BRITISH CHEMICAL ABSTRACTS

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General, Physical, and Inorganic Chemistry.

Revision of Rowland's preliminary tables of solar spectrum wave-lengths. C. E. St. John (Proc. Nat. Acad. Sci., 1927, **13**, 678—683).—An account is given of the methods adopted in fixing standard wave-lengths, and of the scheme in operation at Mount Wilson Observatory, for the accurate determination of solar wave-lengths in the international system. R. A. Morton.

Intensity and width of spectral lines. B. Trumpy (Z. Physik, 1927, **44**, 156).—By using in error the number of atoms instead of the number of resonators in earlier work (this vol., 179) when calculating the radius r_0 of mercury atoms, values slightly too low were obtained. R. W. Lunt.

Intensities in the hydrogen fine structure. W. V. Houston (Physical Rev., 1926, [ii], 28, 428).—Sommerfeld and Unsöld's treatment of the intensities of the hydrogen fine structure components is criticised. The forbidden components $3p_1-2p_1$, $3p_2-2p_2$, and $3s-2s$ are to be expected in this order of decreasing intensity, and the current in a discharge tube is likely to produce them in hydrogen. These components will increase with an increase in current, and will also show a resultant polarisation. A. A. Eldridge.

Doublet separation and fine structure of the Balmer lines of hydrogen. N. A. Kent, L. B. Taylor, and H. Pearson (Physical Rev., 1927, [ii], **30**, 266—283).—The wave-length difference between the components λ' and λ'' ($\lambda'>\lambda''$) of H_α, H_β, and H_γ are determined as 0·1370, 0·0791, and 0·0666 Å., respectively. Another component in λ' in H_α, H_β, and H_γ is present, and there are indications of other components in λ''. The magnitudes of the components agree with those given theoretically by the new quantum mechanics with the spinning electron. A. A. Eldridge.

Spectral intensity distribution in a hydrogen discharge. E. W. Tschudi (J. Franklin Inst., 1927, **204**, 219—225).—A cold cathode discharge tube has an auxiliary tube attached from which cathode rays are projected against the main cathode. The relative intensity distributions of H_γ and H_δ were measured, by means of a photo-electric cell, from the main cathode through the cathode dark space into the negative glow, with and without excitation of the auxiliary tube. The intensity of spectral illumination in the negative glow is increased by about 20% when the main cathode is bombarded by the electron stream. This increase is attributed to the production of soft X-rays in the gas which are capable of exciting the gas molecules. W. E. Downey.

Emission of light from hydrogen atoms. R. d'E. Atkinson (Proc. Roy. Soc., 1927, A, **116**, 81—103).—Experiments are described in which a non-luminous beam of canal rays, some distance after their entry into the vacuum, were made to emit the Balmer lines by excitation at approximately one point only, so that any interval between excitation and emission could be directly measured. The method of point-excitation used was to pass the canal rays across the mouth of one or more fine jets, from which air, or some other gas, was streaming, and to rely on rapid pumping to keep the general pressure low. It was found impossible to confine the excitation region to less than about 1·5 mm. in length, but the distribution of excitation over the region could be definitely determined, and the position of its maximum fixed within one or two hundredths of a mm. The distribution of intensity in the Balmer lines was measured photographically and compared near the maximum with that to be expected on the assumption that the intensity due to strict point-excitation would begin at the point and would fall off exponentially from the start. The results obtained support this assumption, and are in direct disagreement with the conclusions reached by McPetrie (A., 1926, 652). Several considerations arising out of this result are discussed. It is suggested that the process of excitation consists in an instantaneous placing of the hydrogen ion (or atom) into a definite, and preferably fairly deep, quantised state. A number of further experiments made possible by the success of the method are outlined, including a proposal for observing the "negative radiation effect" postulated by Einstein. L. L. Bircumshaw.

Origin of the nebulium spectrum. I. S. Bowen (Nature, 1927, **120**, 473).—The behaviour of the nebulium lines accords with their identification as regards wave-length, source, and series designation, as follows: 7235·0, O II, $^2D-^2P$; 6583·6, N II, $^3P_2-^1D$; 6548·1, N II, $^3P_1-^1D$; 5006·84, O III, $^3P_2-^1D$; 4958·91, O III, $^3P_1-^1D$; 4363·21, O III, $^1D-^1S$; 3728·91, O II, $^4S-^2D_3$; 3726·16, O II, $^4S-^2D_2$. A. A. Eldridge.

Origin of the nebulium spectrum. A. Fowler (Nature, 1927, **120**, 582—583).—The author's observations lend support to the view (preceding abstract) that the two green lines of the nebular spectra are due to O III. On the whole, the numerical evidence also supports the assignment of nebular lines to N II and O II. A. A. ELDRIDGE.

Transition probabilities in the lithium atom. B. TRUMPY (Z. Physik, 1927, 44, 575—584).—The transition probabilities associated with the $1s-4p$ to $1s-12p$ lines of the principal series of the lithium spectrum have been calculated from experimental determinations of the intensities and widths of these lines as absorbed by lithium vapour. For $1s-9p$ to $1s-12p$ the values agree well with those calculated by Pauli according to Schrödinger's theory, whilst those for $1s-4p$ to $1s-9p$ agree well with those calculated by Sugiura in which Pauli's treatment is modified. R. W. LUNT.

Nitrogen series in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1926, [ii], 27, 801).—Two new series of triplets probably converging to a common head and belonging to the quadruplet system, and two series of doublets also having a common limit and belonging to the doublet system, have been observed in nitrogen. The short wave-length lines of one of the triplet series are given by: $\nu=117353-109677\,(m+0{\cdot}845685-0{\cdot}022749/m^2-0{\cdot}026562/m^4)^{-2}$, where $m=1$, 3, and 4 (known) and 2 (new), and $1S=117353$ (14·48 volts) is the lowest energy level yet observed in neutral nitrogen.

A. A. ELDRIDGE.

First spark spectrum of aluminium, Al II. R. A. SAWYER and F. PASCHEN (Ann. Physik, 1927, [iv], 84, 1—19).—The lines of the spectrum of Al II have been photographed, measured, and analysed into series. The source of the aluminium spectrum was a cylindrical cathode of aluminium in a discharge through pure helium. Complete freedom from water vapour was necessary to obtain the higher members of the series. Spectra were photographed on a quartz prism apparatus, on two grating apparatus, and on a vacuum spectrograph. The observations extend from 7471 to 933 Å. The term-scheme has been worked out for Al II. The ionisation potential of Al^+ is 18·744 volts. W. E. DOWNEY.

Spectral relationships of lines arising from the atoms of the first row of the periodic table. R. A. MILLIKAN and I. S. BOWEN (Phil. Mag., 1927, [vii], 4, 561—579).—The work of Millikan, Bowen, and others on the determinations of the types of spectra arising from different electron configurations is recapitulated and it is shown that the recently developed rules of Russell, Pauli, Heisenberg, and Hund have been of extreme importance in the interpretation of the problems. The rules originally developed from a study of the elements of the first long period of the periodic table have been shown to apply equally well for the spectra produced by the atoms of the first row of the periodic table. The application of the spectroscopic rules to systems comprising from 1 to 7 electrons in the first row of the periodic table is discussed in detail.

A. E. MITCHELL.

Arc spectra of metals in chlorine. M. MIYANISHI (Japan. J. Phys., 1927, 4, 119—131).—In the arc spectra of mercury, cadmium, zinc, magnesium, calcium, strontium, and barium in chlorine a number of combination lines which are forbidden by the selection principle have been observed and classified. The broadening of some of the mercury and calcium lines was found to be similar in nature to that produced by the Stark effect. Since the effects observed in chlorine at a constant arc current are approximately reproducible in air with four times the arc current, it is concluded that the marked broadening and the appearance of enhanced and forbidden lines now recorded are due to the presence of chlorine ions in the arc. R. W. LUNT.

Anomalous dispersion in the principal series of potassium. Ratio of the dispersion constants of the red and violet doublets. W. PROKOFIEV and G. GAMOV (Z. Physik, 1927, 44, 887—892).—The ratio of the dispersion constants of the red and violet doublets of potassium is 111·5±1·5 and is independent of the vapour density over a wide range (1 : 65). The ratio of the probabilities of the transition $2p_1-1s$ to the transition $3p_1-1s$ is 30·7. R. W. LUNT.

Extreme ultra-violet spectrum of titanium. R. C. GIBBS (Physical Rev., 1926, [ii], 27, 799).—The hot spark spectrum of titanium was photographed from 192 to 1718 Å. Lines not due to titanium were eliminated; Lang's 25 titanium lines, and 90 others, were observed. A. A. ELDRIDGE.

New lines in the arc spectrum of manganese at normal pressure between 2300 and 2000 Å. S. PIÑA DE RUBIES and J. DORRONSORO (Anal. Fís. Quím., 1927, 25, 374—377).—Data are given for a new series of lines in the arc spectrum of manganese at normal pressure between 3100 and 2000 Å. They are all reversible and have, hitherto, been unclassified.

G. W. ROBINSON.

Ultra- and extra-ultra-violet spectrum of iron as developed by the inverse photo-electric effect. O. STUHLMAN, jun. (Physical Rev., 1926, [ii], 27, 799).—The following spectral regions were reproduced: spark spectrum of iron (Exner and Haschek, Tabellen), pronounced lines between 2456 and 2213 Å., new lines between 2211 and 2154 Å.; Millikan, Bowen, and Sawyer's spark spectrum, 2152—880 Å.

A. A. ELDRIDGE.

Spark spectrum of nickel (Ni II). A. G. SHENSTONE (Physical Rev., 1927, [ii], 30, 255—265).—The wave-lengths (4362—1812 Å.) and classification of the lines in the spectrum of Ni II are tabulated, as well as the Zeeman effect of 44 lines. The important atomic structures are d^8s and d^8p. The low set of terms comprises $^4F'$, $^2F'$, $^4P'$, $^2P'$, ^2D, ^2G, of which $^4F_5'$ is the lowest. The calculated ionisation potential from d^8s to d^8 is 17·4 volts. The g-sum rule is not confined to terms built on the same ion term.

A. A. ELDRIDGE.

Spectrum of ionised krypton. P. K. KICHLU (Nature, 1927, 120, 549).—Three groups of terms, A, B, and C, are tabulated for the spark lines of krypton, such that A combine with B, and B with C; the values given are arbitrary. A. A. ELDRIDGE.

Hyperfine structure of the terms of the cadmium spectrum. A. SCHRAMMEN (Ann. Physik, 1927, [iv], 83, 1161—1199).—Details are given of the use of a quartz Lummer plate. The best position for the plate is found to be between the collimator and the prism. The optical axis of the plate must be within ±10′ of the perpendicular to the direction of the radiation in order to obtain parallel interference bands. The ultra-violet spectrum of cadmium and the mercury line at 2537 Å. have been examined and the plates measured by means of a registrating photometer. The structure of the lines and the hyperfine structure of the terms are discussed.

W. E. Downey.

Structures of the arc spectra of elements of the oxygen group. J. C. McLennan, A. B. McLay, and J. H. McLeod (Phil. Mag., 1927, [vii], **4**, 486—495).—The wave-lengths in the tellurium arc spectrum have been re-measured in the spectral range 3200—1640 Å. Forty lines of wave-length less than 2080 Å. have been measured for the first time. The lines at 2259·02, 2142·75, 2385·76, and 2383·24 Å. previously observed by Zumstein (A., 1926, 650) have been classified as $5^3P_2-6^5S_2$, $5^3P_2-6^3S_1$, $5^3P_1-6^3S_1$, and $5^3P_0-6^3S_1$, respectively. From the observation of Kimura (this vol., 601) that the lines at 2259·02 and 2142·75 Å. were absorbed by the normal tellurium vapour whilst the other pair were not, it is assumed that the lines at 2385·76 and 2383·24 Å. originate in transitions involving metastable states. The absence of $5^1D_2-6^5S_2$ is explained by the rare observance of singlet–quintuplet intercombination lines. The authors were unable definitely to identify any terms of higher energy than 6^3S_1. In the investigation of the tellurium arc spectrum five wave-lengths were observed that were due to the presence of selenium as an impurity. In accordance with the results of Kimura (*loc. cit.*) these have been classified as the most fundamental lines of the Se I spectrum. The results obtained show that in so far as they are known the Se I and Te I spectra are analogous to those of O I and S I. All four spectra have been shown to conform to the theoretical structures predicted from the Pauli–Heisenberg–Hund theory.

A. E. Mitchell.

Intensity ratio of the blue cæsium doublet. C. F. Hagenow and A. L. Hughes (Physical Rev., 1927, [ii], **30**, 284—287).—Redetermination of the intensity ratio of the members of the blue doublet of cæsium (4555, 4593 Å.) gives results ranging from 2·3 to 3·8 : 1, instead of that (2 : 1) anticipated from Burger and Dorgelo's rule (Z. Physik, 1924, **23**, 258).

A. A. Eldridge.

Intensity ratio for doublets with large frequency differences. L. S. Ornstein, (Frl.) M. Coelingh, and (Frl.) J. G. Eymers (Z. Physik, 1927, **44**, 653—654).—Intensity determinations in the spark spectrum of barium have shown that the addition rule for *ps* and *pd* doublets is valid if the observed intensity is divided by the fourth power of the emission frequency.

R. W. Lunt.

Quenching of mercury resonance radiation by foreign gases. P. D. Foote (Physical Rev., 1927, [ii], **30**, 288—299).—The mechanism of the quenching of mercury resonance radiation by the rare gases or nitrogen differs from that of the quenching by hydrogen. Absorption of radiation 2537 Å. produces $^3P_1$ Hg′ atoms, some of which return to the $1S_0$ state by radiating, and some undergo collision of the second type with foreign gas molecules giving $^3P_0$ atoms. Many of these return to the $^3P_1$ state by collision of the first type with high-speed gas molecules; others return to the normal state through collision with traces of hydrogen impurities, whilst yet others collide with normal mercury atoms producing Hg_2' excited molecules.

A. A. Eldridge.

Depolarisation of resonance radiation. P. D. Foote (Physical Rev., 1927, [ii], **30**, 300—304).—Depolarisation and quenching of mercury resonance radiation are phenomena of different types. Two effects producing depolarisation are described.

A. A. Eldridge.

Selective displacement of 0·0153 Å. in *X*-ray spectral lines. X. F. H. Loring (Chem. News, 1927, **135**, 183—185; cf. this vol., 707).—Theoretical. A revision of the calculation of the atomic weight of silver and of other atomic constants.

W. E. Downey.

General characterisation of phenomena associated with *X*-rays as a function of frequency. R. Glocker (Z. Physik, 1927, **43**, 827—838).—Earlier experiments on the energy of photo- and Compton-electrons as a function of the incident *X*-radiation led to a law that the intensity of any effect due to *X*-rays was directly proportional to any given frequency, and to the product of the electron exchange concerned and the intensity of the incident *X*-radiation. The validity of this relationship has now been examined in a number of phenomena associated with *X*-rays.

R. W. Lunt.

***X*-Ray absorption spectra and chemical linking.** S. Aoyama, K. Kimura, and Y. Nishina (Z. Physik, 1927, **44**, 810—833).—The absorption limits for the K_1-line of calcium, the K_1- and K_2-lines of chlorine, and for the K_1-, K_2-, and K_3-lines of sulphur have been determined from observations on a large number of compounds containing these elements. The results are discussed at length with reference to the grating energies of these compounds and thus to the nature of the linking of these atoms in the compounds investigated.

R. W. Lunt.

Spatial distribution of the intensity of *X*-rays scattered by copper. G. E. M. Jauncey and A. W. Coven (Physical Rev., 1926, [ii], **28**, 426).—The total mass scattering coefficient per unit solid angle in a direction ϕ for *X*-rays λ 0·41 Å. when scattered by copper is determined for various values of ϕ, and the ratio of the experimental to Thomson's value is determined for carbon and copper. The ratio for a given angle and wave-length increases with the atomic number of the scatterer.

A. A. Eldridge.

***X*-Ray absorption in heated silver.** H. S. Read (Physical Rev., 1926, [ii], **27**, 795).—For silver, the transmission is a complex function of the wave-length, increasing or decreasing with the temperature; the results are considered theoretically.

A. A. Eldridge.

Higher multiplets in *X*-ray spectra [of the rare earths]. J. H. van der Tuuk (Z. Physik, 1927, **44**, 737—744).—The $M\alpha$-, $M\alpha'$-, $M\beta$-, and $M\beta'$-lines of the following elements have been determined: tungsten, tantalum, hafnium, lutecium, ytterbium, thulium, erbium, holmium, dysprosium, terbium, gadolinium, europium, and samarium. The $M\alpha_1,\alpha_2,\beta$ doublet degenerates in these elements and changes its structure from element to element. This is discussed with reference to the filling up of the fourth quantum orbit with electrons. R. W. Lunt.

Spectrographical measurements in the intermediate region (*K*-, *L*-, *M*-, *N*-series). J. Thibaud and A. Soltan (Compt. rend., 1927, **185**, 642—644).—Thibaud's method (this vol., 803) has been applied to the photography of additional new lines in the intermediate region, viz., the *K*-lines of nitrogen and boron, and the *N*-doublets of tantalum, tungsten, platinum, and gold. In most cases the maximum error is 0·5—1%. Very soft *X*-rays are shown to obey the laws established by Drude for optical and ordinary *X*-ray frequencies. The inaccuracy of Bragg's law for high wave-lengths, however, involves a difficulty in measurements in which the diffracting properties of crystals are used. J. Grant.

Relative intensities of *X*-ray lines in the *L*-spectrum of thorium. S. K. Allison (Physical Rev., 1927, [ii], 30, 245—254).—The relative intensities of the thorium *L*-series lines were measured at 31·8 kilovolts, and the results, together with the relative intensities at high voltage, and those of *L*-doublets, are tabulated. The additional lines, $L\eta$, $L\beta_7$, and $L\gamma_2$ were found, but not γ_5 or γ_4; observed wave-lengths were 854, 772, 641X, respectively. A. A. Eldridge.

Azimuthal intensity of scattered *X*-rays. W. Friedrich and G. Goldhaber (Z. Physik, 1927, 44, 700—707).—The azimuthal intensity of an *X*-ray beam scattered by water contained in a thin-walled glass vessel has been determined by an ionisation method. The angular distribution of intensity thus observed agrees fairly well with that calculated by Compton's theory. R. W. Lunt.

Quantum theory of the Zeeman effect for band lines. E. C. Kemble (Physical Rev., 1926, [ii], 27, 799—800).—Assuming an electronic angular momentum with fixed components σ and ε along and perpendicular to the axis of figure of a diatomic molecule, the Zeeman term formula $E=E_0+rh\Delta\nu_n[\sigma^2+\varepsilon(j^2-\sigma^2)^{\frac{1}{2}}]/j^2$, where r is the magnetic quantum number, $\Delta\nu_n$ is the Larmor frequency, and j is the total angular momentum, holds. It is inferred that the Zeeman pattern for lines adjacent to a band origin will normally be simple, and the scale may be similar to that for an atomic line; that the outer lines of a band will have very complicated patterns, usually on a scale too small to detect; that if the initial and final values of ε are different, the outer lines of a band will seem to be diffusely broadened in a magnetic field; and that the direction of rotation for the Faraday effect in the neighbourhood of a band line will frequently be different for the *P* and *R* branches of the same band. A. A. Eldridge.

Ratio of intensities of modified and unmodified rays in the Compton effect. Y. H. Woo (Physical Rev., 1926, [ii], 28, 426).—The intensity ratios for silver $K\alpha$ rays (scattering angle 120°) are : lithium ∞, beryllium 8·72, boron 7·02, carbon 5·48, sodium 3·04, magnesium 2·78, aluminium 2·61, silicon 2·33, sulphur 1·91, potassium 1·72, calcium 1·71, chromium 0·75, iron 0·51, nickel 0·40, copper 0·21. A. A. Eldridge.

Disappearance of the unmodified line in the Compton effect. Y. H. Woo (Physical Rev., 1926, [ii], 28, 426—427).—The unmodified peak is present, although faint, in the scattered radiation when silver $K\alpha$ rays are scattered by beryllium at 105° and 120°, by boron at 120° and 135°, and by carbon at 140°. The results are not in accord with the theory or results of Jauncey. A. A. Eldridge.

Intensity distribution in the $K\alpha$-doublet of the fluorescence *X*-radiation. Y. H. Woo (Physical Rev., 1926, [ii], 28, 427).—Assuming each component of the α-doublet to be a single line of the same width, the relative intensities α_1/α_2 are : (third order) zinc 2·00, arsenic 1·98; (fourth order) strontium 1·96, zirconium 1·96, molybdenum 2·00, silver 2·06, tin 2·00, iodine 2·05. A. A. Eldridge.

Ionisation potential and radius of the atom. A. S. Eve (Physical Rev., 1926, [ii], 27, 515).—For the rare gases, the ionisation potential is approximately inversely proportional to the radius of the atom, whether Bragg's or the kinetic theory value is selected. A. A. Eldridge.

Critical potentials of copper by electron impacts. H. B. Wahlin (Nature, 1927, **120**, 585).—Critical potentials for copper were observed at 7·7, 1·61, 3·80, 4·84, 5·65, 6·08, 6·73, 8·26, 8·73, 9·40, 10·07, and 10·91 volts; a critical potential at 2·6 volts does not correspond with any spectroscopic transition, and may be due to impurity. A. A. Eldridge.

Critical potential of iodine. V. Kondratéev and A. Leipunski (Z. Physik, 1927, 44, 708—712).—The critical potential of molecular iodine has been determined by allowing a narrow beam of iodine molecules to flow through the ionisation space so that practically no iodine molecules come in contact with the emitting filament. The values so found are 2·5, 3·8 (very weak), and 5 ±0·4 volts. That these potentials are due only to the iodine molecule has been established in a second series of determinations in which the beam of iodine molecules was heated at 800° before entering the ionisation chamber. At this temperature about half the iodine is monatomic; the potentials observed were : 1, 2·5, 5 (very weak), and 6·5 volts. Dymond and Kuhn have shown that 4995 Å. is the limiting wave-length producing one excited and one neutral iodine atom, and corresponds with 2·47 volts. The work of dissociation of the iodine molecule corresponds with 1·53 volts, and the transition ${}^2P_2-{}^2P_1$ with 0·94 volt; the potential observed at 3·5 volts therefore corresponds with the production of two excited iodine atoms.

The observed critical potential at 1 volt in the second series of experiments is identified with the transition ${}^2P_2-{}^2P_1$ in the iodine atom (0·94 volt), and that at 6·5 is thought to be the resonance potential with the value of 6·92 predicted by Turner from spectroscopic data in the Schumann region. R. W. Lunt.

Ionisation potential of terbium. L. Rolla and G. Piccardi (Atti R. Accad. Lincei, 1927, [vi], **5**, 818—819).—The ionisation potential of terbium determined by the flame method (cf. A., 1926, 769) is 6·74 volts. This again confirms the earlier observation that the ionisation potential of members of the rare-earth group increases with increasing atomic number (cf. A., 1926, 1187). M. Carlton.

Determination of critical potentials and the ionisation potential of mercury vapour. E. O. Lawrence (Physical Rev., 1926, [ii], **27**, 515).—A method of high precision gave a value of 10·4 ($\pm$0·5%) volts for the ionisation potential of mercury vapour. A. A. Eldridge.

Voltage–intensity relations of mercury lines below ionisation. D. R. White and H. W. Webb (Physical Rev., 1926, [ii], **27**, 243—244).—The voltage–intensity relationship for each of 20 mercury lines between 2500 and 5800 Å. is primarily a function of the outer energy level involved. Abrupt changes of slope of the curves apparently correspond with certain critical potentials. A. A. Eldridge.

