amer. Chem. Soc., 1926, 48, 3021—3027).—The solution is preferably carefully evaporated to dryness with nitric acid, the residue extracted with hot ammonia solution (to remove iron), filtered, and the filtrate and ammoniacal washings from the iron residue are neutralised with hydrochloric acid. Five c.c. of 10% potassium thiocyanate solution and a fragment of zinc are added, followed by concentrated hydrochloric acid, drop by drop, until hydrogen is evolved. A red colour (sometimes apparent only after extraction with ether) indicates the presence of molybdenum; the addition of a few c.c. of 10% phosphoric acid solution before the ether extraction destroys any colour thought to be due to iron. The sensitivity is 1 in 10^6, but this is decreased by phosphoric acid, mercuric chloride, and certain organic compounds. Attempts to isolate the red molybdenum thiocyanate were unsuccessful, but a determination of the molybdenum : sulphur ratio in ether solution indicated a formula $Mo(CNS)_3$. S. K. Tweedy.

Method of covering quartz fibres by cathodic pulverisation. J. H. C. Quelle (Arch. Néerl. Physiol., 1926, 11, 350—360).—A detailed description is given of a method for drawing quartz fibres, and subsequently covering them with gold or silver by cathodic pulverisation. The method of attaching such fibres, when required for galvanometers, for which the gold-covered fibres are more suitable than the silver, is also described, as well as the determination of the electrical conductivity of the fibres.

M. S. Burr.

Calibration of resistance thermometers at the oxygen b. p. and the carbon dioxide sublimation point. A. G. Loomis and J. E. Walters (J. Amer. Chem. Soc., 1926, 48, 3101—3107).—The use of another fixed point besides the b. p. of oxygen in the calibration of platinum resistance thermometers obviates a calculation of the resistance at the f. p. of mercury by means of the Callendar equation; a suitable fixed point is the sublimation point of carbon dioxide, which is $-78{\cdot}51\pm0{\cdot}01°$ on the thermodynamic scale. The most probable value of the oxygen point is $-183{\cdot}00\pm0{\cdot}02°$ on the same scale. Details of experimentation are given, including the preparation of pure oxygen from potassium permanganate and of pure carbon dioxide from sodium hydrogen carbonate.

S. K. Tweedy.

Improvement in Victor Meyer apparatus for measuring vapour densities. A. Tian (Bull. Soc. chim., 1926, [iv], 39, 1771—1772).—In order to facilitate sweeping out the apparatus with clean dry air after each experiment, a narrow tube is sealed on to the bottom of the large bulb of the apparatus and is bent twice at right angles, both bends being fairly close to the joint. The bend is filled with a little mercury, and on sucking at the open end of the apparatus, a stream of air is drawn through the mercury, which thus acts as a valve.

S. J. Gregg.

Hygrometer. A. Romberg and L. W. Blau (J. Opt. Soc. Amer., 1926, 13, 717—724).—A sensitive, continuous-indicating hygrometer, based on the difference in density between atmospheric air and air saturated with water vapour, is described.

C. J. Smithells.

Apparatus for m.-p. determinations. H. ter Meulen (Chem. Weekblad, 1927, 24, 36).—The thermometer with the capillary tube attached is supported in a long test-tube, suspended in a wider tube with a constriction near the lower end. A small burner is placed below the constriction, and a piece of gauze above it.

S. I. Levy.

Continuous extraction. M. Wagenaar (Chem. Weekblad, 1927, 24, 36—37).—Diagrams are given of apparatus employed for the extraction of aqueous solutions by means of light and heavy solvents. In the first, the light solvent condensed from the vapour rising through a central tube is carried to the bottom of an outer tube, in which the aqueous solution is contained, surrounding the inner tube through which the vapour ascends, and overflows from the top down the central tube into the distillation flask. In the second, the heavy solvent similarly condensed falls through the aqueous layer and escapes from the bottom into the central tube through a seal tube fused into the latter.

S. I. Levy.

Universal [gas] wash-bottle. W. Kochmann (Z. angew. Chem. [Chem. App.- u. Maschinenw.], 1927, 40, 33).—The tube through which the gas enters the flask terminates at its lower end in an upturned jet through which the gas is injected, together with quantities of wash liquid, into an ascending worm connected at its upper end with a descending worm, from the bottom of which the gas bubbles up through the liquid in the usual way. By this arrangement, the gas and liquid are brought into prolonged intimate contact, so that efficient absorption or washing of the gas is effected in one wash-bottle.

A. R. Powell.

Wash-bottle. W. B. Bollen (Ind. Eng. Chem., 1926, 18, 1290).—The wash-bottle is of the familiar pattern but the liquid is ejected by operating a "scent-bottle" bellows, the flow being terminated when required by opening the end of a third tube passing through the stopper.

R. Cuthill.

Weight burette. G. F. Smith (Ind. Eng. Chem., 1926, 18, 1216).—The instrument described has a narrow neck with a graduation mark, and the ground joints at the two extremities are so designed that they do not become wet with the contents of the burette.

R. Cuthill.

Apparatus for dehydrating volatile liquids. P. Loriette (Bull. Soc. chim., 1926, [iv], 39, 1767—1770).—The liquid is dropped into an evaporator consisting of a bulb and coil heated in a water-bath, and the vapour so formed passes successively through three dehydrating tubes connected in series and also heated in the bath. The vapour then passes through a condenser and the liquid is collected. Each dehydrating tube contains eleven perforated plates carrying lumps of calcium oxide, each plate being separated from the one below by small feet. As the first tube becomes vitiated it is removed and a fresh tube placed at the other end of the train.

S. J. Gregg.

Apparatus for the rapid determination of the conductivity of liquids. F. Goldschmidt (Z. angew. Chem. [Chem. App.- u. Maschinenw.], 1927, 40, 31).—The container for the liquid consists of a small cylindrical flask provided with two insulated metal rings at the upper end, which are engaged by conducting clamps fixed into an ebonite boss, from which emerge the leads connecting with the Wheatstone bridge. The metal rings are each connected by means of glass-covered platinum wires with parallel platinum electrodes securely fixed to the bottom of the flask and each coated with platinum sponge. The four arms of the Wheatstone bridge are made up with a fixed resistance of 700 ohms, a vernier variable resistance of 0—700 ohms, the multiplier for the variable resistance, and the liquid the resistance of which is to be measured. The measurements are carried out by the use of a telephone indicator and condenser across one diagonal of the bridge, energised by high-frequency alternating current from a small transformer placed across the other diagonal.

A. R. Powell.

Micro-sublimation in a vacuum. M. Wagenaar (Pharm. Weekblad, 1927, 64, 10—11).—A simple apparatus for sublimation of very small quantities in a vacuum is described. S. I. Levy.

"Ascarite" as a carbon dioxide absorbent. J. S. Buck (Ind. Eng. Chem., 1926, **18**, 1321).—A simple absorption tube for use with "ascarite" in carbon and hydrogen determinations is described (cf. Marsh, B., 1925, 615). R. Cuthill.

Chinese alchemy. J. R. Partington (Nature, 1927, **119**, 11).—It appears unlikely that Chinese alchemical texts are necessarily derived from Greek or Arabic sources; hence their dates should not be estimated on this assumption. A. A. Eldridge.

Mineralogical Chemistry.

Argon content of the atmosphere. E. Moles (Anal. Fís. Quím., 1926, **24**, 560—566).—The author has calculated the percentage of argon by weight in the air from the values for the litre-weight of crude atmospheric nitrogen and chemically prepared nitrogen, respectively, using the mixture rule. For the atmosphere at sea level, the percentage of argon is 0·909 or 0·946 if the maximum density of nitrogen is assumed in the calculation. G. W. Robinson.

Presence of helium in gases from petroleum wells. D. Butescu and V. Atanasiu (Bul. Soc. Româna Stiinte, 1926, **29**, 43—55).—The natural gases from some Rumanian petroleum wells were examined for helium by a spectroscopic method. Most specimens contained very small quantities of this gas, the richest samples containing two or three times as much as is present in air.

S. K. Tweedy.

Alkali metals in beryl from Ishikawa, Iwaki Province. J. Yoshimura (Bull. Chem. Soc. Japan, 1926, **1**, 239).—The beryl contained Cs_2O 0·085, Li_2O 0·015, K_2O 0·24, Na_2O 0·49%; rubidium was absent. S. J. Gregg.

Lepidolite from Nagatori, Chikuzen Province, and the lithium content of Japanese mica. S. Imori and J. Yoshimura (Bull. Chem. Soc. Japan, 1926, **1**, 237—239).—The sample contained SiO_2 56·79 (some present as quartz), Al_2O_3 21·71, Fe_2O_3 0·73, FeO 0·14, MnO 0·46, CaO 0·26, MgO 0·13, K_2O 6·23, Rb_2O 0·96, Na_2O 2·45, Li_2O 1·94, F 4·69, H_2O 4·67, less O for F 1·97, total 99·19%. The percentages of sodium, potassium, and lithium in a number of Japanese micas have been determined.

S. J. Gregg.

Potash-bearing horizon of the Malagash salt deposit, Nova Scotia. H. V. Ellsworth (Can. Dep. Mines Summ. Rep., 1926, 1924—C, 181—198).—The average potassium chloride content is more than 2%; the magnesium and calcium (other than sulphate) contents are small. The insoluble residues contain much quartz. Chemical Abstracts.

Spectrographic analysis of tufa from Fiuggi. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, **16**, 457—475; cf. A., 1924, ii, 417).—This tufa is found to contain small proportions of zirconium, strontium, chromium, lead, cobalt, nickel, scandium, yttrium, ytterbium, lanthanum, cerium, neodymium, and, probably, niobium and zinc. T. H. Pope.

Spectrographic analysis of certain eruptive products of Stromboli. A. Donati (Annali Chim. Appl., 1926, **16**, 475—487).—Two products of eruptive explosions of Stromboli and one sample of the percolated lava of the same eruptive period (July, 1916) are found by spectrographic analysis to contain silicon, titanium, aluminium, iron, chromium, manganese, vanadium (traces), calcium, strontium, barium, magnesium, potassium, scandium (traces), ytterbium, lead (minimal traces), and cobalt (traces); analysis by the wet way reveals the presence of traces of copper, nickel, arsenic, lithium, and hydrochloric acid, and also of sulphuric and phosphoric acids.

T. H. Pope.

Noteworthy Vesuvian sublimations. G. Carobbi (Atti R. Accad. Lincei, 1926, [vi], **4**, 382—384).—Microscopic and crystallographic investigation of material from the inner wall of a fumarole in a laval channel of a cupola formed on Vesuvius in April—May, 1924, reveals the presence of boric acid in the form of sassoline and of potassium fluoborate as avogadrite (cf. *ibid.*, 306—311). T. H. Pope.

New minerals of the mosandrite group from the Chibine Mountains. E. M. Bonstedt, K. A. Nenadkevitsch, and I. D. Starynkevitsch-Borneman (Bull. Acad. Sci. Leningrad, 1926, [vi], 1181—1198).—To two yellow, greenish-yellow, or brownish-yellow minerals of the mosandrite group, with a pale yellow streak, the names *rinkolite* and *lovtchorrite* are given. Their hardness is about 5 and they melt readily in the blowpipe flame and are easily dissolved by acids. Rinkolite, $d_4^{17·5}$ 3·40, has a vitreous cleavage surface with a fatty fracture, and lovtchorrite, *d* 3·32, a fatty lustre. The percentage compositions of the two are as follows:

	SiO_2.	TiO_2.	ZrO_2.	ThO_2.	CeO_2.	Ce_2O_3,$(DiLa)_2O_3$,	Y_2O_3.
Rinkolite	27·58	11·15	0·35	—	—	18·02	
Lovtchorrite ...	27·61	12·71	0·20	0·23	8·79	5·15	1·36

	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	SrO.	BaO.	MgO.
Rinkolite	1·47	0·99	trace	24·70	3·30	trace	trace
Lovtchorrite ...	0·13	—	0·53	27·26	3·56	—	0·80

	Na_2O.	K_2O.	H_2O.	F.	—O for F.	Total.
Rinkolite	6·73	0·16	1·75	5·99	2·47	99·72
Lovtchorrite ...	7·18	0·28	0·51	6·38	2·68	100·00

No crystallographic measurements were found possible. T. H. Pope.

Organic Chemistry.

Effects exerted by atoms and groups of atoms on the reactivity of molecules and on the strength of linkings within the molecules. M. Tiffeneau and Orékhoff (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 247—321).—A review.

Chemical Abstracts.

Field of applicability of classical stereochemistry and Weissenberg's geometrical stereochemistry. W. Hückel (Ber., 1926, **59**, [*B*], 2826—2838; cf. Weissenberg, A., 1926, 934; Reis, *ibid.*, 934).—There is no positive reason for the extension of Weissenberg's theory to the gaseous phase. The number of isomerides is adequately explained by the laws of classical stereochemistry, and the tetrahedral hypothesis in the form of the strain theory renders good indications of the relative stability of the isomerides, although further expansion is desirable. Weissenberg's theory predicts for the gaseous phase many more isomerides than have been isolated, which, if existent, must be very rapidly transformable; it may possibly be useful in explaining the existence of certain labile compounds such as the three *cis*-cinnamic acids. The differences in the conditions of existence of molecules in the crystalline and gaseous states render doubtful the choice of identical principles for the stereochemistry of both phases, and similar considerations explain why a stereochemistry, developed like the tetrahedral hypothesis for the gaseous phase, can in most cases give no adequate explanation for the behaviour of substances when crystalline. H. Wren.

Preparation of synthetic rubber hydrocarbon [dimethylbutadiene]. W. C. Calvert (India Rubber Rev., 1926, No. 9, 48—50, 52, 54).—It appears almost certain that acetone cannot be reduced to pinacol by ordinary reducing agents. A number of condensation methods were examined. The highest yields (52—55%) in the Holleman method were obtained by Adams' procedure (" Organic Syntheses," 1925, 5, 87), omitting mechanical agitation, or by doubling the amount of mercuric chloride. The order of mixing the reagents must not be reversed. A number of variations were tried without success. It is probable that a mercury compound with pinacol is formed intermediately. Of several methods which were tested for the dehydration of pinacol, the best yield of dimethylbutadiene (58%) was obtained by the hydrogen bromide method, pure pinacol reacting more slowly than impure. Dimethylbutadiene could not be obtained by the dry distillation of magnesium pinacolate. Chemical Abstracts.

Unsaponifiable matter from the oils of Elasmobranch fish. II. Hydrogenation of squalene in the presence of nickel. I. M. Heilbron, T. P. Hilditch, and E. D. Kamm (J.C.S., 1926, 3131—3136).—Complete hydrogenation of squalene using a nickel catalyst at 150° yields dodecahydrosqualene. From the product, 0·2% of an oxygenated neutral *compound*, m. p. 67—68°, was isolated. Hydrogenation of squalene is strongly selective; two of the unsaturated linkings appear to be different from the other four, not only in the rate of hydrogenation, but also in that ring closure does not occur after four double linkings have disappeared. B. W. Anderson.

Unsaponifiable matter from the oils of Elasmobranch fish. III. Tetra*cyclo*squalene and the production of a new naphthalene hydrocarbon. J. Harvey, I. M. Heilbron, and E. D. Kamm (J.C.S., 1926, 3136—3140; cf. A., 1926, 816).—Dehydrogenation of tetra*cyclo*squalene with sulphur at 200—270° gave chiefly a fraction, b. p. 100—160°/13 mm., yielding a *picrate*, $C_{19}H_{17}O_7N_3$, m. p. 139—140°, from which a *hydrocarbon*, $C_{13}H_{14}$, m. p. 33·5°, d_{20}^{20} 1·0103, n_D^{20} 1·6110, $[R_L]_D$ 58·5°, of naphthalene-like odour, was obtained. The pyrogenetic decomposition of tetra*cyclo*squalene gives rise to a mixture of lower terpenes; the sesquiterpene fraction on treatment with sulphur also yielded the above hydrocarbon. The action on squalene of formic acid which had been already used in the formation of tetra*cyclo*squalene gave rise to an *isomeric tetra*cyclo*squalene*, b. p. 228—230°/3 mm., d_{20}^{20} 0·9237, n_D^{20} 1·5098, $[R_L]_D$ 132·7, iodine value 111·3. B. W. Anderson.

Chlorobromoiodomethane. M. Garino and E. Teofili (Gazzetta, 1926, 56, 847—852).—Chlorobromoiodopyruvic acid was obtained, but not isolated, by passing gaseous hydrogen iodide into an aqueous solution containing 50% of chlorobromopyruvic acid (A., 1923, i, 24) and 0·5% of iodic acid. Treatment of its sodium salt with excess of alkali results in the formation of *chlorobromoiodomethane*, m. p. about 5°, *d* 2·932—3·120, which begins, in an atmosphere of carbon dioxide, to emit gas at about 150°, b. p. 180—190° (complete alteration). When pure, it is pale yellow, but in the air it turns violet at once, owing to separation of iodine, carbonyl chlorobromide being also formed. The only solvent in which it remains unchanged is vaseline oil. T. H. Pope.

Action of cyanogen chloride on certain secondary organo-magnesium halides. V. Grignard and K. Ono (Bull. Soc. chim., 1926, [iv], 39, 1589—1594).—Cyanogen chloride reacts with primary organo-magnesium halides in two stages to give the corresponding nitrile and ketone, whereas with secondary organomagnesium halides the main product is the corresponding chloro-derivative, accompanied by a small quantity of nitrile (cf. A., 1911, i, 292; 1920, i, 235). In the aliphatic series, the yields of chloro-derivative and nitrile are about 70% and 8—10%, respectively; in the aromatic series, the yield of chloro-derivative is barely 50%, partly owing to formation of the hydrocarbon obtained by duplication of the organic radical. The following are described: *γ-bromopentane*, b. p. 116·5—117·5°/742 mm., d_4^{19} 1·1993, n_D^{19} 1·4403, and *γ-chloropentane*, b. p. 104—105°/753 mm., $d_4^{14·5}$ 0·8967, $n_D^{14·5}$ 1·4163; *ε-bromononane*, b. p. 98—99°/12 mm., d_4^{14} 1·0845, n_D^{14} 1·4544, *α-butylhexonitrile*, b. p. 99—101°/11 mm., $d_4^{16·5}$ 0·8110, $n_D^{16·5}$ 1·4034, and *ε-chlorononane*, b. p. 85—87°/14 mm., d_4^{15} 0·8639, n_D^{15} 1·4314; α-chloroethylbenzene, d_4^{13} 1·0598, n_D^{13} 1·5337; *α-bromopropylbenzene*, b. p. 112—114°/15 mm., d_4^{19} 1·3098, n_D^{19} 1·5517, and α-chloropropylbenzene, $d_4^{19·5}$ 1·0335, $n_D^{19·5}$ 1·5252; chlorodiphenylmethane, $d_4^{19·5}$ 1·1398, $n_D^{19·5}$ 1·5959. M. Clark.

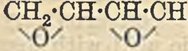
Preparation of αβγ-tribromopropane and propadiene. M. W. Tapley and P. M. Giesy (J. Amer. Pharm. Assoc., 1926, 15, 173—174).—αβ-Dibromopropane (200 g.) and bromine (300 g.) are heated with iron (card teeth) in a reflux apparatus until hydrogen bromide is no longer evolved (1—2 hrs.); the yield of tribromopropane, b. p. 219—221°/760 mm., is 78% of the theoretical. The product is converted by the Gustavson–Demjanoff method into dibromopropylene, from which propadiene is obtained in 78% yield by dropping into a mixture of zinc dust and ethyl alcohol and heating in a reflux apparatus. Chemical Abstracts.

Isomerisation of alkylvinylcarbinols to ethyl alkyl ketones. R. Delaby and J. M. Dumoulin

(Bull. Soc. chim., 1926, [iv], 39, 1578—1584).—See A., 1925, i, 632.

Isomerisation of alkylvinylcarbinols to β-alkylallyl alcohols. R. Delaby (Bull. Soc. chim., 1926, [iv], 39, 1575—1578).—See A., 1926, 45.

Catalytic action of reduced copper on pinacols. S. Yamaguchi (Mem. Coll. Sci. Kyōtō, 1926, 10, 85—87).—See A., 1926, 727.

Cycle of reactions of erythrene derivatives. C. Prévost (Compt. rend., 1926, 183, 1292—1295).—When heated with 75% formic acid, inactive erythritol yields β-hydroxy-Δ^{γ}-butenyl formate, which gives β-hydroxy-Δ^{β}-butenyl alcohol when treated with barium hydroxide. The alcohol and phosphorus tribromide in the presence of cold pyridine yield solely *trans*-αδ-dibromo-Δ^{β}-butene, which, when heated with sodium acetate and acetic acid, gives trans-*αδ-diacetyl-Δ^{β}-butylene glycol*, b. p. 118°/13 mm., m. p. 16°, d_{D}^{20} 1·08015, n_{D}^{20} 1·4772, hydrolysed to trans-*Δ^{β}-butylene glycol*, b. p. 131·5°/12 mm., m. p. 25°, d^{20} 1·0687, n_{D}^{20} 1·4772. When treated with bromine in ethereal solution, the glycol yields the corresponding *dibromohydrin*, m. p. 132·5—133° (corr.), which, with potassium hydroxide, gives butylene dioxide,  $\underset{\diagdown O \diagup}{CH_2\cdot CH}\cdot\underset{\diagdown O \diagup}{CH\cdot CH_2}$, which in turn gives inactive erythritol. L. F. Hewitt.

Partial esterification of polyhydric alcohols. IV. Oxidation of allyl esters to α-monoglycerides. V. α-Structure of alleged "β"-monoglycerides. A. Fairbourne and G. E. Foster (J.C.S., 1926, 3146—3148, 3148—3151).—IV. Oxidation of allyl *p*-nitrobenzoate (*dibromo*-derivative, m. p. 57—58°), and *allyl* 3 : 5-*dinitrobenzoate*, m. p. 50° (*dibromo*-derivative, m. p. 85°), to the corresponding monoglycerides was effected by treating their solutions in acetone with 1% aqueous potassium permanganate. Glycerol α-mono-2 : 4-dinitrophenyl ether was similarly obtained from allyl 2 : 4-dinitrophenyl ether. *Allyl picrate*, m. p. 90° (*dibromo*-derivative, m. p. 106—107°), resisted oxidation to the corresponding glyceride.

V. The two methods proposed by Grün (A., 1910, i, 356) for the synthesis of β-monoglycerides have been found to give α- and not β-products in both cases. In the first case, a specimen of "β"-monochlorohydrin was converted into its *p*-nitrobenzoate, and the product shown to consist chiefly of *glycerol α-monochlorohydrin di-*p*-nitrobenzoate*, m. p. 107—108°, with *glycerol β-monochlorohydrin di-*p*-nitrobenzoate*, m. p. 121—122°, as an impurity. In the second case, glyceryl "β"-monolaurate was shown to have the α-structure. *Glycerol αγ-dibromohydrin* p-*nitrobenzoate*, m. p. 77—78°, being shown not identical with the αβ-dibromohydrin, the possibility of β-substitution in the glycerol molecule was confirmed. *Glycerol αγ-dichlorohydrin* 3 : 5-*dinitrobenzoate*, m. p. 129°, was also prepared. B. W. Anderson.

***cyclo*Hexylglycerol.** R. Delaby and M. Janot (Bull. Soc. chim., 1926, [iv], 39, 1618—1621).—See A., 1926, 165.

Action of water and of alcohols on ethylene oxides in presence of a catalyst. E. Fourneau and I. Ribas (Bull. Soc. chim., 1926, [iv], 39, 1584—1589).—The action of catalysts in promoting the hydration of ethylene oxides is reviewed. Glycerol epichlorohydrin reacts vigorously and almost quantitatively with alcohols in presence of a trace of concentrated sulphuric acid, giving compounds of the type $RO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$. The action is ascribed to the agency of an intermediate product $SO_2[O\cdot CH_2\cdot CH(OH)\cdot CH_2Cl]_2$. This substance, formed when sulphuric acid reacts with an excess of epichlorohydrin, is a colourless oil. It can be substituted for the acid as catalyst in the alcohol–epichlorohydrin reaction. The action is formulated thus: $SO_2[O\cdot CH_2\cdot CH(OH)\cdot CH_2Cl]_2+R\cdot OH\longrightarrow SO_2(OH)[O\cdot CH_2\cdot CH(OH)\cdot CH_2Cl]+RO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$. The acid sulphate then reacts with more epichlorohydrin to regenerate the neutral compound. The latter is readily hydrolysed by water at the ordinary temperature, giving the acid sulphate. Complete hydrolysis takes place at 100°. The following are described: *α-chloro-γ-methoxypropan-β-ol*, b. p. 172°/760 mm.; 95°/20 mm.; *α-chloro-γ-*n*-butyloxypropan-β-ol*, b. p. 115°/20 mm.; *α-chloro-γ-*iso*amyloxypropan-β-ol*, b. p. 118—120°/20 mm. M. Clark.

Dioxan as solvent, particularly for determinations of mol. wt. L. Anschütz and W. Broeker (Ber., 1926, 59, [*B*], 2844—2847).—Dioxan [diethylene dioxide], b. p. 101·2—101·4°/760 mm. m. p. 11°, d_4^{20} 1·0329, is a useful solvent for sparingly soluble substances and particularly valuable in the determination of their mol. wts.; the cryoscopic and ebullioscopic constants are 4950 and 2200, respectively. H. Wren.

Mechanism of chemical transformation. T. M. Lowry (Deuxième Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 135—178).—A discussion.

Chemical Abstracts.

Mechanism of Kolbe's electrosynthesis. D. A. Fairweather and O. J. Walker.—See this vol., 119.

Anhydrides of aliphatic acids. D. Holde (Chem.-Ztg., 1926, 50, 994—996).—A review of the present knowledge of anhydrides and a discussion of their properties, methods of preparation, liability to decomposition, and use for edible purposes.

E. H. Sharples.

Reduction with acetic anhydride. J. B. Menke (Rec. trav. chim., 1926, 45, 908—913).—Hydrated cupric sulphate and chloride when warmed for a short time with acetic anhydride at 60° lose their water of crystallisation and yield the anhydrous salts, whilst refluxing with this reagent for 8 hrs., with the exclusion of moisture, reduces them to the corresponding cuprous salts. A similar reduction occurs with the corresponding mercuric salts, but in this case a complex mercurous *compound* is formed (cf. Sand and Singer, A., 1904, i, 25) which, in the case of mercuric chloride, is obtained in a crystalline form, m. p. about 136° (decomp.), on evaporation of the solution at the ordinary temperature, but the compound obtained from the sulphate is evidently unstable, and the mercurous sulphate resulting from its decomposition yields mercury and mercuric sulphate. Hence, when mercurous sulphate is heated with acetic anhydride, mercury is produced, whilst the solution is coloured with the complex salt. When mercurous chloride is heated with acetic anhydride, no reduction to mercury occurs. J. W. Baker.

Monoacetin. H. A. Schuette and P. P. T. Sah (J. Amer. Chem. Soc., 1926, **48**, 3161—3163).—Monoacetin, b. p. 189—191°/60 mm., d_4^{25} 1·19846, n^{25} 1·4481, is obtained in practically quantitative yield by heating together molar equivalents of glycerol and acetic acid in presence of phosphoric acid or oxide at 170° for 2 hrs., the phosphoric acid being removed by the addition of sodium acetate and filtration before fractionation of the mixture. Diacetin and triacetin are converted into monoacetin when heated with excess of glycerol in presence of phosphoric acid. When glycerol and acetic acid are heated with sulphuric acid, the product is chiefly diacetin, whilst a mixture of about equal amounts of monoacetin and diacetin is obtained when zinc chloride is used as the catalyst. F. G. Willson.

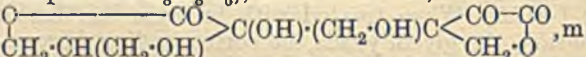
Optical resolution of chlorobromoacetic acid. H. J. Backer and H. W. Mook (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 998—999).—The optically active components of chlorobromoacetic acid have been obtained by the method of "cold crystallisation." With brucine, a lævorotatory acid was obtained, whilst quinine gave a dextrorotatory compound. The latter alkaloid gave the best results. The salts show a rotation of about the same magnitude as that of the acid, but of opposite sign. The highest values of $[M]_D$ so far observed are +8° and −8° for the free acid and ammonium salt, respectively. The tendency to racemisation was found to be much less than anticipated.
J. S. Carter.

Optical activity and the polarity of substituent groups. V. *sec.*-β-Octyl esters of some substituted acetic acids and their behaviour towards solvents. H. G. Rule and R. K. S. Mitchell (J.C.S., 1926, 3202—3209).—β-*Octyl methoxyacetate*, b. p. 120°/15 mm., β-*octyl chloroacetate*, b. p. 119—120°/15 mm.; β-*octyl bromoacetate*, b. p. 121°/15 mm., and β-*octyl iodoacetate*, b. p. 146—147°/17 mm., were prepared and their $[M]_D^t$ (t=20—90°) values tabulated. Values for $[M]_D^{20}$ of the esters in 5% solution in a number of solvents were also tabulated. The relative effect of substituents on the rotation of the acetic ester is given by H<Me<OMe<Et<Cl<Br<I, the order of polarity being followed except for the reversal of the halogens. The relative order for the esters remained unchanged in the various solvents and the effect of various substituents introduced into the solvent benzene molecule in lowering the $[M]_D$ values was in the order Me<H<OEt<Cl<Br<I.
B. W. Anderson.

Crotonic acid series. I. Nitrogen derivatives of crotonic acid. M. A. Phillips (J.C.S., 1926, 2979—2983).—Dry carbamide reacts with α-bromobutyryl bromide to form α-*bromobutyrylcarbamide*, m. p. 156°, the action of aqueous sodium hydroxide on which yields the labile *cis*-form of *crotonylcarbamide*, m. p. 207°. The trans-*isomeride*, m. p. 234°, is obtained by the action of carbamide on crotonyl chloride. B. W. Anderson.

Configuration of oleic and elaidic acids. J. Böeseken and A. H. Belinfante (Rec. trav. chim., 1926, **45**, 914—918).—A preliminary note outlining two methods by which it is hoped to determine the configurations of oleic and elaidic acids. In the first method, the ethyl esters are converted into the octadecenols and thence into octadecenes of similar configurations to the original acids. That obtained from elaidic acid has m. p. +2°, and that from oleic acid m. p. about −15°. The second method is based on a comparison of the glycols obtained by oxidation with alkaline permanganate or with peracids and subsequent hydrolysis of the oxido-acid.
J. W. Baker.

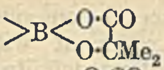
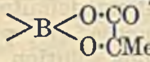
Condensation of pyruvic acid with paraformaldehyde in the presence of sulphuric acid. W. W. Feofilaktow (Ber., 1926, **59**, [*B*], 2765—2777).—Paraformaldehyde is converted by pyruvic acid in the presence of a little sulphuric acid into an acid, $C_9H_8O_6$, m. p. 234° (Kaltwasser assigns the composition $C_8H_8O_6$), and a *dilactone*,



$\begin{array}{l}\text{O}\text{———}\text{CO}\\ \text{CH}_2\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\end{array}\!\!>\text{C(OH)}\cdot(\text{CH}_2\cdot\text{OH})\text{C}<\!\!\begin{array}{l}\text{CO}-\text{CO}\\ \text{CH}_2\cdot\text{O}\end{array}$

,m.p. 140—144° when rapidly heated. The *sodium*, *potassium*, *lead*, and *silver* salts of the corresponding acid are described. The lactone is converted by acetic anhydride and a little sulphuric acid with loss of water into the unsaturated *diacetate*, $C_{14}H_{14}O_9$, m. p. 193°, and by chlorine in the presence of chloroform into the *chloride*, $C_{10}H_{11}O_7Cl$, m. p. 226—227°. With sodium ethoxide, it gives the *compound*, $C_{10}H_{10}O_8N_2$, with phenylhydrazine the *substance*, $C_{22}H_{24}O_6N_4$, m. p. 116—118° (decomp.), and with hydroxylamine (with simultaneous loss of water) the *oxime*, $C_{10}H_9O_6N$, m. p. 198—200° (decomp.). Oxidation of the lactone with hydrogen peroxide in alkaline solution affords a *lactonic acid*, $C_9H_{12}O_7$, m. p. 112—113°, and, apparently, a dihydroxybutyric acid of which the *sodium* and *silver* salts are described. The lactone is reduced by hydrogen in presence of spongy platinum to two *compounds*, $C_{20}H_{20}O_{12}$, needles, m. p. 219—220°, and prisms, m. p. 234—235°, whereas with tin and hydrochloric acid the compound, m. p. 219—220°, is alone produced.
H. Wren.

Mechanism of Claisen's reaction. F. Swarts (Bull. Soc. chim. Belg., 1926, **35**, 411—416).—Ethyl trifluoroacetate condenses with ethyl acetate in presence of sodium ethoxide; since the mechanism suggested by Geuther and Lapworth for the Claisen reaction could not apply in this case, Claisen's original hypothesis as to the course of the condensation is supported. The trifluoroacetate, in fact, forms an additive product with sodium ethoxide, which is isolated by distilling off the ether and unchanged ester and is stable at 130° under reduced pressure. This intermediate compound forms a colloidal solution in ether, the apparent mol. wt. as determined by b.-p. depression being ±930°; it reacts with ethyl acetate to yield ethyl trifluoroacetoacetate. S. I. Levy.

Optically active borohydroxy*iso*butyric acid. J. Böeseken, H. D. Muller, and R. T. Japhongjouw (Rec. trav. chim., 1926, **45**, 919—922).—The resolution of asymmetric boron compounds derived from α-hydroxy*iso*butyric acid,  $>\mathrm{B}<\begin{array}{l}\mathrm{O\cdot CO}\\ \mathrm{O\cdot CMe_2}\end{array}$, and α-hydroxy-α-methylbutyric acid,  $>\mathrm{B}<\begin{array}{l}\mathrm{O\cdot CO}\\ \mathrm{O\cdot CMeEt}\end{array}$, has been effected by means of their brucine salts. A solution of α-hydroxy*iso*butyric acid (2 mols.), boric acid (1 mol.), and brucine (1 mol.) in the minimal quantity of alcohol was heated at 50° in a vacuum desiccator, the vitreous mass dissolved in ether, and the ether evaporated, until the residue after drying over phosphoric oxide was soluble in chloroform. Fractional extraction of this solution with light petroleum yields the l-*brucine* l-*di*(*α-hydroxy*iso-*butyryl*)*borate*, $[\alpha]_D^{18}$ −55·8°, whilst the chloroform residue contains the ld-*salt*, $[\alpha]_D^{18}$ −25·6°, both of which slowly change to the constant value, $[\alpha]_D^{15}$ −42°, of the racemate. By substitution of the appropriate base instead of brucine in the above preparation, the crystalline *aniline*, o-*toluidine*, and *dimethylaniline* salts are obtained. Similar resolution of *brucine di*-(*α-hydroxy-α-methylbutyryl*)*borate* yields the *ll*-isomeride, $[\alpha]_D^{18}$ −44·4°, and the *ld*-form, $[\alpha]_D^{18}$ −16·1°, both changing to the value of the racemate, $[\alpha]_D^{13}$ −28°. J. W. Baker.

***n*-Valerolactone.** H. A. Schuette and P. P. T. Sah (J. Amer. Chem. Soc., 1926, **48**, 3163—3165).—*n*-Valerolactone, b. p. 206—207°, b. p. 125°/60 mm.; b. p. 78°/4 mm., n_D^{25} 1·4301, d^{25} 1·04608, is obtained in 60% yield by reducing sodium lævulate, dissolved in 95% alcohol, with metallic sodium (cf. Losanitsch, A., 1914, i, 657). F. G. Willson.

Microchemical differentiation of maleic and fumaric acids. M. Wagenaar (Pharm. Weekblad, 1927, **64**, 6—10).—Fumaric acid can be identified, with the aid of the microscope, by sublimation or precipitation, and from the ease of formation of its lead, mercury, silver, cadmium, and sodium or ammonium uranyl salts. The appearance of the crystals in each case is described. S. I. Levy.

α-Sulpho-*n*-valeric acid. H. J. Backer and M. Toxopeus (Rec. trav. chim., 1926, **45**, 890—907).—The preparation and resolution of α-sulpho-*n*-valeric acid and its derivatives have been effected, and the dispersions of its salts determined. dl-α-*Sulpho*-n-*valeric acid*, $+1{\cdot}5H_2O$, m. p. 65·5° (*barium*, *cobalt* $+2H_2O$, *nickel* $+2H_2O$, *copper* $+1H_2O$, *copper hydrogen* $+5H_2O$, *silver*, *silver hydrogen*, *aniline*, m. p. 146°, *strychnine* $+4H_2O$, *strychnine hydrogen* $+4H_2O$, *brucine* $+6H_2O$, *brucine hydrogen* $+2H_2O$, salts described), may be obtained by the sulphonation of *n*-valeric acid; it is also obtained in 70% yield by the action of sulphur trioxide on propylmalonic acid, and decomposition of the mixed malonic sulphuric anhydride, which is the initial product of the reaction. d-α-*Sulpho*-n-*valeric acid*, $[M]_{625}$ +1·7° (*aniline*, and *aniline hydrogen* salts), is obtained by repeated crystallisation of the brucine hydrogen salt and is isolated as its *barium* salt $+3H_2O$, $[M]$ +37°, whilst conversion of the mother-liquors into the normal brucine salt and fractional crystallisation yield l-α-*sulpho*-n-*valeric acid*, $[M]_{625}$ −1·7° (*barium hydrogen*, *cobalt* $+2H_2O$, *nickel* $+2H_2O$, *copper* $+1H_2O$, *copper hydrogen* $+5H_2O$ salts), isolated as its *barium* salt $+3H_2O$, $[M]_{625}$ −37°, which is also obtained by crystallisation of the strychnine hydrogen salt of the *dl*-acid. The metal hydrogen salts of the active acids have approximately the same rotation as the parent acids, and show very little dispersion, but the normal salts show a much greater rotation and dispersion in aqueous solutions, but no dispersion in alcoholic solution. On heating aniline sulphovalerate with excess of aniline for 5 hrs., *aniline valeranilide-α-sulphonate*, m. p. 257° (decomp.) (*barium* $+2H_2O$, *cobalt* $+3H_2O$, *nickel* $+3H_2O$, and *copper* salts), is obtained, which on resolution by means of its strychnine salt yields d-*valeranilide-α-sulphonic acid*, $[M]_{625}$ (in water) +2·9°, isolated as its *barium* salt, $+3H_2O$ (*cobalt* $+3H_2O$, *nickel* $+3H_2O$, and *copper* salts). *d*-Sulphovaleric acid heated with excess of aniline yields aniline *l*-valeranilide-α-sulphonate. The metal salts of *d*-valeranilide-α-sulphonic acid in aqueous solution have practically the same rotation as the free acid, but in alcoholic solution the value in each case is increased sixfold, and the cobalt and nickel salts show abnormal dispersion curves in this solvent, due, probably, to the co-ordination of the metal with the nitrogen. The action of *o*-phenylenediamine on α-sulphovaleric acid yields β-benziminazolebutane-α-sulphonic acid (decomp. without fusion) in 70% yield (*barium* $+4H_2O$, *cobalt* $+5H_2O$, *nickel* $+5H_2O$ salts), which is resolved by slow crystallisation in the cold of a mixture of the barium salt and strychnine acetate, which yields the d-*acid* (*barium* salt $+4H_2O$, $\frac{1}{2}[M]_{644}$ 14·8°, *cobalt* salt $+5H_2O$). Treatment of *d*-sulphovaleric acid with *o*-phenylenediamine yields the *l*-benziminazolebutanesulphonic acid, isolated as its *barium* salt. J. W. Baker.

Carbolthionic acids and esters. II. Y. Sakurada (Mem. Coll. Sci. Kyōtō, 1926, **10**, 67—77; cf. A., 1926, 950).—The following thionic esters were prepared, using Matsui's method (A., 1912, i, 261): Thionacetates; *methyl*, b. p. 88—91°/atm., d_4^{23} 0·9002, n_D^{23} 1·4212; *propyl*, b. p. 125—130°/atm., d_4^{23} 0·8952, n_D^{28} 1·4283, η^{23} 0·7823; iso*propyl*, b. p. 119—122°/atm., d_4^{22} 0·8901, n_D^{22} 1·4501, η^{22} 0·7052; *butyl*, b. p. 146—149°/atm., d_4^{29} 0·8883, n^{28} 1·4196, η^{29} 0·8492; iso*butyl*, b. p. 135—140°/atm., d_4^{28} 0·8875, n_D^{30} 1·4316, η^{30} 0·8903; *benzyl*, b. p. 115—120°/27—29 mm., d_4^{25} 1·0296, n_D^{20} 1·5492, η^{25} 2·1711; m-*tolyl*, b. p. 110—112°/25—26 mm.; p-*tolyl*, b. p. 109—110°/25—26 mm.; β-*naphthyl*. Thionpropionates; *propyl*, b. p. 139—144°/atm., d_4^{28} 0·8835, n_D^{28} 1·4396, η^{28} 0·8256; iso*propyl*, b. p. 137—140°/atm., d_4^{22} 0·8714, n_D^{25} 1·4372, η^{22} 0·7318; *butyl*, b. p. 164—167°/atm., d_4^{23} 0·8618, n_D^{28} 1·4303, η^{23} 0·8799; iso*butyl*, b. p. 153—157°/atm., d_4^{25} 0·8678, n_D^{26} 1·4286, η^{25} 0·9001; *benzyl*, b. p. 132—136°/28—30 mm., d_4^{26} 1·0009, n_D^{26} 1·5178, η^{26} 2·0846; *phenyl*. Thionbenzoates; *methyl*, b. p. 112—115°/26 mm., d_4^{28} 1·0710, n_D^{29} 1·5606, η^{28} 1·6866; *propyl*, b. p. 127—132°/29 mm., d_4^{23} 1·0133, n_D^{23} 1·5289, η^{28} 2·4550; iso*propyl*, 117—122°/27 mm., d_4^{27} 1·0060, n_D^{27} 1·5241, η^{27} 2·1376; *butyl*, b. p. 137—142°/23 mm., d_4^{28} 0·9732, n_D^{28} 1·5293, η^{28} 2·6357; iso*butyl*, b. p. 133—137°/27 mm., d_4^{28} 0·9694, n_D^{27} 1·5049, η^{28} 2·5415; iso*amyl*, b. p. 170—175°/54 mm., d_4^{23} 0·9748, n_D^{25} 1·4974, η^{23} 3·1700; *phenyl*, b. p. 155—160°/40 mm.; *benzyl*, b. p. 165—170°/38—40 mm.; β-*naphthyl*. Phenyl-thionacetates; *methyl*, b. p. 145—149°/82—84 mm., d_4^{28} 1·0551, n_D^{30} 1·5612, η^{28} 1·9296; *propyl*, b. p. 130—133°/25 mm., d_4^{27} 1·0139, n_D^{29} 1·5104, η^{27} 2·7187; iso*propyl*, b. p. 140—145°/50 mm., d_4^{22} 1·0078, n_D^{25} 1·5026, η^{22} 2·4672; *butyl*, b. p. 155—160°/36 mm., d_4^{23} 0·9930, n_D^{23} 1·5138, η^{23} 2·9127; iso*butyl*, b. p. 138—143°/25 mm., d_4^{23} 1·0010, n_D^{23} 1·5065, η^{23} 2·7713; iso*amyl*, b. p. 168—169°/50 mm., d_4^{21} 0·9801, n_D^{23} 1·4902, η^{23} 3·1369; *phenyl*, b. p. 202—206°/65 mm.; *benzyl*, b. p. 180—185°/26 mm., d_4^{28} 1·0866, η^{28} 5·2005. Thion-*p*-toluates; *methyl*, b. p. 170—173°/150 mm., d_4^{26} 1·0478, η^{26} 2·5396; *propyl*, b. p. 130—135°/23 mm., d_4^{26} 0·9858, n_D^{23} 1·5289, η^{20} 2·1789; iso*propyl*, b. p. 138—142°/48—50 mm., d_4^{22} 0·9880, η^{22} 1·9882; *butyl*, b. p. 150—152°/23 mm., d_4^{22} 0·9905, n_D^{23} 1·5315, η^{22} 2·7505; iso*butyl*, b. p. 144—148°/38—40 mm., d_4^{25} 0·9757, n_D^{23} 1·5215, η^{25} 2·4254; iso*amyl*, b. p. 155—158°/32 mm., d_4^{23} 0·9856, n_D^{23} 1·5252, η^{22} 2·2020; *benzyl*, b. p. 185—190°/21 mm., d_4^{22} 1·0648, η^{23} 3·8893. Thionoxalates; *dimethyl*, b. p. 50—53°/21 mm.; *diethyl*, b. p. 80—82°/32 mm., d_4^{21} 1·0565, η^{21} 1·1707; *di*iso*propyl*, b. p. 91—93°/43 mm. The ethyl esters of thionacetic, thionpropionic, thionbenzoic, and thion-*p*-toluic acids react with aniline to form the corresponding thianilides in ethereal solution, and phenylimino-esters in alcoholic solution. Thionic esters, hydrolysed with alcoholic potassium hydroxide, yield the unstable thionic acids; *thionacetic*, *thionpropionic*, *thionphenylacetic*, *thion*-p-*toluic*, *thion*-β-*naphthoic*, and *thionoxalic acids* were prepared. B. W. Anderson.