Ionisation by collision and a "photo-electric theory" of the sparking potentials. J. Taylor (Phil. Mag., 1927, [vii], **4**, 505—511).—A reply to criticisms by Huxley (this vol., 709) of the author's theory of sparking potentials (Proc. Roy. Soc., 1927, A, **114**, 73; Phil. Mag., 1927, [vii], **3**, 753). A. E. Mitchell.

Photoelectric emissivity and sparking potentials. J. Taylor (Nature, 1927, **120**, 477—478).—Evidence in favour of the author's photoelectric theory of sparking potentials (preceding abstract) is adduced. A. A. Eldridge.

Diffusion of slow electrons (2—30 volts) in hydrogen and argon. E. Zachmann (Ann. Physik, 1927, [iv], **84**, 20—60).—Electrons of velocities between 30 and 11 volts in argon undergo an increase in diffusion with decreasing velocity. Between 11 and 7 volts velocity the diffusion decreases rapidly and at 6·5 volts it is not noticeable. Between 6·5 and 2 volts velocity, no diffusion is detectable. In hydrogen the diffusion increases with decrease of electron velocity between 30 and 2 volts. W. E. Downey.

Heats of condensation of electrons and positive ions on molybdenum in gas discharges. C. C. Van Voorhis (Physical Rev., 1927, [ii], **30**, 318—338).—A new calorimetric method for measuring the electronic work function of a metal in a gas discharge is described. Values of the heat of electron condensation for molybdenum in argon, hydrogen, and nitrogen are: 4·76; 4·04, 4·35; 4·77, 5·01 volts, respectively, according to the treatment of the surface. The heating effect on molybdenum due to the surface neutralisation of an argon positive ion is about 1 volt. The presence in a low-pressure gas discharge of Langmuir's high-speed "secondary" electrons is indicated. A. A. Eldridge.

Collisions of the second kind in activated ozone. H. D. Smyth (Physical Rev., 1926, [ii], **27**, 108—109).—With ozone some experimental evidence was obtained in support of the view that if an electron collides with an activated molecule, the energy of activation of the molecule may be converted into kinetic energy of the electron by a collision of the second kind. A. A. Eldridge.

Ionic mobility in gaseous mixtures. H. Mayer (Physikal. Z., 1927, **28**, 637—644).—The presence of a trace of impurity in a gas frequently brings about a sudden large change in the mobility of one ion. The values at 760 mm. for k_+ and k_-, the mobilities in pure, dry hydrogen, have been determined as 6·00 and 10·07 cm./sec. per volt/cm., respectively. The addition of chlorine in amounts 0·3, 0·9, 1·5, and 3·0% resulted in the values for k_+ of 5·55, 5·35, 4·95, 4·25, respectively, whereas the corresponding values for k_- were 5·15, 4·60, 4·40, 4·12. A large decrease is thus shown in k_- with the addition of quite small amounts of chlorine, but larger amounts do not maintain the rapid alteration. With small quantities of chlorine in oxygen the mobility of the negative ion decreases fairly rapidly until the chlorine concentration reaches 2% and after this point it falls much more slowly. Water vapour decreases the mobilities in oxygen. For 0, 1·6, 2·4, and 3·0% of water vapour the values of k_+ were 1·38, 1·38, 1·35, and 1·25, respectively, and of k_- 2·11, 2·00, 1·85, and 1·63. Hydrogen–oxygen mixtures have been investigated. For 2·2% of oxygen k_+ is 5·6, k_- 9·3; for 99·3% of oxygen k_+ is 1·44, k_- 2·15. The results are discussed in terms of the cluster theory. R. A. Morton.

Ionisation in flames of various organic substances. J. A. J. Bennett (Trans. Faraday Soc., 1927, **23**, 307—311).—To study the relation between ionisation and detonation the ionisation in flames of hexane, coal-gas, "B.P. petrol," benzene, pentane, acetone, etc., and the effect of adding carbonyls, amyl nitrite, aromatic bases, halogens and halogen compounds, and other substances which alter the highest useful compression ratio of a fuel, have been determined. Although in many cases knock-inducers increase and anti-knocks decrease the ionisation of flames, this is not general. Thus, although ionisation accompanies detonation, there is no simple relation between them, and ionisation does not appear to be either a cause or an effect of detonation, but mainly a temperature effect. This is not in agreement with either Wendt and Grimms' theory (B., 1924, 856) or that of Charch, Mack, and Boord (B., 1926, 570). M. S. Burr.

Ionisation processes in hydrogen, nitrogen, and argon. K. E. Dorsch and H. Kallmann (Z. Physik, 1927, **44**, 565—574).—Previous experiments (this vol., 604) have shown that the ratio of the concentration of H^+ ions to H_2^+ ions formed in hydrogen is approximately constant when produced by electrons of energies corresponding with 16—50 volts. The variation of this ratio produced by the addition of argon, and by increasing the ionisation space, has now been examined over a 1 : 10 pressure range. At any given pressure the ratio is unaffected by these factors, but the ratio $H_3^+ : H_2^+$ is increased by increasing the ionisation space at all the pressures examined. These results show that the primary ionisation process is the formation of H_2^+ ions (no other primary process takes place which is more than

0·5% of this process), that H_3^+ ions are formed in considerable amount according to the reaction $H_2^+ + H_2 = H_3^+ + H$, and that the reaction $H_2^+ = H^+ + H$ takes place only in the neighbourhood of the electrodes.

From measurements of the ionisation in argon–hydrogen, argon–nitrogen, and hydrogen–nitrogen mixtures as function of the electron energies (14—19 volts) relative values of the ionisation potentials have been obtained. By assuming Meissner's recent value for argon, 15·6 volts, computed from optical evidence (this vol., 177), the values 16—16·5 and approximately 16·5 volts are assigned to nitrogen and hydrogen, respectively. R. W. Lunt.

Effect of the medium on gas ion mobility. H. A. Erikson (Physical Rev., 1927, [ii], 30, 339—348).—Addition of carbon dioxide or water vapour to the air through which air ions move diminishes the mobility, that of hydrogen increases the mobility, that of ethylene or chlorine has no effect, whilst that of ammonia results in the formation of a single positive ion of the same mobility as that of the negative ion, which is not affected. Acetylene gives rise to an ion which has a mobility only slightly less than that of the initial air ion. When acetylene remains in air a substance is formed which, when it becomes charged, has a lower mobility. A. A. Eldridge.

Impact of slow cations on lithium chloride in a high vacuum. E. Badareu (Physikal. Z., 1927, 28, 634—637).—When canal rays impinge on a metal collector the galvanometer readings increase rapidly at first and then more slowly as the voltage increases between 0 and 900. If, however, a surface of lithium chloride is used, the galvanometer deflexion becomes constant at about 500 volts if the experiments are conducted in a high vacuum. On the other hand, experiments at pressures of about 0·1—0·5 mm., instead of showing deflexions of the same order of magnitude for the metal and salt surfaces, disclose wide differences; *e.g.*, a copper collector gave at 462 volts a deflexion twenty times as great as that with a collector covered with lithium chloride. The differences between the experiments at relatively low pressure and with high vacuum are ascribed to the fact that the emission of positively-charged particles from the salt increases with increasing current density in the exciting current (cf. Völker, A., 1919, ii, 43). R. A. Morton.

Ionisation probability in collisions between electrons and atoms. F. M. Penning (Physica, 1926, 6, 290—297).—A lecture. Chemical Abstracts.

Divergence of magnetic electrons. W. Bothe (Z. Physik, 1927, 44, 543—546).—A mathematical analysis of the effect of the magnetic moment of electrons on the divergence of a cathode beam. R. W. Lunt.

Charged state of atoms before light emission. E. Rupp (Ann. Physik, 1927, [iv], 84, 154—160).—It is shown that the majority of hydrogen atoms emitting light in canal rays are positively charged before the emission. W. E. Downey.

Luminescence of canal rays. H. Rausch von Traubenberg and R. Gebauer (Z. Physik, 1927, 44, 762—767).—An improved technique is described for examining the fine structure of the hydrogen spectrum emitted by canal rays. The changes produced as the beam moves from the region of an electric field to a region where no field exists are recorded and discussed. R. W. Lunt.

Polarisation of the light from canal rays. II. E. Rupp (Ann. Physik, 1927, [iv], 84, 94—110; cf. *ibid.*, 1926, [iv], 81, 615).

Structure of the radioactive atom and origin of the α-rays. (Sir) E. Rutherford (Phil. Mag., 1927, [vii], 4, 580—605).—For the first time a theory of the structure of the nucleus of a radioactive atom is put forward and discussed in terms of the experimental data. In the radioactive atom one of the neutral α-satellites is regarded as circulating in a quantised orbit round the central nucleus. When for some reason this becomes unstable the satellite escapes from the nucleus, losing its two electrons, and the electric field falls to a critical value. It escapes as a doubly-charged helium nucleus with a velocity which is a function of the quantum orbit and the nuclear charge. The two electrons liberated from the satellite fall towards the nucleus and probably circulate close to the central nucleus and inside the region occupied by the neutral satellites with a speed of the order of that of light. On the occasion of one of these being hurled from the system a disintegration electron results. The disturbance of the neutral satellite system by the liberation of an α-particle or a swift electron may lead to a rearrangement involving the transition of one or more satellites to a different quantum orbit and the emission in the process of γ-rays of frequency determined by quantum relations. It is pointed out that before further progress in the solution of the problem of the origin of the γ-rays can be obtained a knowledge of the precise frequencies of the main γ-rays and their intensities is essential. A. E. Mitchell.

Possible mechanism of atomic disintegration. G. Piccardi (Nature, 1927, 120, 442—443).—The "excess weight" (Harkins' "isotope weight"), $P-2N$, where P is the atomic weight and N the atomic number, is regarded as constituted of $P-2N$ dipoles, externally to the atomic nucleus, formed by one positive and one negative electron sufficiently close together to form an electrically neutral complex. For the inactive gases, and for zinc, cadmium, and mercury, the maximum excess weight (that of the higher isotope of each element) is doubled each time a given atomic structure is repeated, values being: neon 2, argon 4, krypton 14, xenon 28, radon 50, zinc 10, cadmium 20, mercury 44. These elements are also in maximal positions on the curve of ionisation potentials; hence the excess weight is definitely related to the atomic structure. A. A. Eldridge.

Actinium series and the order of stability of radioactive isotopes. A. S. Russell (Nature, 1927, 120, 402—403).—Protoactinium is identified as the most stable isotope of element 91 and actinium as the second stablest isotope of element 89, from relations between atomic mass and stability deducible from Aston's results on non-radioactive elements. It follows that actinium may not have the mass 227 which has been ascribed to it by all of those who consider that the masses of members of the actinium series are of odd number; it follows also that the mass of protoactinium is 233 and therefore that of actinium 229. On the basis of these results the masses of all the actinium products are known unless it can be shown either that one or more α-particles have been overlooked or that a massive particle other than an α-particle is expelled by some member of the series. Two rules, also, are deducible. (1) For a radio-element of even atomic number the masses of its α-ray and of its β-ray isotopes are in decreasing order of stability when arranged in the orders x, $x-2$, $x-1$, $x-4$, $x-3$, etc., and x, $x+2$, $x+1$, $x+4$, $x+3$, etc., respectively, x being an even number and the atomic mass of the stablest isotope. (2) For an element of odd atomic number the masses are in decreasing order of stability when arranged in the same order as the β-ray isotopes of an element of even number. Applied to the isotopes of non-radioactive elements these rules are partly successful only they are inapplicable to the isotopes of tin, magnesium, and silicon, but apply better to those of xenon, cadmium, mercury, sulphur, selenium, krypton, neodymium, and lead. On the theory put forward the end-product of the actinium series has a mass of 209. A. S. RUSSELL.

Radioactive haloes. Possible identification of "hibernium." A. S. RUSSELL (Nature, 1927, **120**, 545—546).—Observations of Joly (Proc. Roy. Soc., 1922, **A**, **102**, 682) and of Iimori and Yoshimura (A., 1926, 990) on the rings of radioactive haloes are considered in the light of Marckwald and Russell's work (A., 1911, ii, 360) on the alteration of radioactive minerals by agencies like percolating water and of Russell's view (preceding abstract) of the atomic masses of the products of the actinium disintegration series. Iimori and Yoshimura ascribed their *Z*-haloes, Joly's *X*-haloes, and possibly Joly's so-called radon haloes to the products of the actinium series. They regard the actinium series as independent of the uranium–radium series; two inner rings sometimes found in *Z*-haloes are ascribed by them to two uranium isotopes at the head of the actinium series. The author criticises this. If uranium minerals have been altered by chemical agencies in the past, different radioactive products may have been isolated from the rest depending on their solubility, etc. From these products three different kinds of haloes should result: the uranium halo resulting from uranium or ionium or radium, the actinium halo resulting from protoactinium, and a lead halo resulting from the end-product of the actinium series if it should be feebly radioactive. Similarly from thorium minerals two haloes may be obtained: the thorium halo and a lead halo due to a possible feebly radioactive end-product. It is concluded that the radius of the ring made by the α-particles from the thorium end-product (mass 208) should be smaller than that from the actinium end-product (mass 209). The hibernium ring is ascribed to the first of these; an unnamed ring discovered by Joly to the second. Some *Z*-haloes are ascribed to protoactinium isolated from uranium minerals; other *Z*-haloes and *X*-haloes to protoactinium and lead separated either from uranium or uranium–thorium minerals. There is no need to regard hibernium, as did Rosseland (Nature, 1922, **109**, 711), as a radioactive element of atomic number approximately 40. If the views put forward are correct the radioactive series are partly extended to mercury; hibernium is identified as thorium-Ω.

A. S. RUSSELL.

Mode of disintegration of radium-*D*, -*E*, and -*F*. S. KIKUCHI (Japan. J. Phys., 1927, **44**, 143—158).—The tracks of rays from an equilibrium mixture of radium-*D*, -*E*, and -*F* have been examined by the Wilson cloud method. Each atom of radium-*E* emits one β-particle only on disintegrating, and the heterogeneous nature of the β-particles so produced cannot be traced to encounters with planetary electrons. The β-particles from radium-*D* are of secondary origin; this substance emits, in addition to radiation of 0·264 Å., radiation of mean wave-length 0·4 Å. which is possibly homogeneous; the *L*-radiation of this element was also detected. R. W. LUNT.

Ionisation produced by radon in spherical vessels. G. GLOCKLER (J. Physical Chem., 1927, **31**, 1322—1331).—Theoretical. A comparison is made of the ionisation produced by radon and its decomposition products as calculated by the average path law (cf. Lind, A., 1912, ii, 1027) and by the method of Mund (A., 1925, ii, 732). For spherical vessels of a diameter up to 10 cm., the two methods give similar results, which are also in agreement with the experimental value obtained by Lind (A., 1919, ii, 210). A new derivation of Mund's original equation is given, but the assumption that the whole of the radium-*A* and the radium-*C* decomposes on the wall of the vessel is modified. Using the experimental value of Lind and Bardwell (A., 1924, ii, 11) for the average path (0·61 × radius of the reaction vessel), it is calculated that 30% of the radium-*A* and 7% of the radium-*C* decompose in the gaseous phase. Mund's efficiency factor is recalculated on this basis and the new values are tabulated.

L. S. THEOBALD.

Scattering of α-particles by helium. (SIR) E. RUTHERFORD and J. CHADWICK (Phil. Mag., 1927, [vii], **4**, 605—620).—Investigations of the collisions of α-particles with helium have shown that in general the collision relations for these particles are similar to those representing the collisions between α-particles and hydrogen nuclei. For large collision distances the forces between the particles are given by Coulomb's law, but with closer approaches (less than $3{\cdot}5\times10^{-13}$ cm. for central collisions and less than 14×10^{-13} cm. for glancing collisions) powerful additional forces are involved. It is suggested that these additional forces originate in the magnetic fields of the nuclei.

A. E. MITCHELL.

Probability law and the α-particle emission of polonium. W. KUTZNER (Z. Physik, 1927, **44**, 655—683; cf. A., 1924, ii, 226).—The α-particle emission of polonium has been re-examined, and it is found that Bateman's expression for the time probability of emission gives values of the emission probability the agreement of which with experiment diminishes as the thickness of the polonium preparation is increased. The discrepancies cannot be accounted for by recoil atoms, and are thought to be due to impurities in the polonium preparation which impede the emission of the true total emission of polonium. R. W. Lunt.

Scattering and absorption of the γ-rays of radium. H. M. Cave and J. A. Gray (Physical Rev., 1926, [ii] 27, 103).—γ-Rays filtered through 2 cm. of lead have an effective wave-length in the neighbourhood of 0·012 Å. A. A. Eldridge.

Internal conversion of γ-rays. (Miss) B. Swirles (Proc. Roy. Soc., 1927, A, **116**, 491—500).—Theoretical. The results of Ellis and Wooster (this vol., 393) are discussed on the lines of quantum mechanics. An expression is obtained for the coefficient of absorption in the *K*-levels.
W. E. Downey.

Variation of radioactivity of hot springs. K. Shiratori (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 613—620).—A comparison is made between the radioactivity of a number of hot springs in Japan before and after a period of eleven or twelve years during which earthquakes have taken place. Changes in temperature are also recorded. M. S. Burr.

Transmutation of elements. A. Smits (Nature, 1927, **120**, 475—476).—Renewed experiments indicate that the mercury found in the earlier experiments, in which a discharge was maintained between lead electrodes under carbon disulphide, originated partly, if not entirely, from the carbon disulphide. Thus there is still no conclusive evidence of the reproducible conversion of lead into mercury. A. A. Eldridge.

Failure of the mercury-to-gold transmutation experiment. H. H. Sheldon and R. S. Estey (Physical Rev., 1926, [ii], 27, 515).—A repetition of Miethe's experiments failed to produce any transmuted gold. A. A. Eldridge.

Radiation arising from the formation of helium from hydrogen. G. E. M. Jauncey and A. L. Hughes (Physical Rev., 1926, [ii], 27, 509).—Four processes are considered: (1) The protons and electrons initially at rest produce a helium nucleus recoiling in the opposite direction of the quantum. (2) The protons and electrons all initially having velocity βc produce a helium nucleus at rest. (3) One proton with velocity βc meeting 3 protons and 2 electrons at rest produces a helium nucleus at rest. (4) One electron with velocity βc meeting 4 protons and one electron at rest produces a helium nucleus at rest. In (1), (2), and (3), $\lambda=0{\cdot}0004$ Å.; in (4), $\lambda=0{\cdot}0008$ Å. In (1) and (2), $\beta=0{\cdot}008$; in (3), $\beta=0{\cdot}03$; in (4), $\beta=0{\cdot}9995$. The reverse of (4) is the photo-electric effect. By analogy with *X*-rays, 0·004 Å. and 0·0008 Å. may be considered as critical absorption wave-lengths. A. A. Eldridge.

Radiation from the mutual annihilation of protons and electrons. A. L. Hughes and G. E. M. Jauncey (Physical Rev., 1926, [ii], 27, 509—510).—The collision of two electrons and one proton results in a recoil electron moving with a minimum velocity $0{\cdot}9999995c$ and a quantum of wave-length $2{\cdot}6\times10^{-5}$ Å., or less. The collision of two protons and one electron results in a recoil proton moving with a minimum velocity $0{\cdot}6c$ and a quantum of wave-length $1{\cdot}9\times10^{-5}$ Å. or less.
A. A. Eldridge.

Application of Schrödinger's wave functions to the calculation of transition probabilities for the principal series of sodium. Y. Sugiura (Phil. Mag., 1927, [vii], 4, 495—504).—In accordance with the result of Kramers (Z. Physik, 1926, 39, 828) that a rational first approximation to the quantum-mechanical calculation may be obtained by using an orbital model fixed by the usual quantum conditions, if in these half-number values are introduced for the radial and azimuthal quantum numbers, the proper functions according to Schrödinger (Ann. Physik, 1926, [iv], 79, 361) have been found for the 3_1, 3_2, and 4_2 states of the sodium atom. These functions have then been used for the calculation of the transition probabilities and the number of dispersion electrons for the principal series of sodium. The result so obtained for each *D*-line of sodium is in close agreement with that deduced from the experimental results of Minkowski (A., 1926, 650).
A. E. Mitchell.

Intensities in the secondary spectrum of hydrogen at various temperatures. J. C. McLennan, H. Grayson-Smith, and W. T. Collins (Proc. Roy. Soc., 1927, **A**, **116**, 277—312).—The intensities of the lines of the secondary spectrum of hydrogen have been studied. A specially constructed discharge tube was arranged in a liquid-air flask with the capillary vertical. Special precautions were taken to obtain pure hydrogen. Photographs were taken at the ordinary temperature and at the temperature of liquid air, nothing else being varied. The intensities were obtained by a Moll self-registering microphotometer and most of the lines measured by Merton and Barratt were examined. Richardson's series system is thereby included and the variation of intensity with temperature is in good agreement with theory. The alternation of intensity between the odd and the even members of the series was observed. Other regularities have been examined and are discussed. W. E. Downey.

Intensity distribution among the lines of certain bands in the spectrum of the hydrogen molecule. O. W. Richardson (Proc. Roy. Soc., 1927, A, **116**, 484—491).—Theoretical. The results of McLennan, Grayson-Smith, and Collins (preceding abstract) are discussed. W. E. Downey.

Bands in the secondary spectrum of hydrogen. II. H. S. Allen and I. Sandeman (Proc. Roy. Soc., 1927, **A**, **116**, 312—327; cf. this vol., 394).—Theoretical. Further work on the system attributed to triatomic hydrogen is described. Further bands have been added and it is concluded that these are only the strongest in an extensive system. The spacing in groups with a difference of 92 wave-numbers is not attributed to the vibration quantum number but possibly is dependent on a new quantum number. W. E. Downey.

Interpretation of the continuous spectrum of hydrogen. Y. Takahashi (Japan. J. Phys., 1927, 4, 103—108).—It is claimed that the difficulties which face the explanation of this spectrum by Bohr's theory are obviated by assuming that it arises from the recombination of two hydrogen atoms of which one at least is excited. R. W. Lunt.

Hydrogen band spectrum in the extreme ultra-violet. T. Hori (Z. Physik, 1927, 44, 834—854).—The band spectrum of hydrogen excited by the glow discharge has been examined with a vacuum spectrograph of dispersion 8·28 Å. per mm. in the range 1027—1249 Å. A large number of lines have been recorded, and arranged according to the term scheme of Dieke and Hopfield. The moment of inertia of the hydrogen molecule in the normal state is found to be $4\cdot67\times10^{-41}$ g. cm.^{2}, and the nuclear spacing $0\cdot75\times10^{-8}$ cm.; for the excited state the corresponding values are $9\cdot2\times10^{-41}$ g. cm.^{2} and $1\cdot06\times10^{-8}$ cm. R. W. Lunt.

Structure of the hydrogen molecule. H. C. Urey (Physical Rev., 1926, [ii], 27, 800).—Dieke's and Takahashi's arrangements of the Fulcher bands of hydrogen are reconsidered. It is assumed that the molecule is symmetrical about the median plane, and that it has no angular momentum in the electron system. It appears necessary to assign the steady states involved to the vibration electron orbits of the median plane. This would give no first-order Zeeman effect as required, and a diamagnetic model for the normal state. A. A. Eldridge.

Structure of the hydrogen molecule ion. H. C. Urey (Physical Rev., 1926, [ii], 27, 800—801).—The energy levels of the vibrational model of the hydrogen molecule ion have been calculated, including the energy contributed by the vibration and rotation of the nuclei. The emitted bands should consist of single band systems, each band having a zero branch only. A. A. Eldridge.

Combinations in the ultra-violet spectrum of the hydrogen molecule. G. H. Dieke and J. J. Hopfield (Physical Rev., 1926, [ii], 28, 849).—Between 1050 and 1650 Å. there are two systems of bands degraded towards the red, and all are of similar structure; they have the same final states, which are the states of lowest energy of the hydrogen molecule. The first system includes a progression which, in a mixture of argon and hydrogen, appears without the rest of the spectrum. In the initial electronic state of this system the nuclei are more tightly bound than in the initial state of the other system, although their distance apart is larger. A. A. Eldridge.

Zero-zero band of the second positive band spectrum of nitrogen. G. Nakamura (Japan. J. Phys., 1927, 4, 109—117).—The band has been analysed by examining the spectrum of a low-tension arc in nitrogen between tungsten electrodes. It is found that the formulæ of Zeit and Lewis (Z. wiss. Phot., 1922, 21, 1) are not applicable to the high members of the band lines. R. W. Lunt.

Structure of the atmospheric absorption bands of oxygen. G. H. Dieke and H. D. Babcock (Proc. Nat. Acad. Sci., 1927, 13, 670—677).—The lines in the A-band (7624·493—7594·970) and the A'-band (7622·998—7603·212), the B-band (6886·743—6869·626), and the α-band (6289·397—6277·533) have been remeasured and Rowland's values for the α'-band have been corrected by subtracting 0·216 Å., so that the wave-lengths given are all expressed on the neon scale. The empirical structure of the bands is worked out in the form

$$\left.\begin{aligned}P_i(j)&=F_i'(j)-F_i''(j+1)\\R_i(j)&=F_i'(j)-F_i''(j-1)\end{aligned}\right\},$$

which makes the bands analogous to other well-known bands. The significance of the empirical structure is not fully elucidated, but the relation $B=h/8\pi^2cJ$ leads to values for the moment of inertia J for the O_2 molecule in the normal and in the excited state of 19·27 and $19\cdot93\times10^{-40}$, respectively, corresponding with 1·205 and $1\cdot225\times10^{-8}$ cm. as distances between the nuclei in the two states.

R. A. Morton.

Half-integral vibrational quantum numbers and rotational energy data for the MgH bands. W. W. Watson (Physical Rev., 1926, [ii], 27, 801).—The magnitude of the isotope effect in the 5211 Å. band accords with the assumption that $n'=\frac{1}{2}$ and $n''=\frac{1}{2}$; the zero points of this band system are represented by the equation $\nu=19217+(1603\cdot5n'-34\cdot75n'^2)-(1493\cdot5n''-31\cdot25n''^2)$, where n' and n'' assume half-integral values from $\frac{1}{2}$ to $3\frac{1}{2}$. For the final state in the 5211 Å. band, the rotational energy $F=\mathrm{B}m^2+\mathrm{D}m^4+\mathrm{F}m^6$, where $m=j+\frac{1}{2}-\varepsilon$ ($\varepsilon=0\cdot47$). The presence of a Kramers and Pauli effect is indicated. The value of ε for the initial state is approx. 0·43.

A. A. Eldridge.

Fine structure of the 4842 Å. band of AlO. W. C. Pomeroy (Physical Rev., 1926, [ii], 27, 640).—The doublet separation of band lines is represented as a function of k (a half integer representing the resultant molecular momentum) of the initial state for both P and R branches by the equation $\Delta\nu=0\cdot0116k+12\times10^{-6}k^2-7\times10^{-11}k^4$. Attributing the doublets to a double energy level in the initial state, $(F')^{+-}=(0\cdot6019\pm6\times10^{-6})m^2-(1\cdot1630\times10^{-6}\pm3\cdot5\times10^{-11})m^4+0\cdot54\times10^{-12}m^6$, where $m=k-0\cdot0074\pm0\cdot00482$; $(F'')=0\cdot6386m^2-1\cdot1094\times10^{-6}m^4-0\cdot43\times10^{-12}m^6-5\cdot2\times10^{-18}m^8$. A. A. Eldridge.

Colouring of glass [containing manganese] in ultra-violet light. C. L. Cross (Physical Rev., 1926, [ii], 27, 108).—The effective light has a wave-length only slightly greater than 2900 Å., the absorption limit of the glass. The tinting takes place only near the surface, and is hastened by heating. Decolorisation is accelerated by heat or visible light.

A. A. Eldridge.

Band spectrum of silicon fluoride. R. C. Johnson and H. G. Jenkins (Proc. Roy. Soc., 1927, A, 116, 327—351).—The discharge through silicon fluoride has been examined. Purified and dry silicon fluoride was streamed through a discharge tube at 1 mm. pressure. The discharge is of a strong blue colour, due to a system of intense bands in the blue region. Several groups of bands have been measured, some being favoured by high current density, others by low. Special precautions were taken to eliminate impurities and it is concluded that the bands are due to SiF_4. The structures of the α-, β-, and γ-systems of bands have been determined. The heat of dissociation as calculated from the vibrational states is found to be 116,000 g.-cal. W. E. Downey.

Structure of Fraunhofer's lines and the dynamics of the sun's chromosphere. A. Unsöld (Z. Physik, 1927, **44**, 793—809).—From an analysis based on the theory of dispersion and on Schwarzschild's theory of radiation equilibria, and by making the assumption that the partial pressure of calcium in the chromosphere is 5×10^{-8} atm., which is in satisfactory agreement in order of magnitude with St. John's data (Astrophys. J., 1910, **32**, 36), the structure of the *H*- and *K*-lines of the singly-ionised calcium atom in the chromosphere has been deduced. R. W. Lunt.

Photochemical absorption of iron salts. J. Plotnikov and M. Karschulin (Z. Elektrochem., 1927, **33**, 212—217).—The absorption bands of potassium ferricyanide and of green and brown ferric ammonium citrate extend into the infra-red, but the region of photochemical sensitiveness does not extend into the infra-red. The use of gelatin coated on glass instead of sized paper as the medium for the light-sensitive substances results in a shift of the sensitivity maximum towards the longer wave-lengths and an alteration in the general sensitivity. The results indicate the invalidity of the Einstein photochemical equivalent law. A simple method of demonstrating the photochemical absorption is given. The photochemically active region of "Ozalid" paper extends from 4750 to 2470 Å., with a maximum at 4000 Å. W. Clark.

Absorption spectra of aragonite and strontianite in the near infra-red. F. I. G. Rawlins and E. K. Rideal (Proc. Roy. Soc., 1927, *A*, **116**, 140—152; cf. this vol., 5).—The absorption spectra of aragonite and strontianite have been examined in the near infra-red by means of two types of apparatus: (*a*) an infra-red spectrometer, thermopile, and moving-magnet galvanometer of the Hill–Downing pattern, and (*b*) an infra-red spectrometer (Littrow principle) and a modified Boys radiomicrometer. From the results it has been found possible to compare the two allotropic modifications of calcium carbonate, and the bi-axial crystals of the alkaline-earth carbonates. In the former case, definite displacements of the three fundamental frequencies of the carbonate ion occur in the two crystal forms. From the overtones of the fundamental at 7 μ it is shown that the frequencies do not follow the order ν_1, $2\nu_1$, $3\nu_1$, but that a correction must be used analogous to the Kratzer correction for an harmonic coupling in gases (Z. Physik, 1920, **3**, 289). This correction is greatest for the less symmetrical form of calcium carbonate. In the bi-axial group, it appears that whereas at ν_1 the absorption wave-lengths increase with the molecular volume, the reverse holds for the bands at ν_2 and ν_3, and the same is true for calcite and aragonite. The values of $\lambda_{\text{ref.}}$—$\lambda_{\text{abs.}}$ have been determined for the various bands with the help of Schaefer's data for $\lambda_{\text{ref.}}$ (cf. this vol., 5). These are generally positive, in confirmation of Schaefer's results, but are smaller than the values obtained by him. L. L. Bircumshaw.

Theory of colour on the basis of molecular strain. II. S. Dutt (J. Indian Chem. Soc., 1927, **4**, 99—109; cf. A., 1926, 830).—The results of a study of the absorption spectra of a number of coloured substances are found to be in agreement with their unsaturation as measured by the ease of hydrogenation in the presence of hydrogen and colloidal palladium. In benzene derivatives, a chromophore is regarded as a seat of strain which may be partly absorbed by dynamic equalisation in the ring, unless the structure is made static by the introduction of an auxochrome. The latter point is illustrated by the comparison of the absorption spectrum of alizarin (dynamic structure) with that of the potassium salt (static, quinonoid structure). The loading effect of substituents in dyes on their absorption spectra is shown to be the greater, the nearer the substituent is to the point of strain. G. A. C. Gough.

Theory of colour on the basis of molecular strain. III. Decomposition of dyes under the influence of solar radiation. K. K. Barat and S. Dutt (J. Indian Chem. Soc., 1927, **4**, 265—270; cf. A., 1926, 830, and preceding abstract).—The absorption spectra of aqueous solutions of a number of typical dyes have been determined during various stages of bleaching by solar radiation. The measurements indicate that the dyes are decomposed to colourless substances without the intermediate formation of less coloured substances. In accordance with the authors' theory, the dyes which absorb the longer wave-lengths decompose most rapidly. G. A. C. Gough.

Vibration frequencies of organic compounds. W. Herz (Z. anorg. Chem., 1927, **166**, 110—112).—The vibration frequencies of the molecules of numerous organic compounds have been calculated by the method previously applied to inorganic compounds (this vol., 817). The frequency decreases on ascending a homologous series and when hydrogen is replaced by the halogens, and for analogous compounds with the same number of carbon atoms is greatest for the one containing a triple linking and smallest for that with single linkings only. R. Cuthill.

Series due to halogens in infra-red absorption spectra of organic compounds. J. W. Ellis (Physical Rev., 1926, [ii], **27**, 639).—The absorption spectra of methylene dichloride and chloroform contain, in addition to the C–H series, bands which fit a linear series starting at 16·8 μ, and bands accounted for by combinations. Similar bands are observed with methylene dibromide and bromoform (17·2 μ) and with methyl iodide and methylene di-iodide (17·5 μ), as well as with more complex molecules containing halogen and hydrogen atoms, but not with carbon tetrachloride or tetrachloroethylene. A. A. Eldridge.

Spectrochemical studies of hydroxyazo-compounds. IV. T. Uemura and S. Tabei (Bull. Chem. Soc. Japan, 1927, **2**, 229—236; cf. this vol., 396).—The absorption spectra of neutral and alkaline solutions of the dyes obtained by coupling diazotised toluidines with each of the three cresols have been examined. The colour changes observed on addition of alkali are due to the change of the substance from the *A*- to the *R*-form. There is but one absorption band when the hydroxyl group in the cresol ring occupies the *p*-position with respect to the azo-group, and two when it occupies the *o*-position. Comparison of the present absorption curves with those of the corresponding hydroxyazobenzenes and benzeneazocresols shows that the methyl group has a hyperchromic influence only when introduced into a non-methylated compound. The effect of a methyl group is apparently independent of its position.

J. S. Carter.

Absorption of ultra-violet rays by the ten isomerides of dichloronaphthalene. H. De Laszlo (Compt. rend., 1927, 185, 599—601).—The absorption curves and m. p. of the ten dichloronaphthalenes fall into three groups according as the chlorine atoms are in the αα-, ββ-, or αβ-positions. As with the *p*-substituted benzene derivatives, the m. p. are highest when the substituents are symmetrically placed, and as far apart as possible. With the exception of that of the 1 : 2-compound, the spectra all show a large electronic interval in the region of about 1420 cm.$^{-1}$, and this is most clearly marked with the ββ- and αβ-derivatives. The absorption bands of the vapours indicate two different states of electronic activation. J. Grant.

Infra-red absorption of fluids. E. N. Gapon (Z. Physik, 1927, 44, 600—602).—If ν_c denotes a characteristic infra-red frequency of a liquid defined so that $u=2\pi r\nu_c$, where u is the velocity of a molecule of mass m in orbital rotation at a radius r about its centre of gravity, then $mr^2\nu_c^2=\text{constant}\times T$, where T is the temperature of the liquid. Since Stefan's law gives $PV_T=\text{constant}\times T$, where P is the internal pressure and V_T the molecular volume of the fluid, the above expression can be written $mr^2\nu_c^2=\text{constant}\times V_T/\beta_T$, where β is the coefficient of compressibility. By substituting $m=M/N$ and $r=\text{constant}\times\sqrt[3]{V_T}$, where N is Avogadro's number, the following expression for ν_c is obtained : $\nu_c=k(V_T^{1/3}/M\beta)^{1/2}$, where the constant $k=0{\cdot}34\times10^{12}$. The values of ν_c have been thus calculated for the following substances : benzene, toluene, *o*-, *m*-, and *p*-xylene, hexane, mesitylene, chloroform, and chlorobenzene. The values so obtained agree fairly well with those calculated from known spectroscopic data by Marton's equation (A., 1925, ii, 1025) for the frequency ν_i of the absorption bands : $\nu_i=\nu_c\sqrt{n}$, where n is an integer and ν_c an infra-red frequency which is identified with that defined by the author.

R. W. Lunt.

Time interval between excitation and emission for fluorescein. L. G. Hoxton and J. W. Beams (Physical Rev., 1926, [ii], 27, 245).—The time elapsing between the beginning of incidence and the beginning of fluorescence emission was $3{\cdot}2\pm0{\cdot}3\times10^{-8}$ sec. for an aqueous solution, and $3{\cdot}7\pm0{\cdot}4\times10^{-8}$ sec. for an alcoholic solution, of fluorescein containing $2{\cdot}5\times10^{-5}$ g. per c.c. A. A. Eldridge.

Absorption and fluorescence of silver bromide and of silver chloride vapour. J. Franck and H. Kuhn (Z. Physik, 44, 607—614).—From an analysis of the absorption and fluorescence spectra of the vapours of silver bromide and chloride it is shown that the size of the nuclear vibrational quanta decreases with increasing quantum number, and that therefore in the vapour state the molecules of these substances are compounds of atoms, as has been established previously for silver iodide. R. W. Lunt.

Fluorescence yield of solutions [of sodium fluorescein]. S. Szczeniovski (Bull. Int. Acad. Polonaise, 1927, *A*, 127—174).—The absorption spectra of solutions of sodium fluorescein in glycerol and in water have been determined over the range 4000—6000 Å. by a photo-electric method. The curves exhibit maxima at 4850—4900 Å. and absorption coefficients near 600, whilst an inflexion near 4600 Å. shows itself most clearly in the glycerol solutions; it is considered that the observed curve is due to the summation of at least two simple bands. Over the concentration range 1×10^{-4}—8×10^{-4} g./litre Beer's law is not obeyed since the absorption increases more slowly with increasing concentration than the law requires, whilst the wave-length of maximum absorption is shorter for the more concentrated solutions. In glycerol solutions the maximum is some 100 Å. nearer the red than is the corresponding aqueous solution.

In order to study the fluorescence it was necessary to prove that Wien's law for the spectral distribution of intensity applies to the visible spectrum from a carbon-filament lamp; the spectral sensitivity curve of the potassium photo-electric cell had also to be determined. It was then possible to measure the fluorescence yield for monochromatic radiations between 4400 and 5100 Å. The yield was independent of concentration over the range of aqueous solutions, but it showed an increase with longer exciting wave-lengths, which was most marked with the glycerol solutions. The fluorescence spectrum exhibits a maximum at approx. 5140 for the aqueous, and 5220 Å. for the glycerol solutions. The fluorescence yield at 5100 Å. for the 4×10^{-4} g./cm.^{3} solution is 0·71, but for the glycerol solution it is nearly 1·00.

R. A. Morton.

Photometric and spectrophotometric studies. VI. Light-intensity measurements in the silent electric discharge. K. Schaum and R. Trautluft (Z. wiss. Phot., 1927, 24, 416—423).—Since chemical change in the silent electric discharge occurs at the brush discharge, a correlation between the intensity of electroluminescence, the electrical conditions, and the chemical reactions seems desirable. Experiments have been carried out on the minimum voltage in a Siemens tube containing oxygen, carbon monoxide, carbon dioxide, ammonia, (*a*) for the discharge merely to pass and (*b*) for it to run continuously. Measurements of the brightness of the luminescence show that this is greater for the streaming gases than for the stationary gases. Alternative mechanisms for the ozonisation process are discussed in connexion with the luminescence. R. A. Morton.

Luminescence of solid nitrogen under cathode-ray bombardment. J. C. McLennan, H. J. C. Ireton, and K. Thomson (Proc. Roy. Soc., 1927, **A**, **116**, 1—15).—Two types of apparatus are described for the examination of the phosphorescence spectrum of solid nitrogen and the spectrum of the light emitted by solid nitrogen when irradiated by cathode rays.

In the phosphorescence spectrum the band N_2 was found to have the components 5240, 5235, 5229, 5224, 5220, 5214, 5210, and 5204 Å., 5214 having the strongest intensity. The band N_4 was shown to be composite and to have the components 5944·47, 5938·8, and 5932·0 Å., the strongest being 5944·47 Å. In addition to the bands N_2 and N_4, the luminescence spectrum contained three diffuse bands, N_1, which shaded into each other and had the mean wave-lengths 5554, 5617, and 5658 Å. A number of faint diffuse bands were also observed, each shaded off towards the red in the blue and violet spectral region between 4573 and 2480 Å. The N_1 bands were found to decrease in intensity after the solid nitrogen had been irradiated for some time, but the groups N_2 and N_4 did not show this phenomenon. The view is held that the solid nitrogen initially deposited in a form *A* is rapidly transformed into a form *B* under electronic irradiation, the phosphorescence investigated being due to form *B*. No trace was observed of the group of wave-lengths N_3 obtained by Vegard (A., 1924, ii, 436). From a study of the structures of the bands N_2 and N_4 the moment of inertia of the molecular system involved in the phosphorescence of solid nitrogen is shown to be 3×10^{-40} g. cm.^{2} approx. It is not considered possible on the evidence obtained to decide whether the band observed by Vegard in the auroral spectrum near 5230 is identical with the band N_2 in the spectrum of solid phosphorescent nitrogen, or with the band 5228, the fourth member in the first negative band system of gaseous nitrogen.

L. L. Bircumshaw.

Spectra of high-frequency discharges in super-vacuum tubes. R. W. Wood and A. L. Loomis (Nature, 1927, **120**, 510).—If a discharge tube, while being exhausted with a Holweck molecular pump, is excited by an oscillating circuit giving a 3-metre wave, a blue hydrogen discharge at first appears, being replaced by the olive-green discharge characteristic of pure oxygen. The walls of the tube phosphoresce with a brilliant ruby-red light. The spectrum includes the line and band spectra of oxygen (possibly from silica) and many carbon lines (doubtless from stop-cock grease).

A. A. Eldridge.

Heat of dissociation of N_2 and N_2^+. H. Sponer (Physical Rev., 1926, [ii], **27**, 641).—The ω^n/n curve for the final state of the first positive group gives $E_e+E_n=11·87$ volts, approx.; for N_2^+, $Q'=9·06$, 9·7 volts, the second value being probably too great. If $I=16·5$ volts, $I'=14·16$ volts.

A. A. Eldridge.

Heat of dissociation of O_2 and O_2^+. R. T. Birge (Physical Rev., 1926, [ii], **27**, 641).—The true heat of dissociation, *Q*, of the molecule O_2 is calculated from the ω^n/n curve for the excited state to be 7·05± 0·03 volts, and from the curve for the stable state to be 6·666±0·5 volts. Values of *Q'* are obtained from the O_2^+ bands as 6·46 volts from the curve for the stable state and 6·49 volts from that for the excited state. The ionisation potential of the atom is 13·54 volts, and that of the molecule 14·1 volts.

A. A. Eldridge.

Critical potentials of nitrogen and the nature of active nitrogen. A. S. Levesley (Trans. Faraday Soc., 1927, **23**, 552—560).—An apparatus for determining the nature of the collisions between nitrogen molecules and electrons, for a range of accelerating voltages from 2·0 to 15·0, is described. The collisions become inelastic when the electrons attain an energy of 6·30 volts, and are then inelastic up to 9·3 volts. The addition of hydrogen produces practically no effect, hence the effect observed is probably due to nitrogen alone, and not to nitric oxide present as an impurity. The wave-length corresponding with 6·3 volts is 1940, and with 9·3 volts 1318, so that the inelastic collisions are probably associated with the excitation of a system of bands in the ultra-violet, having for the final state the normal state of the nitrogen molecule. Down to 2·0 volts, no critical potential was observed which might be associated with the surplus energy of metastable molecules of active nitrogen (cf. Willey and Rideal, A., 1926, 893).

M. S. Burr.

Variation of dielectric constants of certain organic substances with temperature. M. Velasco Durantez (Anal. Fís. Quím., 1927, **25**, 252—305).—On the supposition that a molecule has no permanent electrical moment the relation of Mossotti and Clausius, $(\varepsilon-1)/(\varepsilon+2)\rho=\text{constant}$, follows. If a permanent electrical moment be assumed, the relation of Debye, $(\varepsilon-1)/(\varepsilon+2)\rho=b+a/T$, follows. The dielectric constants of benzene, toluene, xylene, cymene, chlorobenzene, and *cyclo*hexanol have been determined at different temperatures. The dielectric constant of all the compounds studied is a quadratic function of temperature, the coefficient being positive except for benzene. Benzene, toluene, and xylene give results in agreement with the equation of Mossotti and Clausius. The remaining compounds, except *cyclo*hexanol, satisfy Debye's equation. As the constant *a* in Debye's formula is negative for benzene, toluene, and xylene, it is inferred that the molecules of these compounds have no permanent electrical moment.

The effect of asymmetry produced by substitution in the benzene nucleus on electrical moment is discussed. It is concluded that the molecules of the compounds studied which have asymmetric formulæ are electrically bipolar.

G. W. Robinson.

Electrical conductivity of vapours and liquid drops during incipient combustion. J. A. J. Bennett (Trans. Faraday Soc., 1927, **23**, 295—301).—To obtain some insight into the mechanism of the chemical action immediately preceding detonation in an engine cylinder, the electrical conductivity with rise of temperature of mixtures of air with various vapours, viz., ether, *n*-hexane, phenol, aniline, iodine, toluidine, or mixtures of these, has been determined. With rich mixtures of the less volatile substances marked ionisation was obtained above 400° when fogging occurred in the combustion tube. Gold electrodes were used in place of platinum, since the latter caused surface combustion. Similar experiments were carried out in liquid drops–air systems containing mixtures of undecane with a large number of other organic compounds, *e.g.*, alcohols, nitrogen compounds, aromatic bases, and phenols, and also some miscellaneous anti-knockers. The behaviour was similar to that observed in the former systems after fogging had taken place. The conductivity increases exponentially with temperature. The action of ultra-violet light is to lower the temperature of initial combustion without affecting the conductivity. It is suggested that the slow combustion of a disperse system of liquid drops of organic substances in air is accompanied by profuse liberation of electrons, whilst few electrons are present in mixtures of air and vapours. Recombination of electrons and ions may be the source of the energy which causes ignition at a lower temperature in mixtures of gaseous fuels containing liquid drops than in a completely vaporised mixture. M. S. Burr.

Optical dissociation of metallic halides. A. Terenin (Z. Physik, 1927, **44**, 713—736).—The limiting frequencies at which lines characteristic of the metal atoms are emitted when the vapour of the halide is irradiated with intense ultra-violet light have been determined for sodium and thallium iodides: 2450±50 and 2080±20 Å. for the sodium *D*-line and the thallium 3776 line, respectively. The optical dissociation corresponds thus with the formation of an excited metal and a neutral halide atom. The vapours of mercuric chloride, bromide, and iodide and of the iodides of cadmium, zinc, and lead emit a band spectrum when irradiated with light of wave-length shorter than a given limiting value characteristic of the substance. For these substances it is shown that the optical dissociation corresponds with the formation of an excited diatomic molecule and a neutral or an excited halogen atom according to the general equation $MX_2=(MX)'+X$. The band spectra of the mercuric halides observed are given in tabular form with an accuracy of 1—2 Å. R. W. Lunt.