Carbolthionic acids and esters. III. Carbithionic acids and esters. Y. Sakurada (Mem. Coll. Sci. Kyōtō, 1926, **10**, 79—83; cf. Houben, A., 1912, i, 5).—By passing dry hydrogen sulphide into an ethereal solution of the corresponding thio-imino-esters the following carbithionic esters were prepared: ethyl dithioacetate, b. p. 128—132°/atm., d_4^{28} 0·9807, n_D^{29} 1·5303; ethyl dithiopropionate, b. p. 150—155°/atm., d_4^{27} 0·9711, n_D^{27} 1·5259, η^{27} 2·1535; *ethyl dithiobenzoate*, b. p. 122—125°/70 mm.; *ethyl dithiophenylacetate*, b. p. 140—144°/45 mm., d_4^{29} 1·0462, η^{29} 2·9831; *ethyl dithio*-p-*toluate*, b. p. 160—165°/85 mm., d_4^{27} 1·0085, η^{27} 2·3215; *ethyl dithio*-β-*naphthoate*, b. p. 200—205°/45 mm.; *diethyl tetrathionoxalate*, b. p. 90—93°/43 mm. By hydrolysis of these esters with alcoholic potassium hydroxide, dithioacetic, *dithiopropionic*, dithiobenzoic, dithiophenylacetic, *dithio*-p-*toluic*, and *tetrathionoxalic acids* were isolated.

B. W. Anderson.

Constitution of carminic acid. I. Miyagawa (Mem. Coll. Eng. Kyushu Imp. Univ., 1926, **4**, 99—113).—On treatment with ozone in aqueous solution, carminic acid affords an optically active product which on oxidation with barium permanganate yields an optically active *acid*, $C_6H_{12}O_6$, $[\alpha]_D^{23}$ +12·07° (*barium* salt, $[\alpha]_D^{23}$ +4·73°; *potassium* salt, $[\alpha]_D^{22}$ +5·96°). Reduction of this acid with sodium amalgam affords a *sugar*, $C_6H_{12}O_5$, $[\alpha]_D^{25}$ +8·13°, which is not identical with any of the known methylpentoses. The $C_6H_{11}O_5$– side-chain in carmini cacid (cf. Dimroth and Kämmerer, A., 1920, i, 442) accordingly possesses the probable constitution Me·[CH·OH]$_4$·CO–. Octa-acetylcarminic acid and *tetra-acetylcarminic acid*, decomp. 155—170° (obtained by partial hydrolysis of the octa-acetyl compound with *N*-sodium hydroxide), on treatment with ozone in chloroform solution, afford no definite products. Dextrose and penta-acetylglucose are practically unattacked by ozone in aqueous solution. R. Brightman.

Faught test for acetone. H. T. Schaeffer (Amer. J. Pharm., 1926, **98**, 643—645).—The Faught test for acetone (F. A. Faught, " Essentials of Laboratory Diagnosis ") is the most efficient known, dilutions of 1 : 100,000 giving positive results. Further, the test may be used in presence of dextrose and albumin. The costliness of the reagent, however (ethylenediamine hydrate), makes Legal's test the more generally useful. B. W. Anderson.

Mesityl oxide and certain halogen derivatives. J. Doeuvre (Bull. Soc. chim., 1926, [iv], **39**, 1594—1600).—The method of quantitative ozonisation shows that at least 95% of mesityl oxide exists in the form CMe_2:CH·COMe. The system of conjugated double linkings does not appear to affect the value of the parachor (Sugden, A., 1924, ii, 662), since $n_D^{22}=1{\cdot}4425$, $d_4^{22}=0{\cdot}860$, $\gamma^{22}=27{\cdot}7$ dyn./cm., $P=261{\cdot}7$ (calc. 266·2). The products obtained by bubbling a mixture of chlorine and dry air through mesityl oxide in well-cooled carbon tetrachloride include the monochloro-derivative, CMe_2:CCl·COMe, d_4^{17} 1·061, n_D^{17} 1·4703 [*semicarbazone*, m. p. 195° (corr.)], the dichloro-derivative, CMe_2Cl·CHCl·COMe, d_4^{17} 1·170, n_D^{17} 1·4632, and probably a *trichloro*-derivative, CMe_2Cl·CCl_2·COMe, b. p. 104—105°, d_4^{20} 1·313, n_D^{20} 1·4873. The monobromo-derivative, $d_4^{12{\cdot}5}$ 1·376, $n_D^{12{\cdot}5}$ 1·4982 [*semicarbazone*, m. p. 186—187° (corr.)], undergoes slow polymerisation when preserved. M. Clark.

Syntheses by means of inorganic magnesyl derivatives. Q. Mingoia (Gazzetta, 1926, **56**, 839—843).—Just as with aldehydes, magnesium bromohydrosulphide (A., 1926, 388) reacts with ketones, giving additive products, SH·CRR′·OMgBr, which are decomposed by water, giving thioketones, ⟶ SH:CRR′·OH ⟶ CS:RR′. With carbonyl chloride, the reaction gives rise to carbon oxysulphide, and with ethyl oxalate to dithioloxalic acid, $(COSH)_2$ (cf. Auger and Billy, *ibid.*, 1903, i, 310), the *lead* and *ammonium* salts of which were prepared.

The action of magnesium bromohydrosulphide on acetone yields trimeric thioacetone, and that on acetophenone, thioacetophenone. T. H. Pope.

Dioximes. XXXII. G. Ponzio (Gazzetta, 1926, **56**, 701—705).—Methylhydroxyglyoxime can form in acetone complexes of one or two molecules with one molecule of nickelous chloride or sulphate, or cuprous chloride. These differ from the complexes previously described (A., 1925, i, 1041) in that the metal is contained in a complex cation. *Nickel dimethylhydroxyglyoxime chloride*, $[Ni(C_3H_6O_3N_2)_2]Cl_2,H_2O$, emerald-blue, and *sulphate*, $[Ni(C_3H_6O_3N_2)_2]SO_4$, azure, and *cuprous methylhydroxyglyoxime chloride*, $[Cu(C_3H_6O_3N_2)]Cl_2$, greyish-green, are described; all are decomposed by water. Methylhydroxyglyoxime forms a *diacetate*, CMe(:N·OAc)·C(:N·OAc)·OH, m. p. 96—98°, and a *monobenzoate*, CMe(:N·OBz)·C(:N·OH)·OH, m. p. 146—147° (decomp.), which gives a red colour with ferric chloride; the *dibenzoate*, CMe(:N·OBz)·C(:N·OBz)·OH, m. p. 177—178° (decomp.), when heated in alcohol, gives an *isomeride*, m. p. 151—152° (decomp.), reconverted by benzoyl chloride into the original derivative, and hydrolysed to benzhydroxamic acid. Hydrolysis of methylhydroxyglyoxime itself yields α-oximinopropionic acid, from which it can be prepared.

E. W. Wignall.

Dioximes. XXXIII. G. Ponzio and I. De Paolini (Gazzetta, 1926, **56**, 705—709).—Hydroxyglyoxime can be prepared more readily than before (A., 1925, i, 1041) by the action of hydroxylamine on ethyl dichloroacetate. The *sodium*, *potassium*, and *ammonium dihydroxyglyoxime nickelates*, $[(C_2H_2O_3N_2)_2Ni]M_2$, red, crystalline substances, are described, and *nickel dihydroxyglyoxime chloride*, $[Ni(C_2H_4O_3N_2)_2]Cl_2$, emerald-green, are described.

The *diacetate*, CH(:N·OAc)·C(:N·OAc)·OH, has m. p. 113—114°, and is reconverted into hydroxyglyoxime on hydrolysis; the *tribenzoate*, m. p. 142—143°, is hydrolysed to benzhydroxamic acid.

E. W. Wignall.

Dioximes. XXXIV. G. Ponzio and R. Sismondi (Gazzetta, 1926, **56**, 709—713).—Oxaldihydroxamic acid (dihydroxyglyoxime), m. p. 165°, forms complex salts similar to those obtained from other hydroxyglyoximes, and not the compounds described by Hofmann and Ehrhardt (A., 1913, i, 599). The following are described: *sodium bisdihydroxyglyoxime nickelate*, $[(C_2H_2O_4N_2)_2Ni]Na_2$, which forms a *di-* and a *trihydrate*, explosive on heating; the corresponding *potassium* salt, which forms red *di-* and *pentahydrates*; *potassium bisdihydroxyglyoxime cuprate*, coffee-coloured, $[(C_2H_2O_4N_2)_2Cu]K_2$. The dibenzhydroxamic acid, m. p. 161°, described by Schäfer, has m. p. 165—167° (decomp.) and is to be regarded as benzoylated on the oxime groups, viz., HO·C(:N·OBz)·C(:N·OBz)·OH, dibenzoximinoethylene glycol, since with sodium hydroxide it gives benzoic acid, hydrazine, and carbon dioxide, which may be regarded as products of a double Beckmann transformation to an unstable dibenzoylhydrazinedicarboxylic acid.

E. W. Wignall.

Dioximes. XXXIX. G. B. Semeria and B. Bocca (Gazzetta, 1926, **56**, 746—756).—Thermal diagrams obtained by a modified "thaw–melt" method (cf. Rheinboldt, A., 1926, 25) are given for mixtures of glyoxime or its methyl, dimethyl, or methylethyl derivatives, all in the β-forms, which give nickel complexes insoluble in dilute acetic acid, with xanthone, or with antipyrine. Xanthone gives *compounds*: $C_2H_4O_2N_2,2C_{13}H_8O_2$; $MeC_2H_3O_2N_2,C_{13}H_8O_2$; $Me_2C_2H_2O_2N_2,2C_{13}H_8O_2$, and $MeEtC_2H_2O_2N_2,C_{13}H_8O_2$. Antipyrine gives $C_2H_4O_2N_2,C_{11}H_{12}ON_2$; $MeC_2H_3O_2N_2,C_{11}H_{12}ON_2$; $Me_2C_2H_2O_2N_2,C_{11}H_{12}ON_2$; and $MeEtC_2H_2O_2N_2,C_{11}H_{12}ON_2$ and $MeEtC_2H_2O_2N_2,2C_{11}H_{12}ON_2$.

E. W. Wignall.

Dioximes. XL. [Action of bromine on hydroxamic acids.] I. De Paolini (Gazzetta, 1926, **56**, 757—758).—Bromine converts acethydroxamic acid into acetic acid and nitrous oxide; benzhydroxamic acid into benzoic acid and nitrous oxide; phenylacethydroxamic acid into phenylacetic acid; carbamylhydroxamic acid into oxamic acid; phenylcarbamylhydroxamic acid into *p*-bromo-oxanilic acid.

E. W. Wignall.

Reactions between sugars and amines. III. H. von Euler and E. Brunius (Z. physiol. Chem., 1926, **161**, 265—269).—The lowering of f. p. with lævulose–alanine mixtures is greater than would be expected from those of the components. The affinity constant for the reaction is *K* 0·133. On mixing 0·1*N*-solutions, the immediate reaction utilises about 2% of the lævulose present (cf. A., 1926, 714, 822).

P. W. Clutterbuck.

Constitution of the disaccharides. XI. Maltose. W. N. Haworth and S. Peat (J.C.S., 1926, 3094—3101).—Thorough methylation of maltobionic acid yielded *methyl octamethylmaltobionate*, b. p. 170—173°/0·05 mm., n_D^{14} 1·4620, which, on hydrolysis, formed crystalline tetramethylglucose and βγεζ-tetramethylgluconic acid. This acid, when heated, forms βγεζ-tetramethyl-γ-gluconolactone. Mixed m.-p. determinations confirmed the identity of the phenylhydrazide of this acid, m. p. 134—136°, with specimens from two other sources. The constitution of maltose thus seems definitely proved, the oxide ring being amylene oxidic.

B. W. Anderson.

Synthesis of disaccharides. IV. Two β-*d*-glucose tetra-acetates. B. Helferich and W. Klein (Annalen, 1926, **450**, 219—229).—6-Triphenylmethyl-β-*d*-glucose (A., 1925, i, 790), when treated at 0° with hydrobromic acid in acetic acid, gives a triphenylmethyl bromide and β-d-*glucose*-1 : 2 : 3 : 4-*tetra-acetate*, m. p. 128—129°, $[\alpha]_D^{24}$ +12·1° in chloroform, +21·7° in water before mutarotation. This is reconverted by triphenylmethyl chloride into the initial material (thus showing that the 6-hydroxyl group is free) and acetylated by acetic anhydride to β-*d*-glucose penta-acetate, m. p. 134°.

If excess of β-*d*-glucose tetra-acetate is shaken with acetobromoglucose and silver oxide in chloroform, gentiobiose octa-acetate, m. p. 196°, is readily obtained.

If β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate is treated in pyridine with toluenesulphonyl chloride, β-d-*glucose* 1 : 2 : 3 : 4-*tetra-acetate* 6-*toluenesulphonate*, m. p. 203—205°, $[\alpha]_D^{20}$ +23·9° in chloroform, separates.

Study of the mutarotation of β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate at 41·5° shows a gradual decrease in rotation in aqueous solution in ordinary glass vessels, but not in other solvents, or in Jena glass. The product at equilibrium, in which α has decreased to one tenth of its original value, has m. p. 97—98°, and consists of a mixture of the initial material with an isomeride. This is isolated by crystallisation from pyridine; the product containing 1 mol. of pyridine of crystallisation has m. p. 108—110°, $[\alpha]_D^{20}$ —22·0° in water. The pyridine-free β-*d*-*glucose* 1 : 2 : 3 : 6(?)-*tetra-acetate* has m. p. 132°, which is strongly depressed by mixing with the 1 : 2 : 3 : 4-isomeride. The new substance does not form a derivative with triphenylmethyl chloride under the conditions employed with the 1 : 2 : 3 : 4-compound (indicating that the 6-hydroxyl group is not free); it is acetylated in pyridine to β-*d*-glucose penta-acetate, identical with that previously described; it reacts with toluenesulphonyl chloride to give a new β-d-*glucose* 1 : 2 : 3 : 6(?)-*tetra-acetate* 4(?)-*toluenesulphonate*, m. p. 111—112°, $[\alpha]_D^{20}$ $-15·9°$ in chloroform.

Directions are given for the preparation of the reactive silver oxide employed by the authors.

E. W. WIGNALL.

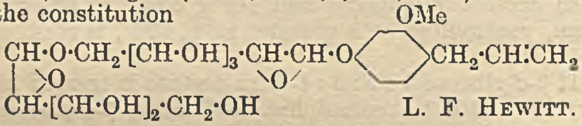
Sugar syntheses. V. Synthesis of trisaccharides. B. HELFERICH and W. SCHÄFER (Annalen, 1926, **450**, 229—237).—The preparation of β-*d*-glucose 1 : 2 : 3 : 4-tetra-acetate (see preceding abstract) has made it possible to prepare trisaccharides. Thus this substance condenses with acetobromocellobiose in chloroform in presence of silver oxide to give 6-β-*cellobiosido*-β-d-*glucose hendeca-acetate*, m. p. 245—247°, $[\alpha]_D^{21}$ $-10·2°$, $-10·4°$ in chloroform, which when hydrolysed by the method of Zemplén (A., 1926, 822) gives 6-β-*cellobiosido*-β-d-*glucose*, m. p. 247—252°, $[\alpha]_D^{20}$ $+15·0°$ to $+8·4°$ in water. A monohydrate, m. p. 200° (decomp.) is described. The sugar has about 42% of the reducing power of dextrose. The *osazone* has m. p. 224°, $[\alpha]_D^{22}$ $-61·5°$ in pyridine. Treatment of the hendeca-acetate with hydrobromic acid in acetic acid yields 6-β-*hepta-acetylcellobiosido-acetobromoglucose*, m. p. 231°.

In a similar manner, from acetobromolactose, 6-β-*lactosido*-β-d-*glucose*, m. p. 257° (decomp.), $[\alpha]_D^{24}$ $+34·7°$ to $+22·6°$ in water, is obtained by way of its *hendeca-acetate*, m. p. 198°, $[\alpha]_D^{22}$ $-2·53°$ in chloroform. The reducing power towards Fehling's solution is about 37% of that of dextrose. The *osazone* has m. p. 233°, $[\alpha]_D^{22}$ $-50·5°$ in pyridine.

Acetobromogentiobiose yields 6-β-*gentiobiosido*-β-d-*glucose hendeca-acetate*, m. p. 221°, $[\alpha]_D^{23}$ $-8·0°$ in chloroform. The free sugar has been obtained as a syrup, of reducing power about 40% of that of dextrose.

E. W. WIGNALL.

Constitution of gein (geoside). H. HÉRISSEY and J. CHEYMOL (Compt. rend., 1926, **183**, 1307—1308).—To gein (cf. A., 1925, i, 487, 1383) is ascribed the constitution



L. F. HEWITT.

Synthesis and degradation of polysaccharides. H. PRINGSHEIM (Ber., 1926, **59**, [*B*], 3008—3018).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Röntgenographic elucidation of the structure of organic substances, particularly those of high mol. wt. H. MARK (Ber., 1926, **59**, [*B*], 2982—3000).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Chemistry of complex organic compounds in the light of Kekulé's theory of structure. H. PRINGSHEIM (Ber., 1926, **59**, [*B*], 3019—3043).—A lecture delivered before the Gesellschaft Deutscher Naturforscher und Ärzte.

H. WREN.

Starch. XIX. Fermentative fission of the polyamyloses. H. PRINGSHEIM, J. LEIBOWITZ, and P. MECHLINSKI (Ber., 1926, **59**, [*B*], 2738—2746; cf. A., 1926, 1128).—Amylase can be removed almost completely and maltase largely from weakly acid taka-diastase solution by β-aluminium hydroxide; the residual solution hydrolyses the polyamyloses readily, giving dextrose and, possibly, maltose. In weakly alkaline solution, the polyamylases are adsorbed by kaolin, which has no effect on maltase and amylase, but elution of the active polyamylases could not be effected. Variation in the nature of the admixed products of taka-diastase renders repetition of the experiments uncertain with different specimens. Complete fission of the polyamyloses to dextrose appears a complicated change, since it does not follow any simple law. Within each polyamylose series the fermentative behaviour of the members is independent of the degree of polymerisation. Hydrolysis of α-di- and α-tetra-amylose or of β-tri- and β-hexa-amylose occurs qualitatively and quantitatively similarly, so that the enzyme appears directly to attack the associated molecule. Under like conditions, tri- and hexa-amylose are more rapidly attacked than di- and tetra-amylose and are smoothly transformed into dextrose in 100% yield, whereas with the α-polyamyloses a "false equilibrium" is somewhat rapidly established and quantitative production of dextrose can be secured only by the use of large amounts of enzyme. Apparently fission of the α- and β-polyamyloses is due to two different enzymes. The enzymes under observation are specifically adapted to certain chemical structures of the substrates and not to definite degrees of association or polymerisation. The observations also bring new indirect evidence of the structural difference of the α- and β-polyamyloses and of their non-identity with the fundamental components of starch.

H. WREN.

Structure of starch. E. PEISER (Z. physiol. Chem., 1926, **161**, 210—217).—Starch, acetylated in the cold, yields a compound, $C_{48}H_{56}O_{42}Ac_{26}$, $[\alpha]^{26}$ $+276·3°$, which on hydrolysis regenerates the original amylose. If the acetylation is carried out at 55°, a substance, $C_{24}H_{28}O_{22}Ac_{14}$, is obtained. A third acetyl derivative, $C_{24}H_{29}O_{22}Ac_{13}$, is obtained by warming the compound $C_{48}H_{56}O_{42}Ac_{26}$ with phosphorus pentachloride, and this on further acetylation yields the higher acetyl derivative, $C_{24}H_{28}O_{22}Ac_{14}$.

P. W. CLUTTERBUCK.

Relation of lichosan to lichenin. H. PRINGSHEIM and O. ROUTALA (Annalen, 1926, **450**, 255—272).—The criticisms of Bergmann and Knehe (A., 1926, 1230) are refuted. In contrast with the grey powder obtained by these authors, pure white lichosan can be dried satisfactorily. The viscosity curve of lichosan in water shows that the particles are smallest at 70°; the mol. wt. determined at this temperature by the Barger–Rast method is 162, that of a glucose anhydride. The viscosity curve resembles that of cellosan, except that with rise of temperature from 70° to 100° the viscosity rises only slightly. At 45°, the mol. wt. is about 486. $[\alpha]_D$ in water 0; in $2N$-sodium hydroxide $+33·5°$; in 95% pyridine $+93·2°$.

Lichosan has been prepared by another method. Lichenin acetylated by acetic anhydride and a trace of sulphuric acid gives lichenin acetate, $C_6H_7O_5Ac_3$, $[\alpha]_D$ $-17·7$ to 23·1° in chloroform (Hess and Schultze, A., 1926, 715), which is hydrolysed to lichenin by methyl-alcoholic ammonia, if this contains a little water. Lichenin acetate heated with naphthalene gives pure white *lichosan acetate*, $C_6H_7O_5Ac_3$, $[\alpha]^{20}_{D}$ −21·8° in chloroform, mol. wt. in phenol 327—445. This hydrolyses under the conditions employed with lichenin to lichosan, identical with that obtained by heating lichenin in glycerol.

The association of molecules in a polysaccharide is considered to be due to molecular valencies. These give with lichosan polymerides of 3—7 mols.; the simple " elementary substance " nevertheless exists, and there is no reason for assuming that chemical changes occur during deassociation.

E. W. Wignall.

[Lignin.] W. Fuchs and E. Honsig (Ber., 1926, 59, [*B*], 2850—2856).—A criticism of the work of Schmidt (A., 1925, i, 1370, and previous abstracts). Treatment of wood with chlorine dioxide and sodium sulphite gives products the total weight of which, calculated to ash-free material, does not differ greatly from the weight of the initial substance. In spite of this, decomposition, oxidation, and hydrolysis occur. Elementary analysis of the initial material and the products derived therefrom shows that about one fourth of the initial carbon is oxidised to carbon dioxide, oxalic acid, etc. In the course of the treatment, the original methoxyl content disappears completely. Hence the decomposition takes place mainly at the expense of the lignin. Elementary analysis also indicates that even if lignin persists in individual fractions, its composition must differ widely from that of original lignin. The greater part of the lignin appears to suffer complete decomposition, as would be expected from the behaviour of phenols under similar conditions. Experience with individual lignin preparations indicates the possibility that they may yield polysaccharides in small amount, but not to the extent assumed by Schmidt. The expression " polysaccharides from lignin " is not admissible. H. Wren.

Crystalline nature of the chief constituent of ordinary coal. C. S. Fox (Nature, 1926, 118, 913).—Coal from the Raniganj coalfield contains one main constituent (" vitro-clarain " or " anthraxylon "), which simulates a crystalline structure, together with resinous substances, fusain, and inorganic matter. A. A. Eldridge.

Crystalline nature of the chief constituent of ordinary coal. M. C. Stopes (Nature, 1926, 118, 913).—Polemical (cf. Fox, preceding abstract).

A. A. Eldridge.

Syntheses of tetramethylenediamine and pyrrolidine. W. Keil (Ber., 1926, 59, [*B*], 2816—2817).—γ-Phthalimido-*n*-butyronitrile is reduced by sodium and alcohol, and the resulting substituted diamine is distilled with concentrated alkali hydroxide, whereby tetramethylenediamine is obtained in more than 60% yield. The corresponding hydrochloride is transformed by dry distillation into pyrrolidine hydrochloride and ammonium chloride. H. Wren.

Additive compounds of halides of bivalent metals with organic bases. III. G. Scagliarini and G. Tartarini (Atti R. Accad. Lincei, 1926, [vi], 4, 387—389; cf. A., 1926, 1113).—In alcoholic solution, hexamethylenetetramine forms with the halides of bivalent metals the *compounds* $CoCl_2,C_6H_{12}N_4$, ultramarine; $CoBr_2,C_6H_{12}N_4$, blue, and $NiCl_2,C_6H_{12}N_4$, greenish-yellow. T. H. Pope.

Action of Grignard reagent on amino-acids. XII. Determination of free carboxyl groups in peptides. F. Bettzieche (Z. physiol. Chem., 1926, 161, 178—190).—Glycylalanine, glycylphenylglycine, benzoylglycylalanine, and benzoylglycylphenylglycine, on esterification and treatment with magnesium phenyl bromide and hydrolysing, respectively, give yields of dibenzyl ketone, 52%; triphenylethanone, 59%; dibenzyl ketone 41%, and triphenylethanone, 50%. The method is adapted to small amounts (40—100 mg.) of the following, the yields with magnesium phenyl and benzyl bromides being tabulated; phenylglycine, glycine, alanine, phenylalanine, leucine, glycylglycine, hippurylglycine, glycylalanine, hippurylalanine, glycylphenylglycine, and hippurylphenylglycine. P. W. Clutterbuck.

Preparation of β-aminoaryl-aliphatic acids. I. W. M. Rodionov and E. T. Malewinskaja (Ber., 1926, 59, [*B*], 2952—2958).—Piperonal is converted by malonic acid and boiling alcoholic ammonia into a mixture of piperonylacrylic acid, methylenedioxystyrenedicarboxylic acid, and β-*amino*-β-*piperonylpropionic acid hydrochloride*, m. p. 232—234°, the relative proportion of the latter increasing with increase in the quantity of alcoholic ammonia. β-Amino-β-piperonylpropionic acid has m. p. 224—225°. Similarly, piperonal, malonic acid, and alcoholic methylamine afford β-*methylamino*-β-*piperonylpropionic acid hydrochloride* (corresponding *acid*, m. p. 199—200°). The following compounds are analogously prepared: β-*amino*-β-*phenylpropionic acid hydrochloride*, m. p. 218°, and the acid, m. p. 228° (also obtained from benzhydramide); β-*amino*-β-m-*nitrophenylpropionic acid hydrochloride*, m. p. 210—211·5°, and the acid, m. p. 226—227°. H. Wren.

Optically active, internally complex salts. H. Ley and T. Temme (Ber., 1926, 59, [*B*], 2712—2719; cf. A., 1917, i, 707).—α-Bromopropionic acid is resolved by means of an excess of cinchonine in acetone solution into its optical isomerides, which are converted by an excess of methylamine at 0° into the corresponding α-methylaminopropionic acid; after treatment with lead hydroxide to decompose any methylamide, the latter are transformed into the *copper* salts, $(C_4H_8O_2N)_2Cu,2H_2O$, $[\alpha]_{\text{blue}}$ +35·2° and 34·1°, respectively. The l-*acid*, m. p. 274° (decomp.), has $[\alpha]_{\text{red}}$ −5·1°, $[\alpha]_{\text{yellow}}$ −6·85°, whereas for the d-*acid* (from the lævorotatory copper salt), $[\alpha]_{\text{yellow}}$ +7·92° is recorded. The *hydrochloride* and *sodium* salt of the *l*-acid have $[\alpha]_{\text{red}}$ −6·25° and $[\alpha]_{\text{red}}$ −2·4°, respectively. With increasing concentration of ammonia, the specific rotation of the copper salt of *l*-methylalanine diminishes to zero, and then attains maximum lævorotation, followed by a decline; a similar behaviour is shown by the corresponding salt of *d*-alanine. Attempts to prepare cobaltic salts of the active methylalanines gave resinous products with high optical activity. With potassium chloroplatinite, the *l*-acid yields the *salt*,

$K[PtCl_2,C_4H_8NO_2]$, $[\alpha]_{red}$ −12·7°, $[\alpha]_{yellow}$ −16·76° in water. The normal *nickel* salt is described. The red *cobaltic* salt of l-*alanine* has $[M]_{red}$ +475°, whereas the corresponding violet *salt* has $[M]_{red}$ −1315° in 50% sulphuric acid. H. WREN.

Action of sodium hypobromite on derivatives of carbamide and guanidine. III. V. CORDIER (Monatsh., 1926, 47, 327—339; cf. A., 1914, i, 258).—The volume of nitrogen (if any) evolved under the prolonged action of sodium hypobromite has been determined for a large number of substances, including derivatives of carbamide, thiocarbamide, guanidine, and the cyclic ureides. The results of this and the previous investigations are collected in tabular form. G. M. BENNETT.

Metal alkyls. F. HEIN and F. A. SEGITZ (Z. anorg. Chem., 1926, 158, 153—174; cf. A., 1925, ii, 217).—Tetraethylammonium iodide and tetrapropylammonium iodide dissolve in zinc ethyl and zinc methyl, and tetraethylammonium iodide also dissolves in cadmium ethyl, forming conducting solutions. With increasing dilution, the molecular conductivity increases, and apparently tends to a limit. The loose *compound*, $NPr_4I,ZnEt_2$, can be separated from the corresponding solution. Since, according to Walden, the tetra-alkylammonium iodides can be regarded as standard electrolytes, the view that the alkali alkyls, considered with respect to their solutions in the above metal alkyls, are salts (cf. *loc. cit.*) is confirmed. An approximate calculation indicates that in all the solutions in metal alkyls the solute molecules are highly polymerised. The behaviour of various metals as anodes in the electrolysis of solutions of sodium ethyl in zinc ethyl has been examined. Antimony, aluminium, magnesium, cadmium, bismuth, thallium, gold, and, in certain circumstances, tin, but not copper, platinum, iron, or tantalum, are attacked almost quantitatively by the ethyl radicals. R. CUTHILL.

Action of tungsten hexachloride on magnesium phenyl iodide. (MLLE.) W. BRYDOWNA (Bull. Soc. chim., 1926, [iv], 39, 1771).—The action of tungsten hexachloride on magnesium phenyl iodide in ether affords diphenyl in 50% yield (cf. A., 1924, i, 381). R. BRIGHTMAN.

Isomeric changes in cyclic compounds with catalysts. I. Hydrocarbons. M. N. DOJARENKO (J. Russ. Phys. Chem. Soc., 1926, 58, 1—15).—The isomeric changes to open-chain structures of cyclic compounds, *e.g.*, hydrocarbons and alcohols, were studied at 250—430° in the presence of alumina as catalyst. The products were fractionated and further separated and identified by treatment with bromine. Methylene*cyclo*butane at 400—430° gave a fraction, b. p. 31—39°/735 mm., containing β-methyl-Δ^β-butene, β-methyl-Δ^α-butene, and isoprene, identified by the physical constants of the bromine derivatives formed. The fractions of higher b. p. gave *p*-cymene and a rubber-like residue. It is probable that isoprene is the main product.

Methyltrimethylene at 340—360° gave a gas, chiefly Δ^β-butene and β-methyl-Δ^α-propene. The liquid portion was probably composed of substances, C_8H_6 and C_4H_6.

By comparing these and other results, the conclusion is reached that in isomeric changes of cyclic to open-chain compounds, the tendency is to increase the number of methyl groups.

The theoretical significance of the reactions is discussed. The catalyst causes, by the influx of external energy, the loosening of a C—C linking, with the formation of intermediate labile forms, which give various products, depending on the external energy conditions. In all cases, the final product has a smaller energy content than the initial compound, as is shown by the values calculated from Fajans' and Hückel's data for C—C and C—H linkings in rings and chains. M. ZVEGINTZOV.

Isomeric transformations of cyclic compounds under the influence of catalysts. I. Isomerisation of cyclic hydrocarbons with aluminium oxide as catalyst. M. DOJARENKO (Ber., 1926, 59, [*B*], 2933—2948).—A more extended account of work already reported (preceding abstract). H. WREN.

Isomeric changes in cyclic compounds with catalysts. II. Dehydration of the alcohols C_4H_8O. III. Dehydration of the alcohols $C_5H_{10}O$. M. N. DOJARENKO (J. Russ. Phys. Chem. Soc., 1926, 58, 16—26, 27—38; cf. preceding abstract).—II. *cyclo*Propylcarbinol, *cyclo*butanol, and allylcarbinol were investigated by the method described in Part I. *cyclo*Propylcarbinol gave a liquid and a gaseous product: propylene (main product), erythrene and butylene (traces). The liquid contained water (which increased with rise of temperature) and an oil (which decreased) consisting of aldehydes, *cyclo*butanone, and polymerides. Some carbon was also deposited. The proportions of the products depend on the temperature. *cyclo*Butanol at 360—390° gave propylene, erythrene, water, carbon, and traces of *cyclo*butanone, aldehydes, and polymerides. Erythrene gave two stereoisomeric tetrabromides, m. p. 39° and 118°. Allylcarbinol (into which *cyclo*propylcarbinol often isomerises) at 400° gave results analogous to the cyclic compounds. The cyclic alcohols isomerise to an open chain, which is then split, giving propylene as the main product.

III. Methyl*cyclo*propylcarbinol was treated at 240—265° and at 350—365°. The effect of rise of temperature was as before. The products were mainly piperylene and divinylmethane, with a little methyl*cyclo*butene (identified by its dibromide, b. p. 66—73°/13 mm., d_4^{17} 1·744, n_D^{17} 1·576), *i.e.*, there was some 3- to 4-ring isomerism.

Methyl*cyclo*butanol at 370—375° and at 410—420° gave mainly isoprene and β-methyl-Δ^β-butene, together with cymene and a rubber-like residue. There was a complete analogy in behaviour and proportions of products obtained with the preceding case.

*cyclo*Butylcarbinol at 415—430° gave mainly *cyclo*pentene, b. p. 43—44°/751 mm., d_4^{10} 0·7776, n_D^{10} 1·4287. No open-chain compounds or polymerides were formed.

By grouping the alcohols according to homologous series, it is found that the dehydration products are also in series. Water is often eliminated in the 1 : 3 positions ("abnormal"), and may be followed by migration of a hydrogen atom.

The energy relations discussed in the previous papers hold good. All the reactions are shown to be in accordance with the principle that the final product has the smaller energy content. M. Zvegintzov.

Condensations of chloral and bromal with phenolic ethers in presence of anhydrous aluminium chloride. E. E. Harris and G. B. Frankforter (J. Amer. Chem. Soc., 1926, 48, 3144—3150).—The following compounds were prepared by condensing chloral, bromal, dibromoacetaldehyde, bromoacetal, and chloral alcoholate with the appropriate aromatic derivatives, in carbon disulphide solution in presence of aluminium chloride at 0° (cf. Frankforter and Kritchevsky, A., 1914, i, 1059): βββ-trichloro-αα-diphenylethane, m. p. 64°; βββ-trichloro-αα-ditolylethane, m. p. 89°; βββ-trichloro-αα-dianisylethane; βββ-trichloro-αα-diphenetylethane, m. p. 105·5°; βββ-*trichloro-αα-di-*(6-*methoxy-*m-*tolyl*)*ethane*, m. p. 159°; βββ-*trichloro-αα-di-*(6-*ethoxy-*m-*tolyl*)*ethane*, m. p. 128°; βββ-tribromo-αα-diphenylethane, m. p. 76°; βββ-*tribromo-αα-ditolylethane*, m. p. 104°; βββ-*tribromo-αα-dianisylethane*, m. p. 115°; βββ-tribromo-αα-diphenetylethane, m. p. 118°; βββ-*tribromo-αα-di-*(6-*methoxy-*m-*tolyl*)*ethane*, m. p. 192°; βββ-*tribromo-αα-di-*(6-*ethoxy-*m-*tolyl*)-*ethane*, m. p. 171°; ββ-*dibromo-αα-dianisylethane*, m. p. 122°; ββ-*dibromo-αα-diphenetylethane*, m. p. 104°; ββ-*dibromo-αα-di-*(6-*methoxy-*m-*tolyl*)*ethane*, m. p. 152°; ββ-*dibromo-αα-di-*(6-*ethoxy-*m-*tolyl*)-*ethane*, m. p. 131°; β-*bromo-αα-dianisylethane*, liquid; and β-*bromo-αα-diphenetylethane*, liquid. The following ethylene derivatives were obtained by treating the above compounds with alcoholic potassium hydroxide: ββ-dichloro-αα-diphenyl-, m. p. 80°; ββ-dichloro-αα-ditolyl-, m. p. 85°; ββ-dichloro-αα-dianisyl-, m. p. 109°; ββ-dichloro-αα-diphenetyl-, m. p. 105°; ββ-*dibromo-αα-diphenyl-*, m. p. 84°; ββ-*dibromo-αα-ditolyl-*, m. p. 118°; ββ-*dibromo-αα-dianisyl-*, m. p. 91°; ββ-*dibromo-αα-diphenetyl-*; β-*bromo-αα-dianisyl-*, m. p. 85°; β-*bromo-αα-diphenetyl-*, m. p. 64°; β-*bromo-αα-di-*(6-*methoxy-*m-*tolyl*)-, m. p. 105°; αα-dianisyl-, m. p. 142°; and αα-*diphenetylethylene*, m. p. 138°. When heated on the steam-bath with sodium ethoxide, the trihalogenodiphenylethanes and the corresponding ditolyl derivatives are converted into diphenylacetic acid and ditolylacetic acid, respectively. The nucleus-substituted trihalogenodiphenylethanes, di- and mono-halogenoethylenes yield, when heated with sodium ethoxide in a sealed tube at 180—200°, the corresponding tolanes; *diethoxytolane*, m. p. 160°, is described. Metallic sodium in boiling benzene converts the trihalogenoethanes into symmetrically substituted stilbenes, and the dihalogenoethylenes into tolanes. When boiled with silver oxide in aqueous suspension, the tribromoethanes are oxidised to substituted benzoic acids, whilst oxidation of the trihalogenoethanes with chromic acid in glacial acetic acid affords substituted benzophenones. F. G. Willson.

Arylsulphonyl chlorides. E. Gebauer-Fülnegg and F. Riesenfeld (Monatsh., 1926, 47, 185—206).—When benzenesulphonyl chloride is treated with sodium iodide in acetone solution (cf. Finkelstein, A., 1910, i, 453), the main products are αα′-diphenyldisulphone and sodium benzenesulphinate, iodine being liberated. A little benzenesulphonyl iodide is also formed. Similar results are obtained in liquid sulphur dioxide solution. When zinc-dust is added to the reaction mixture, benzenesulphinic acid is obtained in 70% yield, with some benzenesulphonic acid. From benzenesulphonyl chloride and pyridine in ether, $C_5H_5N,Ph{\cdot}SO_2Cl$, m. p. 110—112° (Schwartz and Dehn, *ibid.*, 1918, i, 61), is formed, but the compound $(C_5H_5N)_2Ph{\cdot}SO_2Cl$ could not be obtained. In the absence of a solvent, however, owing to the instability of solutions of the additive compound towards moisture, only pyridinium benzenesulphonate, m. p. 132—133°, can be isolated; this is also formed when a solution of benzenesulphonyl chloride in pyridine is electrolysed or treated with sodium iodide. Similarly, when *o*- and *p*-toluenesulphonyl chlorides and *p*-chlorobenzenesulphonyl chloride are heated with pyridine, the corresponding pyridinium salts, m. p. 121—123°, 115—120°, and 137—140°, respectively, are produced, whilst naphthalene-1 : 5-disulphonyl chloride gives *dipyridinium naphthalene-1 : 5-disulphonate*, m. p. 245°, at the ordinary temperature. Quinoline and benzenesulphonyl chloride give *quinolinium benzenesulphonate*, m. p. 126—127°. There is no indication of the formation of free arylsulphonyl radicals in any of the above experiments. An equimolecular mixture of benzenesulphonyl chloride and pyridine affords, on treatment with 0·5—2·0 mols. of potassium hydroxide solution, an intense reddish-violet colour. Homologues of pyridine give a pomegranate-red; other cyclic bases give no coloration. Other sulphonyl chlorides may be used, the colour being discharged by light and oxidising agents in the cold, and by acids on heating. This test is the most delicate colour reaction of pyridine known; it is given by 10 c.c. of 0·01% aqueous pyridine or of a 0·002% solution in 5% alcohol. H. E. F. Notton.

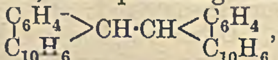
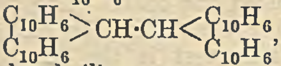
Space formula of diphenyl. E. E. Turner and R. J. W. Le Fèvre (Chem. and Ind., 1926, 831—833).—The literature is reviewed, and a new theory is put forward to explain the existence of optical activity among derivatives of diphenyl.

Photochemical reactions in the *o*-nitrotriphenylmethane series. I. Tanasescu (Bull. Soc. chim., 1926, 39, [iv], 1718—1724).—2 : 4-Dinitrotriphenylmethane on insolation behaves similarly to *o*-nitrotriphenylmethane (A., 1926, 1247), affording in neutral solution the red *o*-quinone derivative and in pyridine the green nitrosocarbinol. Since 2-nitro- and 2 : 4-dinitro-4′ : 4″-diaminotriphenylmethane on insolation in benzene are rapidly isomerised to the corresponding (colourless) nitroso-carbinols, the stability of hexanitrotriphenylmethane under similar conditions is attributed to the electronegative character of the substituent groups, and not to the accumulation of nitro-groups *ortho* to the methine carbon atom. 2 : 4-Dinitrobenzylidene chloride with benzene and aluminium chloride affords 2 : 4-*dinitrotriphenylmethane*, m. p. 93—94°. 2-*Nitro-*4′ : 4″-*diaminotriphenylmethane*, m. p. 64°, and 2 : 4-*dinitro-*4′ : 4″-*diaminotriphenylmethane*, m. p. 132°, are obtained by the condensation of aniline with the nitrobenzaldehyde in chloroform solution in the presence of sulphuric acid. 2-*Nitroso*-4′ : 4″-*diaminotriphenylcarbinol*, colourless, has m. p. 151°, and 4-*nitro*-2-*nitroso*-4′ : 4″-*diaminotriphenylcarbinol*, m. p. 227°.