Molecular scattering of light in a binary liquid mixture. C. V. Raman (Phil. Mag., 1927, [vii], 4, 447—448).—A reply to a criticism by Kar (this vol., 295) of the paper by Raman and Ramanathan (Phil. Mag., 1923, [vi], 45, 213) in which the author's improvement on Einstein's equation for the molecular scattering of light in a binary liquid mixture is justified in that whilst Einstein finds merely the work necessary to change the concentration by an infinitesimal amount from one value to another, both differing from that of the bulk of the mixture, they evaluate directly the total work necessary to change the concentration of a small volume of the mixture from its mean value to one slightly different, the work being done in a strictly reversible manner. It is shown that Kar's assumptions involve a process which is not reversible. A. E. Mitchell.

Valency and additive compounds. J. Perrin (Compt. rend., 1927, **185**, 557—561).—The current theories of valency and of atomic structure are reviewed and correlated with a developed form of Kekulé's conception that chemical action between two substances involves the formation of an intermediate additive compound, which then breaks down in a different sense. Such intermediate compounds are held together by a single electron linking (semivalency), which is weaker than a double electron linking (valency), and is characteristic of a rigid system built up from two octets, or from two closed electronic systems, having in common one instead of two electrons. The theory explains the existence of the Cl_3 molecule and is applied to a few simple reactions. A trimeric formula for polymerised water is obtained, which has the hexagonal symmetry of ice crystals.
J. Grant.

Variability of valency. (Sir) P. C. Rây (J. Indian Chem. Soc., 1927, 4, 89—95).—A discussion of modern conceptions of valency with special reference to the compounds of auric chloride with mercaptans. G. A. C. Gough.

Intramolecular rearrangements in the complex cobalt compounds. A. Uspenski and K. Tschibisov (Z. anorg. Chem., 1927, **164**, 326—334).—It is suggested as a general rule that if a reaction gives rise to stereoisomerides which can be represented by the formula $[Co(NH_3)_4R_1R_2]R_3$ or $[Co\,en_2R_1R_2]R_3$, where R_1, R_2, and R_3 are negative groups, then in the system in equilibrium in the solution a preponderance of the *trans*-form exists. If, however, R_1 and R_2 are electropositive groups, the *cis*-form predominates. The transformation of *trans*-dichlorodiethylenediaminecobaltic chloride into the *cis*-form on evaporation of the aqueous solution, which appears to conflict with the above generalisation, does not, however, occur quantitatively, and is complicated by the unequal solubilities of the two forms. Absorption spectrum observations show that when a strongly acid solution of the *trans*-form is warmed, there is no marked tendency for the formation of the *cis*-form, and on warming an aqueous solution of the aquochlorosulphate an equilibrium with the diaquo-salt is set up. In general, the ratio between the amounts of two stereoisomerides produced in a reaction does not appear to be influenced by their relative solubility, unless the solution becomes saturated in respect of one form. R. Cuthill.

Substitution reactions in the inner sphere of complex compounds. A. Uspenski and K. Tschibisov (Z anorg. Chem., 1927, **164**, 335—340).—The absorption spectra of oxalato-, carbonato-, and diaquo-compounds of the cobalt-tetrammines have been examined. For each of the first two groups, the spectra of the various members are qualitatively similar, being only slightly dependent on the nature of the anion, and with increase in concentration the molecular absorption coefficient increases. If carbon dioxide is passed into a solution of diaquotetramminocobaltic sulphate, the spectrum of the carbonatosulphate is ultimately obtained, but the mechanism of the change is not clear. The action of sulphuric acid on the carbonato-compounds gives absorption curves corresponding with those of the aquo-salts.
R. Cuthill.

Optical absorption and constitution of complex salts. H. Ley (Z. anorg. Chem., 1927, **164**, 377—406).—Solutions of the nickel, cobalt, and cupric salts of the amino-acids, which may be regarded as simple salts with internal complexes, have been investigated by measurements of the conductivity and optical absorption. The dissociation of copper, nickel, and silver aminoacetates as derived from conductivity measurements increases in this order. *E.M.F.* measurements with solutions of the copper salts indicate very low concentrations of the metal ion, but are not wholly conclusive. The behaviour of such compounds in solution depends, not only on the strength of the primary valency between the metal and the group with which it is associated, but also on the character of the subsidiary valency between the metal and the nitrogen, so that as a rule metals giving highly-dissociated ammonia complexes manifest but little tendency to form stable internal complexes with amino-acids. There is no general relation, however, between the degree of dissociation of the internal complex salt and the strength of the acid from which it is formed. Conversion of the copper aquo-complex, [$Cu4H_2O$], into the corresponding ammino-complex, [$Cu4NH_3$], displaces the maximum absorption towards shorter wave-lengths and increases the extinction. The wave-length of maximum absorption of the internal complex with aminoacetic acid is practically the same as that of the ammine, whilst the extinction is intermediate between those of the ammino- and aquo-complexes. Measurements with ammoniacal solutions of copper sulphate indicate that these solutions contain complexes such as [$Cu6NH_3$] and [$Cu2NH_32H_2O$] in addition to the tetrammino-complex. The absorption of nickel sulphate closely resembles that of the acetate. Ammoniacal solutions of the sulphate, which appear from distribution experiments to contain a hexammino-complex, vary in colour with the ammonia concentration. The internal complex with aminoacetic acid occupies an intermediate position between the aquo-complex and the ammino-complex. Both the cupric and nickel salts of aminoacetic acid obey Beer's law over a considerable concentration range, indicating the presence of very stable complexes. Addition of ammonia to solutions of the copper salt, however, increases the extinction, new complexes being formed by the expulsion of aminoacetate ions by ammonia. Determination of the distribution coefficient of ammonia between chloroform and an aqueous solution of cupric aminoacetate points to the addition of two ammonia molecules to the salt. The constitution of such a salt is, however, uncertain. Nickel aminoacetate shows a similar unsaturated character in respect of ammonia. It is suggested in explanation of the optical variability of these internal complex salts that the groups bound by two principal and subsidiary valencies are arranged about the central atom in a plane, in which there is sufficient space for the introduction of, *e.g.*, ammonia molecules. The internal complexes of cobalt, on the other hand, are remarkably inert both chemically and optically, which may be ascribed to an octahedral configuration protecting the metal atom. A complex *compound* of cupric aminoacetate and ethylenediamine, $Cu(C_2H_4O_2N)_2,2\,en,2H_2O$, has been prepared.

R. Cuthill.

Electronic structure of atoms. I. The periodic classification. J. D. Main Smith (J.C.S., 1927, 2029—2038).—It is shown that the feature of the classification of most importance to chemists is the octet arrangement of the elements into eight valency groups, and that modifications of the classification most serviceable in chemistry must give greater prominence to this octet arrangement. It is proposed to abridge the periodic classification by the relegation of the transition elements to a separate transition classification, the abridged classification then including only elements most closely related to the typical elements of the short periods, and consisting of a primitive period of two elements, 5 simple periods of 8 elements each, and a final incomplete period assumed to be also a simple period. The transition elements then form a separate table of 4 periods, each period consisting of 8 valency groups but beginning with Group III and ending with Group II. Each transition period consists of 10 elements, 3 being allotted to Group VIII, but to effect the reduction to 10 elements in the third long period containing 24 transition elements, 14 rare-earths proper to Group III are relegated to a transition sub-series which is not capable of being arranged in a period of 8 groups. The abridged and the transition classifications are then recombined to form a complete periodic classification embodying all the features of the two. The foregoing arrangements and the allocation of the various elements to their proper classifications, periods, groups, and series are discussed, and detailed experimental evidence is cited in support. It is indicated that this classification of the elements is to be the basis of a complete scheme of the distribution of electrons in atomic structures.

F. S. Hawkins.

Rare earths. J. D. Main Smith (Nature, 1927, **120**, 583—584).—The rare earths have no real relation to any other series of elements, and the observed colour resemblances are fortuitous. The sequence of colours of the (tervalent) salts of the first eight rare earths is identical with that of the last eight in the reverse order. Dysprosium salts are yellow; terbium salts are faintly rose in thick layers; illinium salts should be yellow. The identity in the colour sequences indicates that the same colour is obtained in two different ions when one has as many electrons (after deducting 54) more than zero as the other has less than 14, and that the 14 electrons concerned are arranged in only two sub-groups. It is further inferred that gadolinium has electrons in both sub-groups, but also that the second sub-group begins when the first is complete. The author's law of uniform atomic plan is supported.

A. A. Eldridge.

Analogies of scandium with the rare-earth elements and with the tervalent elements of the iron family. G. Urbain and P. B. Sarkar (Compt. rend., 1927, **185**, 593—596).—The resemblance between scandium and the other tervalent elements of the periodic system is discussed. Apart from its simple, anhydrous salts, scandium compounds always differ in composition from the corresponding salts of the rare earths, and no case of isomorphism is known. Scandium acetonylacetate and salts of the types $M_3[ScF_6]$ and $K_3[M(C_2O_4)_3],5H_2O$, however, strongly resemble those of the tervalent elements of the iron family, and the author furnishes evidence of this analogy in the following new *compounds* which are isomorphous with the corresponding compounds of the iron family: $(NH_4)_3[Sc(SCN)_6],4H_2O$, $K_3[Sc(SCN)_6],4H_2O$, and $Na_3[Sc(SCN)_6],12H_2O$. True scandium alums could not be obtained, but microcrystalline double salts with the sulphates of potassium, rubidium, cæsium, and ammonium, which had the composition of anhydrous alums, were prepared. The salt $Tl_3[Sc(SO_4)_3]$, also, is analogous to Étard's salt, $K_3[Cr(SO_4)_3]$. J. GRANT.

Electron distribution in sodium chloride. A. H. COMPTON (Physical Rev., 1926, [ii], 27, 510—511).—The electron density falls to zero for the sodium ion 1·1 Å. and for chlorine at 2·0 Å. from the centre. Sodium has a group of eight electrons (probably K and $L2_2$) near the centre, with two electrons (probably $L2_1$) at 0·9 Å. from the centre. Near the centre of the chlorine ion are 10 electrons (K and L) outside which are 8 others, resolvable into 4 (?3_3) at 0·74 Å., 2 (?3_2) at 1·14 Å., and 2 (?3_1) at 1·60 Å. A. A. ELDRIDGE.

Relationship of classical stereochemistry to the new work of Weissenberg. M. VON STACKELBERG (Z. angew. Chem., 1927, 40, 1023—1027; cf. A., 1926, 459, 934).—The fundamental postulates of classical stereochemistry are (1) the valencies of the carbon atom are directed towards the corners of a tetrahedron, (2) a substituent group or atom can rotate freely about a single linking; whereas those of Weissenberg are (1) the valencies have no fixed direction or length, but the substituents so arrange themselves that their potential energy is a minimum, (2) every symmetrical arrangement corresponds either with a stable (energy minimum) or a labile (energy maximum) configuration, (3) of the large number of theoretically possible symmetrical arrangements, only those occur in practice in which identical atoms occupy similar positions, and different atoms dissimilar positions. These postulates are difficult to apply, however, since only in the case of the simplest substituents can the symmetry arrangements be definitely worked out, and also it is not always possible to distinguish labile from stable configurations. Further, there are often several configurations giving energy minima.

Optical activity is due to the fact that a plane of symmetry will be absent where the four substituent groups are dissimilar; racemisation is explained by the existence of an " energy mountain " between two equally stable configurations, so that a powerful shattering effect (*e.g.*, thermal agitation) will enable the molecules to surmount the mountain and fall in equal numbers on both sides; the Walden inversion is similarly easily explained.

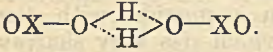
Since free rotation is no longer present, a great number of isomerides are theoretically possible, but are not experimentally observable, owing to the smallness of the " mountains " and " valleys " of the " energy surface "; the possibility of finding such isomerides at low temperatures is thus still open. The final test of the theory lies in X-ray measurements, but since the atomic numbers of the atoms composing organic compounds lie so closely together, the spectrographs are difficult to interpret. S. J. GREGG.

Effective cross-sectional area [of molecules] and molecular structure. E. BRÜCHE (Ann. Physik, 1927, [iv], 83, 1065—1128; cf. this vol., 492).—The previously described experiments have been extended to include oxygen, methane, carbon monoxide, carbon dioxide, nitrous oxide, and nitric oxide. The Ramsauer effect is not characteristic of the rare gases alone, but appears in all the gases examined. The results are plotted as before and the curves can be divided into three groups. Argon, krypton, xenon, hydrogen chloride, and methane all have eight outer electrons and each yields an area against electron velocity curve which slowly rises to a maximum and then more slowly falls away again. Nitrogen and carbon monoxide with ten outer electrons yield curves which rise very sharply to a maximum, followed by an equally sharp descent, which in turn is followed by a very flat maximum. Nitrous oxide and carbon dioxide with sixteen outer electrons yield curves having a small, sharp maximum, followed by a similar but very flat maximum. W. E. DOWNEY.

Effective cross-sectional area of the carbon dioxide molecule against slow electrons. C. RAMSAUER (Ann. Physik, 1927, [iv], 83, 1129—1135; cf. preceding abstract).—It is concluded that the difference between total and absorbing cross-section is in part due to definition and experimental difficulties. The total cross-section would appear to be that given by Lenard. W. E. DOWNEY.

Periodicity of molecular numbers. L. W. TIBYRIÇÁ (Nature, 1927, 120, 585).—Curves indicating the percentage of occurrence in each of four groups of molecular numbers, 4, 12, 20, 28; 6, 14, 22, 30; 0, 8, 16, 24; 2, 10, 18, 26, of a number of gases, acids, bases, and ions exhibit significant differences, which are considered theoretically. A. A. ELDRIDGE.

Activated molecules. L. J. WALDBAUER and I. J. PATTON (J. Physical Chem., 1927, 31, 1433—1434).—The hypothesis is put forward that molecules are in an activated condition when the valency electrons are at their greatest distance from the nucleus and at their lowest speed in their elliptical orbits. Absorption of radiation quanta, on this view, merely moves the valency electron to an outer orbit further removed from the nucleus, and produces a higher degree of activation. The temperature coefficient of a reaction can be explained by an increase in the number and in the force of molecular collisions arising from the increase in velocity of the molecules with a rise in temperature. L. S. THEOBALD.

Constitution of homogeneous acids. A. HANTZSCH (Ber., 1927, 60, [*B*], 1933—1950).—All homogeneous acids, available for investigation, are not " true " acids in the sense of Werner's complex formulæ, $[XO_2]H$, $[XO_3]H$, and $[XO]_4H$ with ionically-combined hydrogen atoms, which are therefore in themselves heteropolar substances and consequently electrolytes, but are rather homopolar hydroxy-compounds, $OX\cdot OH$, $O_2X\cdot OH$, and $O_3X\cdot OH$. Free, ionically-combined hydrogen and free hydrogen ions do not exist. In the unimolecular state, the acids are homopolar non-electrolytes with structurally united hydrogen atoms, and hence are pseudo-acids in accordance with a nomenclature which has become superfluous. This is strictly true only for hydrogen chloride, bromide, and iodide, which are unimolecular as liquids and therefore non-electrolytes; for other acids, it holds only in the gaseous state at a sufficiently high temperature. In the liquid condition the oxygen acids, with certain exceptions, are more or less strongly associated; since the association has an optically bathochromic effect it is not brought about by participation of the oxygen atoms of the acid radical but, as in the case of water and the alcohols, solely by means of the hydroxyl groups; as dimerides they correspond with the formula  $OX{-}O{<}\overset{H}{\underset{H}{}}{>}O{-}XO$. Like bimolecular hydrogen fluoride, they are partly converted into electrolytes by association, since, in consequence of a restricted displacement of the hydrogen atoms according to the scheme $(OX{\cdot}OH)_2 \longrightarrow [X(OH)_2]^+[O_2X]^-$, they yield acylium salts, which are dissociated in the unchanged portion and thus convert such pseudo-homogeneous acids (regarded previously as equilibrium acids from true and pseudo-acids) into electrolytes. Free halogeno-acids do not exist, since, by reason of the non-existence of ionogenic hydrogen, they decompose spontaneously into halogen hydride and the halogen compound of the corresponding element. Their "hydrates" or "alcoholates," like other strong acids, are oxonium salts. All acids behave towards water as "pseudoelectrolytes," since they are more or less completely transformed by addition of water to the "acid" hydrogen atoms into hydroxonium salts and dissociated. The phenomena can be most definitely expressed electrochemically by the phrase "only salts and not acids are electrolytes." Acids are compounds of hydrogen with negative atoms or atomic complexes; oxy-acids are at the same time derivatives of water in which a hydrogen atom is replaced by more negative atoms or atomic complexes. Consequently, acids have the tendency to replace their hydrogen atoms by more positive atoms (metals) or atomic complexes and thereby to pass into salts. Their degree of acidity (strength) is measured by their tendency towards salt formation. The acidity of the acids XH or X·OH increases with increase in the negative nature of the substituent X and is also determined by the differingly strong tendency of the acids towards salt formation or, conversely, by the differing stability of their salts. The strength of acids is most certainly determined by comparison of their tendencies towards additive salt formation with unsaturated substances, particularly with water and related oxides in the production of oxonium salts.

The absorption curves of tetrahydronaphthalene-2-sulphonic acid, its salts and *ethyl* ester, m. p. 35°, are incidentally recorded. H. WREN.

Electron lattice theory of metals. B. E. WARREN (Physical Rev., 1926, [ii], 27, 797—798).—It is predicted that the metals of Groups I and III should utilise a complete lattice of the rock-salt type, the sub-lattice of the positive ions being face-centred cubic; exceptionally, the sub-lattice of the alkali metals should be face-centred tetragonal. The sub-lattice of the metals of Groups II and IV should be either face-centred cubic or hexagonal close-packed; that of V and VI should be body-centred cubic. The lattice of a Group VII metal should not be of a simple type. The predictions are in agreement with the experimental results. A. A. ELDRIDGE.

Determination of crystal orientation in metallic single crystals. Y. SHIMIZU (Sci Rep. Tôhoku Imp. Univ., 1927, 16, 621—625).—A simple method of determining the crystal orientation of a metallic single crystal, without the use of *X*-rays, is described. The crystal is etched and the direction of brightest reflexion observed. M. S. BURR.

Intensity measurements of *X*-ray reflexions from fine powders. J. BRENTANO (Phil. Mag., 1927, [vii], 4, 620—629).—Measurements of the *X*-ray reflexion from finely-powdered rock salt have been made and the results compared with those of Compton and others obtained from single crystals and from coarse powders. In general, the measurements are in good agreement except that for the most powerful reflexions the present measurements give slightly higher values. This indicates a small amount of primary extinction in the measurements from larger crystals. In general, it is concluded that the reduction of a crystal to a coarse powder is sufficient to eliminate secondary but not primary extinction, and it is only with such substances as sodium chloride, the crystal units of which are initially sufficiently small, that grinding can reduce materially primary extinction. A. E. MITCHELL.

Size of the ideal synthesised lattice-range in true crystals. A. SMEKAL (Ann. Physik, 1927, [iv], 83, 1202—1206).—Polemical against Kast (this vol., 816). W. E. DOWNEY.

Orientation of aluminium crystals. K. TANAKA (Japan. J. Phys., 1927, 4, 137—140).—The orientation of long crystals in commercial aluminium wire in relation to the axis of the test piece has been examined. The (210) axis is more favoured than others for the orientation of crystals, a result not in agreement with the results of Elam (A., 1925, ii, 945).

R. W. LUNT.

Crystallite orientation in aluminium. G. TAMMANN and A. HEINZEL (Z. Metallk., 1927, 19, 338—341).—When commercial aluminium ingots are rolled down to sheet the proportion of cube planes in a section parallel to the direction of rolling gradually decreases to zero with a 66% reduction in thickness, whilst the proportion of octahedral and dodecahedral planes remains practically constant or falls slightly up to a 90% reduction, and the proportion of eicositetrahedral planes rapidly increases. Rolled sheet with 60—90% reduction commences suddenly to develop new crystals with varying orientations after annealing at 350°; the orientation of the new grains remains practically unchanged at higher temperatures and consists of 40—45% of (111), 35—40% of (110), and 18—21% of (100) planes on the surface of the rolled sheet. No twinned crystals are formed and prolonged annealing at a temperature just below the m. p. does not produce cube planes over the entire surface as is the case with copper. Progressive planes cut parallel to the cooling surface of a sand-cast aluminium ingot show little change in the crystal orientation, the (111) planes predominating and few (100) planes occurring on the cut surfaces. In chill-cast ingots, however, the predominating orientation is (100) followed by (111), except very

close to the cooling surface, where the converse is true.
A. R. Powell.

Rhombic sulphur isolated from volcanoes. F. Ranfaldi (Mem. Accad. Lincei, 1927, [vi], **2**, 266—318).—A comprehensive comparative survey of existing crystallographic data referring to the rhombohedral sulphur produced by volcanic eruption.
R. W. Lunt.

Lattice constant of metallic cobalt. S. Sekito (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 545—553).—*X*-Ray examination of annealed cobalt by the powder-photographic method, at ordinary temperatures, indicates that it has a hexagonal close-packed arrangement of lattice constant 2·498 Å. and axial ratio 1·622. At about 700°, however, it has a face-centred cubic lattice with lattice constant 3·558 Å. This confirms Masumoto's conclusion (this vol., 21) that there are two allotropic modifications of cobalt which have a transition point lying between 400° and 500°. Electrolytic cobalt may also consist wholly of the hexagonal form, although Hull found a mixture of the two forms in the powder obtained by rapid electrolysis (A., 1922, ii, 624). The amount of discontinuous change at the transition point, calculated from the lattice constant, is in satisfactory agreement with the result obtained by Masumoto from his elongation–temperature curve.
M. S. Burr.

Coherence of the reflected *X*-rays from crystals. G. E. M. Jauncey and A. H. Compton (Nature, 1927, **120**, 549).—For the *K*α line of molybdenum reflected from the (100) planes of rock-salt in the *n*th order, the ratio of the energy of recoil (given to a sodium atom by the impulse imparted by the reflected quantum) for each order to the energy of a quantum of Reststrahlen is 0·017, 0·067, 0·15, 0·27, 0·42, 0·60, 0·82, respectively, for values of *n* from 1 to 7. The fact that the ratio is always less than unity indicates that the energy of recoil is always less than that of a quantum of thermal agitation; hence the impulse is imparted to the crystal as a whole, and there is no reason to anticipate an absence of coherence in the reflected rays.
A. A. Eldridge.

***X*-Ray analysis of hafnium.** K. Kimura (Z. physikal. Chem., 1927, **128**, 394—398).—The hafnium content of a mixture of hafnium and zirconium oxides or phosphates may be determined by mixing the substance with sufficient lutecium oxide or phosphate to cause the hafnium $L\beta_1$ line and the cassiopeium $L\beta_2$ line to appear of equal intensity. Such a mixture corresponds with a Lu_2O_3/HfO_2 ratio of $2·5_5$ for an oxide mixture, and $2·7_5$—$2·8_5$ for a phosphate mixture. The application of the method to the analysis of alvite is described, together with the method of calculation when other metallic oxides are present.
H. F. Gillbe.