R. Brightman.

Coloured hydrocarbons. I. A. A. Vanscheidt (J. Russ. Phys. Chem. Soc., 1926, 58, 39—54).—A *résumé* of the work of Thiele, Graebe, Kauffmann, and Staudinger on the preparation and properties of coloured hydrocarbons of the diphenylene-ethene type, and a discussion of the possibilities of its extension. Substances of the type  $\begin{matrix}Ar\\Ar\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}Ar\\Ar\end{matrix}$, if symmetrical, can be easily synthesised by the action of metals on halogen derivatives of the fluorenes; if unsymmetrical, by the action of alcoholic potassium hydroxide on a mixture of the appropriate fluorene and halogen derivative in acetone. The resulting hydrogenated derivatives are colourless, crystalline compounds, easily oxidised in pyridine by silver oxide on gentle warming, or by air and alcoholic potassium hydroxide in the cold to the coloured hydrocarbons. Their properties, behaviour, and relation to the colourless hydrogenated derivatives, "hydrobifulvenes," are closely analogous to those of dyes of the indigo series and their leuco-bases.

M. Zvegintzov.

Coloured hydrocarbons. III. Synthesis of naphthalene derivatives of bifluorenyl. A. A. Vanscheidt (J. Russ. Phys. Chem. Soc., 1926, 58, 69—83; cf. preceding abstract).—*Bischrysofluorenyl*,  $\begin{matrix}C_6H_4\\|\\C_{10}H_6\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}C_6H_4\\|\\C_{10}H_6\end{matrix}$, m. p. 221°, and *bisdi-α-naphthofluorenyl*,  $\begin{matrix}C_{10}H_6\\|\\C_{10}H_6\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}C_{10}H_6\\|\\C_{10}H_6\end{matrix}$, m. p. 353—355° (obtained by boiling an acetone solution of the bromide with copper powder), are described. Both symmetrical and unsymmetrical hydrocarbons are synthesised by the action of alcoholic potassium hydroxide on a mixture of the fluorene and its halide in acetone. *Bisdi-α-naphthofluorenyl*, m. p. 353°, *fluorenyldi-α-naphthofluorenyl*, m. p. 270°, and *chrysofluorenyldi-α-naphthofluorenyl*, m. p. 267°, are thus prepared. All three on oxidation with lead oxide give vividly-coloured substances. Chrysofluorene and fluorenyl chloride are not condensed by alcoholic potassium hydroxide in acetone. When the fluorenes are treated with alcoholic potassium hydroxide, colours are developed, probably due to the formation of alkali metal complexes with the active methylene group, which then react with the halogen derivatives to give the hydrocarbons.

M. Zvegintzov.

Alkylanthracenes and "transannular tautomerism." II. E. de B. Barnett, J. W. Cook, and M. A. Matthews (Ber., 1926, 59, [*B*], 2863—2877; cf. A., 1926, 1030).—1 : 5-Dichloroanthrone is converted by magnesium methyl iodide into 1 : 5-*dichloro*-9-*hydroxy*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 115—116°, which is readily transformed by mineral acid in the presence of glacial acetic acid into 1 : 5-*dichloro*-9-*methylanthracene*, m. p. 115°. 1 : 5-*Dichloro*-9-*hydroxy*-9-*ethyl*-9 : 10-*dihydroanthracene*, m. p. 120°, and 1 : 5-*dichloro*-9-*ethylanthracene*, m. p. 108°, are similarly prepared. The action of magnesium *n*- or *iso*-propyl, *n*-butyl, or *iso*amyl bromide on 1 : 5-dichloroanthrone gives either unchanged initial material or 1 : 5-dichloroanthracene; bromination of a viscous oil obtained by the aid of magnesium *iso*propyl bromide affords a *compound*, $C_{17}H_{13}Cl_2Br_3$, m. p. 184°. 1 : 5-Dichloro-9-methylanthracene is converted by bromine (1 mol.) into 1 : 5-*dichloro*-9-*bromomethylanthracene*, m. p. 180—184° (or, possibly, a mixture of this substance with 1 : 5-dichloro-10-bromo-9-methylene-9 : 10-dihydroanthracene), which is also obtained by the action of hydrogen bromide on a solution of 1 : 5-dichloro-9-hydroxymethylanthracene in boiling benzene. 1 : 5-*Dichloro*-9-*chloromethylanthracene*, m. p. 149°, is obtained by chlorination of 1 : 5-dichloro-9-methylanthracene suspended in cold carbon tetrachloride or from 1 : 5-dichloro-9-hydroxymethylanthracene and hydrogen chloride; in the latter action, a *compound*, m. p. about 290° (decomp.), probably di-1 : 5-dichloro-9-anthranyl methyl ether, is also produced. 1 : 5-*Dichloro*-9-*acetoxymethylanthracene*, m. p. 149°, from the bromo-compound, sodium acetate, and acetic acid, is hydrolysed by alcoholic potassium hydroxide to 1 : 5-*dichloro*-9-*hydroxymethylanthracene*, m. p. 138—139° (*phenylurethane*, m. p. 179°), which is reconverted into the original acetate by acetic anhydride and pyridine and oxidised to 1 : 5 : 1′ : 5′-tetrachlorodianthrone. Direct hydrolysis of 1 : 5-dichloro-9-bromomethylanthracene in boiling aqueous acetone in presence of calcium carbonate yields a *hydroxy-compound*, m. p. 133—134° (*phenylurethane*, m. p. 193°), which when treated with acetic anhydride gives the above acetate, m. p. 149° (after repeated crystallisation of the crude product), and is oxidised to 1 : 5 : 1′ : 5′-tetrachlorodianthrone. The following derivatives of 1 : 5-dichloroanthracene are described: 9-*methoxymethyl*-, m. p. 154°; 9-*ethoxymethyl*-, m. p. 105—106°; 9-*anilinomethyl*-, m. p. 190°; 9-*dimethylaminophenylmethyl*-, m. p. 195°. Treatment of 1 : 5-dichloro-9-bromomethylanthracene with pyridine or of 1 : 5-dichloro-9-methylanthracene with pyridine and bromine affords 1 : 5-*dichloro*-9-*anthranylmethylpyridinium bromide*, m. p. 250° (decomp.) after darkening (corresponding *picrate*, m. p. 212°). Nitrogen peroxide converts 1 : 5-dichloro-9-methylanthracene into 1 : 5-*dichloro*-10-*nitro*-9-*methylanthracene*, m. p. 174°. 1 : 5-Dichloro-9-bromomethylanthracene is transformed by magnesium methyl iodide, magnesium phenyl bromide, or by copper powder in boiling xylene into a *substance*, $C_{30}H_{18}Cl_4$, m. p. 287° (decomp.) [a *by-product*, m. p. 205° (decomp.), is also obtained when the Grignard reagents are used].

1 : 5-Dichloro-9-methylanthracene is converted by an excess of bromine into 1 : 5-*dichloro*-9 : 10-*dibromo*-9-*bromomethyl*-9 : 10-*dihydroanthracene*, m. p. 130—132° (decomp.), which is decomposed when heated into 1 : 5-dichloro-9-bromomethylanthracene and 1 : 5-*dichloro*-10-*bromo*-9-*bromomethylene*-9 : 10-*dihydroanthracene*, m. p. 192° (decomp.); the latter compound is also obtained as by-product of the above bromination, but is most conveniently isolated by slowly distilling a solution of 1 : 5-dichloro-9-methylanthracene in benzene containing an excess of bromine. Hydrolysis

of the tribromo-derivative in aqueous acetone in the presence of calcium carbonate affords two *compounds*, $C_{15}H_{10}OCl_2$ and $C_{15}H_{11}O_2Cl_2Br$, m. p. 191—192° and 179—181°, respectively. 1 : 5-*Dichloro*-9-*bromo*-10-*ethoxy*-9-*ethoxymethyl*-9 : 10-*dihydroanthracene*, m. p. 120—121°, and 1 : 5-*dichloro*-9-*bromo*-10-*anilino*-9-*anilinomethyl*-9 : 10-*dihydroanthracene*, m. p. 160—162°, are described. The tribromo-compound is converted by pyridine into the pyridinium bromide described above. 1 : 5-*Dichloro*-10-*anilino*-9-*bromomethylene*-9 : 10-*dihydroanthracene* has m. p. 140—141°. 1 : 5-Dichloro-10-bromo-9-bromomethylene-9 : 10-dihydroanthracene is converted by copper powder in boiling xylene into the *substance*, $C_{30}H_{16}Cl_4Br_2$, m. p. 309° (decomp.).

1 : 5-Dichloro-9-ethylanthracene is converted by bromine (1 mol.) into 1 : 5-*dichloro*-9-α-*bromoethylanthracene*, m. p. 135—136° (decomp.), and by the halogen (2 mols.) into 1 : 5-*dichloro*-9 : 10-*dibromo*-9-α-*bromoethyl*-9 : 10-*dihydroanthracene*, m. p. 126—127° (decomp.), which is converted into the monobromo-derivative in boiling toluene. 1 : 5-*Dichloro*-9-α-*acetoxyethylanthracene*, m. p. 156—157°, is described.

H. Wren.

Structure of the benzene nucleus. V. *meso*-Derivatives of anthracene. C. K. Ingold and P. G. Marshall (J.C.S., 1926, 3080—3089).—The reactivity of the *meso*-carbon atoms of anthracene may be due to disturbance of valency round the central ring, or to a dissociable *p*-linking. In the latter case, 9 : 10-diarylanthracenes might show properties similar to those of hexa-arylethanes. This is found to be the case; the colourless compounds form coloured solutions, and colorimetric determinations of the degree of dissociation yield results consistent with a reversible unimolecular reaction. Further, *p*-substituents influence dissociation, and in ionising solvents dissociation is partly ionic. The following have been prepared: 9 : 10-*dianilino*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 232—234°; 9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 222—225° (*disodio*- and *dipotassio*-derivatives); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*tolyl*-9 : 10-*dihydroanthracene*, softens at 270°, m. p. 275°; 9 : 10-*di*-p-*tolylanthracene*, m. p. 278—279° (*dipotassio*- and *disodio*-derivatives); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene*, m. p. 267° (decomp.); 9 : 10-*di*-p-*chlorophenylanthracene*, m. p. 306—307·5°; 9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene* (isomerides, m. p. about 206° and about 165°); 9 : 10-*dihydroxy*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene*, m. p. 273—274°; 9 : 10-*di*-p-*bromophenylanthracene*, shrinks at 315°, m. p. 326—327°; 9 : 10-*dihydroxy*-9 : 10-*di*-p-*anisyl*-9 : 10-*dihydroanthracene*, m. p. 258—262°; 9 : 10-*di*-p-*anisylanthracene*, m. p. 282°; 2-*chloro*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 220—221°; 2-*chloro*-9 : 10-*diphenylanthracene*, m. p. 193°; 2-*bromo*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 206—209°; 2-*bromo*-9 : 10-*diphenylanthracene*, m. p. 185—187°; 9-*hydroxy*-9-*triphenylmethylanthrone*, m. p. 183—190°; 9 : 10-*dichloro*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene*, m. p. 218°; and a *substance*, $C_{26}H_{15}Cl_2$, m. p. 294—295°, of the 9 : 10-diarylanthracene type.

B. W. Anderson.

Molecular organic compounds. I. Molecular organic compounds of *m*-dinitrobenzene, 2 : 4-dinitrotoluene, and 2 : 4-dinitrophenol. C. A. Buehler and A. G. Heap (J. Amer. Chem. Soc., 1926, 48, 3168—3172).—The following new molecular compounds have been prepared: *benzidine*–2 : 4-*dinitrotoluene* (1 : 1), black, m. p. 127·6—128°; *benzidine*–2 : 4-*dinitrophenol* (1 : 1),brown, m. p. 143·5—143·8°, or yellow ($1H_2O$), m. p. 134° (decomp.); *naphthalene*–2 : 4-*dinitrophenol* (1 : 1), yellow, m. p. 94·7—95·0° (cf. Hepp, A., 1883, 315); and *aniline*–2 : 4-*dinitrophenol* (1 : 1), yellow, m. p. 76·7—77·3° (cf. Kremann, *ibid.*, 1906, i, 834). The following compounds, previously known to exist in solution, have been isolated: *m*-dinitrobenzene–α-naphthylamine (1 : 1), red, m. p. 65·1—65·7°, and –β-naphthylamine, red, m. p. 53·9—55·7° (cf. Kremann, *loc. cit.*); *m*-dinitrobenzene–naphthalene (1 : 1), greenish-yellow, m. p. 50·7—51·6° (cf. Kremann, A., 1905, ii, 77; Hepp, *loc. cit.*); *m*-dinitrobenzene–benzidine (1 : 1), black, m. p. 127·6—128°; and *m*-dinitrobenzene–aniline (1 : 1), red, m. p. 38·3—39·3° (cf. Kremann, *loc. cit.*); 2 : 4-dinitrotoluene–α-naphthylamine (1 : 1), orange-red, m. p. 62·9—63·7°; 2 : 4-dinitrotoluene–naphthalene (1 : 1), colourless, m. p. 60·1—60·9° (cf. Kremann, *loc. cit.*); 2 : 4-dinitrophenol–α-naphthylamine (1 : 1), red, m. p. 107·3—107·7°, and –β-naphthylamine (1 : 1), reddish-orange, m. p. 77·6—77·9°; 2 : 4-dinitrophenol–naphthalene (1 : 1), m. p. 94·7—95·0° (cf. Hepp, *loc. cit*).; 2 : 4-dinitrophenol–aniline (1 : 1), yellow, m. p. 76·7—77·3° (cf. Kremann, A., 1906, i, 834); 2 : 4-dinitrophenol–*o*-phenylenediamine (1 : 1), yellow, m. p. 93·6—94·0°, and –*m*-phenylenediamine (1 : 1), orange-yellow, m. p. 107·9—108·2° (cf. Kremann, *ibid.*, 1921, i, 601).

F. G. Willson.

Interaction of thiocarbonyl chloride and chloro-substituted anilines and the inhibitory action of *ortho*-substituents. G. M. Dyson, H. J. George, and R. F. Hunter (J.C.S., 1926, 3041—3044).—The reaction between thiocarbonyl chloride and chloro-substituted anilines is found to be inhibited when one chlorine atom is *ortho* to the amino-group, and does not take place if there are two. The following new thiocarbimides are described: 2 : 3-*dichlorophenylthiocarbimide*, b. p. 256—258°/760; 3 : 4 : 5-*trichlorophenylthiocarbimide*, b. p. 280° (decomp.); 3 : 4 : 6-*trichlorophenylthiocarbimide*, b. p. 280°. Treatment of the thiocarbimides with warm alcoholic ammonia yields the thiocarbamides, 2 : 3-*dichlorophenylthiocarbamide*, m. p. 148°; 3 : 4 : 6-*trichlorophenylthiocarbamide*, m. p. 162°: treatment with a chloroaniline yields a substituted diphenylthiocarbamide; s-*di*-2 : 3-*dichlorophenylthiocarbamide*, m. p. 140°; s-*di*-3 : 4 : 5-*trichlorophenylthiocarbamide*, m. p. 140°.

Improved methods of preparation of 2 : 6- and 3 : 5-dichloroanilines, 3 : 4 : 5- and 3 : 4 : 6-trichloroanilines, and 2 : 3 : 5 : 6-tetrachloroaniline are given.

H. Burton.

Decomposition of substituted carbamyl chlorides by hydroxy-compounds. III. Influence of substituent groups. T. W. Price (J.C.S., 1926, 3230—3233).—The rate of decomposition by ethyl alcohol at 100° has been studied of the following substituted carbamyl chlorides, prepared by the action of carbonyl chloride on the requisite secondary amine; phenylmethyl-, phenylethyl-, *phenyl*-n-*propyl*-, m. p. 45·5°; *phenyl*iso*propyl*-, m. p. 90—90·5°; *phenyl*-n-*butyl*-, b. p. 165—166°/20 mm.; *phenyl*iso*butyl*-, b. p. 149—151°/19 mm.; *phenyl*iso*amyl*-, b. p. 153—153·5°/10 mm.; phenylbenzyl-, diphenyl-, and o-*tolylethyl-carbamyl chloride*, m. p. 36·5—37°. The mean velocity coefficients of the reaction are, for the phenylalkyl compounds: ethyl, 0·0631; *n*-butyl, 0·0545; *n*-propyl, 0·0527; methyl, 0·0427; *iso*propyl, 0·215; *iso*amyl, 0·0414; *iso*butyl, 0·0295. The replacement of the methyl group in phenylmethylcarbamyl chloride by phenyl or benzyl decreases the reactivity. H. Burton.

Diphenyl series. IV. Halogenation of 4-aminodiphenyl. J. Kenyon and P. H. Robinson (J.C.S., 1926, 3050—3054).—4-Acetamidodiphenyl on bromination in acetic acid solution yields 3-*bromo*-4-*acetamidodiphenyl* (50%), m. p. 161°, together with 4′-bromo-4-acetamidodiphenyl (30%) (cf. Scarborough and Waters, A., 1926, 512). Hydrolysis of the former compound gives 3-*bromo*-4-*aminodiphenyl*, m. p. 66°, which on bromination furnishes 3 : 5-dibromo-4-aminodiphenyl [*acetyl* derivative, m. p. 212° (Scarborough and Waters, *loc. cit.*, give m. p. 162°); *diacetyl* derivative, m. p. 184°]. 4-Dimethylaminodiphenyl on bromination yields (3 ?)-*bromo*-4-*dimethylaminodiphenyl*, m. p. 82°, whilst 4′-nitro-4-aminodiphenyl furnishes (3 : 5 ?)-*dibromo*-4′-*nitro*-4-*aminodiphenyl*, m. p. 184° (*diacetyl* derivative, m. p. 228°). Nitration of 3 : 5-dibromo-4-acetamidodiphenyl gives a *dinitro*-derivative, m. p. 269—270° (*diacetyl* compound, m. p. 140°). Treatment of 4-aminodiphenyl with *N*-bromoacetanilide, followed by hydrolysis, gives 3-bromo-4-aminodiphenyl. Chlorination of 4′-chloro-4-acetamidodiphenyl with sodium hypochlorite gives 4′ : N-*dichloro*-4-*acetamidodiphenyl*, m. p. 128°, which is decomposed by warm acetic acid to 3 : 4′-*dichloro*-4-*acetamidodiphenyl*, m. p. 184°, a small quantity of which was obtained by the action of hot acetic acid on the unstable 3 : *N*-dichloro-4-acetamidodiphenyl. Chlorination of 3 : 4′-dichloro-4-acetamidodiphenyl gives 3 : 5 : 4′-trichloro-4-acetamidodiphenyl. H. Burton.

Reactions of nitroxyl with aromatic nitro-derivatives and with azoxy-compounds. D. Bigiavi (Atti R. Accad. Lincei, 1926, [vi], 4, 457—459).—Arylnitrosohydroxylamines (cf. Angeli, A., 1900, i, 221) may be obtained by the action on nitro-derivatives of nitroxyl, prepared, together with nitrous acid, when the sodium salt of nitrohydroxylamine, $N(ONa){:}NO_2Na$, is gently heated in solution. In this reaction the sodium salt of the nitroxyl is first oxidised to sodium nitrite by the nitro-compound, which is transformed into the nitroso-compound, this reacting immediately with the nitroxyl to form the nitrosoarylhydroxylamine. The reaction has been used to prepare m-*nitrophenylnitrosohydroxylamine*, $NO_2{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}OH$, m. p. 75—76° (decomp.), from *m*-dinitrobenzene; p-*nitrophenylnitrosohydroxylamine*, m. p. 73—75° (decomp.); and p-*phenylenebisnitrosohydroxylamine*, $C_6H_4({\cdot}NO{:}N{\cdot}OH)_2$, blackening, without melting at 90°; the last compound is probably polymerised.

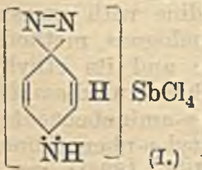
Azoxy-compounds react similarly to the nitro-derivatives with nitroxyl, azoxybenzene yielding azobenzene and a sodium salt apparently of the form $NPh{:}NPh{:}NONa$. *pp′*-Dinitroazoxybenzene and *p*-nitroazoxybenzene give, together with other products, respectively *pp′*-dinitroazobenzene and *p*-nitroazobenzene. T. H. Pope.

o-Chloro- and o-bromo-benzeneazonaphthylhydrazinesulphonic acids. J. Tröger and H. Bertram (J. pr. Chem., 1926, [ii], 114, 269—286).—*o*-Chlorobenzenediazonium chloride couples with α-naphthylamine at 35—40° in presence of sodium acetate, forming yellow 4-o-*chlorobenzeneazo*-α-*naphthylamine*, m. p. 128—129° (*hydrochloride*; *picrate*, decomp. 201°; *perchlorate*; *acetyl* derivative; *benzoyl* derivative, m. p. 193°), which may be diazotised in strong hydrochloric acid solution at 45°, giving 4-o-*chlorobenzeneazonaphthalene*-1-*diazonium chloride*, decomp. 112°. 4-o-*Chlorobenzeneazo*-α-*naphthaleneazo*-m-*phenylenediamine*, decomp. 180°, and 4-o-*chlorobenzeneazo*-α-*naphthaleneazoresorcinol* are described. Brown *sodium* 4-o-*chlorobenzeneazonaphthalene*-α-*diazoniumsulphonate* is reduced by the calculated quantity of stannous chloride to reddish-violet, amorphous 4-o-*chlorobenzeneazo*-α-*naphthylhydrazinesulphonic acid* (*potassium* salt; p-*toluidine* salt, decomp. 161°). Other reducing agents such as ammonium sulphide (cf. A., 1926, 1032) decompose the compound altogether. The hydrazinesulphonic acid readily condenses with aldehydes in presence of hydrogen chloride. In this way, the 4-o-*chlorobenzeneazo*-α-*naphthylhydrazones* of *p*-anisaldehyde, m. p. 170°; cinnamaldehyde, m. p. 182°; salicylaldehyde, m. p. 186°; *p*-hydroxybenzaldehyde, m. p. 134°, and *m*-methoxybenzaldehyde, m. p. 142°, are prepared. 4-*o*-Bromobenzeneazo-α-naphthylamine [*hydrochloride*; *sulphate*; *perchlorate*, m. p. 201° (decomp.); *picrate*, m. p. 198° (decomp.); *acetyl* derivative, m. p. 229°; *benzoyl* derivative, m. p. 196°] is successively converted into 4-*o*-bromobenzeneazonaphthalene-α-diazonium chloride (*loc. cit.*), from which 4-o-*bromobenzeneazo*-α-*naphthaleneazo*-β-*naphthol*, m. p. 217—218°, and 4-o-*bromobenzeneazo*-α-*naphthaleneazoresorcinol*, decomp. 181°, are prepared; *potassium* 4-o-*bromobenzeneazonaphthalene*-α-*diazoniumsulphonate*, 4-o-*bromobenzeneazo*-α-*naphthylhydrazinesulphonic acid* (*potassium* and p-*toluidine*, m. p. 152°, salts), and the 4-o-*bromobenzeneazo*-α-*naphthylhydrazones* of *p*-anisaldehyde, m. p. 164°, *p*-tolualdehyde, m. p. 185°, and cinnamaldehyde, m. p. 176°, are described. The above hydrazinesulphonic acids are more unstable than any previously described. Attempts to prepare the bromo-acid by the method of Tröger and Schäfer (*loc. cit.*) from 4-*o*-bromobenzeneazonaphthalene-1-diazonium chloride and sulphur dioxide were unsuccessful, the products being the corresponding diazosulphonic acid and a *sulphone*, $(BrC_6H_4{\cdot}N_2{\cdot}C_{10}H_6)_2SO_2$. H. E. F. Notton.

Constitution of the azo-dyes. J. S. P. Blumberger (Chem. Weekblad, 1927, 24, 2—12, 42—50).—A critical survey of our present knowledge of the constitution of the hydroxyazo-dyes, indicating that present conceptions of valency render many differences of opinion meaningless (cf. this vol., 55). S. I. LEVY.

as-p-**Nitrophenylethylhydrazine.** G. BARATTINI (Gazzetta, 1926, 56, 821—825; cf. A., 1924, i, 578).—This compound forms a yellow *benzoyl* derivative, m. p. 147°; an *acetyl* derivative, m. p. 144°; a *hydrochloride*, m. p. 212°, and a *picrate*, m. p. 125°. The hydrazones formed with aldehydes and ketones give no coloration with alcoholic potassium hydroxide, the migration of the secondary hydrazinic hydrogen atom to the nitro-group and consequent formation of a quinononitronic complex salt, $NO_2K{:}C_6H_4{:}N{\cdot}N{:}CHR$, which occurs with *p*-nitrophenylhydrazones, being impossible in this case. The formaldehyde compound is obtained in a 1 : 5000 solution of the aldehyde. The as-p-*nitrophenylethylhydrazones* prepared were: formaldehyde, yellow, m. p. 100°; acetaldehyde, pale yellow, m. p. 94°; *o*-nitrobenzaldehyde, orange, m. p. 157°; *m*-nitrobenzaldehyde, pale yellow, m. p. 262°; *p*-dimethylaminobenzaldehyde, bright red, m. p. 187°; cinnamaldehyde, pale yellow, m. p. 160°; salicylaldehyde, pale yellow, m. p. 175°; anisaldehyde, yellow, m. p. 162°; vanillin, orange-yellow, m. p. 153°; piperonal, pink, m. p. 152°; furfuraldehyde, orange, m. p. 150°. T. H. POPE.

Action of antimony trichloride on diazotised diamines. [Determination of antimony in organic compounds.] W. H. GRAY (J.C.S., 1926, 3174—3182).—Diazotised acetyl-*m*-phenylenediamine and acetyl-*p*-phenylenediamine, when treated with antimony trichloride, form the additive compounds *di-*(m-*acetamidobenzenediazonium chloride*)*antimony trichloride*, m. p. 94°, and *di-*(p-*acetamidobenzenediazonium chloride*)*antimony trichloride*, m p. 147°. The additive compound from the *m*-diamine is decomposed when warmed with dilute acid. Decomposition with cold water followed by treatment with chromic acid gives m-*acetamidobenzenediazonium chromate* (explodes violently on warming or on treatment with ammonia). The additive compound from the *p*-diamine gives p-*acetamidobenzenediazonium chloride*, m. p. 131°, when decomposed by water, whilst boiling dilute hydrochloric acid converts it into *p-diazoiminobenzene hydrochloride–antimony trichloride*, (I), m. p. 179° (decomp.). This substance is decomposed by water, giving p-*diazoiminobenzene hydrochloride*, explodes at 155° (*picrate*, explodes at 160°; *chromate*, explodes at 160°). Acetic anhydride in bright sunlight converts *p*-diazoiminobenzene hydrochloride into *p*-acetamidobenzenediazonium chloride, whilst acetic anhydride and sulphuric acid convert it into a neutral *compound*, $C_{10}H_{13}O_5N_3S$, which when treated with chromic acid or picric acid yields p-*acetamidobenzenediazonium chromate*, m. p. 136° (decomp.), or p-*acetamidobenzenediazonium picrate*, m. p. 146·5° (decomp.).



(I.)

The method for the determination of antimony in organic compounds (see A., 1922, i, 404) has been modified by using oxalic acid to remove manganese oxides and carbamide to remove nitrous acid. To determine chlorine in presence of antimony, 0·2 g. of substance is mixed with potassium permanganate (1 g.), a little water, and concentrated sulphuric acid. The liberated chlorine is absorbed in potassium iodide solution. A small correction has to be applied. H. BURTON.

Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. J. HOUBEN [with G. BLAESE] (Ber., 1926, 59, [*B*], 2878—2891).—In the action of hydrogen chloride and nitriles on phenols the change may affect the hydroxyl group or the *para*-hydrogen atom. These changes are opposed to one another in such a manner that reaction with the hydroxyl hinders the entry of the radical into the nucleus, and nuclear substitution hampers the reactivity of the hydroxyl group. Gattermann's synthesis of hydroxyaldehydes and its extension to higher nitriles appears to depend directly on nuclear substitution. Although phenolic ethers react much more smoothly than phenols in Gattermann's synthesis, this does not necessarily appear to be the case when hydrocyanic acid is replaced by other nitriles and the use of zinc or aluminium chloride is omitted.

Phenol is converted by acetonitrile and hydrogen chloride into *acetiminophenyl ether hydrochloride*, $OPh{\cdot}CMe{:}NH,HCl$, m. p. 160° (decomp.) after change at 145°. *Chloroacetiminophenyl ether hydrochloride*, decomp. 110° after softening at 95—100°, the corresponding *dichloro*-compound, decomp. 80—90°, and the *trichloro*-compound are described. *Benziminophenyl ether hydrochloride*, m. p. 180° (decomp.), *phenylacetiminophenyl ether hydrochloride*, m. p. 155° (decomp.), *acetimino-β-naphthyl ether hydrochloride*, decomp. 200°, and *chloroacetimino-β-naphthyl ether hydrochloride* are analogously prepared (β-*naphthyl chloroacetate*, m. p. 97°, is described incidentally). The arylimino-ether hydrochlorides are exceedingly unstable, so that the free ethers have not been isolated. In acid solution, the hydrochlorides are converted into ammonium chloride and aryl ester or its hydrolytic products, whilst in alkaline solution phenol and nitrile or acylamide are produced. Resorcinol, acetonitrile, and hydrogen chloride in the absence of other condensing agent afford *resacetophenoneimine hydrochloride*, m. p. 228° (decomp.), which is easily converted into the free *imine*, decomp. 239° after blackening at 100°, converted by hydroxylamine hydrochloride into resacetophenoneoxime, m. p. 369°. *Diresacetophenoneimine sulphate* is described. α-Naphthol is converted by acetonitrile and hydrogen chloride into a mixture of *acetimino-α-naphthyl ether hydrochloride*, decomp. above 200°, and 4-*hydroxynaphthyl methyl ketimine hydrochloride*, m. p. 251° (decomp.), converted by boiling water into 4-hydroxynaphthyl methyl ketone, m. p. 198°. Attempts to effect the reciprocal conversion of imino-ether into ketimine were unsuccessful. 4-*Hydroxynaphthyl chloromethyl ketone*, m. p. 185°, and 4-*hydroxynaphthyl chloromethyl ketimine hydrochloride* are described. α-Naphthyl methyl ether is not attacked by chloroacetonitrile. H. WREN.

Nitration by means of a mixture of nitrosulphuric and fuming nitric acids. I. J. RINKES (Rec. trav. chim., 1926, 45, 845—848).—Nitration of *o*-nitrophenol with a mixture of nitrosulphuric and nitric acids under the conditions used by Varma and Kulkarni (A., 1925, i, 238) yields a mixture of 2 : 4- and 2 : 6-dinitrophenols (separated by the difference in solubility of their barium salts), and not 2 : 5-dinitrophenol, as stated by these authors. Further nitration yields only picric acid, and not 2 : 4 : 5-trinitrophenol, whilst nitration of hydroxytoluic acid yields mainly 6-nitro-3-hydroxy-*p*-toluic acid, identical with that obtained by Borsche and Berkhout (*ibid.*, 1904, i, 415; the compound is wrongly called in the abstract 6-nitro-3-hydroxycresotic acid), together with a small quantity of 4-nitro-*m*-cresol, m. p. 56°, which is also formed when the nitration conditions of the last-mentioned authors are employed. J. W. Baker.

Influence of substitution in the nucleus on the stability and reactivity of aromatic compounds. K. von Auwers and P. Bullmann (Ber., 1926, 59, [*B*], 2719—2737).—Further examples are cited in favour of the hypothesis that tenacity of organic residues cannot be considered as the sole measure of affinity demand (cf. A., 1924, i, 1055). 2 : 5-Dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide is converted by potassium hydrogen sulphide into the corresponding benzyl sulphide, m. p. 245—246°; isolation of the thiol appears impossible, although the corresponding alcohol is a stable substance and the thiol of the 4-ethoxy-compound can be prepared. 2 : 5-Dibromo-4-hydroxy-3 : 6-dimethylbenzyl acetate yields the ether of the alcohol under the influence of hydrogen fluoride.

The stability of the condensation products of 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl bromide and aromatic amines towards boiling 5% aqueous sodium hydroxide has been examined, reaction proceeding mainly according to the equation $2OH{\cdot}C_6Me_2Br_2{\cdot}CH_2{\cdot}NHR+H_2O=(OH{\cdot}C_6Me_2Br_2)_2CH_2+CH_2O+2R{\cdot}NH_2$, but frequently giving also 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl alcohol. The presence of a methyl group in the *ortho* or *para* position of the amine nucleus decreases the stability of the compound, whereas the contrary effect is exercised by the group in the *meta* position. The methoxy-group resembles the methyl group. A formulation of the distribution of valency in the derivatives of the three toluidines is put forward with reserve.

2 : 5 - Dibromo - 4 - hydroxy - 3 : 6 - dimethylbenzyl bromide reacts readily with aromatic amines, giving mainly nuclear benzyl derivatives; simultaneously, di - 2 : 5 - dibromo - 4 - hydroxy - 3 : 6 - dimethylphenyl - methane and the polymerised 2 : 5-dibromo-3 : 6-dimethyl-4-methylenebenzoquinone, $O{:}C_6Br_2Me_2{:}CH_2$, are frequently obtained. Explanation of this reaction, which has been investigated with many amines, is difficult, since the mechanism of the change is unknown. All ring-methylated dialkylanilines condense readily with the benzyl bromide. The nature of the radical attached to the nitrogen atom appears unimportant. Methoxy-, hydroxy-, and amino-groups in the amine do not hinder normal condensation, whereas this appears to be generally hindered by the presence of chloro-, bromo-, aldehydic, or carboxymethyl substituents, except in certain cases. With substituted pyrazoles, condensation occurs, but not with indazole. The position of the substituents has the same effect on the condensation of amines with the benzyl bromide as on the coupling with diazonium compounds or the formation of nitroso-derivatives, whereas the nature of the substituent has a different effect in the various processes.

The following condensation *products* are obtained from 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl-bromide : with *o*-anisidine, m. p. 161—162°, *p*-anisidine, m. p. 141—142°, 6-chloro-*o*-toluidine, m. p. 191·5—192·5°, and from the tertiary amines, methylethylaniline (as *hydrobromide*, m. p. 140°), diallylaniline (as *picrate*, m. p. 182°), dimethyl-*o*-toluidine (as *hydrochloride*), dimethyl-*m*-toluidine, m. p. 144°, dimethyl-*p*-toluidine, m. p. 149—151·5°, dimethyl-*o*-anisidine, m. p. 120—121°, dimethyl-*as*-*m*-xylidine, dimethyl-*p*-xylidine, m. p. 147°, dimethyl-*as*-*o*-xylidine, m. p. 144—145°, dimethyl-*s*-*m*-xylidine (as *hydrochloride*, m. p. 207—209°), dimethyl-α-naphthylamine, m. p. 173°, diethyl-α-naphthylamine (as *hydrochloride*, m. p. 225°), *m*-bromodimethylaniline, m. p. 136—137°, *m*-hydroxydimethylaniline, m. p. 154·5—155°, and *m*-aminodimethylaniline. 3-Methylpyrazole yields two 2 : 5-dibromo-4-hydroxy-3 : 6-dimethylbenzyl *derivatives*, m. p. 183° and 206°, respectively. The corresponding 3 : 5-*dimethyl*- (m. p. 248—249°), 5 : 3-*phenylmethyl*- (m. p. 181—183°), and 3 : 5-*diphenyl-pyrazole* (m. p. 165—167°) compounds are described. p-*Nitrobenzeneazo*-N-*dimethyl*-m-*toluidine*, m. p. 179·5—180·5°, p-*nitrobenzeneazo*-N-*dimethyl*-o-*anisidine*, m. p. 132—133°, *benzeneazo*-m-*bromo*-N-*dimethylaniline*, m. p. 92—93°, and m-*bromo*-p-*nitrosodimethylaniline hydrochloride*, m. p. 163° (decomp.), have been prepared. H. Wren.

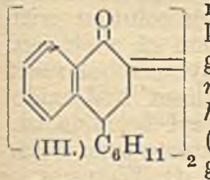
Amidines of the holocaine type. II. Ester-substituted amidines. A. J. Hill and M. V. Cox (J. Amer. Chem. Soc., 1926, 48, 3214—3219; cf. A., 1926, 516).—Substituted amidines of the types $CR({:}N{\cdot}C_6H_4{\cdot}OEt)(NH{\cdot}C_6H_4{\cdot}CO_2Et)$ and $CR({:}N{\cdot}C_6H_4{\cdot}CO_2Et)(NH{\cdot}C_6H_4{\cdot}CO_2Et)$ are obtained in good yields by treating an appropriate acylamino-derivative with phosphorus pentachloride in benzene in the cold, and treating the resulting chloride with an amine. The product is best isolated by evaporating off the benzene, dissolving the residue in just sufficient alcohol, and precipitating the amidine with excess of concentrated ammonia. An analogous method gave 70—95% yields of holocaine and its ethyl, propyl, and *iso*butyl homologues. Substituted *amidines* were prepared from ethyl *p*-aminobenzoate and the following acylamines: acetyl-*p*-phenetidine (m. p. 142°; *hydrochloride*, m. p. 182—183°); propionyl-*p*-phenetidine (m. p. 146°; *hydrochloride*, m. p. 147—148°); butyryl-*p*-phenetidine (m. p. 97°); *iso*valeryl-*p*-phenetidine (m. p. 106°); *n*-valeryl-*p*-phenetidine (m. p. 91°), and benzoyl-*p*-phenetidine (m. p. 117; *hydrochloride*, m. p. 220°); from ethyl aminosalicylate and acetyl-*p*-phenetidine (m. p. 103°; *hydrochloride*, m. p. 152°); and from ethyl *p*-aminobenzoate and ethyl *p*-acetamidobenzoate (m. p. 156°; *hydrochloride*, m. p. 214—215°) and ethyl *p*-propionamidobenzoate (m. p. 135°; *hydrochloride*, m. p. 184—185°). *Ethyl* p-*propionamido*-

benzoate, m. p. 111°, *ethyl* p-*butyramidobenzoate*, m. p. 87°, and n-*valeryl*-p-*phenetidine*, m. p. 92°, are described.
F. G. Willson.

Derivatives of thymol. R. Delaby (Bull. Soc. chim., 1926, [iv], 39, 1612—1618).—Reaction of methylene bromide with the sodium derivative of thymol in alcoholic solution gives a 43% yield of odourless, crystalline dithymoxymethane, m. p. 52° (Arnhold, A., 1887, 911, gives m. p. 36°). A lower yield is obtained using methylene sulphate in alcoholic solution, and a by-product is formed, thymoxyethoxymethane. αγ-*Dithymoxypropane*, obtained in 53% yield by reaction of trimethylene bromide with the sodium derivative of thymol in alcoholic solution, has b. p. 249·5°/21 mm., d_4^{17} 0·9944; n_D^{18} 1·5326.
M. Clark.

Homologous naphthols, their oxidation and hydrogenation products. B. Alberti (Annalen, 1926, 450, 304—318).—α-Naphthol and *cyclo*hexanol condense under the influence of zinc chloride to give a resinous product containing 4-cyclo*hexyl*-α-*naphthol* (I), m. p. 142—143°, b. p. 228°/14·5 mm., 11% of theoretical, and 2-cyclo*hexyl*-α-*naphthol* (II), m. p. 99—100°, b. p. 218°/14 mm., 15% of theoretical. Concentrated sulphuric acid containing nitrous acid dissolves both to a deep green solution, which becomes colourless on dilution in the case of (I), but red in that of (II). The *sodium* salt of (I) crystallises from dilute alkali; that of (I) is more soluble.

Oxidation of (I) with ferric chloride, ferricyanide, or chromic acid yields "*bis*-4-cyclo*hexylnaphthalene-indigo*" (4 : 4′-*di*cyclo*hexyl*-2 : 2′-*dinaphthyl*-1 : 1′-*quinone*) (III), dark violet crystals with red reflex, m. p. 192°. Similar oxidation, or keeping in the air for several months, gives from (II) "*bis*-2-cyclo*hexyl-naphthalenelignone*" (3 : 3′-*di*cyclo*hexyl*-1 : 1′-*dinaphthyl*-4 : 4′-*quinone*), (IV), ruby-red crystals with golden-green reflex, m. p. 199°. Both these substances are reduced only very slowly by hyposulphite; (IV) is reduced by zinc and acetic acid to the corresponding "*dihydrolignone*," m. p. 216—218° (not sharply), which is also obtained during the above-mentioned oxidation by air.


(III.)

Catalytic hydrogenation of a solution of (I) in hexahydrotoluene at 210° and 27 atm. for 40 min. gives 4-cyclo*hexyldecahydro*-α-*naphthol*, m. p. 166—167°, with other products. If the total hydrogenation product is dissolved in decahydronaphthalene and heated with zinc chloride, water is eliminated (the clouding due to the separation of which may be used as a test for the secondary hydroxyl group) and 1-cyclo*hexyl*-Δ^4-*octahydronaphthalene*, b. p. 162—163°/12 mm., d_4^{20} 0·9546, n_D^{20} 1·51754, is obtained. Hydrogenation of this at 160° and 25 atm. gives α-cyclo*hexyldecahydronaphthalene*, b. p. 161—162·5°/12 mm., d_4^{20} 0·9438, n_D^{20} 1·49951.

Similar treatment of (II) at 180° and 25 atm. for 30 min. yields a product from which 2-cyclo*hexyldecahydro*-α-*naphthol*, m. p. 156—157°, is obtained; and at 215°, 26 atm., and 25 min., employing a regenerated catalyst, a second form, m. p. 120—121°. Treatment of this with zinc chloride and rehydrogenation gives β-cyclo*hexyldecahydronaphthalene*, b. p. 160·5—162°/12 mm., d_4^{20} 0·9315, n_D^{20} 1·49951.