***X*-Ray study of the β-transformation in copper–zinc alloys.** A. Phillips and L. W. Thelin (J. Franklin Inst., 1927, **204**, 359—368).—Diffraction data have been obtained for β-brasses at the ordinary temperature and at 520°. The lattice of β-brass is body-centred and the lattice parameter increases with zinc content. Above the transformation temperature β-brass retains a body-centred lattice, but the parameter has the value d_{100} 3·007 Å. against d_{100} 2·956 Å. at the ordinary temperature. The values are for brass containing 51·1% of copper.
W. E. Downey.

Hexagonal structure of thallium crystals. G. R. Levi (Z. Physik, 1927, **44**, 603—606).—The contention of Becker (this vol., 503) that crystalline thallium has a tetragonal structure is contradicted by photographs and crystallographic measurements of actual crystals, which show that the structure is hexagonal.
R. W. Lunt.

Crystal structure of magnesium telluride. W. Zachariasen (Z. physikal. Chem., 1927, **128**, 417—420).—The crystals of magnesium telluride belong to the wurtzite type, with $a=4·52\pm0·02$, $c=7·33\pm0·04$ Å.; u is approx. $\frac{3}{8}$; $d_{calc.}$ is 3·86. The distance between neighbouring magnesium and tellurium atoms is 2·76 Å.
H. F. Gillbe.

Crystal structure of potassium dihydrogen phosphate. S. B. Hendricks (Amer. J. Sci., 1927, [v], **14**, 269—287).—The space-group of ammonium and potassium hydrogen phosphates is D_{2d}^{12} (Hassel, A., 1925, ii, 1130). The unit cell of the potassium salt contains 4 molecules. Using Wyckoff's notation, the phosphorus atoms are at (*a*), the potassium atoms at (*b*), and the oxygen atoms at (*e*), the locations of the latter being fixed by the parameter ranges: $x=0·045-0·075$; $y=0·120-0·135$; $z=0·145-0·165$ Å. The eight hydrogen atoms are at (*c*) and (*d*), the parameter u not being determined. This structure offers evidence against the assumption that the shape of a phosphate group is independent of its ionic surroundings. In the rotating-crystal method of analysis the duration of exposure varies for different parts of the photographic plate. The method of calculating the effective times of exposure is described.
S. K. Tweedy.

Crystal structures of ammonium, potassium, and rubidium cupric chloride dihydrates. S. B. Hendricks and R. G. Dickinson (J. Amer. Chem. Soc., 1927, **49**, 2149—2162).—*X*-Ray methods indicate that the unit cell contains 2 molecules of hydrate, the space-group symmetry probably being D_{4h}^{14} with $u=0·213$, $v=0·217$ for the potassium and rubidium salts and 0·217 and 0·221 for the ammonium salt. The 2Cu are probably at (*a*), 4K at (*d*), 4Cl at (*f*), 4Cl at (*g*), and $4H_2O$ at (*e*) (Wyckoff's notation). This structure, which is in agreement with the behaviour of the substances in solution as double rather than complex salts, represents a new type.
S. K. Tweedy.

Crystal structure of zirconium oxide. W. P. Davey (Physical Rev., 1926, [ii], 27, 798).—Of the several forms in which zirconium oxide may crystallise, one is a face-centred cubic lattice of ZrO_2, $a=5·098$ Å.; the second is a triangular close-packed lattice of ZrO_2, $a=3·598$, $C=1·633$. Both structures give d 6·13.
A. A. Eldridge.

Oxides. Density and crystal structure of the oxides of antimony, and the nature of the oxygen linking. IV. A. Simon (Z. anorg. Chem., 1927, **165**, 31—40).—The oxides Sb_2O_3, Sb_2O_4, Sb_6O_{13}, and Sb_2O_5 all have approximately the same type of lattice. The elementary antimony tetroxide cell contains eight double molecules; antimony tetroxide and the oxide Sb_6O_{13} have a similar type of lattice to the trioxide, whilst the Debye diagram of the pentoxide indicates that this substance is partly colloidal; the fifth atom of oxygen is held much more loosely than the others, and its introduction into or removal from the molecule has but little influence on the dimensions of the lattice. These facts accord with the chemical properties of the pentoxide and its derivatives, notably with the influence of heat on the hydrated form, and with the production of the tetroxide from antimony by the action of nitric acid. The density of antimony trioxide, determined pyknometrically, is 5·19, whilst the *X*-ray method gives the value 5·49. That of the tetroxide increases with increase of time of heating, at 840°: after 1 hr., the density is 5·99, and after 150 hrs., 7·50. The change is ascribed to the production of the crystalline form from the amorphous. Similar irregularities are found when the densities of Sb_6O_{13} and antimony pentoxide are determined; the values from the *X*-ray diagrams are 7·52 and 7·86, respectively. H. F. GILLBE.

Crystal structure of palladium oxide (PdO). W. ZACHARIASEN (Z. physikal. Chem., 1927, **128**, 412—416).—Palladous oxide crystallises in the tetragonal system, with $a=3·029\pm0·005$, $c=5·314\pm0·005$ Å. The elementary cell contains two atoms of palladous oxide, the palladium atoms forming a body-centred lattice; the positions of the oxygen atoms have not been determined on account of the smallness of the scattering. Palladous oxide is probably isomorphous with stannous oxide and red lead monoxide. H. F. GILLBE.

Crystal structure of tetramethylammonium chloroplatinate. M. L. HUGGINS (Physical Rev., 1926, [ii], 27, 638).—The structure has cubic symmetry; $a_0=12·65$ Å. Each platinum atom is surrounded by six chlorine atoms (24*a*) at the corners of a regular octahedron, and each nitrogen atom by four carbon atoms (32*a*) at the corners of a regular tetrahedron. The symmetry is that of the space-group O_h^3 or O^3. The platinum–chlorine distance is 2·35 Å. if the nitrogen–carbon distance is assumed to be 1·47 Å. A. A. ELDRIDGE.

Crystal structure of mercuric oxide. W. ZACHARIASEN (Z. physikal. Chem., 1927, **128**, 421—429).—Powder measurements of the rhombic form of mercuric oxide indicate the existence of two molecules in the elementary cell, of dimensions $a=3·296$, $b=3·513$, and $c=5·504$, with an error of $\pm0·006$ Å.; $d_{\text{calc.}}=11·22$. The mercury atoms form a body-centred lattice, but it is not possible to differentiate between the numerous possible positions of the oxygen atoms on account of the small scattering. H. F. GILLBE.

Crystal structure of heteropolar compounds of the composition $MG_6·LR_6$, $MG_5D·LR_6$, and $MG_4D_2·LR_6$ which crystallise in the trigonal system. O. HASSEL and J. R. SALVESEN (Z. physikal. Chem., 1927, **128**, 345—361).—The crystal structures of the hexahydrates of the following compounds have been determined; *b* is the semidiagonal of a face of the rhombohedron and *D* is the diagonal through the crystal in Å.: magnesium fluosilicate, $b=9·56$, $D=9·89$; manganous fluosilicate, $b=9·66$, $D=9·75$; ferrous fluosilicate, $b=9·62$, $D=9·68$; cobaltous fluosilicate, $b=9·31$, $D=9·69$; nickelous fluosilicate, $b=9·62$, $D=9·50$; zinc fluosilicate, $b=9·32$, $D=9·64$; magnesium titanium fluoride, $b=9·77$, $D=9·85$; zinc titanium fluoride, $b=9·55$, $D=9·88$; zirconium zinc fluoride, $b=9·77$, $D=10·11$; magnesium fluostannate, $b=9·77$, $D=10·02$; zinc fluostannate, $b=9·71$, $D=10·19$. Measurements for other co-ordination compounds are:
$Co(NH_3)_6Co(CN)_6$, $b=10·89$, $D=10·81$;
$Co(NH_3)_6Cr(CN)_6$, $b=11·15$, $D=10·90$;
$Co(NH_3)_5H_2OCo(CN)_6$, $b=10·74$, $D=10·85$;
$Co(NH_3)_5H_2OFe(CN)_6$, $b=10·74$, $D=10·84$;
$Co(NH_3)_4(H_2O)_2Co(CN)_6$, $b=10·62$, $D=11·01$. These compounds are all of very similar structure, one ion being at the corner and the other at the centre of a rhombohedron of about 96° inclination. The arrangement of the six surrounding groups is probably such that the true elementary cell is a rhombohedron of four times the size of the simple one and of inclination about 112°. Replacement of one or two of the ammonia molecules in the hexammine compounds by water produces very little alteration in the *X*-ray diagram. H. F. GILLBE.

Structure of xenotime and the relation between chemical constitution and crystal structure. L. VEGARD (Phil. Mag., 1927, [vii], 4, 511—525).—The structure of xenotime has been investigated by means of the powder method and the previous result that xenotime and zircon have practically identical space lattices confirmed. Both belong to the space-group D_{4h}^{19}. In the xenotime lattice all four oxygen atoms are of equal consequence, whilst the old chemical constitution formula would assign to one of them a singular position. On the octet theory of molecular structure the atomic arrangement in the solid state is in agreement with the constitutional formula. The close packing necessary for the stability of a lattice of the zircon type indicates that such crystals may be stable under high pressures. Xenotime is gradually changing its crystal structure with maintenance of its external form, and it is concluded that crystals of this type have probably been formed under very high pressures.
A. E. MITCHELL.

Quartz. A. MEISSNER (Physikal. Z., 1927, 28, 621—625).—If a quartz plate cut at right angles to one of the electric axes is subjected to high-frequency oscillations of variable frequency, two characteristic oriented oscillations manifest themselves at 1665 and 1160 metres. By dusting the quartz surface with lycopodium powder a clear pattern appears on excitation, and a photograph of the pattern discloses orientation in two directions from the optical axis, $\alpha=-48\pm2°$ (1160 metres), $\beta=+71\pm2°$ (1665 metres). The effect is connected with the inclination of planes of like atoms against the optical axis and the values $\alpha=-44\pm2°$ and $\beta=+63\pm2°$ are calculated from the not unequivocal *X*-ray data. Piezo-electric observations considered in the light of the foregoing lead to values for the modulus of elasticity of $E=7 \cdot 8\times10^{11}$ and $15 \cdot 6\times10^{11}$ cm.$^{-1}$ sec.$^{-2}$ for the conditions corresponding with the angles β and α, respectively, the separations of the planes concerned in the phenomena being 2·3 and 3·4 Å., respectively.

R. A. MORTON.

Equilibrium position of the atoms in β-quartz and its relation to double refraction and optical rotation. E. A. HYLLERAAS (Z. Physik, 1927, **44**, 871—886).—The following values of the oxygen parameters α and u in β-quartz have been computed from an electrostatic evaluation of the grating energy and from data referring to double refraction and to optical rotation, respectively: 77·9°, 0·216; 77·4°, 0·215; 77·1°, 0·214. The values are in satisfactory agreement with those of Bragg, but those of Wyckoff are thought to be in error.

R. W. LUNT.

Structure of silicates. W. L. BRAGG (Proc. Roy. Inst., 1927, **25**, 302—310).

Crystal structure of tetrahedrite. J. PALACIOS (Anal. Fís. Quím., 1927, **25**, 246—251).—Data are given for the crystal structure of tetrahedrite by the methods of Bragg and of Debye and Scherrer, respectively. The unit cell contains four molecules in a cube, $a=10 \cdot 39$ Å.; it is considered that the formula should be $3Cu_2S,Sb_2S_3$, and not $4Cu_2S,Sb_2S_3$, as supposed by Rose, Dana, and Moissan.

G. W. ROBINSON.

Crystal structures of anatase and rutile. M. L. HUGGINS (Physical Rev., 1926, [ii], **27**, 638).—Vegard's and Greenwood's results for rutile, and Vegard's for anatase, have been verified. Anatase has a_0 3·78, c_0 9·50 Å., with titanium atoms at $(0, 0, 0)(0, \frac{1}{2}, \frac{1}{4})(\frac{1}{2}, 0, \frac{3}{4})(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and oxygen atoms at $(0,0,u)(0,\frac{1}{2},u+\frac{1}{4})(\frac{1}{2},0,u+\frac{3}{4})(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})(0,0,\bar{u})(0,\frac{1}{2},\frac{1}{4}-u)(\frac{1}{2},0,\frac{3}{4}-u)(\frac{1}{2},\frac{1}{2},\frac{1}{2}-u)$, where $u=0 \cdot 20\pm0 \cdot 01$; space-group D_{4h}^{19}. Rutile has $a_0=4 \cdot 58$, $c_0=2 \cdot 95$ Å., with titanium atoms at $(0, 0, 0)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and oxygen atoms at $(u, u, o)(\bar{u}, \bar{u}, o)(\frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2})(u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2})$, where $u=0 \cdot 30\pm0 \cdot 01$; space-group D_{4h}^{14}.

A. A. ELDRIDGE.

***X*-Ray diffraction in liquids. Primary normal alcohols.** G. W. STEWART and R. M. MORROW (Physical Rev., 1927, [ii], **30**, 232—244).—Two significant distances are measured by the molybdenum $K\alpha$ X-ray diffraction curves for the primary normal alcohols containing from 1 to 11 carbon atoms; the first is linearly dependent on the number of carbon atoms, and the second is the distance of separation perpendicular to the chain. The first distance increases about 1·3 Å. for each carbon atom, the second is 4·6 Å. for lauryl alcohol, decreasing slowly to 4·4 Å. for butyl alcohol, and then rapidly to 3·8 Å. for methyl alcohol. It is concluded that the diffraction is produced by planes containing the polar groups, which are not perpendicular to the direction of the parallel chain molecules. The effect is not caused by crystal fragments, but is ascribed to a non-crystalline molecular space array termed "cybotaxis." The cybotactic state permits mobility, but not random motion; the molecules have the same orientation in groups too small to produce optical anisotropy. The universality of cybotaxis in liquids is not, however, claimed. Computed values of the densities of the alcohols are recorded.

A. A. ELDRIDGE.

***X*-Ray diffraction in liquids.** C. V. RAMAN and C. M. SOGANI (Nature, 1927, **120**, 514).—A general account of experiments being described elsewhere. When the benzene ring is unsymmetrically loaded there is a broadening of the halo. Acetic acid and glycerol each give two haloes, corresponding respectively with the mean distance between neighbouring molecules which lie side by side, and that between those lying end to end.

A. A. ELDRIDGE.

Electrolytic crystallisation processes. I. V. KOHLSCHÜTTER. **II. Aggregation forms of incoherent metal deposits.** V. KOHLSCHÜTTER and A. GOOD. **III. Formation and properties of coherent metallic films.** V. KOHLSCHÜTTER and F. JAKOBER (Z. Elektrochem., 1927, **33**, 272—277, 277—289, 290—308).—I. In characterising cathodic metal deposits, the mode of arrangement of the individual crystals to form the aggregate (aggregation form) must be considered as well as the form, habit, and size of the individuals. As in other crystallisation processes, growth of existing crystals and formation of new nuclei are differently affected by changing conditions, and wide variations in the character of such deposits are possible. In reviewing theories as to the mechanism of the formation of cathodic metal deposits, it is shown that numerous factors may possibly operate in determining their character, the growth of the deposit being affected, not only by the forces of crystallisation (cf. Blum and Rawdon, A., 1923, ii, 732), but also probably by forces in the solution. An attempt is to be made to determine the dependence of the character of electrodeposited metals on the nature of the metal and the conditions of deposition.

II. The electrodeposition of metals giving incoherent, outgrowing deposits (cadmium, zinc, tin, silver, and thallium) has been investigated with reference to the character and rate of formation of the outgrowths. In previous work (A., 1924, ii, 528) Kohlschütter and Uebersax showed that under suitable conditions lead is deposited from nitrate solutions in the form of thread-like chains of minute octahedra attached to one another by their apexes. This form is favoured by high current density, low electrolyte concentration, and low temperatures. Raising the temperature leads eventually to the formation of leafy structures difficult to characterise. The chains of octahedra probably arise by the convergence of current lines at the apex of the octahedron, resulting in the formation of a new nucleus at that point. From a comparison of the forms exhibited by various metals under various conditions it is concluded that the deposits obtained with a given metal belong to a characteristic morphological type by which the metal can be recognised, in spite of modification due to variation of conditions. The size of the individual crystals is determined by the relation between rate of crystal growth and rate of nucleus formation, which in turn depends on current density, electrolyte concentration, and temperature. High chemical polarisation is known to be an accompaniment of low rate of crystal growth, but this effect cannot be referred to complex formation, since the latter is found to favour crystal growth in some cases. High rate of crystal growth favours regular orientation of the crystals in the chains. The attachment of one to another occurs in a favoured crystallographic direction and depends therefore on the habit of the individuals, which is itself largely determined for a given metal by the composition of the electrolyte. The development of regular chains seems to be favoured by a certain current density and is, no doubt, connected with the chemical polarisation, the magnitude of which affects the distribution of current lines. With silver, chains of crystals were not obtained, there being no favoured direction of growth of the crystals, and probably a suitable relation between rate of growth and rate of nucleus formation was not attained under the experimental conditions. It is concluded that even incoherent cathodic metal deposits exhibit definite regularities and that their formation can be referred to the operation of forces at the crystal surface and in the electrolyte. The observations are discussed in detail and are compared with the results of Glocker and Kaupp (A., 1924, ii, 518) on the *X*-ray examination of coherent metallic deposits possessing a fibrous structure.

III. Mechanical strains developed during the cathodic deposition of thin films of nickel have already been investigated by the "contractometer" method (A., 1922, ii, 648). This method has now been improved and applied to the deposition of other metals which give very fine-grained coherent deposits. The magnitude of the "contraction" developed during the deposition of films of nickel, cobalt, iron, chromium, and palladium on platinum cathodes has been determined under various conditions of current density, temperature, and composition of electrolyte. Deposits obtained on platinum cathodes previously coated electrolytically with very thin films of copper or silver were coarser grained and exhibited a smaller contraction. Cathodic evolution of hydrogen at a contracted nickel deposit causes it to expand. The effect of superimposing alternating current on the direct current during metal deposition has also been examined. In the deposition of zinc and lead, metals which tend to give coarse-grained deposits, expansion was observed instead of contraction under all conditions. With silver deposited from cyanide solutions, contractions occur only when the current density is very high or when the solution contains a large excess of potassium cyanide: these conditions are the reverse of those leading to fine-grained, coherent deposits, and in the formation of such deposits a notable expansion occurs. The various factors which may determine the observed contraction and expansion phenomena are discussed in the light of theories of the mechanism of cathodic metal deposition.

H. J. T. Ellingham.

Recrystallisation of silver and platinum. O. Feussner (Z. Metallk., 1927, 19, 342—345).—As is the case with most other metals, there is a lower temperature limit below which platinum and silver will not recrystallise on annealing. This limiting temperature is higher the smaller is the amount of deformation to which the metal has been subjected; for silver, the minimum temperature lies between 250° and 300° and for platinum it is about 650°. Annealing at temperatures just above the limit yields a fine grain which becomes rapidly coarser with rise of temperature. For silver the relation between annealing temperature and grain size is almost linear above 350°, whereas for platinum the curve is hyperbolic and concave to the axis of temperature, *i.e.*, a relatively small rise in temperature between 800° and 900° causes a large increase in the size of the crystals, but a similar rise of temperature between 1200° and 1500° has a very slight effect on the size of the crystals. By plotting the grain size against the logarithm of the deformation a straight line is obtained in both cases for all temperatures.

A. R. Powell.

Tyndall's experiments on magne-crystallic action. (Sir) W. Bragg (Proc. Roy. Inst., 1927, 25, 162—184).

Grating theory of the electrolytic conductivity of rock salt. W. Braunbek (Z. Physik, 1927, 44, 684—699).—From a statistical analysis of the energy distribution of sodium ions in the rock-salt grating an expression is derived for the probability that an ion will move from the grating, *i.e.*, for the number of ions crossing a given boundary per sec. A consideration of this movement in a uniform electric field leads to an expression for the ionic conductivity, χ, in the following form: $\log\chi=\log 2e^2/3\tau ac\phi_0-\phi_0/kT$, where e is the electronic charge, τ the time period of the ions in the grating, a the grating constant, c a grating distortion factor, k the gas constant per mol., T the temperature Abs., and ϕ_0 the minimum shearing energy per unit cell. The value of c has been calculated from grating theory, that of τ from the frequency of residual rays, and that of ϕ_0 from the melting temperature. The above expression then becomes $\log\chi=27{\cdot}7-10{,}400/T$, from which values of the conductivity χ have been calculated in the range 20—500°, which agree well with those observed by von Seelen (Z. Physik, 1924, 29, 125) for which the relationship $\log\chi=25{\cdot}9-10{,}700/T$ obtains.

R. W. Lunt.

Magnetic susceptibility of some binary alloys. J. F. Spencer and (Miss) M. E. John (Proc. Roy. Soc., 1927, A, 116, 61—72).—The magnetic susceptibilities of silver, lead, cadmium, tin, gold, aluminium, bismuth, and a number of their alloys have been measured by means of the Curie–Cheneveau magnetic balance. The values for the pure metals agree with those obtained by Honda (Ann. Physik, 1920, [iv], 32, 1027). The susceptibility values are plotted against composition in the case of the alloys (silver–lead, gold–lead, gold–tin, gold–cadmium, aluminium–tin, bismuth–tin, cadmium–tin, and lead–tin), and well-defined maxima and minima are obtained, the compositions at which correspond in a number of cases with compounds, and in a few cases with compounds known to exist from a study of f.-p. curves. The magnetic susceptibility of an alloy system may lie well inside the paramagnetic region although both constituents are diamagnetic (lead-silver). The susceptibility curve for the lead–tin system is almost linear. L. L. Bircumshaw.

Magnetic susceptibility of the alkali metals. J. C. McLennan, R. Ruedy, and (Miss) E. Cohen (Proc. Roy. Soc., 1927, A, **116**, 468—483).—The magnetic susceptibilities of sodium, potassium, cæsium, and rubidium have been determined. The metals were purified by distillation in a vacuum. The cæsium and rubidium were prepared by the action of calcium on the halides; sodium was also prepared by electrolysis through glass. The susceptibility was measured by weighing the metals in the presence and absence of a strong uniform magnetic field. The atomic susceptibilities of sodium, potassium, rubidium, and cæsium were found to be 14×10^{-6}, 19×10^{-6}, 17×10^{-6}, and 28×10^{-6}, respectively. The susceptibilities of sodium and cæsium were found to be constant down to −190°. The theoretical bearing of these results is discussed. W. E. Downey.

Distortion of crystals of aluminium under compression. II. Distortion by double slipping and changes in orientation of crystal axes during compression. III. Measurements of stress. G. I. Taylor (Proc. Roy. Soc., 1927, A, **116**, 16—38, 39—60).—II. Changes in the orientation of crystal axes during compression of a disc cut from a single aluminium crystal are found to be in accordance with the prediction made on the assumption that the crystal slips as determined by distortion measurements. The bearing of the results on the structure of rolled sheets of metal is discussed, and distortions of cubical blocks of material, due to various types of double slipping, are compared, to discover which is most likely to occur.

III. Experiments are described for measuring the internal shearing stresses in a compressed disc. Formulæ are developed for analysing shear stresses parallel to slip planes and distortion due to double and single slipping. It is shown that the material hardens more rapidly when a given total amount of slipping is divided equally between two planes than when it is all on one plane. The experiments cover a large range, and indicate that the resistance to shear increases steadily up to the greatest amounts of distortion used. L. L. Bircumshaw.

Nickel–chromium solid solutions. F. C. Blake and A. E. Focke (Physical Rev., 1926, [ii], **27**, 798).—The amount of distortion of the nickel lattice by substitution of chromium, and *vice versa*, has been determined. A. A. Eldridge.

Influence of time and temperature on the mechanism of the mechanical fracture of large crystals of iron, aluminium, copper, and brass. F. Sauerwald and G. Elsner (Z. Physik, 1927, **44**, 36—57).—Measurements have been made of the extensibility, tensile strength, and shearing strength of rods of iron, aluminium, copper, and brass, each containing at most two or three single crystals, at temperatures from 0° to 1000°. The crystalline nature of the fracture produced by stretching and by shearing has been examined, and recorded photographically. The results show that the general statement that at lower temperatures the fracture is crystalline and at higher temperatures intercrystalline does not represent experimental observation. R. W. Lunt.

Sub-grain boundaries in nickel. E. S. Davenport (Nature, 1927, **120**, 478).—An example of the formation of sub-boundaries in nickel is described and illustrated. A. A. Eldridge.

Synthesis of nematic fusions. W. Kast (Ann. Physik, 1927, [iv], **83**, 1200—1201).—A correction.

Mol. wt. of gelatin in cresol. R. O. Herzog and H. Cohn (Z. physiol. Chem., 1927, **169**, 305).—Owing to the difficulty in obtaining trustworthy results with the cryoscopic method (cf. Troensegaard and Schmidt, this vol., 785; Cohn and Conant, A., 1926, 891), the rate of diffusion of gelatin dissolved in cresol is used. A. Wormall.

Metal crystals. V. Thermal and electrical conductivity of crystals belonging to the regular system. E. Grüneisen and E. Goens (Z. Physik, 1927, **44**, 615—642; cf. A., 1926, 784).—The thermal and electrical conductivities of gold, copper, platinum, rhodium, aluminium, iron, and tungsten in the finely-crystallised state and as single crystals have been determined at 0°, −190°, and −252°. For metals of high conductivity the thermal conductivity is determined principally by the purity and to a small extent only by the crystal size. The thermal resistivity, w, can be expressed by $w=w_i+\rho/ZT$, where ρ is the electrical resistivity, Z a constant, T the absolute temperature. The quantity w_i is identified as the non-metallic component of the resistivity, and, at temperatures at which superconductivity occurs, is the predominating term; its value is approximately constant for the metals examined, and is thus independent of purity, hardness, and crystal size. The quantity ρ/ZT is termed the metallic component of the resistivity and predominates except at very low temperatures; for pure, or nearly pure, metals Z has the value $2{\cdot}2\times10^{-8}$; it is therefore in this component that the basis of the Wiedemann–Franz–Lorenz law is to be sought. R. W. Lunt.

Measurement of light absorption. H. von Halban and J. Eisenbrand (Proc. Roy. Soc., 1927, A, **116**, 153—162).—The relative merits of the photographic and photo-electric methods for the measurement of light absorption in the ultra-violet are discussed. The photographic method is characterised by a definite absolute difference in extinction, not by a definite relative error. The accuracy with which the extinction coefficient can be determined depends on the absolute magnitude of the extinction used, and the error may be made very small by employing a sufficiently large extinction. In the photo-electric method it is possible, under favourable conditions, to make the sensitivity to differences of extinction about a hundred times as great as that of the photographic method. The photo-electric method is thus superior to the photographic method for the qualitative or quantitative determination of small changes in light absorption, and is to be preferred as an instrument for the elucidation of problems in chemical dynamics. The method is not so suitable for absolute measurements, since the purity of the light and the degree of definition in respect of wave-length are much poorer than in the photographic method, owing to the high intensity of light needed. The photographic method is entirely suitable for the quantitative exploration of absorption spectra, and on account of its greater rapidity is preferable to the photo-electric method. The large differences which have been found between the results of the two methods at wave-lengths below 300 $\mu\mu$, especially for solutions of nitrates (cf. Baly and Riding, this vol., 183), have been traced to a systematic source of error in the photo-electric measurements, due to the use of a glass relatively opaque to short-wave light in the cells employed in the measurements. The results of the two methods are now found to be in satisfactory agreement. L. L. Bircumshaw.

Specific heat of hydrogen. G. H. Dieke (Physical Rev., 1926, [ii], **27**, 639).—The assumptions necessary in a recalculation of the specific heat of hydrogen on the basis of the new development in band spectra are considered. A. A. Eldridge.

Relation between the difference of the specific heats at constant pressure and constant volume and properties of liquids. W. Herz (Z. anorg. Chem., 1927, **166**, 155—160).—Combination of Trouton's rule with the rule that the molecular heat at constant pressure of a liquid exceeds that at constant volume by 10 g.-cal. (Tyrer, A., 1914, ii, 425; Schulze, A., 1915, ii, 221) leads to the relation $c_p-c_v=L/2T$, where c_p and c_v are the specific heats at constant pressure and constant volume, respectively, and L is the latent heat of evaporation at the b. p. (Abs.), T. Somewhat similar relationships can be deduced connecting c_p-c_v and the internal pressure at the b. p., zero volume, capillary constant, critical data, molecular elevation of the b. p., surface tension at the b. p., and the molecular refraction, and, in general, these are in satisfactory agreement with the experimental data. R. Cuthill.

True specific heats at high temperatures by heating with thermionic electrons. H. Klinkhardt (Ann. Physik, 1927, [iv], **84**, 167—200).—The effect of thermionic emission in raising the temperature of various substances has been used to determine specific heats at high temperatures. The substance was heated in a vacuum furnace to any desired temperature. The heating effect of the controlled emission from a tungsten wire on the hot body was measured by means of a thermocouple embedded in the substance. Copper, solid and liquid lead, zinc, ammonium chloride, iron, nickel, and six iron–manganese alloys have been examined. The method is particularly applicable to the determination of specific heats near the m. p. or conversion point of a substance. W. E. Downey.

Calorimetric researches on some salts. E. Cane (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **32**, 83—86).—Using Bunsen's calorimeter, the specific heats of various metallic molybdates have been determined and by application of the addition law the specific heat of the group MoO_4 has been deduced. Results indicate that this law holds for molybdates. M. Carlton.

Latent heat of evaporation of sulphur. J. H. Awbery (Proc. Physical Soc., 1927, **39**, 417—420).—The quantity of sulphur boiled off from a vessel when a known amount of energy is supplied has been determined. Heat losses were prevented by immersing the vessel in sulphur vapour. Another method of estimating the heat loss, involving the use of a dummy vessel with a smaller heating coil so that the differences in energy and weight evaporated could be equated, proved unsatisfactory. The latent heat was found to be 79 with an estimated accuracy of 2%. R. A. Morton.

Heat of formation of the K_2 molecule. A. Carrelli and P. Pringsheim (Z. Physik, 1927, **44**, 643—652).—The concentration of K_2 molecules in potassium vapour at temperatures from 240° to 310° has been determined from the intensity of the red fluorescence band, excited by a constant source of white light, which is assumed proportional to the concentration of K_2 molecules. By providing that the vapour is saturated, these data give the vapour-pressure curve for K_2 molecules from which the heat of vaporisation, λ_2, is obtained. The heat of formation, Q, is then given by $Q=2\lambda_1-\lambda_2$, where λ_1 is the heat of vaporisation of monatomic potassium; the value thus found is 0·63 electron volt. The variation of the concentration of K_2 molecules with temperature at constant pressure has been employed to calculate Q directly; the value obtained is 0·53 electron volt; that calculated from the convergence frequency of the band is 0·68 electron volt. R. W. Lunt.

Heat of transformation of nickel and cobalt. S. Umino (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 593—611).—The heat content–temperature curves of nickel and cobalt have been determined by a calorimetric method. The heat of magnetic transformation of nickel has hence been found to be 2·01 g.-cal./g., whilst that of cobalt is 2·00 g.-cal./g. and the heat of transformation of cobalt from the hexagonal close-packed to the face-centred cubic lattice is 1·05 g.-cal./g. The mean and true specific heats at different temperatures have also been calculated. M. S. Burr.

New base point on the thermometric scale and the $\alpha\rightleftharpoons\beta$ inversion of quartz. F. Bates and F. P. Phelps (U.S. Bur. Standards Sci. Paper 557, 1927, **22**, 315—327).—The heating and cooling curves for crystalline specimens of quartz from widely-separated sources have been investigated, temperature measurements being made by means of thermocouples inserted in small holes drilled in crystalline plates. It was found that the $\alpha\rightleftharpoons\beta$ inversion is accompanied by superheating and supercooling. Inversion commences sharply at $573{\cdot}3_0$° on heating, and this temperature is always recorded regardless of the origin of the quartz specimen, whilst the inversion on cooling begins at $572{\cdot}3_8$°, but the exact temperature varies slightly with conditions in the crystal. The true inversion temperature may be taken as $572{\cdot}6_7$°. The heat of transition at the inversion temperature is estimated to be 0·165 g.-cal. The change at $573{\cdot}3_0$°, it is suggested, might well replace the m. p. of antimony (630·5°) as a reference point on the thermometric scale, specially suitable for the standardisation and checking of thermocouples. R. A. MORTON.

M. p. of sodium. J. R. NIELSEN and R. BIEBER (Proc. Oklahoma Acad. Sci., 1927, 6, 295—296).—Sodium prepared by electrolysis through glass has m. p. 97·6°. CHEMICAL ABSTRACTS.

Vapour pressure of diphenyl and aniline. F. J. GARRICK (Trans. Faraday Soc., 1927, 23, 560—563).—If, by making use of Jaquerod and Wassmer's vapour-pressure data (A., 1904, ii, 538), the ratio T_1/T_2 is plotted against T_1, where T_1 and T_2 are the temperatures Abs. at which diphenyl and mercury, respectively, have the same vapour pressure, the curve obtained shows a sharp change of slope at about 224°. Measurements of the vapour pressure of diphenyl, between 153° and 254°, have therefore been made by a modification of Ramsay and Young's method. The results are not in agreement with those of Jaquerod and Wassmer, and no discontinuity is observed on plotting in accordance with the Ramsay–Young rule. Vapour pressures of aniline have been determined between 91° and 151°. The results do not agree with those of Kahlbaum (Z. physikal. Chem., 1889, 26, 603). The Ramsay–Young graph is a smooth curve, the curvature being in the usual direction and more pronounced at the lower temperatures. M. S. BURR.

Influence of insoluble materials on the physical properties of liquids. J. B. PEEL, P. L. ROBINSON, and H. C. SMITH (Nature, 1927, 120, 514—515).—Baker's observations (J.C.S., 1927, 949) of the change in vapour pressure and surface tension of liquids in presence of insoluble catalysts are substantiated by density determinations. The density of water at 14·1° in contact with carbon increases by 0·000080 in 48 hrs., 0·00019 in 96 hrs., and 0·00020 in 150 hrs.; the increase with ethyl ether and carbon at 14·8° is 0·0009 in 18 hrs., 0·0011 in 42 hrs., and 0·0013 in 90 or 130 hrs. Water at 18·5° in contact with thoria gave the following results: −0·00017 in 24 hrs., −0·00002 in 48 hrs., +0·00001 in 96 hrs., +0·00011 in 192 hrs., +0·00015 in 209 hrs.; at 23·3°, −0·00040 in 24 hrs., +0·00004 in 209 hrs. A. A. ELDRIDGE.

Relation between orthobaric densities. J. HORIUCHI (Bull. Chem. Soc. Japan, 1927, 2, 213—224; cf. A., 1926, 1198).—The previously-derived relationship between the molecular volumes of a substance in the liquid and gaseous states is shown to be applicable to 22 more substances; the relationships between the quantities A and E and the critical constants are confirmed. The additive nature of the quantity E is established. J. S. CARTER.

Surface tension of molten metals and alloys. Y. MATUYAMA (Sci. Rep. Tohôku Imp. Univ., 1927, 16, 555—562).—An apparatus is described for determining the surface tension of molten metals by the drop-weight method. The surface tensions of tin, bismuth, cadmium, lead, zinc, and antimony fall linearly as the temperature rises. The surface tension–temperature curves are practically parallel for the range of temperature considered, but Eötvös' law is not obeyed. Surface tension–composition curves are given for the binary alloys of antimony with cadmium, zinc, and lead. There is a break in each of the first two curves, showing that the intermetallic compounds formed, CdSb and Zn_3Sb_2, respectively, have not decomposed in the liquid state. M. S. BURR.

Viscosity of liquids above their b. p. IV. T. TITANI (Bull. Chem. Soc. Japan, 1927, 2, 225—229; cf. this vol., 819).—The additive nature of the constant B in the author's previously-derived volume relation is established. When expressed in a reduced form by the introduction of critical data the author's volume and temperature relations become $\phi_r=k_r(v_r^{2/3}-b_r^{2/3})$ and $1-\phi_r=c_r(1-t_r)^{1/5}$, respectively, where ϕ_r, t_r, etc. represent reduced quantities or constants. The reduced constants k_r, b_r, and c_r are now independent of the nature of the substance and have the values 1·84, 0·308, and 1·09, respectively. They are related to the original constants and to the critical constants as follows: $k_r=KV_c^{2/3}/\Phi_c$; $b_r=B/V_c$; $c_r=CT_c^{1/5}/\Phi_c$. Further reduced equations are obtained from a consideration of the dimensions of viscosity. These equations are: $\phi_r'=k_r'(v_r^{2/3}-b_r^{2/3})$ and $\phi_{c_r}'-\phi_r'=c_r'(1-t_r)^{1/5}$, where the reduced constants k_r', c_r', and ϕ_{c_r}' have the values $4·03\times10^4$, $2·40\times10^4$, and $2·19\times10^4$, respectively, and are related to the original constants, critical constants, and mol. wt. by the equations $k_r'=KM^{1/2}T_c^{1/2}V_c^{1/3}$, $c_r'=CM^{1/2}T_c^{7/10}/V_c^{1/3}$, and $\phi_{c_r}'=\Phi_cM^{1/2}T_c^{1/2}/V_c^{1/3}$. J. S. CARTER.

Viscosity of nickel, aluminium, and light alloys. J. COURNOT and M. S. SILVA (Compt. rend., 1927, 185, 650—652).—The viscosities of commercial nickel, "calypso," aluminium, "alpax," and duralumin wires of varying diameters have been studied at 15—700° by the method previously described (B., 1926, 161). Nickel has a viscosity at 500—600° about double of that of an ordinary soft or semi-soft steel, and the limiting viscosities are low in all cases compared with the ordinary rupture loads. If the diameter of the wire is doubled the limiting viscosity is increased by a constant amount independent of the temperature (500 g./mm.² and 1 kg./mm.² for aluminium and duralumin, respectively). J. GRANT.

Theory of the streaming of an elastic liquid in the Couette apparatus. M. REINER and R. RIWLIN (Kolloid-Z., 1927, 43, 1—5; cf. A., 1926, 678).—From the equation for the internal tangential tension of a hypothetical "elastic liquid," $\tau=\theta+\eta dv/dr$, the following formulæ have been derived for the relation between the torsion angle of the suspension wire ϕ and the angular velocity Ω in the Couette apparatus: $\phi-\phi_0\log_e\phi=\phi_0-\phi_0\log_e\phi_0+2(\eta/\theta)\phi_0\Omega$ (1) and $\phi=(\eta/n)\Omega+(\phi/n)\log_e R_E/R_A$ (2), where η is the viscosity constant, θ the "flow solidity," $\phi_0=(2\pi lR_A^2/D)\theta$, $n=D(R_E^2-R_A^2)/4\pi R_E^2\,.\,R_A^2l$ (the apparatus constant), R_E and R_A are the radii of the outer and inner tubes, respectively, l is their length, and D the torsion modulus of the suspension wire. The relation (1) holds below the values ϕ_1 and Ω_1, relation (2) above these values, and $\phi_1=\phi_0\,.\,R_E^2/R_A^2$, $\Omega_1=(\theta/2\eta)[R_E^2/R_A^2-(\log_e R_E^2/R_A^2)-1]$. A criterion for the elasticity of a liquid is that its ϕ–Ω curve cuts off a certain value $\phi_0>0$ from the ϕ axis.

L. L. BIRCUMSHAW.

Viscosities, electrical conductivities, and specific volumes of acetic acid–stannic chloride solutions. J. D. Stranathan and J. Strong (J. Physical Chem., 1927, **31**, 1420—1428).—The viscosities, electrical conductivities, and specific volumes of solutions of stannic chloride in acetic acid have been measured at 25·2° for concentrations of the former up to a mol. fraction 0·4111 at which two layers are formed. Mixing is accompanied by a large evolution of heat, and by a large contraction in volume which, at a mol. fraction 0·3608 of stannic chloride, is 32·1% of the volume calculated on the additive law. The viscosity–concentration curve shows a pronounced maximum which is 282 times the viscosity calculated additively. The maximum occurs at the concentration corresponding with the compound $SnCl_4,3AcOH$, to the formation of which the change in the properties of the system is attributed.

L. S. Theobald.

Constitution of certain salts and acids in solution as determined by observations of critical solution temperatures. S. R. Carter and N. J. L. Megson (J.C.S., 1927, 2023—2028).—The elevation of the critical solution temperature in the systems phenol–water and *iso*butyric acid–water by the addition of other substances (Patterson, A., 1925, ii, 389) is used to detect complex formation in hydrochloric acid solution. For mixtures of hydrochloric acid with sulphur dioxide, selenium dioxide, ferrous chloride, and cupric chloride, the rise of the critical solution temperature is normal and there is no complex formation. Mixtures of hydrochloric acid with ferric chloride, mercuric chloride, and cuprous chloride show, however, considerable complex formation, the compounds $FeCl_3,3HCl$ and $HgCl_2,HCl$ being indicated.

F. S. Hawkins.

Interdiffusion of immiscible solid salts. C. Tubandt and W. Jost (Z. anorg. Chem., 1927, **166**, 27—30).—Immiscible solid salts may diffuse into each other when in contact if the ion carrying the current has the same kind of charge in each, and if each salt is able to form mixed crystals by exchanging its own mobile ion for that of the other salt. These conditions are fulfilled by the forms of cuprous sulphide and silver iodide which are stable at higher temperatures, diffusion occurring in this case by exchange of the metal atoms. Diffusion is slowest at the surface of contact of the solids, indicating a not inconsiderable resistance to the transfer of ions from one lattice to another of a different type.

R. Cuthill.

Determination of solubilities by potentiometric titration, and the "insoluble" form of silver chloride. F. L. Hahn and R. Schulze (Z. anorg. Chem., 1927, **166**, 213—218).—Determinations of the solubility of silver chloride by the potentiometric method previously described (this vol., 743) have failed to confirm the existence of the particularly insoluble form reported by Lorenz and Bergheimer (A., 1924, ii, 757).

R. Cuthill.

Solubility of cupric sulphide in alkali sulphides in presence of sulpharsenates. C. Davies and A. D. Munro (J.C.S., 1927, 2385—2386).—The amount of cupric sulphide dissolved by yellow ammonium sulphide increases steadily with the amount of arsenic present, sufficient copper being dissolved to cause an error in qualitative analysis. Colourless ammonium sulphide does not dissolve cupric sulphide under the same conditions. With solutions of sodium polysulphide the influence of arsenic on the solubility of cupric sulphide is much less pronounced.

F. S. Hawkins.

Effect of one salt on the solubility of another in ethyl alcohol solution. I and II. F. E. King and J. R. Partington (Trans. Faraday Soc., 1927, **23**, 522—535).—The influence of lithium iodide and sodium thiocyanate on the solubility of sodium iodide in ethyl alcohol at 25° has been investigated, and conductivities and viscosities of the sodium iodide–sodium thiocyanate solutions have been determined. The solubility data for sodium thiocyanate and those for lithium iodide, at concentrations below one equivalent per litre, may be represented by the ordinary salting-out formula, $\log s/s_0=kc$, where s_0 and s are the solubilities in g./litre of saturated solution of sodium iodide, alone and in presence of an added salt of concentration c equiv./litre, respectively. Methods of calculating the ionised and un-ionised fractions in the mixture of sodium iodide and thiocyanate are described and compared, and certain values adopted. As the concentration of sodium thiocyanate increases, both the concentration of undissociated sodium iodide and the solubility product of the ions decrease at approximately the same rate.

M. S. Burr.

Influence of electrolytes on the solubility of other electrolytes in non-aqueous solvents. C. A. Kraus and R. P. Seward (Trans. Faraday Soc., 1927, **23**, 488—491).—The solubility of sodium chloride in *iso*propyl alcohol in the presence of sodium nitrate and ammonium nitrate, respectively, has been determined at 25°, and also the solubility of sodium bromide in acetone in presence of sodium nitrate. The results show that addition of a second salt with a common ion depresses the solubility, whilst addition of a salt without a common ion increases it. The magnitude of the effects is not in accordance with that required by the Debye–Hückel theory. It is possible that, in solvents of lower dielectric constant, it will be necessary to abandon the assumption that the simple ions are the only molecular species present.

M. S. Burr.

Physico-chemical analysis by ebullition of saturated solutions. E. Cornec and P. Klug (Bull. Soc. chim., 1927, [iv], **41**, 1009—1017).—The b. p. of solutions which are saturated with regard to pairs of salts are said to afford information concerning the state of the salts in solution. Sodium and potassium chlorides, or nitrates, do not combine in solution; sodium (or potassium) chloride and bromide form a continuous series of mixed crystals; ammonium and copper sulphates, and ammonium and zinc sulphates, form double salts, $CuSO_4,(NH_4)_2SO_4,2H_2O$ and $ZnSO_4,(NH_4)_2SO_4,6H_2O$, respectively, exhibiting congruent solubility.

S. K. Tweedy.

Partition coefficients and the influence of salts. W. Herz and E. Stanner (Z. physikal. Chem., 1927, **128**, 399—411).—The partition coefficients of trimethylamine between benzene and aqueous solutions of lithium, sodium, potassium, strontium, and barium chlorides, and sodium and potassium bromides, iodides, and sulphates have been determined at 25°. The salting-out effect is greatest for chlorides and least for iodides, *i.e.*, it decreases with rising atomic volume, whereas the effect of the cations increases with increasing atomic volume. Neutral salts have a corresponding influence on the solubility of dipropylamine in water. Measurements of the partition coefficients of phenol and of benzoic acid between benzene and aqueous salt solutions indicate that in the case of acidic substances the sodium ion has the greatest influence and the potassium ion the least, the other cations giving intermediate values. The salting-out effect for a neutral substance such as acetone is greatest for the sodium and potassium ions. H. F. GILLBE.

Actinium. L. IMRE (Z. anorg. Chem., 1927, **166**, 1—15).—Experiments on the distribution of the nitrates of thorium and radioactinium between nitric acid solutions and ethyl ether reveal a close similarity in the behaviour of the two salts. A method of removing cerium from actinium preparations has been worked out (cf. this vol., 844). R. CUTHILL.

Dynamics of salting out. E. A. HAFNER (Biochem. Z., 1927, **188**, 259—269).—Phenol is salted out of aqueous solution by ammonium sulphate, more readily in presence of glycine, carbamide, and acetone, less readily in presence of glycerol and alcohol, whilst dextrose and sucrose have but little effect. The salting out of euglobulin and total globulin by magnesium, ammonium, and sodium sulphates is investigated and the results are discussed theoretically (cf. A., 1925, ii, 283). P. W. CLUTTERBUCK.

Adsorption of gases on the surface of mercury. M. L. OLIPHANT and R. S. BURDON (Nature, 1927, **120**, 584—585).—Measurement of the change of the concentration of carbon dioxide in admixture with hydrogen or helium when subjected to a shower of mercury droplets indicates that for 5, 10, and 15% of carbon dioxide a complete unimolecular layer of the gas is formed in 0·2 sec. after formation of the surface. For 0·5% the adsorption is less, and for 50% more, than that which corresponds with a unimolecular layer. It seems possible that the drop-weight method for measuring surface tension gives different values according to whether the liquid wets the tube or not. A. A. ELDRIDGE.