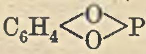
β-Naphthol condensed with *cyclo*hexanol gives 1-cyclo*hexyl*-β-*naphthol* (V), m. p. 107—108°, and 6-cyclo*hexyl*-β-*naphthol* (VI), m. p. 161—162°. The former colours nitrous sulphuric acid green, which changes to brown, and the latter deep red, changing to dark brown. Aërial oxidation of (V) yields a yellow *substance*, $C_{16}H_{18}O_3$, sintering at 153°, m. p. 162—163°, which liberates iodine from potassium iodide, is rapidly coloured an intense yellow by insolation, and readily resinifies. In the hydrogenation of (V) as before, intermediate products could not be isolated; the product of the series of operations, β-*cyclo*hexyldecahydronaphthalene, had b. p. 160·5—162°/12 mm., d_4^{20} 0·9448, n_D^{20} 1·50559. From (VI) by hydrogenation, 6-cyclo*hexyldecahydro*-β-*naphthol*, m. p. 114—115°, is obtained, from which the β-*cyclo*hexyldecahydronaphthalene has b. p. 160·5—162·5°/12 mm., d_4^{20} 0·9282, n_D^{20} 1·49835.

ar-Tetrahydro-β-naphthol on condensation with *cyclo*hexanol gives ar-*tetrahydro*-3-cyclo*hexyl*-β-*naphthol* (VII), m. p. 103°, b. p. 209°/7·5 mm., the distillate being a resin which crystallises very slowly. Sodium nitrite added to a sulphuric acid solution gives a brown colour, which at once becomes lighter; if a little water is added, the liquid turns an intense sky-blue, and a blue amorphous substance is deposited, soluble in acetic or sulphuric acid to give a red colour and a strong fluorescence. Catalytic hydrogenation of (VII) gives a resin, b. p. 182—184·5°/7·5 mm., which acetylates to a mixture, m. p. 117—118°, of stereoisomeric 3-cyclo*hexyldecahydro*-β-*naphthyl acetates*, from which 3-cyclo*hexyldecahydro*-β-*naphthol* is isolated in two forms: A, plates, m. p. 99—100°; B, tables, m. p. 116—117°, somewhat less soluble than A in light petroleum. Dehydration by zinc chloride gives 3-cyclo*hexyl*-Δ^2-*octahydronaphthalene*: from A, b. p. 163—164°/13 mm., d_4^{20} 0·9422, n_D^{20} 1·51029; from B, b. p. 161—164°/12 mm., d_4^{20} 0·9454, n_D^{20} 1·49960.
E. W. Wignall.

Diphenyl series. III. Derivatives of 4-hydroxydiphenyl. F. Bell and J. Kenyon (J.C.S., 1926, 3044—3050).—4-Hydroxydiphenyl reacts with nitrous acid, yielding 3-nitro-4-hydroxydiphenyl; with diazotised aniline, forming 2-*hydroxy*-5-*phenylazobenzene*, m. p. 129°, which on reduction with sodium hyposulphite gives 3-amino-4-hydroxydiphenyl; with chloroform and aqueous sodium hydroxide, furnishing 4-*hydroxy*-3(?)-*aldehydodiphenyl*, m. p. 102° (*phenylhydrazone*, m. p. 210°). These results are claimed to indicate that there is no permanent linking between the 4- and 4′-positions in diphenyl (see Turner, A., 1923, i, 1085).

4-Methoxydiphenyl on nitration with fuming nitric acid in acetic anhydride solution yields mainly 3-*nitro*-4-*methoxydiphenyl*, m. p. 91—92°, together with 4′-*nitro*-4-*methoxydiphenyl*, m. p. 111°. The identity of these nitro-compounds was established by methylation of 3-nitro-4-hydroxydiphenyl and 4′-*nitro*-4-*hydroxydiphenyl*, m. p. 203°. The latter compound was obtained from diazotised 4′-nitro-4-aminodiphenyl. Further nitration of these isomeric nitro-methoxydiphenyls yields 3 : 4′-*dinitro*-4-*methoxydiphenyl*, m. p. 171°. 3 : 5-*Dinitro*-4-*methoxydiphenyl* has m. p. 137—138°. Nitrous acid converts 4′-nitro-4-hydroxydiphenyl into 3 : 4′-*dinitro-4-hydroxydiphenyl*, m. p. 172° (p-*toluenesulphonate*, m. p. 147—148°), whilst bromine converts it into (3 : 5 ?)-*dibromo-4′-nitro-4-hydroxydiphenyl*, m. p. 232—234°. 4-p-*Toluenesulphonyloxydiphenyl*, m. p. 177°, on nitration gives 4′-*nitro*-4-p-*toluenesulphonyloxydiphenyl*, m. p. 156—158°.

Attempts to resolve diphenic acid and methyl hydrogen diphenate have been unsuccessful, indicating that free rotation of the two nuclei in diphenyl is possible in lightly-substituted diphenyl derivatives. The hypothesis is put forward that when free rotation is inhibited, the two nuclei adopt a configuration in which they have a common axis, but are not co-planar. H. Burton.

Aromatic derivatives of the hypothetical orthophosphoric acid $P(OH)_5$. L. Anschütz and W. Brocker (Ber., 1926, 59, [*B*], 2848—2849; cf. Zetzsche and Aeschlimann, A., 1926, 1225).—The following substances are obtained by the action of phosphorus pentachloride on pyrocatechol in an indifferent solvent; *phosphorus pyrocatechyl trichloride*,  $C_6H_4{<}^{O}_{O}{>}PCl_3$, b. p. 132°/11 mm., m. p. 61—62°, which is converted by methyl alcohol into *methyl* o-*phenylene phosphate*, b. p. 148°/11 mm. (corresponding *ethyl* ester, b. p. 157°/12 mm.); *phosphorus dipyrocatechyl monochloride*, unimolecular *form*, m. p. 166—168°, b. p. 194°/11 mm., bimolecular *variety*, m. p. (indef.) 180—210° (decomp.); o-*phenylene orthophosphate*, $P_2(O_2C_6H_4)_5$, m. p. 200—240° (decomp.). *Pentaphenyl orthophosphate*, $P(OPh)_5$, m. p. 46—52°, is obtained by the action of phenol on phosphorus triphenoxydichloride. H. Wren.

Condensation of resorcinol with ethylene dicyanide [succinonitrile]. J. Murai (Sci. Rep. Tôhoku, 1926, 15, 675—678).—See A., 1926, 951.

Alleged nitration of *S*-methylthioguaiacol. Criticism. A. Pollard and R. Robinson (J.C.S., 3090—3093).—Nitric acid acts on *S*-methylthioguaiacol, giving 2-methoxyphenyl methyl sulphoxide, and then 5-*nitro-2-methoxyphenyl methyl sulphoxide*, m. p. 144—145°. These results are contrary to the statement of Holmes, Ingold, and Ingold (A., 1926, 947). Hydrolysis of 5-nitro-2-methoxyphenyl methyl sulphoxide or the corresponding sulphone, m. p. 149—150°, with boiling aqueous sodium hydroxide gives 5-*nitro-2-hydroxyphenylmethylsulphone*, m. p. 167°, which on further nitration yields 3 : 5-*dinitro-2-hydroxyphenylmethylsulphone*, m. p. 166° H. Burton.

Action of nitric acid on *S*-methylthioguaiacol. Correction. C. K. Ingold and E. H. Ingold (J.C.S., 1926, 3093—3094).—The compound previously described (A., 1926, 947) as 6-nitro-2-methoxyphenylmethylsulphone, m. p. 144—145°, is shown to be 5-nitro-2-methoxyphenyl methyl sulphoxide (cf. preceding abstract). The action of nitric acid on *S*-methylthioguaiacol may be to convert it first into the sulphoxide, or nitration may occur through the thionium nitrate with subsequent oxidation. H. Burton.

Sinomenol and disinomenol. K. Goto (Proc. Imp. Acad. Tokyo, 1926, 2, 414—416; cf. A., 1926, 1160).—Mol. wt. determinations of the low-melting (*A*) and high-melting (*B*) series of dibenzoyl-, diacetyl-, and dimethyl-sinomenols (*diacetylsinomenol*-B has m. p. 285°, and *dimethylsinomenol*-A has m. p. 122°) show that the members of series *B* have approximately the same empirical formulæ as, but twice the mol. wt. of those of series *A*. The colour reactions of each series in sulphuric acid are characteristic, and compounds of series *B* are sparingly soluble in methyl alcohol. The author regards sinomenol-*B* as disinomenol (annexed formula), which is produced from sinomenol (m. p. 279°) by atmospheric oxidation during the action of 66% potassium hydroxide on sinomenine. The amount of disinomenol formed is almost trebled by doubling the duration of alkaline fusion. Dibenzoylsinomenol-*B* cannot be converted into the *A*-form. J. M. Gulland.

Side-chain oxidations by means of nitro-compounds. L. T. Smith and R. E. Lyons (J. Amer. Chem. Soc., 1926, 48, 3165—3167).—When benzyl alcohol (10 g.) is heated with nitrobenzene (12 g.) and sodium hydroxide (10 g.) for 4 hrs. at 138—140° in an autoclave, benzoic acid is obtained in 86·8% yield, together with an equivalent amount of azobenzene. *o*-Nitrotoluene reacts to a rather less extent under the same conditions. Reduction of the proportion of alkali present, or addition of water, reduces the extent of reaction. *m*-Dinitrobenzene reacts with benzyl alcohol in alkaline solution, with evolution of ammonia and formation of a charred mass, whilst picric acid and benzyl alcohol react explosively when mixed with sodium hydroxide. Toluene, benzyl chloride, and benzyl bromide are not oxidised by nitrobenzene or *o*-nitrotoluene under the above conditions. F. G. Willson.

Removal of the amino-group from aromatic amino-alcohols. M. Tiffeneau and J. Lévy (Compt. rend., 1926, 183, 969—971).—When β-amino-α-phenyl-*n*-butyl, β-amino-α-phenyl-γ-methyl-*n*-butyl, β-amino-α-phenyl-*n*-amyl, and β-amino-α-phenyl-*n*-hexyl alcohols are treated with nitrous acid, phenyl *n*-propyl ketone, phenyl β-methyl-*n*-propyl ketone, phenyl *n*-butyl ketone, and phenyl *n*-amyl ketone, respectively, are formed. Intermediate formation of unsaturated compounds is probable, but no transposition of the phenyl group occurs. L. F. Hewitt.

Coloured salts of the di- and tri-phenylmethane series. III. Basic coloured salts of diphenylmethane derivatives in which the central carbon atom is united to hydrogen or an aliphatic residue. W. Madelung and F. Völker (J. pr. Chem., 1927, [ii], 115, 24—44).—The formation and reactions of coloured salts obtained from *pp*′-tetramethyldiaminobenzhydrol, the corresponding diphenylalkylcarbinols, and the ethylene derivatives obtained from them, have been studied with the object of elucidating their constitutions, and their relationships are discussed from the point of view of the authors' colour theory (Madelung, A., 1925, i, 1459; this vol., 54). *pp'*-Tetramethyldiaminobenzhydrol forms a blue crystalline *perchlorate*, $C_{17}H_{21}O_4N_2Cl$, and a *double zinc chloride*, $C_{17}H_{21}N_2Cl_3Zn$. The action of magnesium alkyl halides on *pp'*-tetramethyldiaminobenzophenone yields, not the carbinol, but the corresponding ethylene derivative in all cases except with *tert.*-butyl chloride, which yields pp'-*tetramethyldiaminodiphenyl*-tert.-*butylcarbinol*, m. p. 147°. Benzyl chloride yields as-pp'-*tetramethyldiaminodiphenylstyrene*, m. p. 129°, as the chief product, together with pp'-*tetramethyldiaminodiphenylbenzylcarbinol*, m. p. 173°. Dilution with water of the solutions of the carbinol in acids precipitates the styrene derivative. The same coloured solutions are obtained when a solution of either a *pp'*-tetramethyldiaminodiphenylalkylcarbinol or its corresponding ethylene derivative in acetic acid or alcohol is treated with less than one equivalent of a mineral acid. Addition of water to these solutions first decolorises them and ultimately precipitates the ethylene base. The addition of 0·33 mol. of a 0·5% alcoholic solution of perchloric acid to a hot, saturated solution of *as-pp'*-tetramethyldiaminodiphenylethylene yields a blue *perchlorate* of composition 3B,1A (B=base, A=acid). On the other hand, the coloured solutions obtained by the action of oxidising agents, or sodium nitrite, on solutions of diphenylethylene bases (cf. Lemoult, A., 1909, i, 836) retain their colour on dilution with water, and on addition of alkali the corresponding carbinol is precipitated. Thus *αα'-pp'*-tetramethyldiaminodiphenylpropylene, treated in acetic acid solution with sodium nitrite, yields a coloured solution from which the green carbonium *perchlorate* is precipitated on treatment with perchloric acid. This is a true ethylene derivative of the constitution $[CR_2{\cdot}CH{:}CH_2]ClO'_4$ ($R=C_6H_4{\cdot}NMe_2$), from which is obtained the corresponding colourless *carbinol* $CR_2(CH{:}CH_2){\cdot}OH$, m. p. 160°. Similar treatment of *pp'*-tetramethyldiaminodiphenylstyrene yields pp'-*tetramethyldiaminodiphenylhydroxybenzyl perchlorate*, $[CR_2{\cdot}CHPh{\cdot}OH]ClO'_4$, from which is obtained the corresponding αα'-pp'-*tetramethyldiaminodiphenyl* β-*phenyl glycol*, m. p. 141°. Benzhydrol in concentrated sulphuric or perchloric acid solution exhibits halochromism, and dilution with water yields the unchanged carbinol, whilst diphenylmethylcarbinol yields a yellow solution from which the diphenylethylene is precipitated on dilution, the latter compound itself behaving in a similar manner.

J. W. Baker.

Catalytic hydrogenation of aromatic acids and their salts. V. N. Ipatiev and G. A. Rasuvaev (J. Russ. Phys. Chem. Soc., 1926, 58, 122—128).—The hydrogenation of lithium, calcium, barium, zinc, ferrous, and nickel benzoates, as also of the sodium salts of salicylic, *p*-hydroxybenzoic, and mandelic acids, was carried out by Ipatiev's method (A., 1908, ii, 342) in the solid state, nickel sesquioxide being used as catalyst. The alkali and alkaline-earth salts hydrogenated smoothly and rapidly, giving a 60—70% yield of hexahydrobenzoic acid, but the ferrous, nickel, and zinc salts decomposed with the formation of an orange sublimate. The residual gases contained more than 90% of hydrogen. Salicylic and *p*-hydroxybenzoic acids gave 80% yields of *cyclo*hexanol, through loss of the carboxyl group. The residual gas contained much methane. Mandelic acid gave, with decomposition, a 40% yield of phenylacetic acid, with traces of *cyclo*hexylacetic acid, *i.e.*, in this case it is the hydroxyl group which is removed.

M. Zvegintzov.

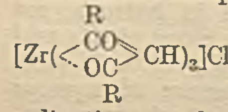
Stereochemistry of hydronaphthalenes. I. Decahydro-β-naphthamides. F. W. Kay and N. Stuart (J.C.S., 1926, 3038—3041).—Decahydro-β-naphthoic acid should exist in four racemic forms, two being derivatives of the *cis*-modification, and two of the *trans*-modification, assuming Mohr's theory of the isomerism of the decahydronaphthalenes to be correct. Reduction of *ar*-tetrahydro-β-naphthoic acid with sodium and amyl alcohol at 150° gave a decahydro-acid, which after conversion through the chloride into the amide was examined for isomeric constituents. An amide, m. p. 195—196° (cf. Borsche and Lange, A., 1924, i, 32), was obtained, together with a small quantity of another amide, m. p. 171—174°. When sodium and ethyl alcohol were used for the reduction, two amides, m. p. 169—171° and m. p. 139—140°, were obtained.

H. Burton.

α-Selenobenzoic acid. Q. Mingoia (Gazzetta, 1926, 56, 835—839).—Passage of a current of dry hydrogen selenide through an ethereal solution of magnesium ethyl bromide (cf. A., 1926, 388) results in the formation of ethane and magnesium bromohydroselenide. The latter is readily decomposed by water, giving hydrogen selenide and magnesium hydroxybromide, and may be isolated in the form of the additive product; it yields with *pyridine*, $MgBr{\cdot}SeH,2C_5H_5N$ (cf. Oddo, *ibid.*, 1904, i, 920; 1907, i, 549, 668). The action of benzoyl chloride on magnesium bromohydroselenide gives *α-selenobenzoic acid*, Ph·COSeH, which is moderately stable and obtainable from methyl alcohol in lustrous, red crystals, m. p. 133°. Some of the esters of this acid were described by Taboury (*ibid.*, 1906, i, 834). Evaporation of the acid in presence of aqueous ammonia results in decomposition, selenium, ammonium benzoate, and ammonium hydroselenide being formed.

T. H. Pope.

Addition and substitution reactions with zirconium chloride. G. Jantsch (J. pr. Chem., 1927, [ii], **115**, 7—23).—Additive and substitution products of zirconium chloride with various aldehydes, ketones, esters, and phenols, analogous to those obtained from thorium chloride (Jantsch and Urbach, A., 1919, i, 566), have been prepared, the rigid exclusion of moisture being necessary. Additive compounds (1 mol. of zirconium chloride and 2 mols. of the secondary component) could be isolated only at low temperatures, since the elimination of hydrogen chloride to form substitution products occurs with much greater ease than in the case of the thorium compounds. As in the earlier investigation, substitution occurs in stages which depend mainly on the temperature. The action of acetophenone and benzophenone on zirconium chloride in ethereal suspension at −5° yields the *additive compounds* of the type $ZrCl_4,2Ph{\cdot}COR$. Benzoic acid in boiling benzene solution yields the *tetrabenzoate*, $Zr(CO_2Ph)_4$, in addition to the compounds obtained by Rosenheim and Hertzmann (A., 1907, ii, 271), whose observations are confirmed. Phenol at $-10°$ yields an *additive compound* which is too unstable to be isolated, and in boiling ether yields the *chlorophenoxide*, $ZrCl(OPh)_3$. In boiling benzene, complete substitution of the chlorine occurs to yield the *tetraphenoxide*, $Zr(OPh)_4$. Acetylacetone in light petroleum at $-10°$ yields an unstable *additive compound*, whilst in ether at the ordinary temperature, the *diacetylacetone chloride*, $ZrCl_2(C_5H_7O_2)_2$, is obtained, and in boiling benzene the trisacetylacetone chloride obtained by Morgan and Bowen (*ibid.*, 1924, i, 1079). In anhydrous media the tetra-acetylacetone compound (Biltz and Clinch, *ibid.*, 1904, i, 705) could not be obtained. Ethyl lactate and methyl mandelate yield unstable *additive compounds* at $-10°$, whilst in ether the *dichlorides* of the type $ZrCl_2[CHR(CO_2Me)O]_2$ ($R=Me$ and Ph, respectively) are obtained. Salicylaldehyde yields an additive compound, and in boiling ether the dichloride obtained by Rosenheim and Hertzmann (*loc. cit.*). Higher substitution products could not be obtained. Similar compounds were obtained from methyl salicylate, and in addition the *trismethyl salicylate chloride*, $ZrCl[C_6H_4(CO_2Me)O]_3$, m. p. 222—225°, was obtained in boiling benzene. In boiling xylene, hydrolysis occurs, yielding the *compound* $Zr({\cdot}O{\cdot}C_6H_4{\cdot}CO_2)_2$. Pæonol in ether at $-10°$ yields an *additive compound*, in boiling ether the disubstitution *compound* $ZrCl_2R_2$, m. p. 185° (decomp.), and in boiling benzene the trisubstituted *compound* $ZrClR_3$, where $R=C_6H_3(OMe)(COMe){\cdot}O{\cdot}$. Since with all compounds in which the hydroxyl group is in the β- or γ-position to the carbonyl group it was found impossible to form tetrasubstitution products, it is assumed that the trisubstituted compounds are co-ordination complexes of the type



$[Zr(<\overset{\overset{R}{|}}{CO}\!\!>CH)_3]Cl$ ($\underset{\underset{R}{|}}{OC}$), in which the metal has a co-ordination number of 6. With benzoin only an additive compound could be obtained.

J. W. BAKER.

Chlorides and amides of hexahydrodiphenyl-*o*-carboxylic acid. J. RANEDO and A. LÉON (Anal. Fís. Quím., 1926, 24, 552—559; cf. A., 1925, i, 665).—Hexahydrodiphenyl-*o*-carboxylic acid, obtained by reduction of diphenyl-*o*-carboxylic acid with sodium and amyl alcohol, has m. p. 103—105°, whilst the isomeride obtained by catalytic hydrogenation has m. p. 102—103°. The former compound yields a crystalline acid *chloride*, m. p. 85—86°, and a crystalline *amide*, m. p. 137°. The other isomeride yields a *chloride*, b. p. 184—186°/38 mm., and a crystalline *amide*, m. p. 101—103°.

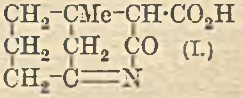
G. W. ROBINSON.

Reactivities of some tertiary bromides. W. H. CAROTHERS (J. Amer. Chem. Soc., 1926, 48, 3192—3197).—*Methyl diphenylbromoacetate* (I), m. p. 38·5—38·8° (decomp. when kept), is obtained by the action of phosphorus tribromide (43·3 g.) and bromine (25·6 g.) on methyl benzilate (38·5 g.). When boiled with potassium thiocyanate in acetone, it affords *methyl diphenylthiocyanoacetate*, m. p. 82·5—83·5°. Bromination of dimethyl phenylmalonate in chloroform yields *dimethyl phenylbromomalonate* (II), b. p. 170—174°/8 mm., m. p. 45·5—46·5°. Similar bromination of tricarbomethoxymethane yields *bromotricarbomethoxymethane* (III), m. p. 50·5—51°, b. p. 116—117°/5 mm. The relative reactivities of (I), (II), (III), and triphenylmethyl bromide (IV) towards silver nitrate in acetonitrile and silver nitrate in absolute methyl alcohol are in the order (IV)>(I)>(II)>(III), whilst the relative reactivities towards potassium thiocyanate in absolute acetone are in the order (IV)>(III)>(I)>(II).

F. G. WILLSON.

Manufacture of intermediates [nitro- and amino-4-hydroxy-3-carboxydiphenyl sulphide] and [azo] dyes. BRITISH DYESTUFFS CORP., LTD., K. H. SAUNDERS, and M. MENDOZA.—See B., 1927, 8.

Formation and stability of associated alicyclic systems. III. Change from "*meta*"- to "*para*"-bridged rings. E. H. FARMER and J. ROSS (J.C.S., 1926, 3233—3240; cf. A., 1904, i, 509; 1926, 66, 834).—1-Methyl-Δ^1-*cyclo*hexen-3-one condenses with ethyl sodiocyanoacetate, giving *ethyl* 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate*, b. p. 197°/2 mm. (*semicarbazone*, m. p. 166°), together with 1-*methyl*cyclo*hexenylidene*-3-*cyanoacetic acid*, m. p. 183° (*methyl* ester, m. p. 60°). *Methyl* 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate*, b. p. 185°/2 mm. (*semicarbazone*, m. p. 183°), and the ethyl ester, on hydrolysis with aqueous sodium carbonate, yield 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetic acid*, m. p. 106°. This acid is converted by hot hydrochloric acid into *propane*-$^{1:3}$II$^{2:4}$-6-*keto*-4-*methyl*-3 : 4 : 5 : 6-*tetrahydropyridine*-5-*carboxylic acid* (I), m. p. 181° (*bromo*-derivative, m. p. 186°).


(I.)

On complete fission with aqueous potassium hydroxide, (I) yields β-methylpimelic-β-acetic acid, whilst partial fission produces 1-*methyl*cyclo*hexan*-3-*one*-1-*malonamic acid*, m. p. 151°, and β-methylpimelic acid β-acetamide. The latter compound, on treatment with hot dilute hydrochloric acid, passes into β-*methylglutarimide*-β-*butyric acid*, m. p. 139°, identical with the substance obtained by passing dry ammonia through the molten anhydride of β-methylpimelic-β-acetic acid, followed by treatment with hot dilute hydrochloric acid.

H. BURTON.

Acidity and isomerism of thioglycollic acid derivatives. O. BEHAGHEL (J. pr. Chem., 1926, [ii], 114, 287—312).—In general, introduction of oxygen or sulphur into carboxylic acids greatly increases their strength (cf. A., 1889, 818; 1894, i, 325; 1902, ii, 643; 1909, i, 286; 1925, i, 397). Replacement of carbonyl or hydroxylic oxygen by sulphur increases the acidity, but in the case of ethereal oxygen, the opposite effect is observed. Thus, derivatives of phenoxyacetic acid are 2·4—3·6 times as strong as the corresponding phenylthiolacetic acids. The following new values are recorded for the dissociation coefficients [*K* (acetic acid)=0·18] of some derivatives of phenoxyacetic acid: *o*-methyl-, 6·819; *m*-methyl-, 6·632, *p*-methyl-, 7·026; *o*-methoxy-, 5·845; o-*chloro*-, m. p. 145—146°, 10·24; *p*-chloro-, 9·617; and of phenylthiolacetic acid, 2·971: *o*-methyl-, 2·819; m-*methyl*-, m. p. 103—104°, 2·728; *p*-methyl-, 2·464; o-*methoxy*-, m. p. 114—115°, 1·822; *o*-chloro-, 3·04; *p*-chloro-, 2·41; *o*-nitro-, 5·546; *p*-nitro-, 6·927; o-*methylthiol*-, m. p. 120°, 1·81; p-*methylthiol*-, m. p. 106—107°, 1·767; *p*-amino-, 0·1403; p-*ethyldithiocarbonato*-, m. p. 101—102°; p-*thiol*-, m. p. 108·5—109·5°; also *p*-phenylenedioxydiacetic acid, 37·64; bis-p: p′-*thiophenylthiolacetic acid*, $(\cdot S\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H)_2$, m. p. 166·5°; and p-*phenylenedithioldiacetic acid*, 4·507. The last occurs in two modifications, (*a*) colourless, m. p. 210—214°, (*b*) yellow, m. p. 214°, after sintering at 208—209°. Microscopical examination of *o*-methylthiolphenylthiolacetic acid shows that this also is polymorphic. H. E. F. Notton.

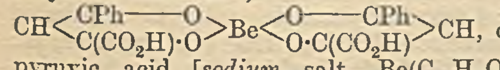
Synthesis of 6-chloro-3-hydroxybenzoic acid. V. I. Minaev (J. Russ. Phys. Chem. Soc., 1926, 58, 115—118).—The method consists in nitrating *o*-chlorobenzoic acid, reducing, diazotising, and decomposing the diazo-compound by heat in aqueous solution. The author discusses the various conditions of diazotisation and decomposition, so as to avoid resinification. If sulphuric acid is used, the diazo-solution, prepared at 5°, must be added very slowly to much water at 80°, when a 60% yield of pure product, m. p. 173°, is obtained. Using hydrochloric acid, the water should be at 60°, then cautiously heated to 90°. The yield is 70%.

M. Zvegintzov.

Carbylamines. XV. Reactions with aliphatic carbylamines. M. Passerini (Gazzetta, 1926, **56**, 826—829; cf. A., 1926, 952).—The reactions of the aromatic carbylamines already described may be extended to the aliphatic carbylamines. *Benzoylmandelylpropylamide* [*α-benzoyloxyphenylacetpropylamide*], Ph·CO·O·CHPh·CO·NHPr, prepared by the interaction of propylcarbylamine, benzaldehyde, and benzoic acid in ethereal solution, m. p. 117—119°, on hydrolysis yields benzoic acid and *mandelylpropylamide*, OH·CHPh·CO·NHPr, m. p. 64—65°. *Trichlorolactylpropylamide*, $CCl_3\cdot CH(OH)\cdot CO\cdot NHPr$, obtained from chloral hydrate and propylcarbylamine, has m. p. 116—118° (decomp. and gas), and yields trichlorolactic acid and propylamine on hydrolysis.

T. H. Pope.

Optical activity dependent on co-ordinated beryllium, copper, and zinc. W. H. Mills and R. A. Gotts (J.C.S., 1926, 3121—3131).—The beryllium derivative,



$$CH{<}\begin{matrix}CPh\text{——}O\\C(CO_2H)\cdot O\end{matrix}{>}Be{<}\begin{matrix}O\text{——}CPh\\O\cdot C(CO_2H)\end{matrix}{>}CH$$

, of benzoylpyruvic acid [*sodium* salt, $Be(C_{10}H_6O_4Na)_2,H_2O$] forms a crystalline brucine salt showing mutarotation in chloroform or alcoholic solution (cf. A., 1925, i, 46). Anhydrous *brucine* d-*berylliobenzoylpyruvate* [hydrated salt, $Be(C_{10}H_7O_4,C_{23}H_{26}O_4N_2)_2,8H_2O$] has m. p. 212—215° (decomp.). It gives $[\alpha]^{20}_{5461}$ +25·06° ⟶ +5° in chloroform and +39·9° ⟶ +13·1° in alcohol. *Brucine* l-*berylliobenzoylpyruvate* gives $[\alpha]^{20}_{5461}$ −11·8° ⟶ +5° in chloroform. The mutarotation was proved to be due to the disappearance of an unstable optical activity associated with the co-ordinated beryllium, since the greater part of the brucine could be removed (by precipitation as hydrochloride from absolute-alcoholic solution) without a corresponding diminution of the optical activity of the solution. *Dimethylammonium berylliobenzoylpyruvate*, thus obtained, has m. p. 95—96°. The strychnine salt of the copper derivative of benzoylpyruvic acid and the brucine salt of the zinc derivative show analogous mutarotation in chloroform solution, and variation takes place, as in the case of the beryllium compounds, in accordance with the unimolecular law. It is concluded that co-ordinated copper and zinc, as well as beryllium, can give rise to optical activity, and that, in the cases considered, the four oxygen atoms are disposed tetrahedrally about the metallic atom, although the valencies of copper and zinc are differently directed in compounds in which their co-ordination number is six.

Strychnine cupribenzoylpyruvate, $+4H_2O$, has m. p. 97—98° (decomp.). *Brucine zincibenzoylpyruvate* decomposes at 185°. M. Clark.

Reactions with fulminic acid. I. Nitriles from naphthols and 2-methylindole. M. Passerini and B. Grulis (Gazzetta, 1926, 56, 829—835).—Although fulminic acid is analogous in structure to the carbylamines, neither the acid nor its mercury salt reacts with α- or β-naphthol, but the additive compounds formed by mercury fulminate with potassium cyanide, potassium iodide, and ammonium thiocyanate readily react, giving good yields of the nitriles of α-naphthol-2-carboxylic and β-naphthol-1-carboxylic acids with α- and β-naphthols, respectively. Similarly, the additive product of mercury fulminate with potassium iodide or cyanide reacts with 2-methylindole, giving the *nitrile* of 2-methylindole-3-carboxylic acid, m. p. 207—210° (browning). T. H. Pope.

Action of hydrochloric acid on desmotroposantonin. P. Bertolo (Gazzetta, 1926, **56**, 852—855).—Although dihydroartemisic acid appears to be formed as an intermediate compound in the conversion of desmotroposantonin into artemisic acid by the action of iodine (A., 1925, i, 546), it has not been found possible to isolate it by moderating the reaction. *Dihydroartemisic acid*, $C_{15}H_{18}O_3$, m. p. 97—98°, may, however, be obtained by heating either desmotroposantonin or santonin in acetic acid solution with concentrated hydrochloric acid in presence of zinc chloride. If the solution in acetic acid is replaced by a suspension in absolute alcohol, *ethyl dihydroartemisate*, m. p. 74—75°, is obtained.

T. H. Pope.

Product of the scission of artemisic acid (1:4-dimethyl-7-ethyl-β-naphthol). P. Bertolo (Gazzetta, 1926, 56, 856—859).—The compound obtained when artemisic acid is fused with potassium hydroxide and considered to be identical with 1:4-dimethyl-β-naphthol, which is formed on fusion of santonous acid with potassium hydroxide or on reduction of artemisin with stannous chloride (A., 1902, i, 814), is now shown to be 1:4-*dimethyl*-7-*ethyl*-β-*naphthol*, m. p. 126° (*methyl ether*, m. p. 72°).

The difference in behaviour of santonous acid and artemisic acid is explained by the fact that in the former the propionic acid radical is united to a carbon atom of the hydrogenated naphthalene nucleus, so that fusion with potassium hydroxide yields 1 : 4-dimethylnaphthol, propionic acid, and hydrogen; in artemisic acid, however, the carbon atom with which the propionic acid radical is connected is not hydrogenated, so that, on fusion with potassium hydroxide, this radical undergoes partial decomposition into carbon dioxide, which is eliminated, and the ethyl group, which remains. T. H. Pope.

Preparation of *d*-santonous acid from desmotroposantonin. P. Bertolo (Gazzetta, 1926, 56, 859—861).—The action of hydriodic acid and red phosphorus on hyposantonin yields dihydrosantinic acid (cf. Gucci and Grassi-Cristaldi, A., 1892, 869), but similar treatment of desmotroposantonin gives, not dihydroartemisic acid, but an almost theoretical yield of an acid which agrees in all its characters with *d*-santonous acid and is regarded by the author as true desmotroposantonous acid. T. H. Pope.

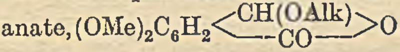
***cyclo*Propenedicarboxylic acids.** F. Feist and C. A. Chen (Ber., 1926, 59, [*B*], 2707—2709).—Ethyl 3-phenyl*cyclo*propane-1 : 2-dicarboxylate reacts very incompletely with bromine at 180° in presence of phosphorus pentachloride, iron, and iodine (cf. Haerdi and Thorpe, A., 1925, i, 923). The free acid with water and bromine at 50° gives 1-bromo-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 226°, which is reduced by sodium amalgam to 3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid and transformed by molten potassium hydroxide into 1-*hydroxy*-3-*phenyl*cyclo*propane*-1 : 2-*dicarboxylic acid*, m. p. about 65° (*methyl* ester, b. p. 210—215°/3 mm.). H. Wren.

***cis*-*o*-Carboxy*cyclo*hexaneacetic acid.** G. A. R. Kon and M. Qudrat-i-Khuda (J.C.S., 1926, 3071—3073).—*cyclo*Hexenyl methyl ketone condenses with ethyl sodiomalonate, giving *ethyl* 1 : 3-*diketodecahydronaphthalene*-4-*carboxylate*, m. p. 114°, which on hydrolysis with alcoholic alkali passes into 1 : 3-*diketodecahydronaphthalene*, m. p. 142°. Sodium hypobromite converts the diketone into *cis*-*o*-carboxy*cyclo*hexaneacetic acid, m. p. 146—147° (anhydride, m. p. 57°), whilst alkaline potassium permanganate oxidises it to *trans*-*cyclo*hexane-1 : 2-dicarboxylic acid, m. p. 222°. H. Burton.

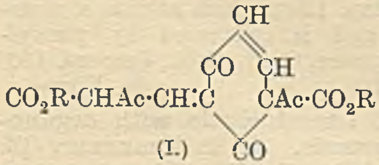
Derivatives of succinic and glutaric acids with cyclic, quaternary carbon atom. W. Hückel and F. Wiebke (Ber., 1926, 59, [*B*], 2838—2844).—*trans*-1-Ketodecahydronaphthalene is converted by ethyl cyanoacetate and alcoholic ammonia into trans-*decahydronaphthalene*-1 : 1-*dicyanoacetimide*, m. p. 261—263° (decomp.), which is hydrolysed by concentrated hydrochloric acid at 150—160° to trans-*decahydronaphthalene*-1 : 1-*diacetic acid*, m. p. 169°, converted by acetic anhydride into the corresponding *anhydride*, m. p. 94°. *trans*-1-Ketodecahydronaphthalene is converted by anhydrous hydrocyanic acid into the corresponding *cyanohydrin*, m. p. 82°. With methyl bromoacetate and zinc, *trans*-1-ketodecahydronaphthalene affords the two theoretically possible *methyl* 1-*hydroxydecahydronaphthalene*-1-*acetates*, m. p. 106° and 45°, respectively (corresponding *acids*, m. p. 144° and 150°). The hydroxy-ester, m. p. 106°, is converted by loss of water and subsequent hydrolysis into an *acid*, $C_{12}H_{18}O_2$, m. p. 155°. Subsequent efforts to prepare the hydroxy-esters were accompanied by loss of water during distillation, and the product when hydrolysed gave an oily *acid*, b. p. 198—210°/33 mm. [*methyl* ester, $C_{13}H_{20}O_2$, $d_4^{14\cdot2}$ 1·0371, $n_D^{13\cdot0}$ 1·50019; *amide*, m. p. 119°; *dibromide*, m. p. 172—173° (decomp.); *methyl* ester of dibromo-acid, m. p. 53°]. *cis*-2-Ketodecahydronaphthalene gives successively cis-*decahydronaphthalene*-2 : 2-*dicyanoacetimide*, m. p. 238—239°, cis-*decahydronaphthalene*-2 : 2-*diacetic acid*, m. p. 167°, and the corresponding *anhydride*, m. p. 91°. cis-2-*Ketodecahydronaphthalene cyanohydrin*, m. p. 81°, is converted by ethyl sodiocyanoacetate and subsequent hydrolysis into cis-*decahydronaphthalene*-2-*acetic*-2-*carboxylic acid*, m. p. 168—170° (decomp.) (*anhydride*, m. p. 97°). trans-2-*Ketodecahydronaphthalene cyanohydrin*, m. p. 108°, trans-2-*carboxydecahydronaphthalene*-2-*acetic acid*, m. p. 149—150°, and its *anhydride*, m. p. 91°, are described. 2-*Carboxy*-1-*methyl*cyclo*hexane*-2-*acetic acid* has m. p. 166° (decomp.) after softening at 135°. H. Wren.

Orientation of the bromine atom in bromodimethoxybenzoic acid. G. P. Rice (J. Amer. Chem. Soc., 1926, 48, 3125—3130).—Bromination of γ-2 : 4-dimethoxybenzoylpropionic acid, and subsequent elimination of hydrogen bromide, yields 5-*bromo*-2 : 4-*dimethoxybenzoylacrylic acid* (cf. A., 1926, 270), the orientation of the bromine atom in which was determined by the following transformations. On oxidation with permanganate, the acid affords 5-*bromo*-2 : 4-*dimethoxybenzoic acid*, m. p. 193°, of which the *methyl* ester, m. p. 117°, yields, when treated with activated magnesium and carbon dioxide, methyl 5-bromo-2-hydroxy-4-methoxybenzoate (cf. Späth, A., 1914, i, 650). Elimination of carbon dioxide from the 5-bromo-2 : 4-dimethoxybenzoic acid could not be effected. Bromination of β-resorcylic acid in glacial acetic acid (cf. Hemmelmayr, A., 1912, i, 977) affords 5-*bromo*-2 : 4-*dihydroxybenzoic acid* (+1H_2O), m. p. 204° (anhydrous), together with a *dibromo*-derivative which yields a soluble dibromoresorcinol when boiled with water. The former yields, on treatment with methyl sulphate and alkali, the above 5-bromo-2 : 4-dimethoxybenzoic acid, m. p. 193°, and the methyl 5-bromo-2-hydroxy-4-methoxybenzoate, m. p. 143°, together with 5-*bromo*-2-*hydroxy*-4-*methoxybenzoic acid*, m. p. 247° (decomp.), which, when boiled with water, yields 4-*bromoresorcinol* 3-*methyl ether*. By elimination of carbon dioxide, 5-bromo-2 : 4-dihydroxybenzoic acid is converted into 4-*bromoresorcinol*, m. p. 103° (cf. Zehenter, A., 1882, 193; 1887, 924), of which the *dimethyl ether*, b. p. 135°/18 mm., and the 1-*methyl ether*, b. p. 152°/25 mm., are described. The dimethyl ether yields the dimethyl ether of β-resorcylic acid, m. p. 108°, when treated with magnesium and carbon dioxide. 3-Bromo-2 : 4-dihydroxybenzoic acid (cf. Hemmelmayr, *ibid.*, 1914, i, 283) yields 2-*bromoresorcinol*, m. p. 102·5°, when boiled with water. The action of methyl sulphate and alkali on 2 : 6-dibromoresorcinol affords the *dimethyl ether*, b. p. 155°/15 mm., and, presumably, 2 : 6-*dibromoresorcinol 3-methyl ether*, b. p. 160°/24 mm. Treatment of 3-bromo-2 : 4-dihydroxy-5-nitrobenzoic acid with warm, concentrated nitric acid affords 2-bromo-4 : 6-dinitroresorcinol, m. p. 189—191° (cf. Dahmer, *ibid.*, 1904, i, 871), whilst 5-bromo-β-resorcylic acid yields similarly 2 : 4 : 6-trinitroresorcinol. F. G. Willson.

Action of arsenic acid on gallic acid. L. F. Iljin (J. pr. Chem., 1927, [ii], **115**, 1—7; cf. A., 1919, i, 908).—The reaction between arsenic and gallic acids in methyl-alcoholic solution (*d* 0·796) yields, by a method of isolation similar to that previously employed, *methyl trigalloylarsenate*, $(C_8H_7O_5)_3AsO$, obtained both as an amorphous powder and in a crystalline form (the former being converted into the latter by slow crystallisation from methyl alcohol–ether solution), and methyl gallate, m. p. 195—196°, which is also obtained by the action of hydrogen sulphide on a solution of the arsenic compound in dilute sulphuric acid. The trigalloylarsenate is converted by methyl sulphate into a *dimethyl ether*, $(C_7H_2O_5Me_3)_3AsO$, which with hydrogen sulphide yields methyl 5-hydroxy-3 : 4-dimethoxybenzoate, m. p. 83—84° (cf. Herzig and Pollak, A., 1903, i, 89). Hydrolysis of methyl trigalloylarsenate with alcoholic potassium hydroxide in an atmosphere of hydrogen yields the corresponding free *acid*. J. W. Baker.

Opianic acid. W. M. Rodionov and A. M. Fedorowa (Ber., 1926, **59**, [*B*], 2949—2952; cf. A., 1924, i, 1196).—Opianic acid is readily converted by thionyl chloride into *opianyl chloride*, m. p. 93—94°, from which methyl opianate is obtained by the action of methyl alcohol and pyridine. The ester or the corresponding ethyl ester is transformed by potassium hydroxide in the requisite alcohol into methyl or ethyl ψ-opianate,  $(OMe)_2C_6H_2{<}\begin{matrix}CH(OAlk)\\CO\end{matrix}{>}O$. Phenol and potassium hydroxide do not react with methyl opianate, whereas opianic acid is transformed by phenol at 120° into a *substance*, m. p. 145—146°. H. Wren.

Xanthophanic acids. I. F. Feist, D. Delfs, and B. Langenkamp (Ber., 1926, **59**, [*B*], 2958—2972; cf. Liebermann and others, A., 1906, i, 556; 1907, i, 889; 1908, i, 548; 1909, i, 403, 405).—The constitution assigned by Liebermann (*loc. cit.*) to xanthophanic acid obtained by Claisen by the action of solid ethyl sodioacetoacetate on ethyl ethoxymethyleneacetoacetate is unsatisfactory, since it assumes the presence of the resacetophenone nucleus. The reactants, however, do not yield ethyl resacetophenonecarboxylate, but ethyl methenyldiacetoacetate, which, by internal ring closure, affords ethyl hydrogen *m*-hydroxyavitinate. Further, xanthophanic acid cannot be synthesised from the diethyl ether of ethyl resacetophenonecarboxylate and ethyl ethoxymethyleneacetoacetate. A guide to the constitution of the substance is found in its production in good yield from ethyl methenyldiacetoacetate and ethyl ethoxymethyleneacetoacetate with elimination of alcohol. It is shown by variation of the alkoxy-groups of the esters that the alkoxy-group of alkoxymethyleneacetoacetic esters and that of one of the two ·CO_2Alk groups of the diester are removed during the action, whereas the remaining ·CO_2Alk groups remain intact. Further, the hydrogen atoms of the acetyl group of ethoxymethyleneacetoacetic esters are not involved. On the basis of these observations, the constitution (I) (R=Et) or one of its three other desmotropic forms is ascribed to xanthophanic acid.