Heats of adsorption on poisoned and heat-treated catalysts. G. B. KISTIAKOWSKY, E. W. FLOSDORF, and H. S. TAYLOR (J. Amer. Chem. Soc., 1927, **49**, 2200—2206).—The curves representing the heat of adsorption of hydrogen by copper catalysts as a function of the amount adsorbed (cf. this vol., 426) exhibit a maximum, which corresponds with a smaller amount of adsorbed gas when the catalyst is partly de-activated (by heat treatment) and disappears when the de-activation is complete. The curve for adsorption by a poisoned copper catalyst is typical of that for adsorption without activation. These results support the theory that a catalyst surface contains variable elementary spaces and that adsorption, accompanied by an endothermic activation process, occurs on the most active spaces. Since, in adsorption, that reaction which involves the smaller free energy decrease is favoured, the question arises as to whether free energy change is a true measure of adsorption velocity. S. K. TWEEDY.

Hydrolytic adsorption by spongy platinum and charcoal. A. FRUMKIN and A. DONDE (Ber., 1927, **60**, [*B*], 1816—1820; cf. this vol., 106).—Spongy platinum, prepared by the action of magnesium on chloroplatinic acid and purified by successive washings with hydrochloric acid and conductivity water in an atmosphere of hydrogen, adsorbs alkali from a solution of sodium sulphate; the alkali is not completely removed by washing with a considerable quantity of water, so that the amount of acid liberated is always in excess of that of the alkali. It has not been found possible to prepare spongy platinum in presence of oxygen which adsorbs acid and liberates alkali. Charcoal treated with platinum and activated in air adsorbs acid from potassium chloride solution and liberates alkali, whereas the opposite effect is observed in an atmosphere of hydrogen. Addition of thiocarbamide to the potassium chloride solution poisons the platinum and the charcoal then adsorbs only acid independently of the gaseous atmosphere. H. WREN.

Adsorption of ions and of sols at interfaces and its application to certain problems of colloid chemistry. N. R. DHAR (J. Indian Chem. Soc., 1927, **4**, 173—181).—The adsorption of ions by sols of mercuric and antimony sulphides, aluminium and ferric hydroxides, and vanadium and manganese oxides shows that the greater the valency of the ion the less is the amount of adsorption. No experimental support is found for the view that ions of greater valency have greater coagulating power. Although sols are capable of adsorbing ions carrying the same charge as the sol, the adsorption is greatest when there is chemical affinity between the ion and the sol. Sols of ferric hydroxide, silver and lead chromates, but not sols of manganese oxide, antimony and cadmium sulphides, are adsorbed readily by their respective solids. The theory of Liesegang rings (A., 1925, ii, 959) based on the last observations is extended. G. A. C. GOUGH.

Physical chemistry of colour lake formation. I. General principles. [Adsorption of anions and hydrogen-ion concentration.] H. B. WEISER and E. E. PORTER (J. Physical Chem., 1927, **31**, 1383—1399).—As a preliminary to the study of colour lake formation, the adsorption of sulphate and oxalate ions, both separately and together, by the hydrated oxides of iron, aluminium, and chromium at various hydrogen-ion concentrations has been investigated. Preparation of the oxides in sol form by a special method gave products of much greater purity than the precipitated gels usually employed in adsorption experiments with dyes. The p_H values were measured by means of the hydrogen electrode. An increase in concentration of the hydrogen ion increases the positive charge on the sol particles, thus enhancing their adsorption capacity for anions. The adsorption of the latter diminishes rapidly on the alkaline side of the neutral point, becoming zero at p_H 9·2. Further, the p_H–adsorption curves show no evidence of the formation of a compound between the ion adsorbed and the hydrous oxide. In the simultaneous adsorption of sulphate and oxalate by hydrous chromic oxide sol, the sulphate is adsorbed more strongly than the oxalate in the alkaline and neutral ranges, but from a basic solution no measurable amount of the former is adsorbed in presence of excess of the oxalate. From a neutral solution, however, the adsorptions are equal when the ratio of sulphate to oxalate concentrations is 128 : 1. In an acid solution this ratio approximates to 1·1—1 at p_H 2·5. The sum of the simultaneous adsorptions of sulphate and oxalate approaches a mean between the separate adsorptions at the same p_H value, which disagrees with the finding of Mehrotra and Sen (this vol., 408) that the sum of the adsorptions of two ions from a mixture is always greater than the adsorption of either when present alone in the solution. The relationship between hydrogen-ion concentration and the precipitation concentrations of sulphate and oxalate has also been investigated, and the conclusion of Miller (A., 1925, ii, 192), that the taking up of anions by hydrous oxides is a solid solution phenomenon, is disputed. Finally, it is pointed out that since both hydrogen and hydroxyl ions are strongly adsorbed by the hydrous oxides, precipitation or adsorption data should be obtained at the same hydrogen-ion concentration if conclusions of any value are to be deduced. L. S. THEOBALD.

Experimental test of Gibbs' adsorption theorem. Study of the structure of the surface of ordinary solutions. J. W. McBAIN and G. P. DAVIES (J. Amer. Chem. Soc., 1927, 49, 2230—2254).—The experiments of Donnan and Barker (Proc. Roy. Soc., 1911, A, 85, 557) are criticised adversely and a simple quantitative method of determining the absolute adsorption of substances at gas–liquid interfaces, giving results only a few per cent. too large, is described. Results are recorded for the adsorption of *p*-toluidine in the nitrogen–water interface and of camphor and *iso*amyl alcohol in the air–water interface. The adsorption is constant over a fairly wide range of concentration. In every case the amount adsorbed greatly exceeds that required for a unimolecular film, so that the surface of these solutions must consist of such a film resting on a comparatively thick layer of concentrated solution, which is decreasing to the bulk concentration with increasing depth. This thick layer probably consists of chains of oriented, contiguous molecules extending downwards into the solution. The higher the bulk concentration the less is the disparity between it and the unimolecular film at the surface and the less is the interfacial tension. Thus the surface tension of a solution attains a definite value as saturation is approached. The actual adsorption for such solutions is the same as for more dilute solutions, whereas the "simplified" Gibbs adsorption isotherm predicts zero adsorption ($d\sigma/dc=0$). On the whole, this equation represents the observed results only to a first approximation; it requires that only two components are present everywhere in the system, a condition never realised in practice. The fundamental equation of Gibbs provides for more than two components: $(d\sigma)_T=-\Gamma_1 d\mu_1-\Gamma_2 d\mu_2-\ldots$; it is shown, however, that other, electrical, terms should be included in this equation. S. K. TWEEDY.

Displacement of the chemical equilibrium at an interface. I. M. KOLTHOFF (Kolloid-Z., 1927, 43, 51; this vol., 732).—The results obtained by Deutsch have been confirmed, but the phenomena observed are believed to be due to a preferential adsorption of the indicator acid or base at the water–benzene interface. Deutsch's explanation is criticised. L. L. BIRCUMSHAW.

Displacement of the chemical equilibrium at an interface. D. DEUTSCH (Kolloid-Z., 1927, 43, 52).—A reply to Kolthoff (cf. preceding abstract). Kolthoff's explanation is considered to be identical with the author's. L. L. BIRCUMSHAW.

Solubility and surface tension. J. TRAUBE, I. SCHÖNING, and L. J. WEBER (Ber., 1927, 60, [*B*], 1808—1814).—Measurements are recorded of the solubility of aniline, paracetaldehyde, amylene, and ethyl acetate in sodium salicylate solution, of *iso*amyl, *iso*butyl, and octyl alcohols, ethyl acetate, aniline, paracetaldehyde, heptoic acid, amyl acetate, and nitrobenzene in sodium benzoate solution, of chloroform in sodium acetate, of *iso*amyl alcohol in sodium benzenesulphonate, hippurate, naphthionate, *p*-hydroxybenzoate, butyrate, tartrate, succinate, citrate, and acetate, of aniline and ethyl acetate in sodium butyrate, and of *iso*amyl alcohol and paracetaldehyde in aniline hydrochloride solution. In general, greater increase of the solubility of the non-electrolyte is observed as the diminution of the surface tension of water by the salt employed increases. Examination of the systems sodium cinnamate–water–*iso*amyl alcohol and sodium cinnamate–water–*iso*butyl alcohol shows that in each case the effect of the alcohol and salt in causing increases in solubility is reciprocal. H. WREN.

Films responsible for oxidation tints on metals. U. R. EVANS (Nature, 1927, 120, 584).—The separated lead oxide film is transparent, and shows interference colours. Iron oxide films are less transparent; that which gives the first-order yellow tint is perceptibly yellowish-grey. The oxide films also reproduce all the surface irregularities of the metal. The difference in the colours of the separated film and of the film on the metal is considered. A. A. ELDRIDGE.

Collodion membranes. II. Relation between membrane structure and permeability to water. N. BJERRUM and E. MANEGOLD (Kolloid-Z., 1927, 43, 5—14).—It has been found that a given membrane is characterised by the membrane thickness, *d*, the water content per c.c. of membrane, *W*, and the permeability to water in c.c. for 1 sq. cm. of membrane surface in 1 sec. under a pressure of 1 cm. of water, *D*. By the use of these three quantities, formulæ are derived from which the pore radius or fissure width can be calculated for hypothetical membrane structures in which (*a*) the pores or fissures all run perpendicular to the membrane surface; (*b*) the pores or fissures are distributed uniformly among three directions perpendicular to one another, and run parallel or perpendicular to the surface; and (c) the pores or fissures are distributed irregularly throughout the membrane. The derived equations contain, besides a constant, only the quotient dD/W, and are used to calculate the dimensions of the capillaries in collodion membranes from the experimental values of d, D, and W. In the membranes investigated, the calculated pore radius varies from 1 to 90 $\mu\mu$, the number of pores from 2×10^9 to 1×10^{12} per sq. cm., the fissure width from 0·8 to 80 $\mu\mu$, and the fissure length from 1×10^5 to 32×10^5 cm. per sq. cm. Possible explanations, based on the contraction of the membrane with increased drying, are suggested for the fact that the number of capillaries per sq. cm. increases rapidly with decreasing water content. L. L. Bircumshaw.

Density of solutions of sodium in liquid ammonia. C. A. Kraus, E. S. Carney, and W. C. Johnson (J. Amer. Chem. Soc., 1927, 49, 2206—2213).—Measurements at −33·8° for concentrations ranging from 32·6 mols. of ammonia per atom of sodium up to saturation (5·48 mols. of ammonia per atom of sodium) show that the solutions have a density lower than that of either constituent. The volume change per atom of sodium is 40·96 c.c. at saturation; this value passes through a maximum with progressive dilution and then diminishes to a limiting value somewhat less than 40 c.c. The large volume change is attributed to the relatively large volume occupied by the free electrons known to exist in these solutions. S. K. Tweedy.

Refractometric evidence for the existence of undissociated molecules and complex ions in solutions of strong electrolytes. K. Fajans (Trans. Faraday Soc., 1927, 23, 357—375).—From a study of the refractivity of salts in solution and in crystal form, it may be shown that, when ions in solution at infinite dilution unite to form crystals, marked deviations from additivity take place, indicating mutual influences between the ions or between the ions and the solvent. Considering the anions, the refractivity of which is lowered by neighbouring cations, if ΔR is the diminution in the refractivity of a given anion in the alkali halide lattice, r the distance between oppositely-charged ions, and k_A a constant, then $\Delta R\times r^4=k_A$. For the iodine, bromine, and chlorine ions the constant k is approximately proportional to the square of the respective refractivities. From the available data it may be shown that the refractivities of salts and hydrogen chloride undergo, with increasing concentration, changes analogous to those which accompany the association of ions into crystals or molecules. These changes are attributable to the polarising action of the ions on each other, and from their magnitude they must be attributed to oppositely charged ions in direct contact with each other, *i.e.*, undissociated molecules. It follows from the refractivity data that in solution the least distance possible between chlorine and sodium ions is greater than between chlorine and lithium. Since, therefore, the characteristic parameter introduced into the formulæ of Debye and Hückel has a greater value for lithium than for sodium, this parameter does not indicate the distance of nearest approach of the ions as required by the theory. From a comparison of the partial vapour pressures of hydrogen chloride and hydrogen cyanide over their aqueous solutions, it is concluded that, up to concentrations of about 5 g.-mol. of hydrogen chloride per 1000 g. of water, the decrease in refractivity with increasing concentration is due only to a very slight extent to the formation of undissociated hydrogen chloride, possibly being caused by the complex ion H_2Cl^+. At still higher concentrations undissociated hydrogen chloride appears to be formed in increasing quantities. M. S. Burr.

Optical properties of coloured substances which exhibit colour changes in concentrated solutions of neutral salts. F. Vlès (Compt. rend., 1927, 185, 644—647).—The observations relate to substances which are not necessarily p_H or r_H indicators, but change colour or are precipitated in the presence of concentrated solutions of neutral salts. The absorption ratio (ϕ) for the two extreme spectral forms has been measured for solutions of sulphonecyanine-5*R* in potassium chloride solutions of various strengths (3·5—0·000001*N*) in which the concentration of the dye was $3{\cdot}5\times10^{-5}$. Curves in which ϕ is plotted against the logarithm of the salt concentration show clearly the gradual change in colour from rose (saturated to *N*-solutions) to violet. The observations suggest the existence of a potassium salt of the dye, or of some complex substance. J. Grant.

Nature of solutions of cobalt halides. A. Hantzsch (Z. anorg. Chem., 1927, 166, 237—243).—Gróh's theory (this vol., 728) that the blue colour of cobalt chloride solutions is due to $CoCl_4''$ ions is in conflict with some of the experimental facts. Thus although above 28° solutions of cobalt chloride in pyridine are blue, conductivity measurements show that even at 85° very few ions are present. The colour change is, however, readily explained by supposing that the red pseudo-salt $Co(C_5H_5N)_4Cl_2$ passes into the blue pseudo-salt $Co(C_5H_5N)_2Cl_2$ on heating (cf. this vol., 327). Even in solutions of cobalt chloride in acetone or ethyl alcohol, where Gróh's data show that some blue true salt is present, it seems probable that it is in equilibrium with a much larger amount of the blue pseudo-salt. It is suggested that the violet dihydrate of cobalt chloride passes in solutions into a blue form, which is unstable in the solid state. This would answer Benrath's objection to the theory that the blue colour produced by the addition of certain chlorides to pink solutions of cobalt chloride is due to the formation of lower hydrates (this vol., 829). R. Cuthill.

Stability of suspensions of coarsely-dispersed particles in solutions. II. Determination of colloids with the aid of the rate of clarification. H. Werner (Ber., 1927, 60, [*B*], 1920—1933; cf. this vol., 620).—Starch in concentration of less than 0·0005% and other colloids may be determined by the addition of a suspension of *Bolus alba* in 5*M*-sodium chloride solution and observation of the rate of sedimentation under standard conditions.

H. Wren.

Lability in ferric oxide hydrosols. C. H. Sorum (Science, 1927, 65, 498—499).—A ferric oxide sol prepared by hydrolysis of ferric chloride at 100°, and containing 3·5788 g. of iron per litre, was partly coagulated by shaking, stirring, or addition of mechanically coagulated ferric oxide. After removal of the coagulum, the supernatant sol, which contained 3·2 g. of iron per litre, was completely stable towards agitation and inoculation. Dilution decreased the coagulation until a limiting concentration was reached below which coagulation did not occur.

A. A. Eldridge.

"Photo-sols." I. S. S. Bhatnagar, N. A. Yajnik, and V. D. Zadoo (J. Indian Chem. Soc., 1927, 4, 209—219).—The reactions of gold and silver sols with arsenic and antimony trisulphide sols are shown to be photo-sensitive and therefore similar to the reaction between silver and sulphur sols (Freundlich and Nathansohn, A., 1921, ii, 536). Excepting cases when silver sol and arsenic or antimony trisulphide sols are mixed in certain proportions, no changes are observed when the mixtures are kept in the dark. Rapid colour change is produced by exposure to sunlight, and the product is found to consist of metallic sulphides, free sulphur, and arsenious or antimonious acids. G. A. C. Gough.

Stability of suspensions. II. Rate of sedimentation of kaolin suspensions containing colloidal silicic acid. W. O. Kermack and W. T. H. Williamson (Proc. Roy. Soc. Edin., 1927, 47, 202—221; cf. A., 1925, ii, 523; B., 1925, 464).—The rates of sedimentation of kaolin suspensions have been examined in presence of salts of the alkali metals. In acid suspensions, the inhibiting action is least in the case of cæsium and greatest in the case of sodium. The influence of small quantities of colloidal silicic acid has also been examined at various hydrogen-ion concentrations and in presence of univalent, bivalent, and tervalent cations. Small quantities of silicic acid appear normally to have a protective action, but under certain conditions produce precipitation of a film of insoluble material over the surface of the particles. An abnormally rapid rate of sedimentation of the particles is then observed, as, for example, in presence of certain salts of the alkali metals or of calcium at $p_H > 7·5$. In presence of calcium phosphate between p_H 4·5 and 9·2 the effect of silicic acid is to prevent formation of a precipitate, and in this case the abnormal sedimentation occurring in the absence of silicic acid tends to disappear.

W. O. Kermack.

Rigidity and other anomalies in colloidal solutions. E. Hatschek (Proc. Roy. Inst., 1927, 25, 245—259).

Protected silver hydrosols. V. Reduction of silver nitrate solution by irradiation with ultraviolet light in the presence of protective colloids. J. Voigt (Kolloid-Z., 1927, 43, 30—35).—Gum arabic has no reducing action on pure silver nitrate solution in absence of light or in diffused daylight, but illumination by ultra-violet light leads to the formation of a silver hydrosol. The greater the concentration of gum arabic the more finely divided is the sol, and sols obtained by illuminating solutions in quartz tubes are less homogeneous than those obtained by illumination in tubes of Jena glass. No sol-formation occurs on exposing pure silver nitrate solution to ultra-violet light unless a protective colloid is present. A series of experiments was made using a protein degradation product as the protective colloid, and the results are compared with those obtained with gum arabic.

L. L. Bircumshaw.

Colloidal mixed solutions of calcium carbonate and calcium phosphate. G. Stella (Kolloid-Z., 1927, 43, 21—26; cf. A., 1926, 1204).—Colloidal mixtures of calcium carbonate and calcium phosphate have been prepared by mixing sodium carbonate, sodium phosphate, and calcium chloride solutions in aqueous gelatin solution at 95°. The ratio of the two salts in the mixture can vary within wide limits, and the highest concentration which either salt can reach depends both on the gelatin concentration and on that of the second calcium salt. The calcium carbonate may not exceed a maximum concentration of 0·005—0·006M above half the calcium phosphate concentration. The phosphate may reach a concentration two or three times as great as that which it could possess alone at the same gelatin concentration. The mixed precipitates of the two salts form a gel in water (provided that the carbonate does not exceed half the phosphate), which is readily peptised by gelatin at 80—90°. The excess of calcium carbonate separates slowly from the colloidal solution in a crystalline state, without causing any change in the appearance or stability of the solution. The results support the hypothesis that a complex salt, or a homochemical compound (in von Weimarn's sense), is formed, in which two calcium atoms of the phosphate are bound with one of the carbonate. Peptisation experiments show that the mixed precipitate is more readily peptised, and offers a greater resistance to the modifying action of temperature, than the phosphate alone. L. L. Bircumshaw.

Investigation of colloidal systems. N. N. Andreev (Kolloid-Z., 1927, 43, 14—17).—A modification of the method used by Lottermoser (*ibid.*, 1914, 15, 145). The scattering of the light which passes through a colloidal solution is measured by means of a potassium photo-element. From observations with colloidal solutions of colophony, suspensions of barium carbonate, and emulsions of *Staphylococcus albus*, it is found that the galvanometer deflexions become relatively smaller with increasing concentration, due to the fact that the light scattered from the lower particles is intercepted by the upper particles. The method has been used to investigate the formation of colloidal sulphur solution and the coagulation of mastic with barium chloride solution. It has the advantage over tyndallometric measurements in that it gives absolute values. Some applications of the method are discussed.

L. L. Bircumshaw.

Theory of peptisation of metallic hydroxides in presence of non-electrolytes. K. C. Sen (Kolloid-Z., 1927, 43, 17—21).—Experiments on the peptisation of cerium, iron, and chromium hydroxides in presence of non-electrolytes (sucrose and glycerol)

show that if an exactly equivalent quantity of alkali is added to the solution, precipitation occurs even in the presence of the protective non-electrolyte. A minimum excess of hydrogen or hydroxyl ions is necessary for peptisation. It is inferred that the protective action of the so-called protective colloids and non-electrolytes is dependent on the presence of easily adsorbable ions in the solution. The protective action of the non-electrolyte appears to be subordinate to that of the ions. It probably acts only on the surface of the colloid particles, diminishing the surface energy, increasing the hydration, and preventing the growth of the particles.
L. L. Bircumshaw.

Peptisation of metallic hydroxides in the presence of sugars. M. R. Mehrotra and K. C. Sen (J. Indian Chem. Soc., 1927, 4, 117—129; cf. A., 1923, ii, 834).—The minimum amount of dextrose or of lævulose necessary to prevent the precipitation of metallic hydroxides when sodium hydroxide (3 mols.) is added to a solution of the metallic chloride and the sugar, is found to increase in the order Cu, Fe, Hg, Ce in both cases. Sucrose and lactose give the orders Cu, Ce, Fe, Hg, and Cu, Fe, Ce, Hg, respectively. At low concentrations there is a direct proportion between the amount of metallic hydroxide peptised and the sugar required, but at higher concentrations a greater proportion of sugar is needed. This, together with the fact that peptisation is a specific effect, indicates that the formation of metallic sucrates is improbable. In the case of mercuric chloride, the effect of a larger excess of alkali is to increase the sugar required, whereas cupric chloride, under the same conditions, requires less sugar. Whilst the peptisation of cupric and ferric hydroxides requires considerable time, the keeping of peptised mercuric hydroxide causes precipitation. G. A. C. Gough.

Peptisation of iron and chromium hydroxides in presence of non-electrolytes and influence of acid and alkali on the peptisation. K. C. Sen (J. Indian Chem. Soc., 1927, 4, 131—135).—Experiments in presence of glycerol show that an excess of alkali is necessary to prevent precipitation; this excess can be reduced by the addition of larger amounts of glycerol to a limit beyond which further addition is ineffectual. The specific protecting powers of non-electrolytes (preceding abstract) are apparent only when the minimum amount of alkali necessary for peptisation is present. G. A. C. Gough.

Sensitisation of cholesterol sols. R. Stern (Biochem. Z., 1927, 187, 315—323).—Further experiments (cf. A., 1926, 576) on the flocculation of cholesterol sols by acetate, lactate, and tartrate buffers in presence of electrodialysed ox serum confirm the author's view that the coagulation point is dependent on the concentrations of cholesterol, protein, and hydrogen ions (cf. Rona and Deutsch, A., 1926, 792). P. W. Clutterbuck.

Aluminium hydroxide gels of Willstätter Kraut, and co-workers. R. Zsigmondy and D. G. R. Bonnell (Ber., 1927, 60, [*B*], 1916—1918).—Aluminium hydroxide *C*, regarded as a colloid, is composed of very coarse particles; it is gradually dissolved to aluminium chloride by dilute hydrochloric acid, but is not peptised. The hydroxide *A* readily forms true hydrosols and therefore contains very small primary particles which, when combined in large numbers to secondary particles, form the suspension of the preparation *A*. H. Wren.