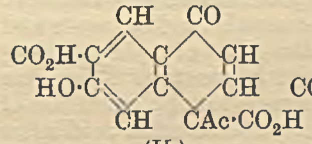


(I.)

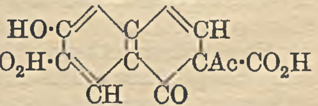
The following substances are incidentally described : *methyl αγ-diacetylglutaconate*, m. p. 85°, from methyl sodioacetoacetate and methyl ethoxymethyleneacetoacetate; *γ-methyl α-ethyl αγ-diacetylglutaconate*, m. p. 87°, from ethyl sodioacetoacetate and methyl ethoxymethyleneacetoacetate; *α-methyl γ-ethyl αγ-diacetylglutaconate*, m. p. 73°, from methyl sodioacetoacetate and ethyl ethoxymethyleneacetoacetate; *ethyl ethoxymethylenebenzoylacetate*, b. p. 203°/13 mm.; ethyl 2 : 4-diketo-1-acetyl-3-β-carbethoxy-β-acetylethylidene-Δ⁵-*cyclo*hexene-1-carboxylate (Claisen's diethylxanthophanic acid), m. p. 144°, from ethyl diacetylglutaconate and ethyl ethoxymethyleneacetoacetate in presence of sodium ethoxide, and the corresponding dimethyl ester, m. p. 179°; *ethyl* 2:4-*diketo*-1-*acetyl*-3-β-*carbomethoxy*-β-*acetylethylidene*-Δ^5-cyclo*hexene*-1-*carboxylate*, m. p. 167°; *methyl* 2 : 4-*diketo*-1-*acetyl*-3-β-*carbethoxy*-β-*acetylethylidene*-Δ^5-cyclo*hexene*-1-*carboxylate*, m. p. 151°; *ethyl* 2 : 4-*diketo*-1-*benzoyl*-3-β-*carbethoxy*-β-*acetylethylidene*-Δ^5-cyclo*hexene*-1-*carboxylate* (*diethylerythrophanic acid*), m. p. 157°, from ethyl diacetylglutaconate and ethyl ethoxymethylenebenzoylacetate; the *copper* salt, $(C_{18}H_{19}O_8)_2Cu$, and *benzoyl* derivative, m. p. 146°, of "diethylxanthophanic acid."

The "transformation product," $C_{17}H_{18}O_8$, m. p. 161—162°, obtained by the action of magnesium methoxide on xanthophanic acid (cf. Liebermann, *loc. cit.*), is converted by phenylhydrazine into the *phenylhydrazone* of *methyl resacetophenonecarboxylate*, which appears to exist in two forms, m. p. 242—243° and m. p. 248—249°.

Xanthophanic acid is converted by concentrated sulphuric acid into a substance, $C_{14}H_{10}O_7$, m. p. 187° (cf. Liebermann, *loc. cit.*), and an isomeric *compound* (*barium* salt). The product, which is acidic and does not contain an ethoxy-group, appears to have the constitution (II) or (III).



(II.)

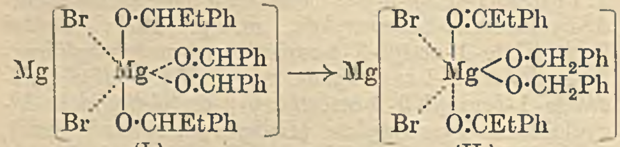


(III.)

Liebermann's "hydrazone," from diethylxanthophanic acid or ethylglaucophanic acid, m. p. 194—195°, has the composition $C_{12}H_{12}O_4N_2$, and is therefore obtained from the diethyl compound by loss of an acetoacetic residue. It contains an ethoxy-group and is hydrolysed to an *acid*, $C_{10}H_8O_4N_2$, m. p. 331—333°. It is converted by silver oxide and ethyl iodide into a neutral *compound*, $C_{14}H_{16}O_4N_2$, m. p. 75—76°. The hydrazone and nitric acid afford a *product*, m. p. 214°, whereas the ethylated hydrazone yields a *mononitro*-derivative, $C_{11}H_{15}O_4N_2(NO_2)$, m. p. 98—99°.

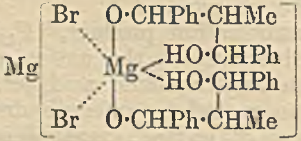
Diethylxanthophanic acid is reduced by zinc and dilute sulphuric acid to a *dihydro*-derivative, $C_{18}H_{22}O_8$, m. p. 60—70°, decomp. 120°, which affords a *monobenzoyl* compound and is converted by phenylhydrazine into a *substance*, $C_{18}H_{20}O_4N_2$, decomp. 140° after softening at 110°. H. Wren.

Condensation of benzaldehyde with organomagnesium compounds. A. P. Terentjev (Z. anorg. Chem., 1927, 159, 226—230).—An attempt to explain the formation of the various products resulting from the reaction between benzaldehyde and magnesium ethyl bromide (Marshall, A., 1915, i, 409; Hess and Rheinboldt, *ibid.*, 1921, i, 777; Meisenheimer, *ibid.*, 1925, i, 527). The scheme suggested by Meisenheimer (*ibid.*, 1926, 68) explains the appearance of propiophenone and benzyl alcohol, but fails to account for the formation of αγ-dihydroxy-αγ-diphenyl-β-methylpropane. The present explanation is based on the author's co-ordination formula (*ibid.*, 1130) and the assumption that the individual hydrogen atoms of the co-ordinatively bound components are extremely mobile and can wander from one component to another. Meisenheimer's scheme now becomes:



(I.) (II.)

By the wandering of a hydrogen atom from each of the two ethyl groups, formula (I) becomes:



which explains the appearance of αγ-dihydroxy-αγ-diphenyl-β-methylpropane. The essential difference between this reaction scheme and that of Meisenheimer is that in the present instance two molecules of benzaldehyde are bound co-ordinatively, and by the wandering of an atom of hydrogen can condense to form benzyl benzoate. In support, it is found that by using an excess of benzaldehyde, benzyl benzoate can be isolated from the products of the reaction. As a result of interaction between benzyl benzoate and the magnesium bromoalkoxide of phenylethylcarbinol, phenylethylcarbinyl benzoate is a possible reaction product. The evidence for the existence of this ester is indirect (detection of benzoic acid after hydrolysis of a small fraction boiling above 330°) and inconclusive. J. S. Carter.

p-Dimethylaminobenzylidenepentaerythritol. A. Fairbourne and J. W. Woodley (J.C.S., 1926, 3240—3241).—*p*-Dimethylaminobenzaldehyde condenses with pentaerythritol in presence of warm 50% sulphuric acid, giving p-*dimethylaminobenzylidenepentaerythritol*, m. p. 140° (decomp.) (*methiodide*, decomp. 175°). Condensation of this benzylidene derivative with another mol. of the aldehyde yields bis-*p*-dimethylaminobenzylidenepentaerythritol (*methiodide*, decomp. 220°). Attempts to condense the mono-*p*-dimethylaminobenzylidene derivative with different aldehydes caused elimination of the *p*-dimethylaminobenzylidene radical and the formation of spirans identical with those from 2 mols. of the aldehyde. p-*Dimethylaminobenzaldehyde methiodide* decomposes at 160°. H. Burton.

5-Methoxy-α-naphthaldehyde. J. B. Shoesmith and H. Rubli (J.C.S., 1926, 3241—3243).—5-Hydroxy-α-naphthoic acid, prepared by fusing 1-cyanonaphthalene-5-sulphonic acid with sodium hydroxide, is converted into 5-methoxy-α-naphthoic acid by methyl sulphate. Treatment of the potassium salt of this acid with thionyl chloride yields 5-*methoxy-α-naphthoyl chloride*, b. p. 194°/11 mm., m. p. 80—81°. Reduction of this compound with hydrogen in presence of palladium produced 5-*methoxy-α-naphthaldehyde*, m. p. 66° (p-*nitrophenylhydrazone*, m. p. 246°; *semicarbazone*, m. p. 246°; *oxime*, m. p. 104°). H. Burton.

Acyl migration during the partial hydrolysis of acylated polyphenolic aldehydes. E. Passu and L. von Vargha (Ber., 1926, 59, [*B*], 2818—2824; cf. A., 1923, i, 338).—3 : 4-*Diacetoxybenzaldehyde*, m. p. 54° [*phenylhydrazone*, m. p. 135°; *semicarbazone*, m. p. 200—202° (decomp.)], is prepared in 95% yield by the action of acetic anhydride on 3 : 4-dihydroxybenzaldehyde in aqueous alkaline solution. It is converted by partial hydrolysis into 4-*hydroxy*-3-*acetoxybenzaldehyde*, m. p. 109—110° (p-*nitrophenylhydrazone*, m. p. 195°), which is obtained in better yield by the partial acetylation of 3 : 4-dihydroxybenzaldehyde. The constitution of the substance is established by its conversion by diazomethane into 3-acetoxy-4-methoxybenzaldehyde, m. p. 88°, which is hydrolysed to *iso*vanillin, m. p. 115—116°. 4-*Benzoxy*-3-*acetoxybenzaldehyde*, m. p. 109° (*phenylhydrazone*, m. p. 158°), prepared by the action of benzoyl chloride and aqueous potassium hydroxide on 4-hydroxy-3-acetoxybenzaldehyde dissolved in acetone, is hydrolysed in acid or aqueous solution with migration of the benzoyl group to 4-*hydroxy*-3-*benzoxybenzaldehyde*, m. p. 136—137° (*phenylhydrazone*, m. p. 192°), which, when acetylated, affords 4-*acetoxy*-3-*benzoxybenzaldehyde*, m. p. 68° (*phenylhydrazone*, m. p. 166°). 4-Hydroxy-3-benzoxybenzaldehyde is converted by diazomethane into 4-methoxy-3-benzoxybenzaldehyde, m. p. 75°, from which *iso*vanillin is obtained by hydrolysis. H. Wren.

Alkyl*cyclo*-pentanones and -hexanones. Action of benzaldehyde and other aromatic aldehydes on cyclanones. Differentiation of the αα- and αα′-dimethylcyclanones. A. Haller and R. Cornubert (Bull. Soc. chim., 1926, [iv], 39, 1621—1643).—A review of previous work (cf. A., 1914, i, 291; 1920, i, 390, 441; 1924, i, 1203; 1925, i, 1070, 1071). M. Clark.

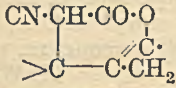
Alkyl*cyclo*-pentanones and -hexanones. II. Alkylation of 1-methyl*cyclo*pentan-2-one. A. Haller and R. Cornubert (Bull. Soc. chim., 1926, [iv], 39, 1724—1732; cf. preceding abstract).—Re-examination of the products obtained on methylating

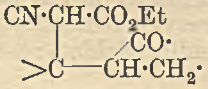
1-methyl*cyclo*pentan-2-one with methyl iodide and sodamide indicates that the dimethylation product consists of at least 95% of 1 : 1-dimethyl*cyclo*pentanone and only 5% of the 1 : 3-dimethyl isomeride. The trimethylation product reacts with benzaldehyde in presence of hydrochloric acid and appears to contain di- and tetra-methyl*cyclo*pentanones. 1 : 1 : 3-Trimethyl*cyclo*hexanone, like 1 : 1 : 3-trimethyl*cyclo*pentanone, does not react under these conditions. 1 : 1 : 3 : 3-Tetramethyl*cyclo*pentanone, b. p. 155—156°/770 mm., d_4^{20} 0·8653, n_D^{20} 1·4288, probably contains traces of the trimethyl derivative. It is concluded that *gem*-methylation takes place more readily than symmetrical methylation. Ethylation under similar conditions affords about 80% of condensation products and a fraction which is apparently a mixture of mono- and di-ethyl-1-methyl*cyclo*pentan-2-ones.

R. BRIGHTMAN.

Three-carbon system. X. Mobility of some cyclic ketones. G. A. R. KON and J. H. NUTLAND (J.C.S., 1926, 3101—3111 ; cf. *ibid.*, 1923, **123**, 1361).—2-Δ^1-*cyclo*Hexenyl*cyclo*hexanone gives two semicarbazones, one form m. p. 200—201°, and a small amount of another form, m. p. 172° (cf. A., 1907, i, 220; 1923, i, 142). The ketone regenerated from the semicarbazone of m. p. 200—201° by oxalic acid had b. p. 145°/17 mm., $d_4^{15\cdot1}$ 1·00404, $n_D^{15\cdot1}$ 1·50692, $[R_L]_D$ 52·81, and gave, on oxidation with ozone, adipic acid, indicating the stable βγ-form. Methylation by "molecular" sodium and methyl iodide yielded 2-*methyl*-2-Δ^1-cyclo*hexenyl*cyclo*hexanone*, b. p. 150°/18 mm., $d_4^{19\cdot4}$ 0·98804, $n_D^{19\cdot4}$ 1·50320, $[R_L]_D$ 57·51 (*semicarbazone*, m. p. 204°). Oxidation of the methylated ketone gave adipic acid and δ-acetylvaleric acid (identified as semicarbazone, m. p. 145—146°). The original ketone, when condensed with ethyl sodiocyanoacetate, gave a small amount of a *cyanolactone*, m. p. 112°, of type (I), formed by the loss of alcohol from the expected cyano-ester (II) [cf. Vorländer, A., 1906, i, 362).

(I.)

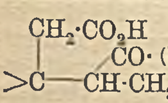




(II.)

Concentrated sulphuric acid converts the lactone into an *imide*, m. p. 166°.

2-*cyclo*Pentylidene*cyclo*pentanone (semicarbazones, m. p. 223° and 207°) on oxidation gives *cyclo*pentanone and glutaric acid, showing the αβ-formula. Ethylation converts it into 2-*ethyl*-2-Δ^1-cyclo*pentenyl*cyclo*pentanone*, b. p. 140°/22 mm., $d_4^{22\cdot4}$ 0·983385, $n_D^{22\cdot4}$ 1·49756, $[R_L]_D$ 53·07 (*semicarbazone*, m. p. 202°). Oxidation of the ethylated ketone gave glutaric acid and 2-ethyl*cyclo*pentanone formed by decomposition of an acid, probably 2-ω-carboxybutyryl-2-ethyl*cyclo*pentenone, with boiling water. The ethyl sodiocyanoacetate condensation gave a *cyano*-ester [type (II)], b. p. 164—165°/20 mm., which on hydrolysis furnished an *acid* [type (III)], m. p. 135° (*semicarbazone*, m. p. 197°). 2-*iso*Propylidene*cyclo*pentanone (semicarbazone, m. p. 217—218°; oxidation products, acetone and glutaric acid) on ethylation gave 2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, b. p. 97—98°/20 mm., $d_4^{19\cdot7}$ 0·94132, $n_D^{19\cdot7}$ 1·47892, $[R_L]_D$ 45·84 (*semicarbazone*, m. p. 199°; oxidation gave formic acid and probably δ-acetylheptoic acid, identified as the *semicarbazone*, m. p. 141—142°). Ethyl sodiocyanoacetate yielded a *cyano*-ester, b. p. 135°/20 mm., which on hydrolysis gave an *acid*, m. p. 133°. Camphorphorone on ethylation gave 5-*methyl*-2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, b. p. 95—96°/16 mm., $d_4^{18\cdot7}$ 0·91131, $n_D^{18\cdot7}$ 1·46533, $[R_L]_D$ 50·46 (*semicarbazone*, m. p. 184°; oxidation products, formic acid, and δ-acetyl-α-methylheptoic acid, identified as *semicarbazone*, m. p. 147—148°). An *acid*, m. p. 135°, was obtained from the cyanoacetate condensation. Both pulegone and *iso*pulegone, on methylation give 2 : 5-*dimethyl*-2-iso*propenyl*cyclo*hexanone* (2-*methyl*iso*pulegone*), b. p. 108°/19 mm., $d_4^{18\cdot8}$ 0·92081, $n_D^{18\cdot8}$ 1·47163, $[R_L]_D$ 50·51, $[\alpha]_D$ (in alcohol) $-122\cdot1°$ (*semicarbazone*, m. p. 203—204°), whilst condensation with ethyl sodiocyanoacetate gives a cyanolactone. This on hydrolysis yields an imide, m. p. 129°. 5-*Methyl*-2-*ethyl*-2-iso*propenyl*cyclo*hexanone* has b. p. 110°/15 mm., $d_4^{19\cdot1}$ 0·90362, $n_D^{19\cdot1}$ 1·46433, $[R_L]_D$ 55·05, $[\alpha]_D$ (in alcohol) $-174\cdot0°$ (*semicarbazone*, m. p. 207—208°).



(III.)

*iso*Pulegone is lævorotatory when prepared from pulegone hydrobromide, whereas the natural ketone is dextrorotatory. The results show that the cyclic ketones examined react both as αβ- and βγ-unsaturated ketones.

H. BURTON.

Condensations of *p*-dimethylaminobenzaldehyde with special reference to *p*-dimethylaminobenzylideneacetone and its reduction products. H. THOMS and H. SEEBE (Z. angew. Chem., 1926, 39, 1464—1465).—The observation of Meyer and Beer (A., 1913, i, 617) that *p*-dimethylaminobenzaldehyde undergoes the Perkin condensation only in presence of potassium acetate, not the sodium salt, is confirmed. From this and other evidence on condensations with aldehydes and ketones to give *p*-dimethylaminocinnamaldehyde and *p*-dimethylaminostyryl methyl ketone, it is concluded that the introduction of the *p*-dimethylamino-group reduces the reactivity of benzaldehyde, particularly in the case of the cinnamic acid synthesis, and causes a corresponding tendency to form by-products. *p*-Dimethylaminostyryl methyl ketone gives only normal oximes, semicarbazones, and phenylhydrazones, the double linking in the side-chain giving no reaction, as in the case of many αβ-unsaturated ketones. Reduction of this compound with sodium and amyl alcohol gives α-p-*dimethylaminophenylbutan*-γ-*ol*, whilst reduction with sodium amalgam in weak acetic acid solution under pressure gives a trace of that alcohol, 80% of β-p-*dimethylaminophenylethyl methyl ketone*, and 10—20% of δε-*di*-p-*dimethylaminophenyloctane*-βη-*dione*. Besides these was found a trace of a yellow *product*, m. p. 190°, not further investigated.

E. HOLMES.

Semipinacolic transformations; comparative stability of secondary and tertiary hydroxyl groups. M. TIFFENEAU and J. LEVY (Compt. rend., 1926, **183**, 1112—1114).—Since αγ-diphenyl-β-benzylpropane-αβ-diol and γ-phenyl-α-anisyl-β-benzylpropane-αβ-diol when treated with sulphuric acid of any concentration, and the latter when simply heated, yield only the corresponding ketone, in accordance with the scheme $CHAr(OH){\cdot}CR_2{\cdot}OH \longrightarrow CHAr{\cdot}CR_2O^- \longrightarrow CHArR{\cdot}CO{\cdot}R$ (I), and no aldehyde, in accordance with the scheme $CHAr(OH){\cdot}CR_2{\cdot}OH \longrightarrow CHArO{\cdot}CR_2 \longrightarrow CArR_2{\cdot}CHO$ (II) (cf. Orékhov, A., 1919, i, 271); and since α-phenyl-β-methylbutane-αβ-diol yields the ketone with concentrated sulphuric acid, the aldehyde with 8% sulphuric acid, and a mixture with acids of intermediate concentrations, the semipinacolic mechanism (I) for the formation of the ketones is probably correct, since the conversions of trisubstituted aldehydes into ketones (Orékhoff and Tiffeneau, *ibid.*, 1926, 171) occurs only on treatment with concentrated sulphuric acid. The following compounds are obtained: *benzyl β-phenyl-α-anisylethyl ketone* (*oxime*, m. p. 90—91°; *semicarbazone*, m. p. 138—139°); *β-phenyl-αβ-dimethylpropaldehyde*, b. p. 228—230° (*semicarbazone*, m. p. 158—159°). J. W. Baker.

Dehydration of *cyclo*hexylhydrobenzoin and the isomerisation of aldehydes to ketones. S. Danilov (J. Russ. Phys. Chem. Soc., 1926, 58, 129—147).—Another account of work described elsewhere (A., 1926, 519—520). Benzhydryl *cyclo*hexyl ketone (αα-diphenyl-β-*cyclo*hexylethan-β-one, *loc. cit.*) forms an *oxime*, m. p. 164°, and a *semicarbazone*, m. p. 213°. M. Zvegintzov.

α-Phenyl ββ-di-*p*-tolylethylene glycol and di-*p*-tolylacetophenone. S. Danilov (J. Russ. Phys. Chem. Soc., 1926, 58, 148—155; cf. A., 1926, 519, 726).—*α-Phenyl ββ-di-*p*-tolylethylene glycol*, m. p. 157°, prepared from methyl mandelate and magnesium *p*-tolyl bromide, on dehydration with dilute sulphuric or oxalic acid, gives only traces of the expected phenyldi-*p*-tolylacetaldehyde, but almost exclusively the ketone, *di-*p*-tolylacetophenone*, m. p. 57·5°, decomp. to benzoic acid and di-*p*-tolylmethane by alcoholic potassium hydroxide, giving an *oxime*, m. p. 188°, and a *semicarbazone*, m. p. 186°, which seems to exist in two isomeric forms. This behaviour is in accordance with the author's theory that the acid nature of groups, as shown by the conductivities of the acids they form, determines the mechanism of glycol dehydration. Groups which give acids having approximately the same conductivity do not tend to migrate, when present together, even if they belong to the aromatic series, which, in general, favour structural changes. M. Zvegintzov.

ω-Chloro-*o*-hydroxyacetophenone. K. von Auwers and M. Leo (Ber., 1926, 59, [*B*], 2899).—ω-Chloro-*o*-hydroxyacetophenone has m. p. 73—74°, in agreement with the observations of Fries and Pfaffendorff (A., 1910, i, 149). The product, m. p. 101°, described as such by Tutin (J.C.S., 1910, 97, 2503) is coumaranone. H. Wren.

Syntheses of chalkones. H. Simonis and C. Lear (Ber., 1926, 59, [*B*], 2908—2913).—Phenolic ethers, particularly those containing a substituent in the *para*-position to the alkoxy-group, are converted by suitable acid chlorides in the presence of aluminium chloride (1 mol.) into alkylated chalkones; the use of a further mol. of aluminium chloride causes removal of the alkyl group, with production of the chalkone. Thus *p*-tolyl methyl ether, cinnamoyl chloride, and aluminium chloride afford *4-methoxy-*m*-tolyl styryl ketone*, m. p. 55—56°, and 4-hydroxy-*m*-tolyl styryl ketone, m. p. 111° (cf. Auwers and Döll, A., 1920, i, 871). Quinol diethyl ether gives *2-hydroxy-5-ethoxyphenyl styryl ketone*, m. p. 83°, converted by sodium hydroxide into 6-ethoxyflavanone. *p*-Tolyl methyl ether, phenylpropiolyl chloride, and aluminium chloride in molecular proportions give *4-methoxy-*m*-tolyl β-phenylethinyl ketone*, m. p. 62°, whereas with a double proportion of aluminium chloride, *4-methoxy-*m*-tolyl β-chlorostyryl ketone*, m. p. 95·5°, is obtained; the latter compound is converted by dilute sodium hydroxide into 6-methylflavone. H. Wren.

Applicability of the Friedel–Crafts reaction to the production of flavones. H. Simonis and S. Danischewski (Ber., 1926, 59, [*B*], 2914—2919; cf. preceding abstract).—Quinol dimethyl ether, aluminium chloride, and cinnamoyl chloride yield *2 : 5-dimethoxyphenyl styryl ketone*, m. p. 43°, which is converted by aluminium chloride in presence of benzene into *2-hydroxy-5-methoxyphenyl styryl ketone*, m. p. 49°, transformed by alkali hydroxide into 6-methoxyflavanone. *2 : 5-Dimethoxyphenyl β-phenylethinyl ketone*, m. p. 57°, is converted by aluminium chloride into *2-hydroxy-5-methoxyphenyl β-chlorostyryl ketone*, m. p. 90°, or, if hydrogen chloride is also used, into an isomeric *ketone*, m. p. 80°; both ketones are transformed by sodium hydroxide into *6-methoxyflavone*, m. p. 154°. Resorcinol dimethyl ether and cinnamoyl chloride afford *2 : 6-dimethoxyphenyl styryl ketone*, m. p. 80°, and thence *2-hydroxy-6-methoxyphenyl styryl ketone*, m. p. 105°, which could not be converted into the corresponding flavanone. *2-Hydroxy-6-methoxyphenyl β-chlorostyryl ketone*, m. p. 95°, and *5-methoxyflavone*, m. p. 133°, are described. *2-Methoxy-5 : 6-dimethylphenyl styryl ketone*, m. p. 78°, is demethylated to *2-hydroxy-5 : 6-dimethylphenyl styryl ketone*, m. p. 116°, which is with difficulty transformable into *5 : 6-dimethylflavanone*, m. p. 89°. *2-Hydroxy-3 : 5-dimethylphenyl styryl ketone*, m. p. 78°, readily yields *6 : 8-dimethylflavanone*, m. p. 108°. H. Wren.

Formation of chloranil from aromatic compounds. L. Denis (Bull. Soc. chim. Belg., 1926, 35, 375—379).—In continuation of work by Michiels and Hingot (Bull. Acad. roy. méd. Belg., 1925, 213). the author finds that chloranil is also produced by the action of hydrochloric acid and potassium chlorate on *p*-hydroxybenzoic, 2 : 5-dihydroxybenzoic, and picrolonic acids. The introduction of a nitro-group into benzoic acid or benzaldehyde inhibits the reaction, negative results being obtained with the three nitrobenzoic acids and nitrobenzaldehydes, 2 : 4 : 6-trinitro- and 2 : 4-dinitro-benzoic acids. Similarly, nitro-*p*-cresol and the nitro-*o*- and -*p*-toluidines all give a negative test. None of the nitrotoluenes or nitroxylenes examined affords chloranil in this way, and negative results are similarly obtained with trinitrobenzene, tetrabromo-*p*- and -*m*-xylene, neutral-red, 2-nitroresorcinol, 2 : 4 : 6-trinitroresorcinol, *p*- and *m*-nitrocinnamic acids, 2 : 4-dihydroxybenzoic acid, and 2 : 4-dinitro-α-naphthol. On the other hand, a positive chloranil reaction is obtained with the three nitroanilines and nitrophenols, with 2 : 4-dinitroaniline, *o*- and *p*-nitroacetanilides, *o*- and *p*-nitroanisole, with alizarin-yellow-GG, and with nitron. Of the three dihydroxybenzenes, only quinol gives a positive reaction. R. BRIGHTMAN.

Alkylation of hydroxynaphthaquinone. II. Carbon alkylation. L. F. FIESER (J. Amer. Chem. Soc., 1926, 48, 3201—3214; cf. this vol., 59).—Whilst alkylation of hydroxynaphthaquinone (through the silver salt) by means of saturated alkyl halides leads to one or both of the isomeric *O*-ethers, similar reaction with allyl, benzyl, and diphenylmethyl halides yields, in addition, *C*-alkyl derivatives, whilst triphenylmethyl and cinnamyl halides yield the *C*-alkyl derivative exclusively. Treatment of the silver salt of hydroxynaphthaquinone with allyl bromide in boiling benzene affords mainly 4-*allyloxy*-β-*naphthaquinone*, m. p. 125°, with 2-*allyloxy*-α-*naphthaquinone*, m. p. 98·5°, and 3-*hydroxy*-2-*allyl*-α-*naphthaquinone* (I), yellow, m. p. 116°, which is also produced, exothermically, when either of the isomeric *O*-ethers is heated above the m. p. A normal acetyl derivative of (I) could not be obtained. When treated with acetic anhydride and sodium acetate, (I) yields a *compound*, $C_{17}H_{14}O_5$, the reaction being apparently analogous to that recorded for lapachol by Paternò and Minnuni (A., 1890, 607) and Hooker (J.C.S., 1892, 61, 611). Reduction of (I) with zinc dust and acetic acid in presence of acetic anhydride affords the corresponding *quinol triacetate*, m. p. 155·5°, whilst heating with hydrochloric and acetic acids yields 3-*hydroxy*-2-β-*chloropropyl*-α-*naphthaquinone*, yellow, m. p. 147° (*acetyl* derivative, m. p. 102°) (cf. Hooker, *loc. cit.*), together with 1-*methyl*-4 : 5-*benzocoumaran*-3 : 6-*quinone*, yellow, m. p. 166—167°, which is also formed to a slight extent when the above chloro-derivative is boiled in glacial acetic acid. Treatment of (I) with cold, concentrated sulphuric acid affords 1-*methyl*-5 : 6-*benzocoumaran*-3 : 4-*quinone*, red, m. p. 133·5°, which is also obtained from the above chloro-derivative by the action of sulphuric acid at 80°, and is converted into the chloro-derivative by treatment with hydrochloric acid at 55°, whilst the action of cold alkali affords 3-*hydroxy*-2-β-*hydroxypropyl*-α-*naphthaquinone*, yellow, m. p. 108—110° (*acetyl* derivative, m. p. 127°). Benzyl chloride and the silver salt of hydroxynaphthaquinone yield analogously 4-*benzyloxy*-β-*naphthaquinone*, orange-yellow, m. p. 182·5°, 2-*benzyloxy*-α-*naphthaquinone*, yellow, m. p. 145°, and 3-*hydroxy*-2-*benzyl*-α-*naphthaquinone*, golden-yellow, m. p. 175—176°. Diphenylmethyl bromide yields similarly 2-*diphenylmethoxy*-α-*naphthaquinone*, yellow, m. p. 150—151°, and 3-*hydroxy*-2-*diphenylmethyl*-α-*naphthaquinone*, yellow, m. p. 186·5° (*acetyl* derivative, m. p. 170·5°; *quinol triacetate*, m. p. 215°), the latter being also obtained by boiling hydroxynaphthaquinone with benzhydrol in glacial acetic acid in presence of sulphuric acid (cf. Möhlau and Klopfer, A., 1899, i, 912). 3-*Hydroxy*-2-*triphenylmethyl*-α-*naphthaquinone*, yellow, m. p. 211° (decomp.) (*sodium* salt, red), is obtained as above. Treatment of the silver salt of hydroxynaphthaquinone with cinnamyl chloride and sodium carbonate in cold benzene affords 3-*hydroxy*-2-*cinnamyl*-α-*naphthaquinone*, yellow, m. p. 170°, which, when treated with cold, concentrated sulphuric acid, yields what is probably 2-*phenyl*-7 : 8-*benzochroman*-5 : 6-*quinone*, red, m. p. 167°. F. G. WILLSON.

Derivatives of naphthaquinones [1-imino-4-arylimino-2-hydroxy-α-naphthaquinones]. SOC. ANON. DES MAT. COL. ET PROD. CHIM. DE ST.-DENIS, R. LANTZ, and A. WAHL.—See B., 1927, 39.

Preparation of 1 : 4-dichloroanthraquinone from phthalic anhydride and *p*-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1926, 48, 3198—3199).—Phthalic anhydride (1 mol.) is heated with *p*-dichlorobenzene (0·5 mol.) and aluminium chloride (1·5 mol.) at 110—120° for about 4 hrs. The product, o-2′ : 5′-*dichlorobenzoylbenzoic acid*, m. p. 169°, is isolated and heated with excess of sulphuric acid at 150° for 4 hrs., when an 83% yield of 1 : 4-dichloroanthraquinone, m. p. 187·5°, is obtained (cf. Ullmann and Billig, A., 1911, i, 490). F. G. WILLSON.

Fritzsch's reagent [β-dinitroanthraquinone]. E. BÖRNSTEIN, H. SCHLIEWIENSKY, and S. V. SZCZESNY-HEYL (Ber., 1926, 59, [*B*], 2812—2815).—β-Dinitroanthraquinone, m. p. 290—291° (decomp.), prepared by the action of nitric acid on anthracene, gives additive *compounds* containing the components in equimolecular ratio with the following substances: anthracene, m. p. 263—264°; 1-methylanthracene, m. p. 259°; 2-methylanthracene, m. p. 219°; 1 : 6(or 1 : 7)-dimethylanthracene, m. p. 224—225°; 1 : 3 : 6 : 8-tetramethylanthraquinone, m. p. 260—261° (decomp.); dibromo-2-methylanthracene, m. p. 241° (decomp.); phenanthrene, m. p. 218—219°; acenaphthene, m. p. 227—230°; carbazole, m. p. 260—261°; stilbene, m. p. 248°; chrysene, m. p. 302—303°; retene, m. p. 225—226°; diphenylamine, m. p. 243—244° (decomp.); di-*p*-tolylamine, m. p. 212—213°; di-β-naphthylamine, m. p. 176—177°; xenylamine (diphenylylamine), m. p. 241°; benzidine, m. p. 240—241°; *o*-tolidine, m. p. 202°. It does not form additive compounds with diphenyl, di-*p*-tolyl, fluorene, di- or tri-phenylmethane, naphthalene, tetra- or deca-hydronaphthalene, acetophenone, benzophenone, coumarin, isatin, azobenzene, azoxybenzene, diphenyl sulphide, sulphoxide, or sulphone, diphenol sulphide, carbanilide, thiocarbanilide, pyridine, quinoline, indole, acridine, the three phenylenediamines, and naphthidine. H. WREN.

Genetic relationship of aliphatic to cyclic perfumes; geraniol. H. THOMS (Oesterr. Chem.-Ztg., 1926, 29, 228—229).—When geraniol is heated with 20% sulphuric acid at 200—210° for 6 hrs., or when it is stirred with three times its weight of 65% sulphuric acid at —15° and the product heated to 60°, it yields a *hydrocarbon*, b. p. 183—195°/16 mm., 147—152°/3 mm., d^{20} 0·9116, n_D^{19} 1·50338, which corresponds in its physical properties with a sesquiterpene. On catalytic reduction with palladium, it yields a *tetrahydro*-derivative, $C_{15}H_{28}$, b. p. 175—180°/16 mm., d^{20} 0·8758, n_D 1·47547. The unsaturated hydrocarbon yields an unstable *tetrabromide*, which spontaneously loses hydrogen bromide. J. W. BAKER.

Dehydrogenation of menthol. G. CUSMANO (Atti R. Accad. Lincei, 1926, [vi], 4, 385—387).—

When a solution of sodium in fused menthol is heated at about 300°, hydrogen is evolved in large proportion, the sodium menthoxide losing two atoms of hydrogen to give a sodiomenthone, which afterwards gives up four hydrogen atoms to form sodium thymoxide, possibly by way of a menthenone derivative.

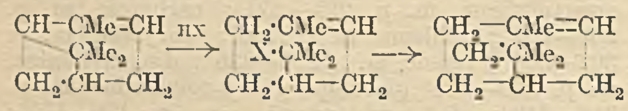
T. H. POPE.

Terpene and sesquiterpene of Mitsubazeri. N. HIRANO (Sci. Rep. Tôhoku, 1926, 15, 661—670).—See A., 1926, 408.

Liquid hydrochlorides of pinene. M. DELÉPINE and C. CACHAT (Bull. Soc. chim., 1926, [iv], 39, 1745—1755).—Repeated fractional distillation has established the presence of limonene and limonene hydrochloride in the "liquid hydrochloride" obtained in the treatment of Aleppo turpentine (α +41·8°) with hydrogen chloride in the cold or in alcoholic solution, in addition to the products previously observed (cf. A., 1907, i, 630; 1910, i, 400; 1921, i, 795; 1924, i, 1084, 1088; 1926, 1042).

R. BRIGHTMAN.

Hydration of nopinene. II. G. AUSTERWEIL and (MLLE.) O. PETROVICI (Bull. Soc. chim., 1926, [iv], 39, 1732—1744; cf. A., 1926, 619).—The reaction between nopinene and organic acids affording bornyl esters is bimolecular, involving addition at the double linking and at the ruptured bridge linkings; it is always accompanied by a unimolecular reaction, affording *l*-α-pinene by addition of 1 mol. of acid at the double linking. The latter reaction is the first stage in the formation of monocyclic terpenes, the latter being produced from pinene according to the scheme:



Dilution of the organic acid with a neutral solvent such as toluene almost completely suppresses the formation of monocyclic terpenes, and the reaction product consists of *l*-pinene and bornyl esters. These facts support the view that the hemicyclic double linking in nopinene is more reactive than the bridge linking. Under conditions in which nopinene affords bornyl ethers and *l*-pinene, pinene alone affords neither bornyl ethers nor monocyclic terpenes.

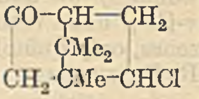
R. BRIGHTMAN.

Nitrogenous derivatives of terpene alcohols [bornyl and menthyl pyridinecarboxylates]. R. WOLFFENSTEIN.—See B., 1927, 28.

Essence of camphor. VI. Dehydration of cyclic terpene alcohols by Japanese acid earth. K. ONO (Bull. Chem. Soc. Japan, 1926, 1, 248—252).—The following products were isolated on dehydrating certain cyclic terpene alcohols with Japanese fuller's earth: dipentene and α-terpineol from terpin hydrate; dipentene from liquid terpineol; *l*-menthene from *l*-menthol; crystalline *d*-camphene and a liquid *d*-camphene from *d*-borneol.

S. J. GREGG.

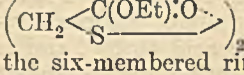
Chromic acid oxidation of bornyl chloride to *p*-ketobornyl chloride. J. BREDT and P. PINTEN (J. pr. Chem., 1927, [ii], 115, 45—55).—Oxidation of bornyl chloride in acetic acid solution with potassium dichromate and sulphuric acid at 60—70° yields *p*-ketobornyl chloride (annexed formula), m. p. 158° (*semicarbazone*, m. p. 259°), in 10—30% yield, according to the conditions, the effect of varying these being investigated in some detail. The constitution of the product is proved by its reduction with sodium and boiling alcohol to *epi*borneol (*acetate*, b. p. 114°/19 mm., d_4^{14} 0·988, $[\alpha]_D^{13}$ +15·63°), which is oxidised by chromic and acetic acids to *epi*camphor (*semicarbazone*, m. p. 236—237°; oxime, m. p. 103°). The optical activity of the products obtained varied with the specimens of pinene used for the original preparation of the bornyl chloride.



J. W. BAKER.

Co-ordinated mercaptides. A. M. DRUMMOND and D. T. GIBSON (J.C.S., 1926, 3073—3077).—The metallic derivatives of mercaptans containing the CO group are not of the simple type RSM′, but are co-ordinated ring compounds, showing non-ionisable character, solubility in anhydrous organic solvents, anomalous colour, and, in certain cases, stability towards heat.

Thiolcamphor [*cadmibromide*, $C_{10}H_{15}OBrSCd$; *stannochloride*, $(C_{10}H_{15}OSH)_3,Sn_2Cl_4$, m. p. 187°], yields, on treatment with alcoholic silver nitrate, *silver thiolcamphor argentinitrate*, $C_{10}H_{15}O{\cdot}SAg,AgNO_3,H_2O$, charring at 200—210°, $[\alpha]_{5461}^{19}$ +21° in chloroform. This substance reacts with a solution of thiolcamphor in dry benzene, giving a *compound*, $(C_{10}H_{15}O{\cdot}SAg)_2,AgNO_3,H_2O$, decomp. above 230°, $[\alpha]_{5461}^{15}$ +64° in chloroform. The following are also described: *nickel thiolcamphor*, $(C_{10}H_{15}O{\cdot}S)_2Ni,C_{10}H_{15}O{\cdot}SH$; *methyl* β-*thiolpropionate*, b. p. 54—55°/14 mm., n^{19} 1·4628, giving *methyl silver* β-*thiolpropionate argentinitrate*, $C_4H_7O_2{\cdot}AgS,AgNO_3{\cdot}H_2O$, and *methyl nickel* β-*thiolpropionate*, $(C_4H_7O_2S)_2Ni$. The five-membered ring compound, *ethyl nickel thiolacetate*,



$$\left(CH_2<\begin{matrix}C(OEt){:}O\\S\end{matrix}>\right)_2Ni$$

shows greater stability than the six-membered ring compounds, melting without decomposition at 101°. *Nickel* β-*thiolpropionate*, $(C_3H_5O_2S)_2Ni$, resembles the previous compounds in colour only and is insoluble in organic solvents.

An improved method for the preparation of thiolcamphor is described.

M. CLARK.

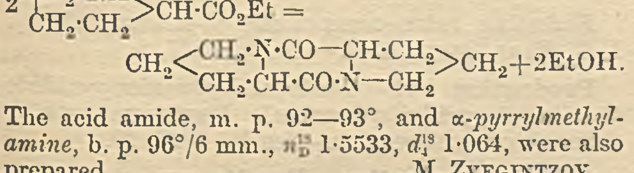
Ring opening and closing in coumarandione derivatives. K. VON AUWERS and W. HERBENER (J. pr. Chem., 1926, [ii], 114, 313—336; cf. A., 1908, i, 477; 1911, i, 168).—4 : 6-Dimethylcoumaran-3-one and benzenediazonium chloride in acetic acid solution yield orange-red 4 : 6-*dimethylcoumaran*-2 : 3-*dione*-2-*phenylhydrazone*, m. p. 155—156°. This does not further react with phenylhydrazine. Benzoylation in hot pyridine converts it into the *as*-*benzoylphenylhydrazone*, m. p. 182—183°, the constitution of which is proved by its quantitative reduction to benzanilide. 4 : 6-Dimethylcoumarandione and phenylhydrazine acetate give the 3-*phenylhydrazone*, m. p. 151—152°, which is hydrolysed by cold 2% alcoholic sodium hydroxide to 2-*hydroxy*-4 : 6-*dimethylphenylglyoxylic acid phenylhydrazone*, m. p. 117°, the reverse change being brought about by heating or desiccation. The

3-benzoylphenylhydrazone, 3-acetylphenylhydrazone, and 3-anil of 4 : 6-dimethylcoumarandione could not be prepared; even in anhydrous solvents the corresponding *derivatives* of 2-hydroxy-4 : 6-dimethylphenylglyoxylic acid, m. p. 96—98°, 141—142°, and 123—124°, respectively, are obtained. The *benzoylphenylhydrazone*, m. p. 147°, and *anil*, m. p. 110—111°, of methyl 2-methoxy-4 : 6-dimethylphenylglyoxylate are unexpectedly resistant towards hydrolysis. 4 : 6-*Dimethylcoumarandione*-3-*methylphenylhydrazone*, m. p. 142°, is immediately soluble in aqueous sodium hydroxide; the free acid rapidly undergoes lactonisation. The corresponding *benzylphenylhydrazone*, m. p. 148—150°, was obtained as a mixture of lactone and free acid. 2-*Hydroxy*-4 : 6-*dimethylphenylglyoxanilide anil*, m. p. 194—195°; 2-*hydroxyphenylglyoxylic acid benzoylphenylhydrazone*, m. p. 60—70°, and *anil-anilide*, m. p. 177—178°, and *ethyl* 2-*hydroxyphenylglyoxylate*-p-*nitrophenylhydrazone*, m. p. 129—130°, are described. The factors affecting the stability of the lactone rings in the above compounds and the corresponding ones from coumarandione and its 5-methyl derivative (*ibid.*, 1911, i, 585; 1912, i, 204) are fully discussed.

[In part with W. Gaertner].—In order to prove that *o*-hydroxyphenylglyoxylic acids have not the constitution of 2 : 2-dihydroxycoumaran-3-ones, some pairs of mixed ether-esters have been prepared. 2-*Methoxy*-5-*methylphenylglyoxylic acid*, m. p. 114—115°, affords a liquid *ethyl* ester, b. p. 168—170°/11 mm.; 2-*ethoxy*-5-*methylphenylglyoxylic acid*, m. p. 142—143°, yields a *methyl* ester, m. p. 53°. If the cyclic formula is correct, these should have been identical. This formula also fails to explain the rapid lactonisation of 2-hydroxy-4 : 6-dimethylglyoxylic acid in presence of water (A., 1921, i, 578). 2-*Methoxy*-4 : 6-*dimethylphenylglyoxylic acid*, m. p. 126—127° (*methyl* ester, m. p. 48°; *ethyl* ester, b. p. 180°/15 mm.), gives a *benzoylphenylhydrazone*, m. p. 143—144°, which is converted through the *silver* salt into a *methyl* ester, m. p. 147°, identical with that obtained above from dimethylcoumarandione. 2-*Ethoxy*-4 : 6-*dimethylphenylglyoxylic acid*, m. p. 141—142° (*methyl* ester, m. p. 85—86°), decomposes on distillation in a vacuum into 3 : 5-dimethylphenetole and 2-*ethoxy*-4 : 6-*dimethylbenzoic acid*, m. p. 125—126°.

H. E. F. Notton.

Derivatives of pyrrole. Pyrrolidine. N. J. Putochin (J. Russ. Phys. Chem. Soc., 1926, 58, 119—121).—The ethyl ester of proline, on keeping for 2—3 months, deposits colourless needles, m. p. 183—184°. The mother-liquor, on distillation, gives a quantitative yield of ethyl alcohol, according to the equation :



$$2\left.\begin{matrix}\mathrm{CH_2{-}NH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CH{\cdot}CO_2Et} = \mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}N{\cdot}CO{-}CH{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH{\cdot}CO{\cdot}N{-}CH_2}\end{matrix}\right\rangle\mathrm{CH_2}+2\mathrm{EtOH}.$$

The acid amide, m. p. 92—93°, and α-*pyrrylmethylamine*, b. p. 96°/6 mm., n_D^{15} 1·5533, d_4^{18} 1·064, were also prepared.

M. Zvegintzov.

Hydrogenated phenylquinolines and determination of the constitution of "decahydroatophan." A. Skita and C. Wulff [with C. Fehr, W. Winterhalder, and A. Meetz] (Ber., 1926, 59, [*B*], 2683—2691; cf. A., 1916, i, 835).—2-Phenylquinoline-4-carboxylic acid (atophan) is converted by hydrogen at 1—1½ atm. pressure in glacial acetic acid in the presence of colloidal platinum into 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, m. p. 163—165° (*hydrochloride*, m. p. 235°; *nitroso*-compound, m. p. 110°; *acetyl* derivative, m. p. 193—194°; *ethyl* ester, b. p. 170—180°/0·25 mm.). The acid is converted by distillation with soda-lime into 2-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 341—343° (*benzoyl* derivative, m. p. 101°), obtained also by hydrogenation of 2-phenylquinoline under 2 atm. in presence of colloidal platinum.

The action of hexahydrobenzaldehyde and pyruvic acid on aniline in boiling alcoholic solution yields 2-cyclo*hexylquinoline*-4-*carboxylic acid*, m. p. 137° (*methyl* ester, m. p. 54—55°), and a *substance*, m. p. 230°; the acid, which is also obtained from pyruvic acid and *hexahydrobenzylideneaniline*, b. p. 179°/70 mm., is decarboxylated to 2-cyclo*hexylquinoline*, b. p. 180—183°/20 mm.

Catalytic hydrogenation of atophan under 3 atm. affords 2-*cyclo*hexyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (decahydroatophan, *loc. cit.*); the *nitroso*-derivative, m. p. 89°, *acetyl* compound, m. p. above 300°, *amide*, m. p. 156°, *methyl* ester, m. p. 71°, and *ethyl* ester, b. p. 165—173°/0·5 mm., are described. Decarboxylation of the acid affords 2-cyclo*hexyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 314—315° (non-crystalline *nitroso*-derivative; *benzoyl* compound, m. p. 134°; *picrate*, m. p. 204°), also prepared by hydrogenation of 2-phenylquinoline in presence of colloidal platinum at 60° and 3 atm. or, with greater difficulty, from 2-*cyclo*hexylquinoline in presence of spongy platinum.

Hydrogenation of atophan usually ceases at the decahydro-stage, but if fresh platinum is then added, 2-cyclo*hexyldecahydroquinoline*-4-*carboxylic acid* (perhydroatophan), m. p. above 300°, is obtained; the *nitroso*-derivative, decomp. 69°, *ethyl* ester, m. p. 62—63°, and its *hydrochloride*, m. p. 269°, are described. Decarboxylation of the acid gives 2-cyclo*hexyldecahydroquinoline*, b. p. 165°/13 mm. (hygroscopic *hydrochloride*; *nitroso*-derivative, m. p. 179°), also obtained by hydrogenation of 2-phenylquinoline in presence of colloidal platinum at 3 atm. and 60°.

Benzaldehyde and cyclo*hexylamine* yield *benzylidene*cyclo*hexylamine*, b. p. 136°/16 mm. (cyclo*hexylamine benzoate*, m. p. 169°, is incidentally described). With pyruvic acid, benzylidene*cyclo*hexylamine yields a *compound*, $C_{16}H_{19}O_2N$, m. p. 144°, which is readily hydrolysed to benzaldehyde and *cyclo*hexylamine.

H. Wren.

Homologues of indole in coal tar. O. Kruber (Ber., 1926, 59, [*B*], 2752—2760).—The presence of 2-, 3-, 5-, and 7-methylindole in coal tar is established. The residues obtained from the technical isolation of indole are fractionally distilled under reduced pressure. The individual fractions are converted successively into their sodium derivatives and carboxylic acids. The latter compounds are purified by crystallisation and subsequently decarboxylated to the parent indoles. The following new compounds are described : 7-*methylindole*-3-*carboxylic acid*, m. p.

228° (decomp.); 7-*methylindole*, b. p. 266°, m. p. 85° (*picrate*, m. p. 176°); 1-*benzoyl*-7-*methylindole*, m. p. 84°, obtained in very poor yield from benzoyl chloride and the sodium derivative of 7-methylindole and oxidised by permanganate to 2-*benzamido*-m-*toluic acid*, m. p. 178°. The constitution of 7-methylindole is established as follows: 7-methylindole-3-carboxylic acid is reduced by sodium and alcohol to 7-*methyl*-2 : 3-*dihydroindole*-3-*carboxylic acid*, m. p. 237°, from which 7-*methyl*-2 : 3-*dihydroindole*, b. p. 120—122°/10 mm., d_4^{20} 1·044, is prepared (*picrate*, m. p. 186°; *hydrochloride*, m. p. 199—200°; *benzenesulphonyl* derivative, m. p. 131°; *benzoyl* derivative, m. p. 106°). The acid is readily transformed by benzoyl chloride in presence of sodium hydrogen carbonate into 1-*benzoyl*-7-*methyl*-2 : 3-*dihydroindole*-3-*carboxylic acid*, m. p. 163—164°, oxidised by permanganate to 2-*benzamido*iso*phthalic acid*, m. p. 217—218° (also *dihydrate*), whence 2-amino*iso*phthalic acid, m. p. above 340° (*methyl* ester, m. p. 103—104°); the latter acid is identical with that prepared by reduction of 2-nitro*iso*phthalic acid, obtained by oxidation of 2-nitro-*m*-xylene. 7-Methylindole is obtained synthetically by converting the *o*-tolylhydrazone of ethyl pyruvate by means of zinc chloride into ethyl 7-methylindole-2-carboxylate and hydrolysis of the latter to 7-methylindole-2-carboxylic acid, m. p. 170°, followed by decarboxylation. 3-Methylindole is isolated through the sparingly soluble sodium salt of the corresponding carboxylic acid. 5-Methylindole, b. p. 267°, m. p. 65°, is obtained by decarboxylation of 5-*methylindole*-3-*carboxylic acid*, m. p. 202° (decomp.), and synthesised from the *p*-tolylhydrazone of ethyl pyruvate. 2-Methylindole-3-carboxylic acid has m. p. 190°. H. WREN.

3-Methoxy-2-phenylindole and 3-benzamido-2-phenylindole. R. ROBINSON and S. THORNLEY (J.C.S., 1926, 3144—3145).—3-*Methoxy*-2-*phenylindole*, m. p. 106°, and 3-*benzamido*-2-*phenylindole*, m. p. 206°, are readily obtained through the phenylhydrazones of ω-methoxyacetophenone and ω-benzamidoacetophenone, respectively, showing that Fischer's method can be extended to the synthesis of indole derivatives in which an oxygen or a nitrogen atom is directly attached to the pyrrole nucleus. ω-*Benzamidoacetophenonephenylhydrazone* has m. p. 153°. M. CLARK.

Reactions of aldehydes with magnesium [magnesyl] indole. Q. MINGOIA (Gazzetta, 1926, 56, 772—781).—Aromatic aldehydes react with the magnesium compounds of indole and its derivatives to give substituted phenyldi-indolylmethanes. Magnesium indole yields with vanillin *di*-3-*indolyl*-p-*hydroxy*-m-*methoxyphenylmethane*, $(C_6H_4{:}C_2H_2N)_2CH\cdot C_6H_3(OH)\cdot OMe$, m. p. 141—142°; with piperonal *di*-3-*indolylmethylenedioxyphenylmethane*, m. p. 89—91° (*diacetyl* derivative, m. p. 99—100°; *dibenzoyl* derivative, m. p. 70°); and with *m*-nitrobenzaldehyde *di*-3-*indolyl*-m-*nitrophenylmethane*, m. p. above 260°. The magnesium compound of 2-methylindole reacts with benzaldehyde to give *di*-2-*methylindolylphenylmethane*, m. p. 250—251°; with vanillin to give *di*-2-*methylindolyl*-p-*hydroxy*-m-*methoxyphenylmethane*, m. p. 220° (*triacetyl* derivative, m. p. 170°); with piperonal to give *di*-2-*methylindolylmethylenedioxyphenylmethane*, m. p. 211—213° (*diacetyl* derivative, m. p. 112°; *dibenzoyl* derivative, m. p. 135—140°), and with *m*-nitrobenzaldehyde to yield di-2-methylindolyl-*m*-nitrophenylmethane (m. p. 271°; cf. Fischer, A., 1888, 284). The magnesium compound of 3-methylindole reacts with piperonal to give a poor yield of *di*-3-*methylindolylmethylenedioxyphenylmethane*, m. p. 94°, and with *m*-nitrobenzaldehyde to give a little of a *substance*, m. p. 160° (decomp.), which is probably the corresponding di-indolylphenylmethane. G. M. BENNETT.

Syntheses by means of magnesium [magnesyl] pyrrole. II. Reactions with inorganic anhydrides and chloroanhydrides and formation and constitution of some sulphur derivatives of indole. B. ODDO and Q. MINGOIA (Gazzetta, 1926, 56, 782—797).—Sulphuryl chloride reacts with magnesium pyrrole in ether to give dark brown, amorphous, insoluble products, whilst with magnesium indole the product is *di*-3-*indolylsulphone*, m. p. 151—152°, not reduced by zinc and acetic acid to a sulphide. *Di*-2-*methyl*-3-*indolylsulphone* (decomp.) results from the corresponding reaction using 2-methylindole. Magnesium indole reacts with sulphur dioxide to give di-indolylsulphoxide, m. p. 157° (Madelung and Tencer, A., 1915, i, 719), reduced by zinc and acetic acid to the corresponding sulphide, m. p. 232°, which is also formed as a by-product in the above reaction. Benzenediazonium chloride converts this sulphide into a *bisbenzeneazo*-derivative, m. p. 158°. The corresponding product from 2-methylindole is di-2-methyl-3-indolyl sulphide, m. p. 225—226°. Magnesium pyrrole reacts with carbon disulphide with production of *pyrrole*-2-*dithiocarbonic acid*, a reddish-brown oil (brick-red *lead* and greenish-yellow *mercury* salts described), which is readily oxidised in neutral solution to its *disulphide*, $[C_4H_4N\cdot CS\cdot S\cdot]_2$, m. p. 133°. In the same way, by the action of carbon disulphide on magnesium indole, *indole*-3-*dithiocarbonic acid* (*ammonium* and orange-red *lead* salts described) is obtained, which is readily oxidised to the *disulphide*, m. p. 155° (*bisbenzeneazo*-derivative, m. p. 107°), and is converted by fusion with potassium hydroxide into indole-3-carboxylic acid, m. p. 218°. From the magnesium compound of 2-methylindole there is obtained 2-*methylindole*-3-*dithiocarbonic acid* (*ammonium*, orange-yellow *lead*, and brick-red *mercury* salts described) and its *disulphide*, m. p. 183°.

G. M. BENNETT.

[Condensation products of 2-aminopyridine with aliphatic-aromatic ketones.] L. SCHMID and B. BANGLER (Ber., 1926, 59, [*B*], 2805).—A reply to Tschitschibabin (A., 1926, 1153).

Reducing nitro-compounds [3-nitropyridine]. I. G. FARBENIND. A.-G.—See B., 1927, 8.

Production of 5-nitro-2-hydrazinopyridine [5-nitro-2-pyridylhydrazine]. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT.—See B., 1927, 29.

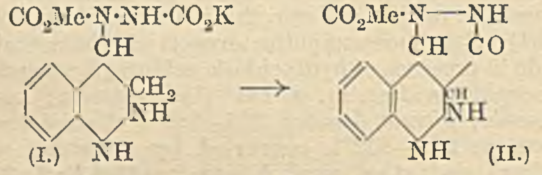
6-Methoxyquinoline. E. MASCHMANN (Ber., 1926, 59, [*B*], 2825—2826).—6-Methoxyquinoline has b. p. 153°/12 mm., 284°/749 mm., m. p. 26·5°. The discoloration observed when it is preserved is caused by light, particularly ultra-violet rays, and not by air. H. Wren.

Quinoline derivatives. VI. 2-Phenylquinoline-4-carboxylic acid. H. John [with V. Fischl and E. Wünsche] (Ber., 1926, 59, [*B*], 2709—2712).—Dry distillation of barium 2-phenylquinoline-4-carboxylate yields 2-phenylquinoline, m. p. 84°, and, apparently, *di-2-phenylquinolyl*, m. p. 303° (*hydrochloride*; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *chloroplatinate*, which does not melt below 300°; *picrate*, m. p. 234°). The product of high m. p. is also obtained by distillation of the lithium, ammonium, sodium, potassium, calcium, strontium, aluminium, and tin salts, but not from the magnesium, iron, copper, silver, zinc, cadmium, lead, or bismuth compounds. 4-Chloro-2-phenylquinoline is converted by copper powder in boiling nitrobenzene into 2-phenylquinoline, whereas distillation with zinc dust transforms it into the substance, m. p. 303°, in poor yield. H. Wren.

Behaviour of 2-substituted 8-methoxy-3-arylsulphonylquinolines towards nascent hydrogen. J. Tröger and F. Krückeberg (J. pr. Chem., 1926, [ii], **114**, 249—268).—The reactivity of 2-amino-3-arylsulphonylquinolines is decreased by the introduction of an 8-methoxyl group. Further study of the 2-amino-8-methoxy-3-arylsulphonylquinolines (cf. A., 1926, 68) shows that they do not form methiodides, that their *hydrochlorides* and *nitrates* decompose when heated at 105—120°, and that their *hydrogen sulphates* are hydrolysed by water. 2-Amino-8-methoxy-3-benzenesulphonylquinoline is converted by nitrous acid into 2-*hydroxy*-8-*methoxy*-3-*benzenesulphonylquinoline*, m. p. 250°. When the latter is heated at 150° with phosphorus pentachloride, it yields the corresponding 2-*chloro*-derivative, m. p. 195°. This does not react with metallic benzenesulphinates or thio-*p*-tolyloxides (cf. *ibid.*, 1924, i, 556), but with aniline, potassium hydrosulphide, and sodium ethoxide it affords 2-*anilino*-, m. p. 185°, 2-*thiol*-, m. p. 183°, and 2-*ethoxy*-8-*methoxy*-3-*benzenesulphonylquinoline*, m. p. 191°, respectively. The following derivatives are prepared by analogous methods: of 8-methoxy-3-*p*-toluenesulphonylquinoline: 2-*hydroxy*-, m. p. 262°; 2-*chloro*-, m. p. 197°; 2-*anilino*-, m. p. 187°; 2-*thiol*-, m. p. 186°; of 8-methoxy-3-*p*-chlorobenzenesulphonylquinoline: 2-*hydroxy*-, m. p. 275°; 2-*chloro*-, m. p. 212°; of 8-methoxy-3-*o*-anisolesulphonylquinoline: 2-*hydroxy*-, m. p. 237°; 2-*chloro*-, m. p. 188°; 2-*anilino*-, m. p. 184°; 2-*thiol*-, m. p. 189°; of 8-methoxy-3-*p*-phenetolesulphonylquinoline: 2-*hydroxy*-, m. p. 269°; 2-*chloro*-, m. p. 174°, and 2-*hydroxy*-8-*methoxy*-3-p-*bromobenzenesulphonylquinoline*, m. p. 262°. When reduced with tin and concentrated hydrochloric acid, these compounds behave in the usual way (cf. A., 1926, 524), the 2-substituent being removed in combination with hydrogen, the 3-arylsulphonyl-group as the corresponding arylthiophenol (75—80% yield), whilst the quinoline nucleus remains as 8-*methoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline hydrochloride*, m. p. 220° (decomp.) (*benzoyl* derivative, m. p. 136°). The 2-hydroxy-8-methoxy-3-arylsulphonylquinolines, however, do not give a tetrahydroquinoline derivative. In this case, the methoxycarbostyril first produced probably resists further reduction. H. E. F. Notton.

Derivatives of acenaphthpyridine. I. S. U. Nair and J. L. Simonsen (J.C.S., 1926, 3140—3143).—Whilst α-naphthylamine itself fails to condense with paracetaldehyde, its derivatives substituted in the 4-position readily undergo this reaction (cf. A., 1926, 1154). 5-Aminoacenaphthene reacts with paracetaldehyde in presence of hydrochloric acid to give 2-*methylacenaphthpyridine*, m. p. 131° (*hydrochloride*; *hydrobromide*; *picrate*, decomp. 225—226°; *chloroplatinate*, decomp. 251—252°), converted by reduction with sodium and ethyl alcohol into 2-*methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine*, m. p. 88—89°, b. p. 215—217°/14 mm. (*hydrochloride*, decomp. 260—261°; *benzoyl* derivative, m. p. 187—188°). 5-Aminoacenaphthene condenses with ethyl acetoacetate in alcoholic solution in presence of a trace of piperidine, giving *ethyl* β-5-*acenaphthylaminocrotonate*, m. p. 83—84°. When heated at 220°, this compound is converted into 4-*hydroxy*-2-*methylacenaphthpyridine*, m. p. above 330°. Condensation of 5-aminoacenaphthene and ethyl acetoacetate at 170° gives, besides a small quantity of s-*di*-5-*acenaphthylcarbamide*, m. p. 318°, β-5-*acenaphthylaminocroton*-5-*acenaphthylamide*, m. p. 189—190°, which is hydrolysed by dilute hydrochloric acid to 5-*acetoacetamidoacenaphthene*, m. p. 142—143°. This compound is converted by treatment with concentrated hydrochloric acid into 2-*hydroxy*-4-*methylacenaphthpyridine*, m. p. above 350° (*hydrochloride*). The hydroxy-compound reacts with phosphorus pentachloride to give 2-*chloro*-4-*methylacenaphthpyridine*, m. p. 200—201°, which yields on reduction with sodium and ethyl alcohol 4-*methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine*, m. p. 87—88° (*hydrobromide*). M. Clark.

Causes of the "azo-ester reaction." O. Diels and K. Alder (Annalen, 1926, 450, 237—254; cf. Diels and others, A., 1925, i, 976).—An investigation of the 1 : 4 addition of azodicarboxylates to conjugated unsaturated hydrocarbons, a reaction which is considered to be a test for the presence of partial valencies in the 1 : 4 position. With isoprene, ethyl azodicarboxylate gives *ethyl* 5-*methyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 2-*pyridazine*-1 : 2-*dicarboxylate*, b. p. 115°/0·15 mm., which reacts violently with bromine. Ethyl azodicarbamidoacetate, $(CO_2Et{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}N{:})_2$ (Blom., Diss., Kiel, 1923), gives the corresponding 1 : 2-*dicarbamidoacetate*, m. p. 158°, which with bromine forms *ethyl* 4 : 5-*dibromo*-4-*methylhexahydro*-1 : 2-*pyridazine*-1 : 2-*dicarbamidoacetate*, m. p. 175°. Myrcene reacts with methyl azodicarboxylate to give *methyl* 5-δ-*methyl*-Δγ-*amylidene*-1 : 2 : 3 : 6-*tetrahydropyridazine*-1 : 2-*dicarboxylate*, b. p. 145°/0·2 mm.; this reacts readily with bromine or with permanganate. With styrene, the conjugated system is continued in the benzene ring; addition of methyl azodicarboxylate occurs, but the product at the same time regains benzenoid character by reducing and combining with a second molecule of the azo-ester to give *methyl* 4-*hydrazino*-1 : 2 : 4 : 4-*tetrahydrocinnoline*-N : N′ : N″ : N‴-*tetracarboxylate* [*methyl* 4-*hydrazino*-1 : 2 : 4 : 4-*tetrahydro*-1 : 2-*benzdiazine*-N : N′ : N″ : N‴-*tetracarboxylate*], m. p. 178°, which gives no reactions of an unsaturated compound. Hydrolysis of this by potassium hydroxide gives *potassium 4-carbomethoxyhydrazinotetrahydrocinnoline-ω-carboxylate* (I), m. p. 146—147° (decomp.), which on treatment with acetic acid yields *methyl* ar-*hexahydrocinnolo*-1 : 2 : 3-*pyrazolone*-1-*carboxylate* (II), m. p. 183° (decomp.).


(I.) (II.)

In contrast to styrene, stilbene does not react with ethyl azodicarboxylate. It is thus assumed that a 1 : 4 conjugated system is required for the condensations. Correspondingly, *as*-diphenylethylene adds on 2 mols. of the methyl ester to give the unsaturated compound *methyl di*-[o-*hydrazinophenyl*]-*ethylene*-N : N′ : N″ : N‴-*tetracarboxylate*, $CH_2{:}C[\cdot C_6H_4\cdot N(CO_2Me)\cdot NH(CO_2Me)]_2$, m. p. 188°. γ-Phenylpropene yields a product which is probably *methyl* γ-2 : 6-*dihydrazinophenylpropenetetracarboxylate*, $CHMe{:}CH\cdot C_6H_3[N(CO_2Me)\cdot NH(CO_2Me)]_2$, m. p. 142°. β-Phenylpropene yields *methyl* β-o-*hydrazinophenylpropene*-N : N′-*dicarboxylate*, m. p. 82°. This gives by catalytic hydrogenation the corresponding *propane* derivative, m. p. 62°, and by addition of bromine the αβ-*dibromopropane* derivative, m. p. 164°; ozonisation yields o-*dicarbomethoxyhydrazinoacetophenone*, m. p. 104° (*phenylhydrazone*, m. p. 156°).

Indene combines with 1 mol. of the ethyl ester to give a product which is probably *ethyl 2-hydrazinoindene*-N : N′-*dicarboxylate*, m. p. 107°.

Substituted butadienes give rise to compounds which are regarded as pyridazine derivatives: thus *trans*-1 : 4-diphenylbutadiene gives *methyl* 3 : 6-*diphenyl*-1 : 2 : 3 : 6-*tetrahydropyridazine*-1 : 2-*dicarboxylate*, m. p. 182°. This adds on bromine to give *methyl* 4 : 5-*dibromo*-3 : 6-*diphenylhexahydropyridazine*-1 : 2-*dicarboxylate*, m. p. 183—184°. It is hydrolysed by methyl-alcoholic potassium hydroxide to 3 : 6-*diphenyl*-1 : 2 : 3 : 6-*tetrahydropyridazine*, m. p. 157°, feebly basic (*hydrochloride*, m. p. 185°), which is reduced by zinc and hydrochloric acid to 1 : 4-diamino-1 : 4-diphenyl-Δ^β-butene (picrate, decomp. 230°, cf. Wieland and Stenzl, A., 1908, i, 518).

Phenylacetylene and diphenylacetylene scarcely react with the azo-ester.

Considering the addition of the azo-ester to heterocyclic compounds containing a co-ordinated system, pyrrole reacts violently and forms a complex grey amorphous substance, derived from at least 3 mols. of ethyl azodicarboxylate to 1 mol. of pyrrole.

Thiophen is inert towards the azo-ester, but furan reacts very readily, indicating that ring oxygen co-ordinates much less readily with free partial valencies than does sulphur. E. W. WIGNALL.

Synthesis of 1-acylindazoles [and related substances]. K. VON AUWERS and E. FRESE (Annalen, 1926, 450, 273—303).—Derivatives of *o*-aminobenzaldoxime of the formula $R'\cdot CO\cdot NH\cdot C_6H_4\cdot CH{:}N\cdot O\cdot CO\cdot R$ when heated, yield nitriles, $R'\cdot CO\cdot NH\cdot C_6H_4\cdot CN$; when heated with anhydrous sodium carbonate, the nitriles are obtained if R=alkyl, but 1-acylindazoles, $C_6H_4{:}(\cdot CH{:}N\cdot N\cdot COR')$ if R=alkoxyl. Thus *o*-acetamidoacetylbenzaldoxime, m. p. 131—132° (cf. Gabriel and Meyer, A., 1882, 188), when heated alone or with sodium carbonate, is converted into *o*-acetamidobenzonitrile. *Methyl* o-*aminobenzaldehyde*-N-*carboxylate*, m. p. 89—90°, which is obtained from *o*-aminobenzaldehyde and methyl chloroformate, and when treated with sodium carbonate gives various products, including a *substance*, $C_{14}H_{12}ON_2$, m. p. 132—134° (decomp.), gives an *oxime*, m. p. 129°, which is converted by acetic anhydride into an *isomeride*, m. p. 121—123°. The corresponding *methyl* o-*aminobenzaldoxime*-ON-*dicarboxylate*, m. p. 135—136°, which is obtained from *o*-aminobenzaldoxime and methyl chloroformate, yields, when heated alone, *methyl* o-*aminobenzonitrile*-N-*carboxylate*, m. p. 94·5—95·5°, but in presence of sodium carbonate, methyl indazole-1-carboxylate, m. p. 59—60°, b. p. 151—152°/13 mm. (cf. A., 1921, i, 808; 1925, i, 1460).

The following were similarly prepared, using ethyl chloroformate: *ethyl* o-*aminobenzaldoxime*-N-*carboxylate*, m. p. 115—116°; *ethyl* o-*aminobenzaldoxime*-ON-*dicarboxylate*, m. p. 88·5—89°, which yields *ethyl* o-*aminobenzonitrile*-N-*carboxylate*, m. p. 103—104°, and ethyl indazole-1-carboxylate (see above); *methyl* o-*amino*-O-*carbethoxybenzaldoxime*-N-*carboxylate*, m. p. 78·5—79·5°, which yields methyl *o*-aminobenzonitrile-*N*-carboxylate, and methyl indazole-1-carboxylate.

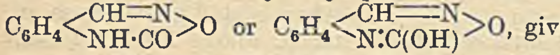
Methyl o-*aminoacetylbenzaldoxime*-N-*carboxylate*, m. p. 104·5—105·5°, is converted by alcoholic alkali into a heptaoxadiazine (see below); when heated alone, it gives methyl *o*-aminobenzonitrile-*N*-carboxylate; with sodium carbonate, unidentified products were obtained.

Methyl o-*acetamidobenzaldoxime*-O-*carboxylate*, m. p. 122—123° (decomp.), from *o*-acetamidobenzaldoxime, yields o-*acetamidobenzonitrile* and 1-acetylindazole. o-*Chloroacetamidochloroacetylbenzaldoxime*, m. p. 156·5—157·5°, converted by alcoholic alkali into an octaoxadiazine (see below), is hydrolysed by alcoholic hydrochloric acid to o-*chloroacetamidobenzaldoxime*, m. p. 182—183°. *Ethyl* o-*chloroacetamidobenzaldoxime*-O-*carboxylate*, m. p. 120—120·5°, obtained from the latter, yields o-*chloroacetamidobenzonitrile*, m. p. 115—116°, and with alkali, 1-chloroacetylindazole. *o*-Aminobenzaldoxime is benzoylated to a mixture of 5 parts of *o*-benzamidobenzaldoxime and 1 part of o-*benzamidobenzoylbenzaldoxime*, m. p. 141—143°; *ethyl* o-*benzamidobenzaldoxime*-O-*carboxylate*, m. p. 129—130°, obtained from the former, yields *o*-benzamidobenzonitrile and 1-benzoylindazole.

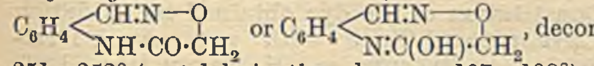
By the action of potassium cyanate on *o*-aminobenzaldoxime in acetic acid, *o*-carbamidobenzaldoxime, m. p. 161° (which gives an *ethyl* O-*carboxylate*, m. p. 166°), and a *substance*, $C_{16}H_{15}O_4N_5$, m. p. 216—217° (decomp.), are obtained. Using phenylcarbimide, the product is o-*benzamidobenzaldoxime*, m. p. 174—176° (*acetyl* derivative, m. p. 141—142°). Attempts to convert this by the action of potassium carbonate into 1-carbamylindazole have given no pure product. 2-*Carbamylindazole*, prepared from indazole and potassium cyanate, is labile, melting at

132—133°, resolidifying and melting again at 155°, being largely converted into 1-*carbamylindazole*, m. p. 166—167°.

o-*Benzamidoacetophenoneoxime*, m. p. 40—50°, gives an O-*carbomethoxy*-derivative, m. p. 93—94°, which, when heated with potassium carbonate in light petroleum gives some *o*-*benzamidoacetophenoneoxime benzoate*, m. p. 133°, and 1-*benzoyl*-3-*methylindazole*, m. p. 66—67°, identical with that prepared from 3-methylindazole.

The heptaoxadiazine mentioned above can also be obtained by heating *o*-carbomethoxyamidobenzaldoxime with dilute sodium hydroxide and acidifying, It is 4 : 5-*benzo*-7-*hydroxyhepta*-1 : 2 : 6-*oxadiazine*,  $C_6H_4{<}\begin{array}{l}CH{=}N\\ NH{\cdot}CO\end{array}{>}O$ or $C_6H_4{<}\begin{array}{l}CH{=}N\\ N{:}C(OH)\end{array}{>}O$, giving a *dihydrate*, decomp. 242—243°. This forms with ethyl chloroformate an O(?)-*carbethoxy*-derivative, m. p. 60—70° (decomp.), hydrolysed by alkali, but partly converted into a N(?)-*carbethoxy*-derivative, m. p. 181—182° or up to 193° (decomp.), according to the temperature at which heating begins; this substance may be obtained quantitatively by prolonged heating in benzene.

Acetic anhydride converts the heptaoxadiazine into *o*-acetamidoacetylbenzaldoxime, but by careful treatment, evaporating with methyl or with ethyl alcohol, *methyl* or *ethyl* *o*-*acetamidobenzaldoxime*-N-*carboxylates*(?), $CO_2R{\cdot}NAc{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH$, m. p. 158—159° (decomp.) and 164—164·5°, are respectively obtained. The free N-*carboxylic acid* (?), m. p. 153—154°, is obtained by slow evaporation without alcohol; it is converted by sodium carbonate into the heptaoxadiazine. Action of hydroxylamine on the latter yields *o*-ω-*hydroxycarbamidobenzaldoxime*, m. p. 205° (decomp.).

The octaoxadiazine mentioned above, obtained from *o*-chloroacetamidochloroacetylbenzaldoxime by treatment with alkali and acidification, is 4 : 5-*benzo*-7-*hydroxyocta*-1 : 2 : 6-*oxadiazine*,  $C_6H_4{<}\begin{array}{l}CH{:}N{-}O\\ NH{\cdot}CO{\cdot}CH_2\end{array}$ or $C_6H_4{<}\begin{array}{l}CH{:}N{-}O\\ N{:}C(OH){\cdot}CH_2\end{array}$, decomp. 251—252° (*acetyl* derivative, decomp. 197—198°).

In an attempt to prepare labile 2-acylindazoles, *o*-aminobenzyl alcohol was diazotised and treated first with sodium sulphite, and then with (*a*) zinc and acetic acid; the product was a substance of high m. p. containing sulphur; or (*b*) sodium hydroxide, which gives a crystalline *sodium* salt, decomposed by acid to indazole and sulphuric acid, and thus an *indazole*-N-*sulphonate*.

o-Nitrobenzylamine (obtained in varying yields by the Gabriel reaction) gives *o*-*tolu*-*o*-*nitrobenzylamide*, m. p. 131—132°, which is reduced by ammonium sulphide to *o*-*tolu*-*o*-*hydroxylaminobenzylamide*, m. p. 114—115°; this on heating or treatment with alcoholic alkali loses water to form an *anhydro*-derivative, $C_{30}H_{30}O_3N_4$, m. p. 189—190°, and a *substance*, m. p. 110—112°.

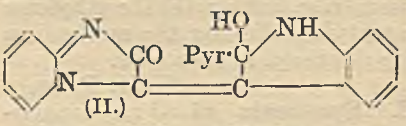
o-Hydrazinocinnamic acid, m. p. 196—197°, is better obtained by the method of Fischer and Kuzel (A., 1884, 440) than by that of Fischer and Tafel (*ibid.*, 1885, 540). The colour changes reported by these authors have not been confirmed. Attempts to acetylate this acid to a pure derivative from which a 2-acetylindazole might be obtained have not been successful.

E. W. Wignall.

Products of the action of aromatic aldehydes or pyriminazol-2-one and cyclic 1 : 2-dicarbonyl compounds. F. Reindel and A. von Putzer-Reybegg (Ber., 1926, 59, [*B*], 2926—2932).—*Pyriminazol-2-one*, m. p. 169° (decomp.), is prepared by addition of barium chloride to an aqueous solution of the sodium salt and decomposition of the *barium* salt by carbon dioxide. The corresponding hydrochloride is converted by benzaldehyde in boiling, absolute alcoholic suspension into 3-*benzylidene*-*pyriminazol*-2-*one hydrochloride*, m. p. 253° (decomp.), from which the free *base*, m. p. 233°, is derived; if the latter compound is crystallised from alcohol in presence of a little sodium salt, a *substance*, $C_{28}H_{26}O_3N_4$, m. p. 233° (decomp.) after becoming yellow at 190°, is obtained. Catalytic hydrogenation of the benzylidene derivative yields 3-*benzylpyriminazolone hydrochloride*, m. p. 216° (decomp.) [corresponding *picrate*, m. p. 189° (decomp.)]. Bromine converts the benzylidene compound into the *perbromide*, $C_{14}H_{10}ON_2Br_2$, m. p. 171—173° (decomp.). The following derivatives of pyriminazol-2-one are prepared analogously; 3-*o*-*nitrobenzylidene*, m. p. 214° (decomp.); *hydrochloride*, m. p. 239° (decomp.); 3-*m*-*nitrobenzylidene*, *sulphate*, m. p. 236° (decomp.); 3-*o*-*hydroxybenzylidene*, *hydrochloride*, m. p. 245° (decomp.): 3-*p*-*hydroxybenzylidene*, m. p. 278° (decomp.); *sulphate*, m. p. 237° (decomp.); *sodium* salt: 3-*p*-*dimethylaminobenzylidene*, m. p. 275° (decomp.); *hydrochloride*, m. p. 256° (decomp.). The pyriminazole ring appears to have chromophoric properties similar to those of the indole ring.

3-Benzylidenepyriminazolone hydrochloride is transformed by boiling aqueous sodium acetate into benzaldehyde and (?) *di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazylphenylmethane*, m. p. 207° (decomp.), which is converted into a *substance*, m. p. 248° (decomp.), when crystallised from alcohol. Both substances are converted by phenylhydrazine into benzaldehydephenylhydrazone and by concentrated sodium hydroxide into a crystalline *sodium* salt converted by benzoylation into the *dibenzoyl* derivative of the methane, m. p. 204° (slight decomp.). Direct benzoylation of the substances, m. p. 207° and 248°, affords the benzoyl derivative of pyriminazolone, whereas oxidation of them with potassium ferricyanide gives *di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazylphenylmethene*, m. p. 207° (decomp.) (*sodium* salt). *Di*-2-*keto*-2 : 3-*dihydro*-3-*pyriminazyl*-2′-*hydroxyphenylmethane* (+H_2O), m. p. 216° (decomp.), is oxidised by ferricyanide to a red, non-crystalline methene.

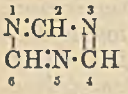
In cold alcoholic suspension, isatin and pyriminazolone hydrochloride afford 3-*pyriminazyl*-3′-*dioxindole*, m. p. 170° (decomp.) (*hydrochloride*, m. p. 230°), whereas in boiling suspension and with an increased proportion of the hydrochloride, di-3 : 3-pyriminazyloxindole, m. p. 249° (decomp.) (*hydrochloride*), is obtained. The latter compound is isomerised in boiling alcohol or converted by sodium hydroxide to the *dye* (II), m. p.



281° (decomp.) (*dibenzoyl* derivative, m. p. 241°). Analogous *dyes* are prepared from 5 : 7-dibromoisatin, 5-bromoisatin, and acenaphthaquinone, and have m. p. (decomp.) 294°, 287°, and 280°, respectively.

H. WREN.

Cyanurin group. O. DIELS and R. LICHTE (Ber., 1926, **59**, [*B*], 2778—2784).—It is proposed to base the nomenclature of all cyanuric compounds on "cyanurin," $C_3H_3N_3$. Cyanuric acid itself is therefore 2 : 4 : 6-trihydroxycyanurin. *iso*Cyanuric compounds are regarded as hydrogenated cyanurins; thus, *iso*cyanuric acid is designated 2 : 4 : 6-triketohexahydrocyanurin.



$$\begin{array}{l}\overset{1}{N}\!:\!\overset{2}{C}H\cdot\overset{3}{N} \\ \underset{6}{C}H\!:\!\underset{5}{N}\cdot\underset{4}{C}H\end{array}$$

Acetylcarbamide, obtained in 80% yield by the acetylation of carbamide in presence of a small amount of sublimed aluminium chloride, is converted by formaldehyde in presence of concentrated sulphuric acid at −15° into *methylenediacetylcarbamide*, $CH_2(NH\cdot CO\cdot NHAc)_2$, m. p. 255°, which is hydrolysed by concentrated aqueous potassium hydroxide to *methylenedicarbamide*, m. p. 207°. The latter substance is transformed by concentrated hydrochloric acid into 2 : 4-*diketohexahydrocyanurin*, m. p. 245°, the salts of which are readily hydrolysed by water. Acetylthiocarbamide and formaldehyde afford *methylenediacetylthiocarbamide*, m. p. 167°, from which *methylenedithiocarbamide*, m. p. 152°, and 2 : 4-*dithiohexahydrocyanurin* are successively derived; the *silver*, *cuprous*, and *mercurous* (decomp. 230°) salts of the latter compound are described. The mercurous compound adds methyl iodide at the three nitrogen and two sulphur atoms, whilst the imino-group between the two CS groups is also methylated, thus giving the *compound* $C_9H_{20}N_2S_2I_5Hg_2$, m. p. 101°; ethyl iodide affords the analogous *substance* $C_{15}H_{32}N_3S_2I_5Hg_2$, m. p. 73°. The compounds are readily hydrolysed by water with separation of mercuric iodide. 2 : 4-Dithiohexahydrocyanurin and methyl iodide give the *substance* $C_7H_{16}N_3I_3S_2$, m. p. 115°.

Thioacetanilide and methyl iodide yield the *compound* NHPh·CMe:SMeI, m. p. 135—137°.

H. WREN.

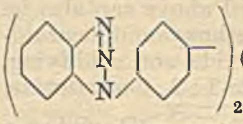
Condensations of unsaturated compounds with diazomethane. R. ROTTER (Monatsh., 1926, **47**, 353—356).—Freshly-distilled (unimolecular) carbodianil combines with diazomethane in ethereal solution to yield 5-anilino-1-phenyltriazole, m. p. 142° (cf. Dimroth, A., 1909, 269).

G. M. BENNETT.

Syntheses with azoimide and mechanism of the reactions. E. OLIVERI-MANDALÀ (Mem. R. Accad. Lincei, 1926, [vi], **2**, 132—150).—A summary is given of the syntheses effected by addition of azoimide to (1) compounds with two contiguous double linkings in the molecule, such as carbodiphenylimide, carbimides, and thiocarbimides, ketens, carbon disulphide, and nitrous acid, (2) compounds containing bivalent carbon, such as carbylamines and fulminic acid, (3) the nitrilic linking, (4) the ethylenic linking, and (5) the acetylenic linking, the mechanism of the reaction being discussed in each case.

T. H. POPE.

Dicarbazyls. I. Synthesis of 3 : 3′-dicarbazyl. S. H. TUCKER (J.C.S., 1926, 3033—3038).—NN′-*Di*-o-*nitrophenylbenzidine*, m. p. 240° (NN′-*diacetyl* derivative $+2C_6H_6$, m. p. 80—85°; +EtOH, m. p. 120°; $+MeCO_2H$, m. p. 100—105°; +MeOH, m. p. 125—130°), is obtained, together with a little N-o-*nitrophenylbenzidine* (N′-*acetyl* derivative, m. p. 222°), by condensation of benzidine and *o*-chloronitrobenzene, or, alternatively, by oxidation of *o*-nitrodiphenylamine with sodium dichromate. Reduction gives NN′-*di*-o-*aminophenylbenzidine*, m. p. 218° (*dihydrochloride* becoming greenish-blue at 230—260°), converted by treatment with nitrous acid into 4 : 4′-*di*-1″ : 2″ : 3″-*benztriazolyldiphenyl* (I), m. p. 299°, which, when heated above its m. p., yields 3 : 3′-*dicarbazyl*, m. p. above 350° (9 : 9′-*diacetyl* derivative, m. p. 247—249°).



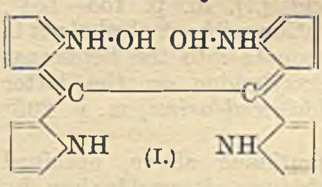
(I.)

M. CLARK.

So-called "substituted dihydropentazines" of Chattaway and Parkes. R. STOLLÉ (J. pr. Chem., 1926, [ii], **114**, 348—349).—Since α-hydrazinobenzaldehydebenzylideneazine, CHPh:N·N:CPh·NH·NH₂, is converted by nitrous acid into 1-benzylideneamino-5-phenyltetrazole (A., 1914, i, 750), the product obtained in a similar way from α-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone by Chattaway and Parkes (*ibid.*, 1926, 308) is probably 1-dibromoanilino-5-phenyltetrazole, and not 1-dibromophenyl-5-phenyl-1 : 4-dihydropentazine.

H. E. F. NOTTON.

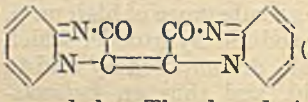
Action of ethyl oxalate on magnesium pyrryl iodide. T. N. GODNEV and N. A. NARYSCHKIN (Ber., 1926, **59**, [*B*], 2897—2898; cf. A., 1926, 183).—The isolation of "tetra-2-pyrrylethylene glycol" as a blackish-brown powder indicates that it is the true dye base (I).



(I.)

H. WREN.

Constitution of the dye obtained by oxidation of pyriminazol-2-one with potassium ferricyanide. F. REINDEL and H. RAUCH (Ber., 1926, **59**, [*B*], 2921—2925; cf. A., 1924, i, 1235; 1925, i, 438; Tschitschibabin, *ibid.*, 1925, i, 158).—In relation to the constitution of the dye, inconclusive attempts to synthesise a substance (I), by the action of ethyl dibromomaleate on 2-aminopyridine are recorded. The dye derived from 3 : 3-dibromopyriminazol-2-one and pyriminazol-2-one is not identical with that described previously. The yellow sodium salt obtained by the action of air on the sodium salts of pyriminazol-2-one (Reindel, *loc. cit.*) is not an intermediate product in the formation of the dye, since the latter cannot be produced from it by oxidation with potassium ferricyanide in alkaline solution. Treatment of the yellow salt with a little hydrochloric acid gives a *compound*, $C_{14}H_{10}O_3N_4,HCl,2H_2O$, m. p. 176° (decomp.), which is transformed by boiling water into pyriminazolone and a *substance*, decomp. 215—220°, giving 2-aminopyridine and oxalic acid when treated with sodium hydroxide.



(I.)

H. WREN.

Action of cyanogen halides on phenylhydrazine. X. Derivatives of oxadiazole. G. Pellizzari (Gazzetta, 1926, **56**, 695—700).—α-Cyanophenylhydrazine reacts in boiling benzene solution with acyl chlorides to give imino-oxadiazole derivatives. With benzoyl chloride the product is 2-*imino*-3 : 5-*diphenyloxa*-3 : 4-*diazole*, m. p. 124° (*benzoyl* derivative, m. p. 165°; *acetyl* derivative, m. p. 111°; *nitroso*-derivative explodes at about 80°), soluble in acids and converted by nitrous acid in boiling solution into the 3 : 5-diphenyloxa-3 : 4-diazol-2-one, m. p. 113°, of Freund and Goldsmith (A., 1888, 1187). In the same way, acetyl chloride yields the corresponding 2-imino-3-phenyl-5-methyloxa-3 : 4-diazole (Freund and Kuh, A., 1890, 1442) [*hydrochloride*, m. p. 190° (decomp.), and *picrate*, m. p. 174°, described], hydrolysed to the oxadiazolone, m. p. 93—94°. Ethyl chloroformate reacts to give 2-*imino*-5-*ethoxy*-3-*phenyloxa*-3 : 4-*diazole*, m. p. 75°, which has weak basic and acidic properties, and is hydrolysed by aqueous sodium hydroxide to 2-*imino*-5-*hydroxy*-3-*phenyloxa*-3 : 4-*diazole*, m. p. 262—263° (decomp.). G. M. Bennett.

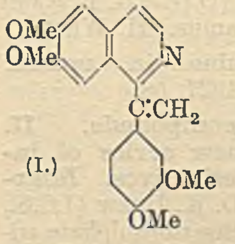
1 : 3-Benzoxazines. II. Conversion of *iso*nitrosocoumaranones into derivatives of 1 : 3-benzoxazine. E. Mameli (Gazzetta, 1926, **56**, 759—772).—The conversion of an *iso*nitrosocoumaranone derivative, by means of the Beckmann transformation, into a diketo-1 : 3-benzoxazine (A., 1922, i, 669) has been extended to a number of other cases. 2-*iso*Nitrosocoumaran-3-one yields 2 : 4-diketo-1 : 3-benzoxazine (m. p. 227°), and 2-*iso*nitroso-6-methylcoumaran-3-one is converted into 7-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 232° (*potassium* and *silver* salts described), which is hydrolysed by sodium hydroxide to the amide (m. p. 182°) of 2-hydroxy-*p*-toluic acid. 2-*iso*Nitroso-5-methylcoumaran-3-one yields 6-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 233°, which is hydrolysed by alkali to the amide (m. p. 178°) of 2-hydroxy-5-methylbenzoic acid. 2-iso*Nitroso*-7-*methylcoumaran*-3-*one*, m. p. 194°, obtained by the action of nitrite in acetic acid solution on 7-methylcoumaranone, is converted by the Beckmann reaction into 8-*methyl*-2 : 4-*diketo*-1 : 3-*benzoxazine*, m. p. 207° (*potassium* and *silver* salts described), which is hydrolysed by alkali to the amide (m. p. 112°) of 2-hydroxy-3-methylbenzoic acid. Contrary to statements in the literature (*e.g.*, J.C.S., 1920, **117**, 1534), better yields of these coumaranones are obtained from the phenols by the action of sodium acetate on the *o*-hydroxyphenyl chloromethyl ketone than by the action of aluminium chloride on the phenoxyacetyl chloride. G. M. Bennett.

Synthesis of coniine. G. Koller (Monatsh., 1926, **47**, 393—396).—α-Trichloro-γ-2-pyridylpropan-β-ol, from picoline and chloral, is reduced with zinc dust in aqueous methyl alcohol to α-propenylpyridine (picrate identical with the picrate of Ladenburg's "allylpyridine"). Reduction of this base by means of hydrogen and colloidal platinum, followed by sodium and ethyl alcohol, gives *dl*-coniine, b. p. 59—63°/17 mm. (*m*-nitrobenzoyl derivative and nitrosoamine, oils; hydrochloride, m. p. 211—212°), from which *d*-coniine hydrogen tartrate, m. p. 53—54°, is obtained. G. M. Bennett.

Yohimba alkaloids. L. Spiegel (Ber., 1926, **59**, [*B*], 2706—2707).—It appears doubtful whether justification exists for assigning to yohimbine the composition $C_{21}H_{26}O_3N_2$ (cf. Field, J.C.S., 1923, **123**, 3003) instead of $C_{22}H_{28}O_3N_2$ suggested by the author. Criticism is directed against the observations of Hahn and Brandenberg and of Warnat (A., 1926, 1263). The identity of *iso*yohimbine with *meso*yohimbine and with corynanthine is regarded as impossible. H. Wren.

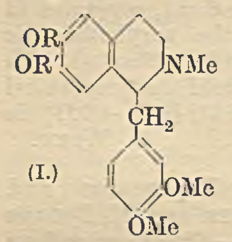
Corydalis alkaloids. VII. Syntheses of corybulbine and *iso*corybulbine. E. Späth and H. Holter (Ber., 1926, **59**, [*B*], 2800—2805; cf. A., 1925, i, 1085).—Corydaline is partly demethylated by treatment with hydrochloric acid (*d* 1·19) at 100°, and the separated mixture of phenolic bases is preserved in methyl-alcoholic solution, when corybulbine, m. p. 242—243°, $[\alpha]_D^{15}$ +304·9° in chloroform, separates in 8% yield. The residue from the corybulbine is dissolved in ether and fractionally extracted with aqueous hydrochloric acid; the final fractions afford *iso*corybulbine, m. p. 187·5—188·5°, $[\alpha]_D^{15}$ +301° in chloroform, in small amount. H. Wren.

Opium alkaloids. V. ψ-Papaverine and methylenepapaverine. E. Späth and N. Polgar (Ber., 1926, **59**, [*B*], 2787—2790).—Direct comparison of Hesse's ψ-papaverine (cf. A., 1903, i, 773) and papaverine, their hydrochlorides, m. p. 225—226° (decomp.), hydrobromides, m. p. 213—214° (slight decomp.), picrate, m. p. 186—186·5°, hydrogen oxalates, m. p. 201·5—202° (decomp.), and *chloroplatinates*, m. p. 212—213° (decomp.), establishes the identity of the alkaloids. The name ψ-papaverine should be deleted from the literature. Methylenepapaverine has the constitution (I), since it is oxidised by permanganate to papaveraldine and catalytically reduced to *methylenedihydropapaverine*, m. p. 154°. *Methylenepapaverine methiodide* is described. H. Wren.



(I.)

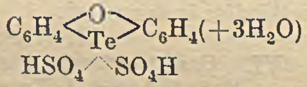
Opium alkaloids. VI. Constitution of codamine and ψ-laudanine. E. Späth and H. Epstein (Ber., 1926, **59**, [*B*], 2791—2800).—Contrary to the observations of Hesse, codamine, m. p. 126°, has the composition $C_{20}H_{25}O_4N$; it contains one hydroxyl and three methoxyl groups. When treated with diazomethane, it affords *d*-laudanosine. To determine the position of the free hydroxyl group, codamine is transformed into its ethyl ether and the latter oxidised by permanganate, whereby veratric acid is obtained, thus indicating the position 6 or 7 for the hydroxyl group in the *iso*quinoline nucleus. To establish the course of the mild oxidation of laudanosine derivatives, *r*-laudanosine is treated with permanganate in faintly alkaline solution under definite conditions, whereby 6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 125—126°, is obtained (cf. Pyman, J.C.S., 1909, **95**, 1617). The synthesis of this substance is accomplished by converting β-3 : 4-dimethoxyphenylethylamine into the corresponding formyl derivative, and thence, by means of phosphoric oxide in the presence of toluene, into 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 204—206°). The base is converted into the corresponding *methiodide*, m. p. 202° (decomp.), and thence into the chloride, from which 6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline is obtained by oxidation. Similarly, 7-methoxy-6-ethoxy-3 : 4-dihydro*iso*quinoline (cf. Späth and Dobrowsky, A., 1925, i, 1085) is transformed into the *methiodide*, m. p. 187—189° after softening, the methochloride, and 7-*methoxy*-6-*ethoxy*-1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 97—97·5°, whereas 6-methoxy-7-ethoxy-3 : 4-dihydro*iso*quinoline (*loc. cit.*) affords successively the *methiodide*, m. p. 170—172°, *methochloride*, and 6-*methoxy*-7-*ethoxy*-1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 120—121°. Oxidation of ethylated codamine affords the product, m. p. 120—121°, thus establishing the constitution (I) for codamine (R=Me, R′=H).


(I.)

Methylation of ψ-laudanine by diazomethane affords *r*-laudanosine in good yield. Energetic oxidation of ethylated ψ-laudanine yields veratric acid and the methyl ethyl ether of nor-*m*-hemipinic acid, thus establishing the presence of the free hydroxyl group in the *iso*quinoline nucleus, whereas mild oxidation affords 7-methoxy-6-ethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 95—96°. The constitution (I) (R=H, R′=Me) is therefore established for ψ-laudanine. H. Wren.

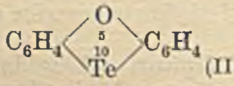
Determination of morphine in opium. F. C. M. J. Hollman.—See B., 1927, 58.

Cyclic organo-metallic compounds. II. Tellurylium compounds, a new series of intensely coloured tellurium derivatives. Migration of anions in solids. H. D. K. Drew (J.C.S., 1926, 3054—3071).—Phenoxtellurine dibisulphate trihydrate (I), combines with phenoxtellurine (II) to



$$\underset{\mathrm{HSO_4}\quad\mathrm{SO_4H}}{\mathrm{C_6H_4{<}\substack{O\\Te}{>}C_6H_4}}(+3\mathrm{H_2O})$$

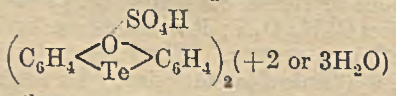
(I).



$$\mathrm{C_6H_4{<}\substack{O\\5\\10\\Te}{>}C_6H_4}$$

(II.)

give a highly-coloured violet compound formulated as diphenoxtellurylium dibisulphate di- or tri-hydrate



$$\left(\mathrm{C_6H_4{<}\substack{\overset{SO_4H}{O}\\Te}{>}C_6H_4}\right)_2(+2\text{ or }3\mathrm{H_2O})$$

(III.)

(III). Similar reactions occur between phenoxtellurine dinitrate, didihydrogen phosphate, or diperchlorate and various organic tellurides or sulphides. In these salts, the tellurium is satisfied with one polar and three non-polar linkings, but in the case of phenoxtellurine dichloride, dibromide, or diacetate, the compounds are non-polar and do not give rise to coloured complexes with tellurides.

A development of intense colour occurs when (I) is rubbed with iron or other base metal. Explanations for the colour changes are offered. The following compounds are described: *phenoxtellurine* 10 : 10-*dinitrate*, m. p. 258° (decomp.); 2-*nitrophenoxtellurine* 10 : 10-*dinitrate*, m. p. 196—197° (decomp.); 2 : 8-*dinitrophenoxtellurine* 10 : 10-*dinitrate*, m. p. 259° (decomp.); 4-*nitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate* (?), m. p. 243°; 4 : 8-*dinitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate* (?), violent decomp. 237—239°.

After cautious addition of water to a solution of phenoxtellurine in concentrated sulphuric acid, red crystals of *diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (IV), decomp. near 165°, are slowly deposited. This compound is converted, on exposure to moist air, into *diphenoxtellurylium dibisulphate di- or tri-hydrate* (III), in which the conditions of drying determine the final degree of hydration. Dilution of the red solution of phenoxtellurine in concentrated sulphuric acid with a greater proportion of water gives a violet precipitate, crystallising from glacial acetic acid as *diphenoxtellurylium hydroxybisulphate monohydrate* (V). This compound loses colour gradually at 205—245°, giving phenoxtellurine and a white solid unmelted at 300°.

Each of the compounds (III), (IV), and (V) is decomposed into its constituents by an excess of water. *Phenoxtellurine* 10 : 10-*diacetate*, m. p. 205—207° (decomp.), is obtained by the action of aqueous hydrogen peroxide on a solution of phenoxtellurine in hot glacial acetic acid. Excess of hydrogen peroxide reacts to give *phenoxtellurone*. When a solution of the diacetate in boiling water is treated with sulphuric acid, a crystalline sulphate separates, giving, on recrystallisation from sulphuric acid, crystals the composition of which depends on the concentration of acid present. With the minimum of acid necessary to cause precipitation, *phenoxtellurine sulphate* is obtained. From more strongly acid solutions, a complex *compound* is deposited, containing two molecular proportions of phenoxtellurine hydroxybisulphate, and one of phenoxtellurine dibisulphate + 1 mol. of water. When the crude sulphate is dissolved in warm concentrated sulphuric acid, and a relatively small proportion of water added, crystals of *phenoxtellurine dibisulphate trihydrate* (I) are obtained. M. Clark.

Organic compounds of arsenic. IV. Reaction between the Grignard reagent and arsenic trisulphide. K. Matsumiya and M. Nakai (Mem. Coll. Sci. Kyōtō, 1926, 10, 57—66; cf. A., 1925, i, 1339).—Magnesium *p*-tolyl bromide and arsenic trisulphide react to form tri-*p*-tolylarsine, di-*p*-tolylarsenious sulphide, and tri-*p*-tolylarsine sulphide, the relative amounts varying greatly according to the mode of preparation of the sulphide. These differences are not shown in the corresponding reaction using magnesium phenyl bromide. Magnesium α-naphthyl bromide reacts with the sulphide to form only *di*-α-*naphthylarsenious sulphide*, m. p. 185—186°; which was also prepared from hydrogen sulphide and di-α-naphthylarsenious oxide or di-α-naphthylchloroarsine. *Triphenylarsine sulphide mercurichloride*, m. p. 239—241°, and *tri*-p-*tolylarsine sulphide mercurichloride*, m. p. 227—229°, were also prepared.

B. W. Anderson.

Manufacture of solutions of aminoaryldichloroarsines or aminoarylarsenious oxides. G. Newbery, and May & Baker, Ltd.,—See B., 1927, 29.

Decomposition of unsymmetrical mercuri-organic compounds: a method of establishing the degree of electronegativity of organic radicals. M. S. Kharasch and R. Marker (J. Amer. Chem. Soc., 1926, 48, 3130—3143; cf. A., 1925, i, 1107).—The failure of Hilpert and Grüttner (A., 1915, i, 729) to obtain unsymmetrical mercuri-organic compounds was due to their use of too large an excess of Grignard reagent, and non-recognition of the instability of these derivatives towards heat. Thus *mercuryphenyl* p-*tolyl*, obtained by the action of 1 mol. of mercuric *p*-tolyl chloride on 2 mols. of magnesium phenyl bromide in ether at 5°, is almost completely decomposed into mercury diphenyl and mercury di-*p*-tolyl if the ethereal reaction mixture be boiled for 30 min. If the proportions of the reactants and the temperature be carefully controlled, the unsymmetrical derivatives can be readily prepared, and the following compounds containing the groups mentioned attached to mercury obtained in this way are described: *phenyl methyl* (liquid), *phenyl* cyclo*hexyl* (solid), *phenyl butyl* (liquid), *benzyl methyl* (liquid), *phenyl naphthyl* (solid, decomp. 110—115°), α-*naphthyl ethyl* (liquid), *methyl butyl* (liquid), *phenyl* o-*anisyl* (solid), cyclo*hexyl methyl* (liquid), *ethyl benzyl* (liquid), *phenyl mesityl* (solid, decomp. 110—120°), *methyl mesityl* (solid), *propyl butyl* (liquid), and *butylmercury* iso*amyl*. The decomposition of the unsymmetrical derivatives, HgR_1R_2, by hydrogen chloride, according to the equation $HgR_1R_2+HCl=R_1HgCl+R_2H$, the great rapidity of which precludes the possibility of side reactions, proceeds in a manner determined by the relative electronegativity of R_1 and R_2, the more electronegative radical combining with the hydrogen atom. It is assumed that the more electronegative radical dissociates first from the mercury and then combines with the hydrogen ion in solution. Examination of the products obtained by the action of hydrogen chloride on a series of unsymmetrical mercury derivatives thus enables the relative electronegativity of the radicals concerned to be determined, and from the results so far obtained the following radicals are listed in the order of their decreasing electronegativity: cyanogen; α-naphthyl, *p*-anisyl, and mesityl; *p*-tolyl; phenyl; methyl; ethyl and *n*-propyl; *n*-butyl; *iso*amyl; benzyl; *cyclo*hexyl and *n*-hexadecyl. Diphenylyl is more electronegative than phenyl, and α-naphthyl than β-naphthyl. Hydrogen chloride converts a mercury dialkyl in which the two radicals are of approximately equal electronegativity into both the possible hydrocarbons in a fixed ratio. Thus, mercury propyl butyl affords 74·2% of mercuric butyl chloride and 25·8% of mercuric propyl chloride, whilst mercury benzyl ethyl yields 94·1% of mercuric benzyl chloride and 5·9% of mercuric ethyl chloride, with a variation of not more than ±1% in each case. The bearing of the above results on the electronic conception of valency is discussed (cf. Kharasch and Sher, A., 1925, ii, 636) and an explanation is offered for the existence of free radicals, according to which the extent of the dissociation of the hexa-arylethanes is determined by by electronegativity of, and is independent of the mass and complexity of, the radicals attached to the methyl carbon atoms. F. G. Willson.

Mercuration of aromatic substances. III. *p*- and *m*-Nitrotoluenes. S. Coffey (J.C.S., 1926, 3215—3224; cf. A., 1926, i, 629).—When excess of *p*-nitrotoluene is heated with mercuric acetate at 140°, a mixture of 2- and 3-acetoxymercuri-4-nitrotoluenes, in which the latter compound may constitute as much as 80% of the product, is obtained. The pure individual products could not be isolated from the mercuration mixture. The proportions of the two substances were determined by conversion through the chloromercuri-*p*-nitrotoluenes into a mixture of 2- and 3-bromonitrotoluenes, the composition of which was determined by comparison with the f.-p. curve obtained from mixtures of the pure bromonitrotoluenes. Improved methods of preparation for these substances are described.

2-*Chloromercuri*-4-*nitrotoluene*, m. p. 230—231° (corr.), is obtained when 4-*nitrotoluene*-2-*sulphinic acid*, m. p. 127—128° (*sodium* salt $+2H_2O$; *ferric* salt), prepared from the corresponding sulphonyl chloride by warming with sodium sulphite, is boiled with a 50% aqueous-alcoholic solution of mercuric chloride. 3-*Chloromercuri*-4-*nitrotoluene*, m. p. 226—227° (corr.), is synthesised by the following method: 4-Nitro-*o*-toluidine yields, on sulphonation with chlorosulphonic acid, 4-*nitro*-2-*aminotoluene*-5-*sulphonic acid* (*ammonium* and *potassium* salts), the constitution of this substance being proved by reduction to 2 : 4-tolylenediamine-5-sulphonic acid. The *diazonium* derivative of the sulphonic acid is extremely stable. The diazonium group is eliminated by means of copper powder and formic acid, yielding 4-*nitrotoluene*-3-*sulphonic acid*, isolated as the *potassium* salt. The sulphonic acid is converted into the corresponding *sulphinic acid*, m. p. 112—113° (*ferric* and *ammonium* salts), and thence into 3-chloromercuri-4-nitrotoluene.

When *m*-nitrotoluene is heated with mercuric acetate for 12 hrs. at 140°, it yields a mixture of acetoxymercuri-*m*-nitrotoluenes. After conversion into the corresponding chloromercuri-derivatives, 4-*chloromercuri*-3-*nitrotoluene*, m. p. 210° (corr.), and 5-*chloromercuri*-3-*nitrotoluene*, m. p. 294° (corr.), can be isolated from the mixture. The constitution of these substances is proved by conversion into the corresponding bromonitrotoluenes. The presence of 6-chloromercuri-3-nitrotoluene is demonstrated by the isolation of 6-bromo-*m*-toluidine from the mixture of amino-compounds obtained by reducing the bromonitrotoluene product derived from the mixture of chloromercuri-derivatives. M. Clark.

Colloidal organomercuric compounds. G. Rossi and C. Bocchi (Gazzetta, 1926, 56, 817—821; cf. A., 1925, i, 601).—*Tetramercuri*-α-*acetonaphthalide acetate*, $NHAc\cdot C_{10}H_3(Hg\cdot OAc)_4$, prepared by heating an intimate mixture of mercuric acetate (4 mols.) free from mercurous salts with α-acetonaphthalide, decomposes at 220°, and forms aqueous solutions which froth abundantly when shaken, are highly viscous, cannot be dialysed, coagulate when heated, and are acid owing to the presence of acetic acid; if much acetic acid is present, coagulation of the solution does not take place. This compound does not yield mercuric oxide when treated with potassium hydroxide. T. H. Pope.

Organo-tin compounds. K. K. Law (J.C.S., 1926, 3243).—*Hexabenzyldistannane*, $Sn(CH_2Ph)_3\cdot Sn(CH_2Ph)_3$, m. p. 147—148°, obtained by heating tribenzylstannic chloride (*ibid.*, 1912, **101**, 2557) with sodium in toluene solution, is decomposed by iodine in benzene solution, giving tribenzylstannic iodide. Dibenzylethylstannic iodide reacts with excess of an ethereal solution of magnesium *n*-butyl bromide, giving, when the product is afterwards heated at 140°, *dibenzylethylbutylstannane*, $SnEtBu(CH_2Ph)_2$, b. p. 207—209°/9 mm. *Benzylethyldibutylstannane*, $SnEtBu_2\cdot CH_2Ph$, b. p. 175—180°/9 mm., is obtained as a by-product from benzylethylstannic iodide present as impurity. M. Clark.

Structure of complex carbohydrates and proteins. M. Bergmann (Kolloid-Z., 1926, **40**, 289—295, and Ber., 1926, 59, [*B*], 2973—2981).—A lecture on the structure of compounds of high mol. wt. E. S. Hedges.

Structure of proteins. E. Waldschmidt-Leitz (Kolloid-Z., 1926, **40**, 295—300, and Ber., 1926, **59**, [*B*], 3000—3007).—A lecture on the structure of proteins studied from the point of view of the products of enzyme action. E. S. Hedges.

Partial hydrolysis of globin. F Haurowitz (Z. physiol. Chem., 1926, **162**, 41—62).—Globin is partly hydrolysed by sulphuric acid (70 vol.-%) after some days at 40°. After 5 days, no free histidine is present in the hydrolysate, but a histidine-rich peptide (containing 68% of its nitrogen as histidine-nitrogen) may be precipitated by mercuric sulphate. Leucine and proline are present, but neither arginine nor lysine. Kirbach's "globinokyrin" is a mixture of peptides. H. D. Kay.

Composition and characterisation of genuine proteins. S. P. L. Sørensen (J.C.S., 1926, 2995—3009).—Hugo Müller Lecture, delivered on Oct. 28, 1926.

Colorimetric determination of tryptophan in proteins. J. Tillmans and A. Alt (Biochem. Z., 1926, **178**, 243—244).—A reply to the criticisms by Fürth (A., 1926, 633) of the author's method (*ibid.*, 189). J. Pryde.

Sources of error in organic elementary analysis. II. The combustion tube. J. Lindner (Ber., 1926, **59**, [*B*], 2806—2812; cf. this vol., 66).—Complete freedom of the current of air from carbon dioxide can be attained only with extreme difficulty and by particular precautions. Many hard glass tubes appear to evolve traces of carbon dioxide when strongly heated, but the amount is insufficient to be of practical importance. The entry of traces of organic matter into the combustion tube from the air aspirator and system is facilitated by the heat from the furnace. Technical copper oxide "for analysis" may contain alkaline impurities which are of much greater importance in micro- than in macro-analysis. H. Wren.

Meulen's catalytic method for the determination of nitrogen in organic compounds. F. L. Smith and A. P. West (Philippine J. Sci., 1926, **31**, 265—275).—A modification of the method (A., 1925, ii, 66) is described involving the separation of the mixture of asbestos fibre and nickel catalyst, by means of asbestos plugs, into four sections, the first of which is heated to dull redness and acts as a preheater to the rest of the catalyst, which is maintained at 350°. This arrangement is claimed to obviate the tendency in the original method for solid compounds to distil unchanged through the reduction tube. E. Holmes.

Influence of chlorides on Denigès' reaction for citric acid. I. M. Kolthoff (Pharm. Weekblad, 1926, **63**, 1453—1455; cf. Wagenaar, A., 1926, 1226).—Small proportions of chlorine do not affect the reaction in aqueous solution. If, however, other organic acids be present, chlorides interfere strongly. The test can be carried out without removing chlorides if manganous sulphate be added. S. I. Levy.

Stahre's reaction for citric acid. N. Schoorl (Pharm. Weekblad, 1926, **63**, 1455—1458).—The detection of citric acid by oxidation with permanganate and treatment with bromine, which gives a white precipitate of pentabromoacetone, is not affected by the presence of other organic acids, or of chlorides, unless these are in great excess. S. I. Levy.

Determination of aniline, especially in dilute solutions. A. V. Pamfiloff.—See B., 1927, 7.

Determination of antimony in organic compounds. W. H. Gray.—See this vol., 143.

Biochemistry.

Regulation of respiration. VI. Continuous electrometric methods of recording changes in expired carbon dioxide and oxygen. R. Gesell and D. A. McGinty (Amer. J. Physiol., 1926, **79**, 72—90).—The "carbon dioxide electrode" consisted of a fine manganese dioxide electrode resting on a peritoneal membrane moistened with potassium chloride solution in connexion with a calomel electrode. The "carbon dioxide electrode" was exposed to a steady stream of expired air and responded to changes in carbon dioxide tension by changes in acidity, the resulting changes in *E.M.F.* being balanced potentiometrically and recorded mechanically. The changes in oxygen tension were measured by supplying to a Bunsen burner a constant mixture of gas and expired air. The changes in heat of the flame were impressed on a constant flow of water and measured and recorded by a thermopile in the same way as with the "carbon dioxide electrode." *In vitro* and *in vivo* experiments demonstrating the accuracy of the methods are recorded and rapid means of calibration described. R. K. Cannan.

Prolonged alterations of oxygen pressure in the inspired air with special reference to tissue oxygen tension, tissue carbon dioxide tension, and hæmoglobin. J. A. Campbell (J. Physiol., 1927, 62, 211—231).—Rabbits were exposed for about 6 weeks to oxygen pressures varying from 60% below to 200% above the normal, the barometric pressure being kept constant. There was no effect on the oxygen consumption. Reduced oxygen pressure depressed the carbon dioxide and oxygen tensions of the tissues notably and increased the hæmoglobin content of the blood. With increased oxygen pressure, inverse effects to the above were noted. In both cases, pronounced after-effects indicated mechanisms concerned with acclimatisation. These, however, did not serve to restore the normal oxygen tension of the tissues. Rabbits, previously acclimatised, tolerated for 10 days an atmosphere containing only 7·5% of oxygen. The carbon dioxide and oxygen tensions of the tissues are regulated by the oxygen content of the arterial blood. Excessive thyroid feeding was without effect on the tension of oxygen or of carbon dioxide in the tissues. R. K. Cannan.

Comparative capacity of the blood and of the tissues to absorb carbonic acid. L. A. Shaw (Amer. J. Physiol., 1926, 79, 91—99).—Cats were caused to breathe air containing 7·5% of carbon dioxide until the carbon dioxide uptake was complete. From this, by subtracting the carbon dioxide in the blood independently determined, the carbon dioxide taken up by the tissues was calculated. This accounted for 87·4% of the total, corresponding with 10 volumes per 100 g. of tissue. The buffering capacity of the blood against a rise in carbon dioxide tension in the inspired air is about twice as great as that of the same weight of tissue. The respiratory quotient was about the same after saturation of the body with carbon dioxide at the increased tension as before the experiment. R. K. Cannan.

Rate of distribution of dissolved gases between the red blood-corpuscle and its fluid environment. I. Rate of uptake of oxygen and carbon monoxide by sheep's corpuscles. H. Hartridge and F. J. W. Roughton (J. Physiol., 1927, 62, 232—242).—The authors' method of determining the velocity of very rapid reactions was employed. Control experiments established that the observed rate of increase in the concentration of oxyhæmoglobin was to be attributed to the rate of the actual reaction within the corpuscle. The effects on the velocity of varying the concentration of dissolved oxygen, the temperature, and the sodium chloride are given. Under parallel conditions, the rate of uptake of carbon monoxide was about half that of oxygen. R. K. Cannan.

Pyramidone in testing for blood. M. Elzas and L. M. Lansberg (Pharm. Weekblad, 1927, 64, 19—22).—By addition of 1 drop of a solution, containing 1 part of blood in 60,000 parts, to 3 c.c. of a 5% solution of pyramidone in alcohol, to which a little acetic acid and hydrogen peroxide have been added, a violet coloration develops on keeping. The test compares well in sensitiveness with the ordinary tests for blood. Comparative tests on blood in fæces are described. S. I. Levy.

Existence of "pinnaglobin." M. Henze (Z. physiol. Chem., 1926, 162, 136—138).—The liquid obtained from *Pinna squamosa* by Griffiths, and believed by him to be blood, is in fact the pericardial fluid. From this fluid a pigment may be isolated which is not of a protein nature and has no respiratory functions, but contains manganese in organic combination. "Pinnaglobin" does not exist. H. D. Kay.

Distribution of diffusible and non-diffusible calcium in blood-serum of normal animals. H. Updegraff, D. M. Greenberg, and G. W. Clark (J. Biol. Chem., 1926, 71, 87—117).—A number of determinations of diffusible and non-diffusible calcium in the blood-serum of man and of various animals have been made by a modification of the method of Moritz (A., 1925, i, 995), whose results are criticised on the ground that he neglected to allow for the diffusible calcium remaining in the collodion sacs. It is found that, of the two fractions, the non-diffusible is the more constant; the non-diffusible calcium is not in equilibrium with the total diffusible calcium, but may be in equilibrium with a small fraction of the latter. Since, in the different sera, the concentration of non-diffusible calcium runs parallel with that of the protein, it is probable that these two are in chemical combination. C. R. Harington.

Colorimetric determination of chlorides, inorganic sulphates, and inorganic phosphates in small amounts of blood. S. Yoshimatsu (Tohoku J. Exp. Med., 1926, 7, 553—559).—The blood (5—10 c.c.) is deproteinised by alcohol, heat, and "dazol," aliquot parts being used for the determination of sulphate (*ibid.*, 1926, 7, 11), phosphate (Satō, A., 1918, ii, 406), and chloride (Isaacs' method, *ibid.*, 1922, ii, 716, author's modification). Chemical Abstracts.

Determination of non-protein sulphur compounds of blood. Determination of sulphur compounds in urine. W. Denis and L. Reed (J. Biol. Chem., 1926, 71, 191—204, 205—208).—Proteins are removed from blood with trichloroacetic acid. Inorganic sulphate is determined by precipitation with barium chloride in presence of gelatin, and nephelometric comparison of the resulting solution with a similarly treated solution of a known amount of potassium sulphate. Application of the method to further portions of the blood filtrate after acid hydrolysis and after incineration with a mixture of zinc nitrate, sodium chloride, and ammonium chloride yields figures for the total sulphates and total sulphur, respectively. The error of the method, as compared with gravimetric determinations, is −10 to +7%. The above method has been applied successfully to suitably diluted urine. C. R. Harington.

Colorimetric determination of blood-sugar. Correction. B. Glassmann (Z. physiol. Chem., 1926, 162, 145—147).—Many specimens of resorcinol, even in absence of dextrose, give a yellow colour when heated with 25% hydrochloric acid. A method of correcting for this possible error in the author's method (A., 1926, 192) is described. H. D. Kay.

Determination of dextrose in blood. A. Hansen (Dansk Tiddsk. Farm., 1927, **1**, 195—205).—Blood is deproteinised and the alkaline ferricyanide oxidation conducted as in the Hagedorn and Jensen method. The ferrocyanide formed is determined by oxidation with 2 c.c. of 0·005*N*-potassium dichromate in presence of 5 c.c. of 10% hydrochloric acid; the excess of dichromate is determined by addition of 3 c.c. of 0·005*N*-sodium arsenite containing 1% of sulphuric acid, and excess of arsenite is titrated with 0·005*N*-potassium bromate in presence of potassium bromide, using 0·0004% methyl-orange as indicator. The stock solutions used are more stable than those in the Hagedorn and Jensen method, but the same results are obtained with both methods. L. F. Hewitt.

Co-zymase. IX. Determination of co-zymase in blood. H. von Euler and R. Nilsson (Z. physiol. Chem., 1926, **162**, 63—71).—Co-zymase, measured by its effect in restoring fermenting power to washed, dried yeast, is present in considerable quantities in human blood. It is present entirely in the red cells, from which it may be extracted by boiling with water. Bird's blood contains more co-zymase than the blood of mammals. The co-zymase content of the blood in man in diabetes, and in the mouse in rickets, remains normal. H. D. Kay.

Reversible hæmolysis. K. Fukushima (J. Biochem. [Japan], 1926, **6**, 315—322).—Reversion of hæmolysis is attributed to the action of electrolytes which apparently combine with the hæmoglobin and either penetrate into or adhere to the stroma. Chemical Abstracts.

Anticoagulating action and nuclear origin of a substance extracted from the mesenteric ganglion. M. Doyon and I. Vial (Compt. rend., 1926, **183**, 1123—1124).—The isolation from the mesenteric ganglions of a bullock of a phosphorus-free nucleoside which, *in vitro*, has a powerful inhibiting action on blood coagulation, is described. It consists essentially of a carbohydrate–purine compound, is acid to litmus, and, after hydrolysis, reduces Fehling's solution. J. W. Baker.

Lactacidogen in heart-muscle. H. Perger (Z. physiol. Chem., 1926, **162**, 122—135).—Heart-muscle contains lactacidogen, which is diminished in quantity when the isolated organ is allowed to beat for a considerable time in a non-nutrient solution before the determination is made. Heart-muscle is able to re-synthesise inorganic phosphate into organically combined phosphoric acid in presence of sodium fluoride. This ability is diminished in the heart-muscle of a sick animal. Potassium cyanide also brings about this synthesis in presence of heart-muscle. Within certain limits, alanine will replace glycogen in the lactacidogen synthesis in presence of sodium fluoride. H. D. Kay.

Non-existence of uncombined adrenaline in fresh suprarenal capsules. G. Mouriquand and A. Leulier (Compt. rend., 1926, **183**, 1353—1355).—The suprarenal capsule (guinea-pig) gives practically no adrenaline reaction with mercuric chloride and sodium acetate directly after removal from the body, but after keeping for 24 hrs., a strong reaction is given. It is suggested, therefore, that adrenaline exists in the capsule in a combined state. L. F. Hewitt.

Fixed oil of the kidney fat of the emu (*Dromaius novæ-hollandiæ*). F. R. Morrison (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 113—118).—The oil obtained from the fatty tissue surrounding the kidneys of the emu has m. p. 30—31°, d_{30}^{30} 0·915, n_D^{20} 1·4700, acid value 1·7, saponification value 195·2, iodine value 95·5, and consists of glycerides of oleic, linolenic, palmitic, and stearic acids. In addition, 0·2% of unsaponifiable matter which gives the colour reactions of cholesterol and a small amount of a mixed glyceride of palmitic and stearic acids (probably glyceryl β-stearate-αγ-dipalmitate) were isolated. J. W. Baker.

Nickel and cobalt content of the pancreas. G. Bertrand and M. Mâchebœuf (Bull. Soc. chim., 1926, [iv], **39**, 1646—1648).—See A., 1926, 869.

Chemistry of the ovary. XI. Fat of ovarian residue. D. Tourtelotte and M. C. Hart (J. Biol. Chem., 1926, **71**, 1—13).—From 247 g. of the acetone-soluble portion of the ethereal extract of ovarian residue there were obtained 100 g. of free fatty acids, 95 g. of fatty acids present as neutral fat, and 46·3 g. of unsaponifiable matter, of which 30·76 g. was cholesterol. The mixed fatty acids comprised 0·4% myristic, 32·4% palmitic, 10·4% stearic, 55·3% oleic, 0·7% arachidonic acids, together with a trace of linoleic acid and 0·7% of an acid, $C_{20}H_{31}O_2$, yielding a *hexabromide*, m. p. 220° (decomp.). C. R. Harington.

Investigation of asparaginase in the testicles of the calf. M. Mario (Arch. Farm. sper. Sci. aff., 1926, **41**, 216—218).—Contrary to the statement of Lang (A., 1904, ii, 427), calves' testicles contain no enzyme capable of deaminating asparagine. T. H. Pope.

Shark's fins. K. H. Lin (J. Biochem. [Japan], 1926, **6**, 323—333).—Commercial, prepared shark's fins are free from fat or carbohydrate; the ash content is 0·84% (of which 0·70% is sulphur) and the nitrogen content 17·18%. Hence it is an incomplete protein, lacking in tryptophan; one third of the total amount of amino-acids consists of arginine, histidine, and lysine. Chemical Abstracts.

Oil from *Mesoplodon bidens*. E. André and H. Canal (Compt. rend., 1926, **183**, 1063—1065).—Oil from the cetacean *Mesoplodon bidens* had the following properties: d_0^{15} 0·8694, n_D^{15} 1·4650, α_D −0·85°, saponification value, 103·4, iodine value (Hanus) 81·5. When saponified, 51% of fatty acids and 49% of unsaponifiable matter were obtained, together with 0·7% of glycerol. From the unsaponifiable matter, m. p. 20—25°, iodine value, 83·4, acetyl index (André) 184, were isolated cetyl alcohol and oleyl alcohol. In the fatty acid fraction, an acid similar to *iso*pelargonic acid is present to the extent of about 1%; oleic acid predominates, together with gadoleic acid and erucic acid. In general, the oil is similar to cachalot oil. L. F. Hewitt.

Chemical composition of the jellyfish *Velella spirans*. F. Haurowitz and H. Waelsch (Z. physiol. Chem., 1926, **161**, 300—317).—A quantitative investigation of the ash, ether-, alcohol-, water-, hydrochloric acid-soluble and insoluble fractions and of the enzymes of the dried jellyfish.

P. W. Clutterbuck.

Comparative chemical investigation of *Holothuria* and *Actinia*. F. Haurowitz and H. Waelsch (Z. physiol. Chem., 1926, **161**, 318).—Tests for carbamide, uric acid, creatine, and creatinine in extracts of *Holothuria tubulosa* and *Actinia equina* were negative. Differing from *Velella spirans*, the entire framework of the above is completely digested by pepsin–trypsin treatment, and is free from cellulose, chitin, and scleroprotein. P. W. Clutterbuck.

Composition of the spawn from *Hemifusus tuba*, Gmel. Y. Komori (J. Biochem. [Japan], 1926, 6, 129—138).—From 2 kg. of the fluid from the egg-sac, 160 g. of " crude vitellin " were obtained, having the following amino-acid composition : alanine 0·71, valine 0·27, leucine 10·29, proline 1·1, phenylalanine 0·22, aspartic acid 1·6, tyrosine 0·8, arginine 3·73, lysine 0·86, tryptophan 1·49%. Glycine, *iso*leucine, glutamic acid, serine, and histidine were absent. Chemical Abstracts.

Amylolytic power of certain digestive secretions in relation to the time of glandular activity. V. Zagami (Arch. Farm. sper. Sci. aff., 1926, **41**, 151—169).—Human saliva, obtained under the influence of an acid stimulus such as 0·1*N*-hydrochloric acid or lemon juice, is secreted in almost uniform quantities during the succeeding periods of intense glandular activity, whilst the amylolytic power increases rapidly during the first 15 min. and subsequently diminishes slowly and continuously. The pancreatic juice of the dog, obtained under the action of various mixed foods and then of 0·4% hydrochloric acid, is secreted in almost uniform quantities during succeeding periods of intense glandular activity, and maintains constant amylolytic power. The enteric juice of the dog, obtained by stimulation with 5% sodium chloride solution, is formed in quantities diminishing almost to zero, whilst its amylolytic power increases to four times the original value. T. H. Pope.

Iodine as a biological element. IV. Iodine content of colostrum and normal milk. E. Maurer and S. Diez (Biochem. Z., 1926, **167**, 161—166).—Both in the cow and in the human the iodine content of colostrum diminishes steadily during the first five or six days of lactation until normal milk is produced. J. Pryde.

Carbon dioxide tension of cerebrospinal fluid. A. T. Shohl and S. Karelitz (J. Biol. Chem., 1926, **71**, 119—126).—For cerebrospinal fluid, the term *pK'* of the Henderson–Hasselbalch equation is found, both by analysis of the fluid after equilibration with a known tension of carbon dioxide and by calculation from the ionic strength of the fluid, to be 6·13±0·03. Assuming equal values for p_H and hydrogen carbonate in blood plasma and cerebrospinal fluid, the carbon dioxide tension in the latter is the higher by 5—7 mm. of mercury. The carbon dioxide tension of the cerebrospinal fluid does not in general, however, bear a definite relation to that of the blood plasma.

C. R. Harington.

Gallodeoxycholic acid from the bile of chickens and its influence on pancreatic lipase activity. S. Yonemura (J. Biochem. [Japan], 1926, 6, 287—296).—Crude bile acid, obtained by boiling fresh bile with potassium hydroxide and precipitating with hydrochloric acid, was kneaded with cold water, dissolved in alcohol, and freed from fatty acids with light petroleum. The dry residue was then boiled with alcoholic sodium ethoxide, acidified with dilute sulphuric acid, and extracted with light petroleum, and this process repeated. *Gallodeoxycholic acid*, prepared from the *barium* salt, $C_{48}H_{78}O_8Ba$, has m. p. 112° (softening at 95°), $[\alpha]_D$ +13·23°. When boiled with chromium trioxide in glacial acetic acid, it affords *gallodehydrodeoxycholic acid*, $C_{24}H_{66}O_4$, m. p. 153—154°. Boiling with concentrated nitric acid affords gallodeoxybilianic acid, m. p. 89—90°, identified as a trimethyl ester of deoxybilianic acid. Gallodeoxycholic acid increases the activity of pancreatic lipase as also does cholic acid.

Chemical Abstracts.

Presence of amino-acids in the gall from a bile duct cyst. T. Takaki (J. Biochem. [Japan], 1926, 6, 27—29).—Bile (1500 c.c.) from a one-year-old child yielded tyrosine (0·03 g.), leucine (0·43 g.), arginine (0·18 g.), and lysine (0·06 g.).

Chemical Abstracts.

Isotopes of chlorine in urine. L. Ambard and A. Chrétien (Bull. Soc. Chim. biol., 1926, 8, 1103—1105).—After injection of sodium chloride, the urinary chloride, purified by fractionation, gave values for the atomic weight of chlorine identical with the normal value. The two isotopes therefore pass through the body and the ratio remains constant.

A. Wormall.

Determination of urea. B. Glassmann (Z. physiol Chem., 1926, **162**, 148).—A correction to the author's volumetric method. H. D. Kay.

Determination of cellulose in human fæces and the digestion of food cellulose. T. Kohmoto and S. Sakaguchi (J. Biochem. [Japan], 1926, 6, 61—76).—The sample (3—5 g.) is digested for 1 hr. with 2·5% potassium hydroxide solution (200 c.c.), acidified with sulphuric acid, diluted, again heated for 1 hr., and filtered hot through fine linen on an asbestos pad. The residue, after being washed with water, alcohol, and alcohol–ether mixture, is mixed with water to 100 c.c., 6 c.c. of 5% sodium hypochlorite are added with stirring, the mixture is filtered after 15 min. through a tared paper, washed, treated with 1% acetic acid, washed with water, alcohol, and ether, and dried at 105°. The loss of cellulose is 5·8%. Persons whose food contained 8·5% of cellulose digested and absorbed 75% of the quantity. Air-dried foods contain cellulose as follows : rice 0·465, bread 0·318, hard bread 0·334, potato 1·904, sweet potato 2·694, beans 5·2%.

Chemical Abstracts.

Extraction of total ether-soluble material from fæces. R. G. Freeman, jun., and E. G. Miller, jun. (Arch. Pediatrics, 1926, **43**, 421—422).—

For the determination of total lipins, the material (1—5 g.) is triturated with concentrated hydrochloric acid (1—3 c.c.) and then with anhydrous sodium sulphate (35—40 g. per g. of fæces), and the mass repeatedly extracted with ether at the ordinary temperature, the residue after evaporation being dried at 98—100°. The free fatty acids are determined by solution in benzene and titration with $0 \cdot 1N$-sodium ethoxide solution. Soaps are determined by difference. CHEMICAL ABSTRACTS.

Lactacidogen metabolism in diabetic muscle. H. LANGE (Arch. exp. Path. Pharm., 1926, **118**, 115—120).—In diabetic muscle, the enzymic processes resulting in the formation and decomposition of lactacidogen proceed under the same conditions with considerably less speed than in normal muscle. W. ROBSON.

Diazo-urine. I. Chemical composition of the diazo-urine in tuberculosis. Y. KOMORI (J. Biochem. [Japan], 1926, **6**, 297—305).—Fifty litres of urine from advanced tuberculous patients contained: antoxyproteic acid 67·33 g., oxyproteic acid 10·79 g., *l*-proline 0·15 g., aspartic acid 0·37 g., glutamic acid 0·024 g., serine 0·04 g., arginine 2·39 g., lysine 3·05 g.; histidine and phenylalanine were present. CHEMICAL ABSTRACTS.

Metabolism during fasting in the human subject. W. G. LENNOX (J. Clin. Invest., 1926, **2**, 609).—The oxygen consumed increases during fasting and runs parallel with the nitrogen excretion. CHEMICAL ABSTRACTS.

Rôle of acetaldehyde in animal metabolism. A. P. BRIGGS (J. Biol. Chem., 1926, **71**, 67—73).—After administration of acetaldehyde and of alcohol, the former substance could be detected in the expired air and in the urine; no acetaldehyde was excreted after administration of pyruvic acid. C. R. HARINGTON.

Action of the sympathetic system on the carbohydrate metabolism of muscle. H. E. BÜTTNER (Z. physiol. Chem., 1926, **161**, 282—299).—By section of the rami communicantes in the frog, the muscle lactic acid is increased by about 40% and the glycogen content by 34%, whereas the lactacidogen content is decreased by 18%. The lactic acid content of the muscle is increased on the operated side when the aorta is ligatured immediately after the operation. Lactic acid formation after injection of caffeine is greater by 50% in the muscle, the sympathetic innervation of which is cut, than in the normal muscle. After injection of carbamide in large doses, the lactic acid content of the muscle becomes 8—10 times the normal value, and that of the muscle, the rami of which are cut, is increased by 44%. P. W. CLUTTERBUCK.

Specific dynamic action of gelatin hydrolysates. D. RAPPORT (J. Biol. Chem., 1926, **71**, 75—86).—When gelatin is administered together with the products of its acid or tryptic hydrolysis, the specific dynamic effect obtained is equal to the sum of that of the gelatin and that of the hydrolysate; if, on the other hand, the protein or its hydrolysate be administered simultaneously with glycine (the latter being given either orally or intravenously), the normal specific dynamic action of the glycine is neutralised. The specific dynamic action of the mixed hydrolytic products of a protein is therefore a property of the original protein, and does not depend on the amount of any given amino-acid which is present. C. R. HARINGTON.

Value of cocoa and chocolate as sources of protein in the diet. H. H. MITCHELL, J. R. BEADLES, and M. H. KEITH (J. Biol. Chem., 1926, **71**, 15—31).—Rats were fed on a diet containing 8% of protein, the whole of which was supplied in the form of cocoa. Under these conditions, the protein was digested to the extent of 38% on the average, and its biological value (*i.e.*, % of absorbed nitrogen which was retained in the body) was 37; neither of these values was altered by the substitution of milk for half the cocoa. Neither by itself nor in combination with milk, therefore, can cocoa be regarded as an important source of food protein. Cocoa was found to contain 0·55% of creatinine and 0·24% of creatine, and the excretion of these compounds was increased in the animals on the cocoa diet. C. R. HARINGTON.

Effect on the kidney of long-continued administration of diets containing an excess of certain food elements. I. Excess of protein and cystine. II. Excess of acid and alkali. T. ADDIS, E. M. MACKAY, and L. L. MACKAY (J. Biol. Chem., 1926, **71**, 139—156, 157—166).—I. At the end of a year on a diet containing 70% of protein, rats showed, as compared with control animals on a diet with 17% of protein, a general deficiency of body-fat, a decrease in the weight of the liver, and an increase in that of the kidneys; these changes were less marked, or absent, in rats on the low-protein diet with the addition of 1% of cystine. Renal lesions were not observed.

II. Rats fed for a year on an " acid diet " containing 2% of calcium chloride showed a reduction in body-weight and a decreased excretion of protein in the urine as compared with normal rats, but no pathological changes in the kidney; on a diet containing 4% of sodium hydrogen carbonate, however, large amounts of blood appeared in the urine, and 30% of the rats so treated showed hydronephrosis. C. R. HARINGTON.

Chemical nature of substances required for cell multiplication. A. CARREL and L. E. BAKER (J. Exp. Med., 1926, **44**, 503—521).—The presence in embryo juice of a hormone that stimulates cell division is improbable. Proteoses separated from peptic digests of fibrin by sodium sulphate determine a more abundant and prolonged multiplication of fibroblasts than that produced by embryo juice. Peptones and smaller split products furnish some nutrient material, but are sometimes toxic. Possibly the effect of embryo juice is due to the splitting of the protein of the juice into proteoses by the cell enzyme, or by other enzymes activated by the presence of living cells. CHEMICAL ABSTRACTS.

Comparative biochemistry. II. Behaviour of aromatic fatty acids and of pyridine in the organism of lower animals. Y. KOMORI, Y. SENDJU, J. SAGARA, and M. TAKAMATSU (J. Biochem. [Japan], 1926, **6**, 21—26).—Frogs eliminate subcutaneously administered benzoic, phenylacetic, and

phenylpropionic acids in the urine as hippuric acid. Turtles eliminate benzoic acid as hippuric acid and pyridine as methylpyridylammonium hydroxide.
Chemical Abstracts.

Comparative biochemistry. III. Behaviour of nicotinic acid in the organism of mammals and birds. Y. Komori and Y. Sendju (J. Biochem. [Japan], 1926, 6, 163—170).—Nicotinic acid, neutralised with sodium carbonate and fed to dogs, is eliminated in the urine partly unchanged and partly as nicotinuric acid and as trigonelline. Trigonelline does not appear in the urine of rabbits given nicotinic acid; birds eliminate the whole of the nicotinic acid unchanged. Chemical Abstracts.

Behaviour of *o*-nitrobenzaldehyde, *o*-aminobenzaldehyde, and anthranil in the animal organism. T. Hosoda (J. Biochem. [Japan], 1926, 6, 171—177).—When *o*-aminobenzaldehyde is administered to rabbits, especially subcutaneously, anthranilic acid appears in the urine. Injections of *o*-amino- and *o*-nitro-benzaldehyde do not produce a reducing urine. The urines contain *o*-nitrobenzoic acid. Anthranil caused the appearance of anthranilic acid in the urine. Chemical Abstracts.

Action of carnosine on gastric secretion. I. P. Rasenkow, G. W. Derwies, and S. E. Ssewerin (Z. physiol. Chem., 1926, 162, 95—102).—Administration of carnosine, either subcutaneously or *per os*, has no effect on the secretion of gastric juice. Only when injected intravenously does carnosine act as a weak stimulator of gastric secretion. Meat extract owes its activity only in the slightest degree to carnosine. Krimberg's results (A., 1926, 752) are probably due to impurities present in his carnosine fractions, and not to the base itself. H. D. Kay.

Production of alcohol in the animal body. II. Amount of alcohol in the blood and liver of asphyxiated animals. M. Aoki (J. Biochem. [Japan], 1926, 6, 307—314).—The blood and tissues of asphyxiated fowls contain an increased amount of alcohol. Chemical Abstracts.

Distribution of iodine in nature and its physiological significance in vegetable and animal organisms. J. Stoklasa [with Dvořák, Bareš, Šilhavý, and Štrupl] (Z. angew. Chem., 1927, 40, 20—27).—Analyses of many different kinds of rocks show that iodine is widely distributed, especially in volcanic rocks and the more recent rocks which contain the fossilised remains of animal- or plant-life. In the case of volcanic rocks, the content varies from 0·458 to 0·984 mg. of iodine per kg. in recent rocks to 0·295—0·428 mg. per kg. in plutonic rocks. The fossils of the silurian and carboniferous formations are especially rich in iodine, some of them containing as much as 1·94 mg. per kg. (*Caulopteris*). The fact that fossilised plants have a relatively high content of iodine indicates that this element played an important part in their growth, and tests made on many plants grown in various soils both with and without an iodine supply substantiate this. Iodine promotes the growth of the nitrifying bacteria in a similar way to radioactive substances, and the simultaneous presence of iron and iodine in a soil causes a much more intensive assimilation of nitrogen, a greater growth of the plant, a larger yield of seed, and a much greater development of the germ, thus resulting in greater fertility. Thus iodine must be considered as an essential biogenic element in the synthesising processes of the living cell. Radishes, tomatoes, and, to a smaller extent, potatoes are particularly rich in iodo-oxydases and are therefore a valuable source of iodine for human food. A. R. Powell.

Trimethylamine oxide as biological hydrogen acceptor. D. Ackermann, K. Poller, and W. Linneweh (Ber., 1926, 59, [*B*], 2750—2751).—Trimethylamine oxide behaves as hydrogen acceptor towards substances containing the thiol group united to carbon, provided the mol. wt. of these substances is not too large, but not towards a variety of compounds such as dextrose, adrenaline, amino-acids, albumin, globulin, hæmoglobin, and ovalbumin. The oxide is indifferent towards hydrogen except in presence of palladised charcoal or other carrier.
H. Wren.

Influence of bile acids on the protein metabolism of the sex glands and the significance of choleic acid. R. Karasawa (J. Biochem. [Japan], 1926, 6, 139—159).—Cholic, and particularly deoxycholic, acids inhibit the proteolysis in autolysing testes, the effect depending on the amount as well as on the concentration. The amount of nitrogen from mono- and di-amino-acids becomes both absolutely and relatively smaller as the quantity of bile acid increases, whilst the cleavage of nucleoproteins is actually stimulated.
Chemical Abstracts.

Relation between bile acids, snake venom, and cholesterol. I. S. Yonemura and M. Fujihara (J. Biochem. [Japan], 1926, 6, 91—100).—Cholic and deoxycholic acids have a strong hæmolytic effect on rabbit red blood-cells, and act plasmolytically on leucocytes. When injected intravenously into rabbits, cholic and deoxycholic acids, like the poison of *Trigocephalus*, reduce the blood cholesterol and the number of leucocytes. Chemical Abstracts.

Effect of parasympathetic poisons on blood-sugar. Problem of the parasympathetic hyperglycæmia. T. Sakurai (J. Biochem. [Japan], 1926, 6, 211—236).—Subcutaneous, but not oral, administration of choline to fasting rabbits produces slight hyper- or hypo-glycæmia, according to the dose (0·1—0·01 g. per kg.). Eserine (1 mg. per kg.) and pilocarpine (5—10 mg. per kg.), injected subcutaneously, produce hyperglycæmia, the hyperglycæmic effect being inhibited by atropine. Eserine does not inhibit the effect of insulin, but the reverse is true.
Chemical Abstracts.

Influence of hydrazine and its derivatives on metabolism. II. Non-protein nitrogen of blood and metabolism of glycine in hydrazine intoxication. H. B. Lewis and S. Izume. **III. Mechanism of hydrazine hypoglycæmia.** S. Izume and H. B. Lewis (J. Biol. Chem., 1926, 71, 33—49, 51—66).—II. After subcutaneous injection into rabbits of 130 mg. per kg. of hydrazine sulphate, the amino-acid nitrogen of the blood was always increased; the total non-protein nitrogen and urea nitrogen of the blood were markedly increased only in those cases in which renal lesions were produced in addition to the hepatic lesions which are a constant effect of the hydrazine. Injection of glycine into rabbits poisoned with hydrazine leads to an abnormal rise in the concentration of amino-acid nitrogen in the blood and no simultaneous increase in the urea; the hyperglycæmia and increased deposition of glycogen in the liver, which follows large doses of glycine in the normal rabbit, did not take place during hydrazine poisoning.

III. In rabbits poisoned with hydrazine the hyperglycæmia following administration of dextrose or of sodium lactate was abnormally great, whilst no deposition of glycogen took place. It therefore appears that the hepatic injury induced by hydrazine interferes both with the process of deamination and with the synthesis of glycogen. It is suggested that the hypoglycæmia produced by a simple injection of hydrazine is due to a failure in the conversion of non-carbohydrate materials into dextrose, with resulting deficiency in the latter substance.

C. R. Harington.

Biothermic action of organic compounds. E. Mameli and E. Filippi (Annali Chim. Appl., 1926, 16, 556—602).—Investigation of about 80 compounds (cf. A., 1925, i, 466) shows that, in general, only few functional groups or molecular groupings impart a distinct and constant biothermic function to the molecules of which they form part. Most of the organic compounds examined exhibit varied thermic behaviour, not only as regards doses, but also in relation to other experimental conditions, such as the character of the solvent used or the mode of suspension, and the method of administration. The carboxyl group in aliphatic chains is predominantly athermic, the acetamido-group mostly hypothermic, and the hydroxyacetyl group hyperthermic. Certain vitamins also have a hyperthermic effect. Glycollic acid and various coumaranone derivatives act similarly to the phenoxyacetic acids, and the hyperthermic effects are neither preceded nor followed by marked or rapid hypothermia, such as is observed with carbazole and certain other compounds, and do not exhibit the considerable oscillations during the rise of temperature which follow the administration of non-toxic doses of strychnine. T. H. Pope.

Rate of sedimentation of red blood cells and shifting in the plasma proteins in animals injected with India ink. S. Tsunekawa (J. Biochem. [Japan], 1926, 6, 237—260).—Injection of the ink is followed by a sudden increase in the fibrinogen content of the plasma, with return to the normal level after 7—10 days. The albumin/globulin quotient similarly diminishes and becomes normal. The absolute and relative increase of the globulin is not always parallel to the change in fibrinogen content. The rate of sedimentation of red cells is greatly increased. Chemical Abstracts.

Chemotherapy. I. Physiological action of leuco-dyes of the triphenylmethane series. M. Coplans and A. G. Green (J. Pharm. Exp. Ther., 1926, 30, 101—119).—The leuco-compounds of brilliant-green, xylene-blue, sulphato-green, and sulphato-violet are much less toxic and less active bactericidal agents than the corresponding dyes themselves. The dyes themselves, however, have no effect on toxins, whilst the leuco-compounds detoxicate diphtheria and tetanus toxins both *in vitro* and *in vivo*. For detoxication *in vitro*, incubation for several hours at 37° is necessary. Lethal doses of toxins thus treated do not produce toxic symptoms or death of the animal. Simultaneous injection of toxin and leuco-dye, or injection of the leuco-dye within a short time of injection of toxin and in the same place, also results in "neutralisation" of the toxin. Previous injection of leuco-compound has no effect. In the case of cobra-venom, detoxication of the toxin could be obtained *in vivo*, but not *in vitro*. In some cases, toxic symptoms were manifested in the animal some days after the introduction of the detoxicated toxin. Hæmoglobin prevents the neutralisation of the toxin by the leuco-compound, owing, it is suggested, to catalytic oxidation of the latter through the agency of the hæmoglobin. The more basic the leuco-compound the greater is its activity in neutralising toxins. The name "contra-toxins" is suggested for such compounds. L. F. Hewitt.

Relation between chemical constitution and therapeutic action. E. Fourneau (Compt. rend. 6me. Conference intern. chim., 1925, 72—211).—A review, chiefly devoted to protozoocidal and spirillicidal substances. A number of dyes, and organic derivatives of mercury and arsenic, are considered, and some general rules are deduced.

Chemical Abstracts.

Pharmacology of iron. E. Starkenstein (Arch. exp. Path. Pharm., 1926, 118, 131—191).—Ferrous compounds are not precipitated in the highest concentrations of protein solutions or in blood-serum, nor do they agglutinate or dissolve washed erythrocytes. They have neither an irritating nor an astringent action on subcutaneous or intravenous injection. Ferric salts are precipitated by very dilute protein solutions, and agglutinate and dissolve washed erythrocytes. The hæmolytic action of ferric salts of organic acids is stronger than that of inorganic ferric salts, whilst as protein precipitants the inverse holds. Ferric salts of hydroxypolycarboxylic acids (at least two carboxyls and one hydroxyl) behave likewise. Their acid-reacting solutions may be neutralised or made slightly alkaline without the separation of ferric hydroxide. These neutral solutions do not precipitate protein, and the iron forms part of a complex anion. These iron-containing acids exist only within a limited range of p_H; they form insoluble calcium and lead salts. The analogous ferrous salts of these acids behave similarly to other ferrous salts. Only the ferro-ions are toxic. After larger doses, the toxic effects are first similar to those of magnesium narcosis, from which the animals recover only to relapse later in convulsions. The toxicity of the ferrous salts is analogous to the behaviour of calcium salts with differing anions. In descending order of toxicity are chloride, sulphate, nitrate, acetate, lactate, indicating that the anion determines the degree of toxicity. The ferric ion is inactive in the organism. The complex salts of the above-mentioned ferrous and ferric hydroxypolycarboxylic acids are formed in the organism after the administration of the ferrous or ferric salts of the corresponding acids. They are stable on account of the buffering action of the organism. In the animal body, the ferro-acids are oxidised to ferri-acids. Ferrous salts and the complex iron-containing anions are rendered non-toxic by calcium chloride.

W. Robson.

Elimination of lead by the secretion of the digestive glands. F. Bricker (Arch. exp. Path. Pharm., 1926, **119**, 129—139).—After the administration of a single dose of white lead (0·4—0·6 g.) to a dog *per os*, a small amount of white lead is eliminated in the bile on the following day and a smaller amount in the pancreatic juice. With long-continued feeding (0·2—0·3 g. of white lead per day), the cessation of lead treatment may give rise to two types of results. Excretion in the bile may persist for some time and then cease, or may cease after a very short time, followed by excretion of traces later. Excretion in the pancreatic juice continues for some time after the lead feeding has stopped, and then ceases. The quantity excreted over an extended period is very small, and thus the liver and pancreas play no significant rôle in eliminating lead. No renewal of lead excretion in the bile can be produced by stimulants, whilst various foodstuffs or hydrochloric acid have no effect on excretion in pancreatic juice.

A. Wormall.

Methods of destroying organic matter in the chemical and biological analysis of poisons. M. A. Mancini (Arch. Farm. sper. Sci. aff., 1926, **41**, 170—184).—The various methods suggested for destroying animal tissue in the investigation of cases of poisoning are discussed. Tryptic digestion serves well for this purpose and effects no change in the chemical or biological properties of alkaloids, glucosides, antipyrin, veronal, trional, or acetanilide.

T. H. Pope.

Ionic changes in the blood with narcotics and stimulants. E. Brauchli and O. Schnider (Arch. exp. Path. Pharm., 1926, **119**, 240—253).—Earlier experiments with dogs showing the changes in blood calcium and potassium in narcosis (cf. Cloetta and Brauchli, A., 1926, 431) are confirmed and applied to man with similar results. A reduction in the calcium content takes place whenever sleep ensues, but the fall is not quite so great if the dog has previously been accustomed to the narcotic by doses *per os* over an extended period. Some relationship thus exists between the condition of sleep and the fall of calcium content of plasma. Caffeine, tetrahydro-β-naphthylamine, and camphor produce a definite rise in plasma calcium, but strychnine gives varying results. The alterations in the potassium content are less constant. In narcosis there is a rise, in light sleep the results vary, and with caffeine, tetrahydro-β-naphthylamine, and camphor there is a tendency for the blood potassium to fall.

A. Wormall.

Toxicological investigation of veronal. G. Sensi (Annali Chim. Appl., 1926, **16**, 510—519).—The viscera (or urine), rendered acid by acetic acid, are extracted with ethyl acetate until a small portion of the solvent leaves no appreciable residue on evaporation. The extract is evaporated and the residue boiled with water and filtered hot. The filtrate is evaporated to dryness on a water-bath and the remaining impure veronal dissolved in boiling alcohol and the solution filtered. The filtrate is treated for 24 hrs. with 7% of activated aluminium, prepared by immersing strips of aluminium sheet for 3 min. in 1% mercuric chloride solution, the filtered liquid being then evaporated to dryness and the residue of highly pure veronal weighed.

T. H. Pope.

Solvent action of carbon disulphide on biliary calculi *in vivo*. G. Galatà (Arch. Farm. sper. Sci. aff., 1926, **41**, 185—201).—Carbon disulphide, ingested in oil by a dog for 25 days in daily doses of 1 c.c. of 10% solution per kg. body-weight, and also injected subcutaneously in daily doses of about 0·8 c.c. per kg., effected no diminution in the weight of two cholesterol calculi deposited in the gall-bladder 25 days previously. Further, daily ingestion for 15 days of a 10% solution of carbon disulphide in oil at the rate of 2 c.c. per kg. body-weight caused no appreciable modification in the volumes of two calculi of cholesterol or of four fragments of calculi encysted under the skin; these calculi were, however, partly dissolved by subsequent subcutaneous injection of carbon disulphide in the same doses, although the injections were made at points distant from the encysted calculi.

T. H. Pope.

Specificity of enzymes. S. Kostytschev (Z. physiol. Chem., 1926, **162**, 139—144).—A reply to Neuberg (A., 1926, 1173). The author restates his criticism of Neuberg's theory of fermentation.

H. D. Kay.

Alteration of liver arginase activity through external factors. S. Hino (J. Biochem. [Japan], 1926, **6**, 335—366).—A temperature of 4—8° does not diminish the activity of a solution of liver arginase even after 10 days; the destructive effect of a higher temperature varies according to the hydrogen-ion concentration. The presence of phosphates does not make liver arginase thermolabile (?). The inhibitory influence of sodium fluoride is a linear function of the logarithm of its concentration. Potassium bromide, cyanide, and iodide are without effect over a wide range of concentration, but free iodine is strongly inhibitory or destructive.

Chemical Abstracts.

Action of enzymes on γ-methylglucoside. R. Kuhn and T. Wagner-Jauregg (Z. physiol. Chem., 1926, **162**, 103—121).—γ-Methylglucoside (1 : 4 ?) has been prepared by a modification of Fischer's method, and from a consideration of the simultaneous polarimetric and titrimetric changes observed during its hydrolysis by dilute hydrochloric acid it is concluded that it is a mixture of the two isomerides. Free γ-glucose cannot be detected in the reaction mixture during this hydrolysis. If γ-glucose plays a large part in carbohydrate metabolism, it might be expected that enzymes capable of hydrolysing γ-glucosides would be widely distributed in nature. This is not the case. Of a large number of enzyme preparations and organ extracts examined, only autolysed yeast and an aqueous extract of pig's liver have a slight hydrolytic effect, the remainder being inactive. H. D. Kay.

Biochemical synthesis of β-5-chlorosalicylglucoside. P. Delauney (Compt. rend., 1926, 183, 990—992).—5-Chlorosaligenol and dextrose dissolved in aqueous acetone are treated with emulsin, when β-5-chlorosalicylglucoside (lævorotatory) is formed. L. F. Hewitt.

Biochemical oxidation of ferrous malate. J. Wolff and J. Loiseleur (Compt. rend., 1926, 183, 1134—1136).—The effect of varying conditions on the oxidation of ferrous malate in the presence of ferrase (Wolff, A., 1926, 322) has been studied. The oxydase effects complete oxidation in air (not in a vacuum) between 20° and 50° (at 95° the ferrase is destroyed). At p_H 5 oxidation is rapid, and still proceeds, but more slowly, at p_H 3. Dialysis of an aqueous extract of ferrase from *Lactarius piperatus* or *Agaricus campestris* causes a large diminution in its activity, but reactivation occurs on the addition of a small quantity of manganese sulphate. J. W. Baker.

Nature of ferrase and certain oxydases. G. Bertrand (Compt. rend., 1926, 183, 1136—1137).—The author does not agree that the observed facts (cf. preceding abstract) constitute sufficient evidence for the real existence of a new oxydase, ferrase, in extracts from the tissues of fungi, but believes that the oxidising power is due to the presence of a small quantity of a quinonoid derivative, volatile or readily destroyed by heat, forming a complex system with laccase (cf. Bertrand, A., 1896, i, 534). J. W. Baker.

Methylglyoxal as a decomposition product of dextrose. E. Toenniessen and W. Fischer (Z. physiol. Chem., 1926, 161, 254—264).—Hexosephosphoric acid (but neither glycogen nor dextrose) is converted by a mixture of muscle and pancreas pulp or by the mixed extracts of these pulps into methylglyoxal by an enzyme present in the muscle, the aldehyde being not further converted into lactic acid owing to the restraining action of the antiglyoxalase of the pancreas. This is regarded as proof of the view that methylglyoxal is an intermediate in carbohydrate metabolism. P. W. Clutterbuck.

Hydrolysis of phosphoric esters in the surviving liver and the influence of drugs on the reaction. Liver lactacidogen. O. Riesser (Z. physiol. Chem., 1926, 161, 149—177).—Liver pulp of frog and rabbit in 2% sodium hydrogen carbonate solution at 43—45° readily eliminates phosphoric acid, the amounts, for frog 0·174%, for rabbit 0·219% of the dry weight, being of the same order of magnitude as the lactacidogen phosphoric acid. An amount of lactic acid equal to or greater than that of the phosphoric acid is simultaneously formed. Hexosediphosphoric acid added to an alkaline solution under the same conditions gives rise to phosphoric, but no lactic acid, whereas added to muscle pulp it gives considerable amounts of phosphoric and a little lactic acid. Liver of frog and rabbit, on keeping in physiological saline, readily splits off phosphoric acid in the first hour, the maximum being reached for frog in Ringer's solution in 3 hrs. and for rabbit in Locke's solution at 39° in 2 hrs. The simultaneous formation of lactic acid is small. In isotonic calcium chloride solution, phosphoric acid formation is inhibited, and in isotonic sodium fluoride solution it is either inhibited completely or may be decreased (indicating synthesis of phosphoric esters). Alcohol, chloroform, adrenaline, and insulin do not affect the rate of spontaneous phosphoric acid formation, and quinine appears slightly to inhibit. P. W. Clutterbuck.

Function of a phosphatase in bone formation. H. D. Kay (Brit. J. Exp. Path., 1926, 7, 177—180).—Normal blood plasma contains a small quantity of an acid-soluble phosphoric ester which is hydrolysable by bone phosphatase. The phosphatase content of whole bone is high in the fœtus, diminishing as the rate of bone formation decreases. In the kidney, the phosphatase is lowest in the fœtal stage. Chemical Abstracts.

Synthetic action of pepsin. T. Oda (J. Biochem. [Japan], 1926, 6, 77—89).—In digests of egg-white, edestin, and fibrin treated with pepsin, the synthesis (measured by changes in the amount of nitrogen unprecipitated by trichloroacetic acid) is complete after incubation for 2 days, and is most rapid at p_H 4. The synthetic process is not affected by lecithin or cholesterol, or by various electrolytes. The free amino-nitrogen is unaltered. Chemical Abstracts.

Adsorption of pepsin. K. Kikawa (J. Biochem. [Japan], 1926, 6, 275—286).—Pepsin is best absorbed on animal charcoal at p_H 1 or 2; it is removed by a phosphate (p_H 6·8) or citrate (p_H 5) solution, but not by a mixture of citrate and hydrochloric acid at p_H 1·8. The charcoal with the adsorbed pepsin digests caseinogen at p_H 1·8, much pepsin being removed. The leaching effect of protein is not due to the lowering of surface tension or to its viscosity; amino-acids, peptone, and diketopiperazine do not show the same effect. Chemical Abstracts.

Auto-digestion. II. Trypsin and "antitrypsin." H. Necheles and F. Fernando (Amer. J. Physiol., 1926, 79, 9—27).—The sera of the chicken, duck, goose, and pigeon and saline extracts of the earthworm were found to have "antitryptic" titres of the same order as that of dog's serum. Injection of pancreas, pancreatic juice, or trypsin did not change the titre. Agents having possible effects on the permeability of the intestine were without effect on the titre. It is concluded that trypsin does not act as an antigen and that antitrypsin is not an antibody. It is suggested that the "antitryptic titre" is the product of the action of a protease and of a trypsin-inhibiting substance. R. K. Cannan.

Trypsin. XV. Enzymes of the pancreas. R. Willstätter, E. Waldschmidt-Leitz, S. Duñaiturria, and G. Künstner (Z. physiol. Chem., 1926, 161, 191—209).—A number of improvements of the gelatin method for determination of trypsin are given, rendering it sufficiently accurate for the determination of the enzyme in fresh pancreas and in glycerol extracts thereof. A new method of preparation of trypsin is given, aiming at the complete separation of accompanying enzymes. Although trypsin is not adsorbed from acid solution by the stable γ-form

of aluminium hydroxide, it is readily adsorbed by the unstable β modification. A new method for the determination of trypsin by caseinogen is described which is regarded as superior to the gelatin method.
P. W. CLUTTERBUCK.

Enzymic cleavage of dipeptides. III. Activation and inhibition of peptidases. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **161**, 270—281).—The hydrolysis of glycylglycine by erepsin (see A., 1926, 388, 1174) is inhibited by calcium chloride at concentrations of 0·02—0·03M upwards. Phosphate inhibits the enzyme of fresh glycerol extracts, but does not inhibit if the extract has been kept. Changes in activity of intestinal and yeast erepsin during dialysis are followed. In the crude enzyme, some substance is present which slightly activates the enzyme, but its effect is small.
P. W. CLUTTERBUCK.

Enzymic hydrolysis of dipeptides. IV. Intestinal erepsin. K. JOSEPHSON and H. VON EULER (Z. physiol. Chem., 1926, **162**, 85—94).—It has been shown previously that in the formation of the enzyme-substrate complex between a peptide and intestinal erepsin which precedes hydrolysis, the free amino-group of the α-amino-acid present in the peptide combines with the enzyme. Evidence is now adduced that the group in the enzyme molecule which combines with the free amino-group of the peptide is an aldehyde group. Phenylhydrazine, potassium cyanide, and sodium sulphite, all of which combine with aldehydes, strongly inhibit the hydrolysis of glycylglycine by erepsin. H. D. KAY.

Effect of amino-acids and other compounds on the activity of urease. W. J. HUSA (J. Amer. Chem. Soc., 1926, **48**, 3199—3201; cf. A., 1923, i, 351).—The promoter effect of α-amino-acids on urease has been confirmed, and is not affected by the introduction of a methyl group in the α-position. δ-Amino-n-valeric acid has no promoter effect, thus supporting the previous conclusion that the degree of the effect is determined by the proximity of the amino- and carboxyl groups. Quinine hydrochloride and ethyl 3-amino-4-hydroxymethylbenzoate slightly decrease the activity of urease. The enzyme is completely inactivated by "Mercurochrome 220 Soluble." F. G. WILLSON.

Enzymic conversion of aldehydes. II. K. MYRBÄCK and W. JACOBI (Z. physiol. Chem., 1926, **161**, 245—253).—The Cannizzaro reaction with acetaldehyde is accelerated by both fresh and dried yeast. The enzyme is not, but an activator is, removed by washing. By addition of the wash-water, the washed yeast is reactivated. This activator cannot be definitely said to be identical with co-zymase or co-reductase. P. W. CLUTTERBUCK.

Oxidoreductase in yeast. A. N. LEBEDEV (J. Russ. Phys. Chem. Soc., 1926, **58**, 184—195).—The power of yeast extract to decolorise methylene-blue was studied quantitatively. Variously treated samples of extract boiled, heated at different temperatures (35°, 60°) with and without addition of chemical reagents and fresh enzyme, were used. Experiments were also performed with maceration extract. Boiled extract was inert, but on autolysis it again became very active. This was shown not to be due to the formation of xanthine substances. Extract heated at 60° was moderately active, but did not ferment, like the fresh extracts, sugar or glyceric acid solutions, although its effect on pyruvic acid was greater. The results confirm the presence of a vigorous oxidoreductase in yeast, but not its participation in fermentation reaction.
M. ZVEGINTZOV.

Bacteria. XI. Development of a systematic analytical method for the comparative study of bacterial cells. T. B. JOHNSON (Amer. Rev. Tuberculosis, 1926, **14**, 164—171).
CHEMICAL ABSTRACTS.

General properties of cryptotoxins; tetanus cryptotoxin. H. VINCENT (Compt. rend., 1926, **182**, 1307—1310).—Cryptotoxins are formed by treating bacterial toxins with soaps, *e.g.*, sodium palmitate. The toxic properties of the toxin are destroyed, but the immunising properties remain. The toxin of tetanus is destroyed by treatment with 0·5% of a 0·2% solution of sodium palmitate at 38° for 10—16 hrs., but the toxic properties are partly recovered by treating the cryptotoxin with dilute hydrochloric acid. The immunising properties of the toxin are not destroyed by treatment with soaps, and the local reaction caused by the first injection disappears after repeated injections. Sodium palmitate is an efficient bactericidal agent for typhoid, paratyphoid A and B, and cholera bacilli, for Shiga's and Flexner's bacilli, *B. coli communis*, and streptococci, but is not hæmolytic. L. F. HEWITT.

Chemistry of insulin. H. PENAU and L. BLANCHARD (Bull. Soc. Chim. biol., 1926, **8**, 383—450).—An account of the preparation, properties, and physiological action of insulin.

Effect of various sugars (and of adrenaline and pituitrin) in restoring the shivering reflex. G. J. CASSIDY, S. DWORKIN, and W. H. FINNY (Amer. J. Physiol., 1926, **77**, 211—218).—Dihydroxyacetone, lævulose, mannose, and galactose restore the shivering reflex in cats in which it has been abolished by insulin hypoglycæmia. Maltose, sucrose, and lactose are also sometimes effective by reason of the products of their hydrolysis. All these substances, with the exception of sucrose and lactose, also abolish insulin convulsions. Adrenaline and pituitrin cause shivering to reappear in hypoglycæmic cats. R. K. CANNAN.

Effect of prolonged administration of parathyroid extract on excretion of phosphorus and calcium. I. GREENWALD and J. GROSS (J. Biol. Chem., 1926, **68**, 325—333).—Prolonged administration of parathyroid extract to a dog led to an increase in the total excretion of calcium and phosphorus; the increase in the excretion of calcium was so large as to indicate that it must have been due, in part at least, to removal of calcium from the bones.
C. R. HARINGTON.

Influence of diet and sunlight on the amount of vitamin-*A* and vitamin-*D* in the milk afforded by a cow. H. CHICK and M. H. ROSCOE (Biochem. J., 1926, **20**, 632—649).—The vitamin-*A* content of milk is at a maximum when the cow is fed on fresh green food, and least when the animal is on a winter ration of cereals and roots; exposure of the cow to sunlight does not affect this vitamin in the milk. The antirachitic value of milk, on the other hand, depends on the degree of insolation of the cow as well as on the character of the diet. Milk contains a maximum amount of both fat-soluble vitamins when the cow is out at pasture in summer. Butter made from milk possessing antirachitic potency preserves this property after storage in the frozen condition for more than 2 years. S. S. Zilva.

Difference in chemical composition of the skeletons of young rats fed (1) on diets deprived of fat-soluble vitamins and (2) on a low-phosphorus rachitic diet, compared with those of normally nourished animals of the same age. H. Chick, V. Kovenchevsky, and M. H. Roscoe (Biochem. J., 1926, **20**, 622—631).—A condition of osteoporosis found in the bones of young rats kept on a diet deprived of fat-soluble vitamins is characterised by (1) a proportion of alcohol- and (fat) ether-soluble material in excess of the normal, (2) a proportion of ash (A) less than the normal, (3) a normal proportion of organic material, cartilage and connective-tissue, etc. (R), (4) a value of the A/R ratio of about 0·9—1·2, the normal value being about 1·5. In the osteoporotic bone, the percentage of calcium, reckoned on the dry weight of the bones, is frequently very low (12—16%), and is found to approach much nearer to the normal if the calculation is made on the fat-extracted bone.

Rachitic bones of rats kept on McCollum's low-phosphorus rickets-producing diet are characterised by (1) a content of mineral ash (A) much below the normal, (2) a water content much above the normal, (3) a very low value of the A/R ratio, *i.e.*, from 0·4 to 0·8, as compared with 1·0, the value found for the bones of rats which receive cod-liver oil in addition to this diet. The value of the A/R ratio is the best chemical criterion in the diagnosis of rickets. S. S. Zilva.

Value of egg-yolk in supplementing diets deficient in calcium. E. Tse (Amer. J. Physiol., 1926, **77**, 192—198).—Contrary to McCollum, it is found that small quantities of egg-yolk effectively supplement diets poor in calcium. This is due to a vitamin-like substance economising available calcium. R. K. Cannan.

Relation of certain soil algæ to some soluble carbon compounds. B. M. B. Roach (Ann. Bot., 1926, **40**, 149—201).—A number of species of algæ have been isolated from the soil and the nutrition of the organisms has been studied in pure culture. The majority of the species show greatly increased growth when provided with dextrose or other suitable soluble organic compounds; and some, at least, are able to develop saprophytically in complete darkness, and must therefore be taken into account in regard to the biological and chemical changes taking place in the soil. A few soil species seem to be completely autotrophic in nutrition. A method for the quantitative study of unicellular algæ is described, involving daily measurements of the size of the cells and the number of cells per unit volume of the culture fluid, and the calculation from these data of the bulk of algal protoplasm present. In media favourable to growth, the logarithmic values of the bulk, plotted against time for a limited period of growth, lie on a straight line within the limits of experimental error, indicating growth at a uniform rate. Deviations from the straight line are still further reduced if the cultures are continuously aërated and the illumination is controlled. The relative average rates of growth of the species *Scenedesmus costulatus*, Chod., var. *chlorelloides*, in media containing mineral salts with 1% of various soluble organic compounds, taking the rate with dextrose as 100%, are: maltose, 100%, with an initial "lag" period; galactose, 94%; sucrose, 84%; lævulose, 73%; mineral salts alone, 60%; mannitol, 13%; xylose, 0%. Xylose is definitely toxic. C. T. Gimingham.

Chlorosis of fruit trees. I. Composition of apple leaves in cases of lime-induced chlorosis. T. Wallace and C. E. T. Mann (J. Pomology, 1926, **5**, 115—123).—Normal apple leaves contain more dry matter and less ash in the dry matter than chlorotic leaves. The percentages of potassium and sodium are always much higher, and of calcium definitely lower, in the ash of chlorotic leaves than in that of normal leaves; the differences are especially great in the case of potassium. Differences in the amounts of magnesium, iron, aluminium, phosphorus, and silica are not so definite. The soils on which chlorosis of apple trees occurred all contained high percentages of carbonates. Spraying chlorotic foliage with a solution of ferrous sulphate restored the normal green colour in several cases. C. T. Gimingham.

Waxes of perfumed flowers. I. Wax of *Rosa Druscky*. A. D'Ambrosio (Annali Chim. Appl., 1926, **16**, 443—451).—This rose contains a yellow wax, m. p. 57—58°. The portion extracted by cold alcohol contains oleic acid and other substances. That extracted by hot alcohol is colourless, m. p. 71—72°, and contains *rosilic acid*, $C_{18}H_{36}O_3$, m. p. 73°. This is ι-hydroxystearic acid, since chromic acid oxidation yields azelaic acid, and probably sebacic acid, whilst hydriodic acid yields *ι-iodostearic acid*, m. p. 56—57°, which is reduced to stearic acid. With the rosilic acid there is present an *acid*, m. p. 70°, forming a *barium* salt which indicates a mol. wt. of 1438. As hydrolysis gives rosilic acid, it is considered that the new acid consists of five rosilic acid molecules united by condensation of the hydroxyl group of one with the carboxyl group of the next and so on (cf. Bougault and Baudier, A., 1909, i, 82).

The portion of the wax insoluble in alcohol has m. p. 57—58°; it is yellow, and contains sulphur compounds, and also 0-hydroxyheptadecane (dinonylcarbinol, Kipping, J.C.S., 1893, **63**, 457). This is the alcohol which would be obtained by loss of carbon dioxide from rosilic acid. E. W. Wignall.

Flower waxes. Rose wax. H. Prophète (Bull. Soc. chim., 1926, [iv], 39, 1600—1610).—See A., 1926, 981, 1281.