Phenomena caused by the low refractive indices of the alkali fluoborates. J. H. de Boer (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 350—354).—The apparent precipitation of potassium fluoborate as a jelly when potassium chloride solution is added to hydrofluoboric acid is due to the low refractive index of the salt. Precipitation of the cæsium salt by the same method yields a perfectly transparent solution, which exhibits brilliant colours owing to the difference of the dispersions of the solid and liquid phases. Cæsium fluoborate has n_D between 1·3563 and 1·3502, in agreement with the theory of the deformation of the electron layers in an ion, which requires the refractive index to be greater than 1·33. The refractive indices of potassium and rubidium fluoborates should be still smaller and experimental values for the latter are about 1·33. The sodium and lithium salts have refractive indices below that of water: for 12% solutions n_D^{20} for sodium fluoborate is 1·3321, and for lithium fluoborate 1·3303. For a 20% solution of the free acid n_D is 1·3284. H. F. Gillbe.

Volumetric chemical observations on forces of aggregation. I. Traube (Ber., 1927, 60, [*B*], 1815—1816).—The theory that complex substances, such as cellulose and the proteins, should be regarded, not as compounds in the sense of the older structural chemistry, but as built up by aggregation from smaller units, is examined from the volumetric chemical point of view. It appears that the forces of aggregation and valency are identical in their mode of action and differ in that the former are not operative from atom to atom, but act solely in causing a greater or less diminution of the co-volume. H. Wren.

Hydration of univalent ions. E. Schreiner and E. B. Schreiner (Z. anorg. Chem., 1927, 166, 219—224).—The calculations of hydration numbers previously made (A., 1924, ii, 524) have been revised, using for the activity, *a*, Bjerrum's formula, $\log a = \log X - kC^{1/3}$, where X is the molar fraction, k the activity constant, and C the concentration in g.-mol./1000 g. of water. R. Cuthill.

Electronic theory of valency. V. Molecular structure of strong and weak electrolytes. (*a*) Complete ionisation. T. M. Lowry (Trans. Faraday Soc., 1927, 23, 508—515).—Theoretical. In general the ions of a strong electrolyte are prevented from neutralising their opposite electric charges by the operation of factors which find expression in the "octet" rule. Badly-conducting solutions may, however, be obtained by dissolving a salt in a medium with a low dielectric constant, when abnormal variations of conductivity with dilution are generally observed. The small "degree of dissociation" is probably due, not to the neutralisation of the ionic charges with the formation of a chemical "bond," but rather to the formation of neutral ionic doublets. Many fused salts, *e.g.*, silver chloride, are good conductors, giving values for the "coefficient of ionisation" which may be above 100%, possibly as a result of the formation of multiply-charged ionic aggregates. Other fused salts, *e.g.*, dimethylaniline hydrobromide, are poor conductors, probably because the crystal lattice breaks down into neutral ionic doublets on fusion. The term "hydrolysis" has no significance from the point of view of the theory of complete ionisation, unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt, with formation of a covalent compound. Subsequently water may be eliminated from this.

M. S. Burr.

Valency. VI. Molecular structure of strong and weak electrolytes. (*b*) Reversible ionisation. T. M. Lowry (Trans. Faraday Soc., Sept. 1927, advance proof; cf. A., 1926, 454).—A review of weak electrolytes from the point of view of recent theoretical developments. It is shown that where partial and reversible ionisation occurs there is, in all the cases considered, a possibility of the formation of a covalent linking between the ions either directly or by means of some molecular rearrangement. Weak electrolytes of this class are found amongst acids and bases, pseudo-electrolytes, co-ordinated salts, substituted methyl halides, and a few simple metallic salts such as mercuric chloride. G. A. Elliott.

Dissociation constants of α- and β-alanine, and the transference velocities of the cations of the two isomerides. A. Bork (Z. physikal. Chem., 1927, **129**, 58—68).—Aqueous solutions of β-alanine possess a very small conductivity, the acid and basic dissociation constants being $9\cdot7\times10^{-11}$ and $4\cdot6\times10^{-11}$, respectively. Comparison of these figures with the corresponding values for α-alanine indicates that weakening of the acidic properties of the β-amino-acids is not accompanied by a decrease of basic properties, although this occurs in the case of the α-amino-acids. The transference velocity of the cation of α-alanine is 25·7, whilst that of the isomeric cation of β-alanine is 37·5. H. F. Gillbe.

Ionisation of polyhydrion acids. C. Morton (Trans. Faraday Soc., Sept. 1927, advance proof).—The variation of p_{H} in the neutralisation of tricarballylic, camphoronic, citric, and acetic acids by sodium hydroxide has been determined in $0\cdot01M$-solution. The observations were made with a new form of apparatus in which the potentiometer is connected in the grid circuit of a valve-amplifier with a galvanometer in the plate circuit. A method of differential titration utilising this device is described by means of which very accurate end-point determinations may be made. The classical mass-action equations for the dissociation of weak electrolytes have been modified by the introduction of activity coefficients derived from the Debye–Hückel theory, and in this way formulæ have been obtained which permit of the calculation of the true dissociation constants of polyhydrion acids for which the various stages of dissociation overlap. The theoretical equations are in accord with previous data for acetic, phthalic, and phosphoric acids, and yield the following values for the dissociation constants of the acids examined: tricarballylic acid, $3\cdot25\times10^{-4}$, $2\cdot65\times10^{-5}$, and $1\cdot48\times10^{-6}$; camphoronic acid, $2\cdot95\times10^{-4}$, $1\cdot05\times10^{-5}$, and $3\cdot7\times10^{-8}$; citric acid, $9\cdot11\times10^{-4}$, $2\cdot69\times10^{-5}$, and $1\cdot35\times10^{-6}$; acetic acid, $1\cdot77\times10^{-5}$. These results are in general agreement with the known effects of substitution on the strength of acids. The methods used by Enklaar (Z. physikal. Chem., 1912, **80**, 620), and by Auerbach and Smolczyk (A., 1925, ii, 118) in computing the dissociation constants of tribasic acids, are criticised.

G. A. Elliott.

Corrections for determination of ionic concentrations in very dilute hydroxide solutions. E. Laue (Z. anorg. Chem., 1927, **165**, 305—324).—The influence of dissolved carbon dioxide on the conductivity of dilute solutions of hydroxides not in equilibrium with the solid has been calculated by application of the mass law. In agreement with Remy's results (A., 1925, ii, 299), it is found that the conductivity is considerably reduced. With sparingly soluble hydroxides, however, where the solid hydroxide is present in equilibrium with the solution, it is calculated that the observed conductivity is very slightly too high. In this instance, Remy's calculations are defective, and the solubility corrections based on them are therefore inaccurate. The concentration of the hydroxide cation is considerably increased by the carbonic acid, however, and this must be taken into account in methods of measuring the solubility dependent on a determination of the cation. The effect of small concentrations of a second hydroxide on the solubility of the hydroxide under consideration may be computed by the application of simple mass action principles, but in calculating the effect of neutral salts the interionic forces cannot be neglected, and it is necessary to utilise the activity theory. All the corrections calculated in this way for the influence of carbon dioxide and electrolytes on the solubility of silver hydroxide prove to be in excellent agreement with experimental data. R. Cuthill.

Amphoteric nature of silver hydroxide. E. Laue (Z. anorg. Chem., 1927, **165**, 325—363).—Kossel's theory of the behaviour of the hydroxides of the metals of the second short series of the periodic system (A., 1916, ii, 243) has been extended to the whole system. From these considerations, it appears probable that silver hydroxide is feebly amphoteric. The mean value of the solubility in water at 25° determined by the conductivity, equilibrium, and usual analytical methods and corrected for the influence of carbon dioxide dissolved in the water (cf. preceding abstract) is $1\cdot36\times10^{-4}$ g.-equiv./litre. By conductivity measurements, the solubility at 18° is found to be $1\cdot14\times10^{-4}$ and at 20° $1\cdot20\times10^{-4}$ g.-equiv./litre. The fact that these values are in general lower than those found in the literature is to be ascribed to the considerable correction for the concentration of the cation necessitated by the dissolved carbon dioxide. From measurements of the solubility of the hydroxide in sodium hydroxide, the activity product is calculated to be $1\cdot85\times10^{-8}$. In the more concentrated solutions, the solubility is greater than in pure water, which is due to the hydroxide functioning as an acid, the activity product of this argentic acid being 2×10^{-18}. The solubility both in solutions of sodium hydroxide and in solutions of potassium nitrate is in good agreement with the requirements of Bjerrum's theory. R. CUTHILL.

Physical significance of the second fundamental law of thermodynamics. J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1927, [v], **13**, 180—184).—If Q_t and Q_0 are the thermal effects at temperatures t and 0, respectively, associated with an isothermal, reversible transformation between the same adiabatics, then $Q_t/Q_0=f(t)$, where $f(t)$ is a universal function. The thermodynamic scale of temperature is not *a priori* an absolute scale. J. S. CARTER.

Computation of the free energy and fugacity in gaseous mixtures of ethylene and argon. G. E. GIBSON and B. SOSNICK (J. Amer. Chem. Soc., 1927, **49**, 2172—2179).—The fugacities are calculated from the experimental results of Masson and Dolley (A., 1923, ii, 462). Lewis and Randall's fugacity rule ("Thermodynamics," p. 197) holds fairly well at low pressures, but at 50 atm. the deviation may attain 20%, and at 100 atm., 100%. S. K. TWEEDY.

Allotropy and internal equilibrium. A. SMITS (Z. physikal. Chem., 1927, **129**, 33—57).—A discussion of intensively-dried substances from the point of view of allotropy, together with new data on the vapour pressure of intensively-dried hexane, carbon disulphide, ethyl bromide, bromine, and nitrogen peroxide. H. F. GILLBE.

Agreement with experiment of the dilution formula deduced from the Debye–Hückel theory. A. FERGUSON and I. VOGEL (Trans. Faraday Soc., 1927, **23**, 404—408).—The value of n in the dilution equation of the general form $\Lambda=\Lambda_0-BC^n$ has been deduced graphically for a large number of electrolytes, from published conductivity data. It is found that n varies in a perfectly regular manner between 0·38 and 0·6, or possibly 1·0, for electrolytes in a related group, and cannot be equal to 0·5 as required by the Debye–Hückel theory. So far as can be seen from the data available, B varies irregularly with temperature, whilst n decreases with rise of temperature, except for potassium bromide and sodium acetate. M. S. BURR.

Activity of electrolytes. J. N. BRÖNSTED (Trans. Faraday Soc., 1927, **23**, 416—432).—A discussion of the activity of electrolytes, taking into consideration the following points: the thermodynamic laws of salt solutions, the principle of the specific interaction of ions as an explanation of the individual behaviour of salts, the theoretical calculation of activity coefficients, especially with reference to the Debye–Hückel theory, the application of the activity conception to the behaviour of weak electrolytes in the presence of strong electrolytes, or when the weak electrolytes themselves are ions, and, finally, the problems of concentrated solutions and of non-aqueous solutions. M. S. BURR.

Significance of the activity coefficient. M. RANDALL (Trans. Faraday Soc., 1927, **23**, 498—502).—A comparison between the thermodynamic and mechanistic treatments of the theory of solutions. If the composition of the solution be expressed in terms of the mol. wt. of arbitrarily chosen molecular species, then the activity coefficient gives a simple numerical statement of the deviation of this solution from the law of perfect solution. The laws based on the various mechanistic hypotheses all tend to approach the law of perfect solution as a limit. The activity concept makes it possible to bring the various colligative properties of a solution into agreement, and thus is a test of the adequacy of any mechanism which may be proposed. M. S. BURR.

Calculation of activity coefficients. M. RANDALL (Trans. Faraday Soc., 1927, **23**, 502—507).—The methods in use for calculating the activity coefficient of the solute from that of the solvent are mentioned, and it is shown how the same curve is applicable to all the different methods. The results thus obtained may be correlated with directly-measured values of the activity of the solute, so that the curves obtained by plotting log γ plus a constant against the square root of the ionic strength may be superimposed and the best average values selected. A method is suggested for interpolating the activity coefficients of strong electrolytes by plotting log $\gamma/\mu^{\frac{1}{2}}$ against $\mu^{\frac{1}{2}}$, where γ is the activity coefficient and μ the ionic strength. The graph thus obtained is approximately a straight line. M. S. BURR.

Use of amalgam electrodes for determining activities in methyl alcohol. J. H. WOLFENDEN, C. P. WRIGHT, N. L. R. KANE, and P. S. BUCKLEY (Trans. Faraday Soc., 1927, **23**, 491—498).—Attempts have been made to determine the *E.M.F.* of the cell $NaHg_x|NaCl$ in $MeOH|AgCl,Ag$ for dilute solutions below 0·16*M*. A streaming amalgam electrode was used, but the *E.M.F.* was found to depend on the rate of flow of the amalgam, apparently without limit and irrespective of the concentration of the solution. It was also found that, at concentrations of about 0·005*M* and lower, an unknown factor intervenes to make the *E.M.F.* 20—40 millivolts lower than corresponds with the ionic activity calculated from Debye and Hückel's equation. Measurements have also been made for three pairs of solutions with the liquid junction concentration cell $Ag,AgCl|NaCl(c_1)|NaCl(c_2)|AgCl,Ag$. When these are combined with the values obtained with the cell without liquid junction, it is again seen that the latter cannot be correct, since the values for the transport number thus obtained are not in agreement with the known mobilities of the two ions. M. S. BURR.

Activity of zinc chloride in concentrated solution. F. FOXTON and W. J. SHUTT (Trans. Faraday Soc., 1927, **23**, 480—488).—The solutions studied were, in most cases, so concentrated as to approach the conditions of molten salts. Cells without liquid junction, $Zn|ZnCl_2|Cl_2,Pt$, and cells with liquid junction, $Zn|ZnCl_2(m_1)|ZnCl_2(m_2)|Zn$ and $Pt,Cl_2|ZnCl_2(m_1)|ZnCl_2(m_2)|Cl_2,Pt$, were examined. The temperature coefficient for the first cell, in a 5*M*-zinc chloride solution, is 0·0007128 volt/degree between 60° and 80°. The heat of formation of zinc chloride in 5*M*-solution, deduced from this, is in good agreement with Thomsen's and Berthelot's values. To determine the change in activity coefficient with temperature, it was assumed that barium and zinc chlorides, at molar concentration, have the same activity coefficient. The curves obtained by plotting activity coefficient against the square root of the concentration show a diminution in the rate of increase at the highest concentrations, *i.e.*, above about 20*M*. This may be due to some type of polymerisation. The zinc concentration cells appear to behave normally, but the chlorine cells are abnormal at comparatively low concentrations, since the chlorine electrode in the more concentrated solution is positive with respect to the other. This is ascribed to the formation of complex anions in concentrated solution.

M. S. Burr.

Activity coefficients of protein ions. G. S. Adair (Trans. Faraday Soc., 1927, 23, 536—537).—A comparison is made between the activity coefficients of the hæmoglobin ion in solution at the isoelectric point p_H 6·8, when the valency is zero, and in solutions of p_H 7·8, when the ion has a negative valency of 8·5. In both cases the activity coefficient increases with increasing concentration, contrary to the requirements of the Debye–Hückel formula, but the first coefficient increases more rapidly than the second.

M. S. Burr.

Activity of hydrogen ion in mixed solvents. H. Millet (Trans. Faraday Soc., 1927, 23, 515—522).—Hydrogen-ion activities in ethyl alcohol–water mixtures containing 0·5*N*-HCl at 25° and 30°, alone and in the presence of sucrose, have been determined by *E.M.F.* measurements, using the ordinary hydrogen electrode. The values obtained pass through a minimum in a mixture containing 30% g.-mol. of alcohol, approaching a composition corresponding with EtOH,$3H_2O$. The hydrogen-ion activity coefficients α for hydrochloric acid in alcohol–water mixtures are connected with the values of the corresponding equivalent conductivities λ_r, and the dielectric constants D of the media, by the relationship $k=\alpha D^2/\lambda_r$, where k is a constant, but the formula has only a limited application. The hydrogen-ion activity of picric acid in alcohol, measured by the quinhydrone electrode, is found to diminish rapidly on the addition of small amounts of water. There is also a corresponding fall in hydrogen-ion mobilities. Calculated values of the hydrogen-ion activities, made on the assumption that hydration of the hydrogen has taken place, agree with the observed values.

M. S. Burr.

Some anomalies in the theory of solution of strong electrolytes and their explanation. N. Bjerrum (Trans. Faraday Soc., 1927, 23, 445—454).—Certain phenomena in dilute solutions of electrolytes do not at first sight appear to be explicable by the Debye–Hückel theory, viz., the variation in the heats of dilution of solutions of strong electrolytes, the values for the partition coefficients of ions between different solvents, the small Soret effect of many electrolytes, the amount of contraction on dissolution of a salt in water, and the negative heat capacity of ions in aqueous solution. All these, however, may be explained quantitatively on the assumption that the effective dielectric constant of the solution decreases in the immediate neighbourhood of the ions. M. S. Burr.

Mixed solutions of electrolytes and non-electrolytes. G. Scatchard (Trans. Faraday Soc., 1927, 23, 454—462).—If the properties of mixed solutions of electrolytes and non-electrolytes are deduced on the assumption that the ions consist of spheres in a continuous medium, they agree more closely than might be expected with the observed properties. The use of the same model may, therefore, be justifiable in the study of other phenomena.

M. S. Burr.

Strong electrolytes in relation to statistical theory, in particular the phase integral of Gibbs. R. H. Fowler (Trans. Faraday Soc., 1927, 23, 434—443).—Mathematical. The theory of Debye and Hückel is developed from the fundamental principles of statistical mechanics, using the method of Gibbs (cf. Kramers, this vol., 626). M. S. Burr.

Interionic attraction theory of Debye and Hückel. D. L. Chapman (Trans. Faraday Soc., 1927, 23, 443—445).—The approximation method adopted in the development of the Debye–Hückel equation does not appear to be justified in the case of small ions. M. S. Burr.

Thermodynamic properties of a few concentrated salt solutions. H. S. Harned (Trans. Faraday Soc., 1927, 23, 462—470).—By a study of *E.M.F.* data for cells of the type $Ag|AgX|MX(m_2)$, $HX(m_1)|H_2|HX(m_0)|AgX|Ag$ and $H_2|MOH(m_0)$, $MX(m)|M_xHg|MOH(m_0)|H_2$, the thermodynamic properties of strong acids in homoanionic salt solutions are contrasted with those of strong bases in homocationic salt solutions. Methods for determining the ionic activity coefficient product and dissociation of water in salt solutions are described. Consideration is also given to the derivation of individual thermodynamic activities for the ions of some simple electrolytes and for hydrogen and hydroxyl ions in pure aqueous halide solutions, or in acid–halide and hydroxide–halide solutions. For a given concentration of halide solution, the hydrogen-ion activity coefficient is greatest, and that of the hydroxyl ion least, when the electrical field intensity has its highest value. The behaviour of the hydroxyl ion is, therefore, contrary to that expected on the basis of an interionic attraction theory. This is attributed to the highly unsymmetrical structure of the hydroxyl ion and hence its ready deformability in an electric field, accompanied by a lowering of the activity coefficient. The unsymmetrical formate ion acts similarly to the hydroxyl ion (this vol., 206).

M. S. Burr.

Computation of partial molal quantities of binary solutions. B. Sosnick (J. Amer. Chem. Soc., 1927, 49, 2255—2257).—An equation is derived which enables partial molar quantities to be obtained from directly-measured molal quantities. A correction term is required which is small for nearly perfect solutions. S. K. Tweedy.

Relation of temperature to hydrogen-ion concentration of buffer solutions. A. G. Olsen (Science, 1927, 65, 477—478).—Published measurements demonstrate the importance of proper selection of the buffer solution where the reactions occur at temperatures other than that at which the acidity is measured. A. A. ELDRIDGE.

Application of the hydrogen electrode to organic bases: piperidine and its use as an alkaline buffer. E. B. R. PRIDEAUX and F. L. GILBERT (J.C.S., 1927, 2164—2168).—The neutralisation of piperidine by hydrochloric acid can be accurately followed by the hydrogen electrode, and the dissociation constant obtained by this method is 1×10^{-3} at 18°. The constant slowly decreases during the neutralisation, but since the addition of sodium chloride has no appreciable influence on the potential, the decrease cannot be attributed to the formation of the salt. The alkalinities of partly neutralised solutions calculated from the constant were checked by colorimetric titration, and found to agree. It follows that such solutions can be used as alkaline buffers. F. S. HAWKINS.

Buffer action. VI. Phase buffers. K. KLINKE (Helv. Chim. Acta, 1927, **10**, 627—642).—The systems considered are distinguished by the presence of weak acids and by the limited solubility of at least one of the substances concerned. Equations representing the change in the hydrogen-ion concentration on the addition of a completely dissociated acid to solutions of salts of sparingly soluble buffer acids and suspensions of sparingly soluble salts of soluble and sparingly soluble buffer acids are derived. Where possible illustrative titration curves are given. J. S. CARTER.

Mechanism of titrations with adsorbed indicators. J. W. HODAKOV (Z. physikal. Chem., 1927, **129**, 128).—The work of Fajans and Wolff (A., 1924, ii, 776) and of Hassel (A., 1924, ii, 738) renders the final conclusion of the author's previous communication invalid (this vol., 743). H. F. GILLBE.

Titration potential curves for precipitation reactions. E. LANGE and E. SCHWARTZ (Z. physikal. Chem., 1927, **129**, 111—127).—The maximum potential change during a titration in which a sparingly soluble uni-univalent precipitate is formed is given by $\Delta E=RT/nF\times p/2v\sqrt{L}$, where $\sqrt{L}$ is the solubility of the precipitate, v the volume of the solution titrated, and p the volume of each successive small quantity of solution added. The greatest slope of the potential curve is at a distance $P=\sqrt{2}\times v\sqrt{L}$ from the end-point, P being the total volume of solution added; the accuracy of determination of the end-point can thus be calculated. The influence of neutral salts on the sharpness of the end-point is in accord with the Debye–Hückel theory. Flattening of the potential curve due to the adsorption of ions is discussed, together with the influence of temperature on the potential in the neighbourhood of the end-point. H. F. GILLBE.

Critical state. I. Critical state of water and of aqueous solutions. E. SCHRÖER (Z. physikal. Chem., 1927, **129**, 79—110).—The most probable value of the critical temperature of water, determined from the temperature–density diagram, is 374·20°± 0·20°. The densities of the liquid and vapour phases do not become identical until the temperature is about 0·5° above the critical temperature. Solutions of the alkali halides exhibit no linear relation between the concentration and elevation of the critical temperature; neither are the elevations produced by different salts at the same equivalent concentrations equal. Experiments with coloured salts prove that at the critical temperature very little salt enters the vapour phase unless the contents of the vessel be stirred, in which case the vapour becomes saturated with salt; the temperature at which the meniscus disappears, however, remains unaltered. H. F. GILLBE.

Ebullioscopic paradox. A. BERTHOUD, E. BRINER, and A. SCHIDLOF (Helv. Chim. Acta, 1927, **10**, 585—588).—The fact utilised in the Landsberger process of mol. wt. determination that vapour of solvent at its b. p. is able to raise a solution to a higher temperature is not at first sight in accordance with the second law of thermodynamics and the suggestion that the necessary heat is supplied by the latent heat given out on condensation is incomplete. Assuming that the external compensating work permitting the heat transfer is the osmotic work caused by the dilution of the solution by the condensed solvent, the authors re-obtain the classical equation of van 't Hoff for the elevation of the b. p.

On passing water vapour at 100° into a concentrated solution of ammonium nitrate contained in a Dewar flask the temperature of the solution is rapidly raised and a b. p. of the order of 120° attained. J. S. CARTER.

Occurrence of points of inflexion in the concentration–vapour pressure curves of aqueous solutions of certain electrolytes. A. J. ALLMAND (Trans. Faraday Soc., 1927, **23**, 477—480).—The concentrations at which the curves connecting lowering of vapour pressure with concentration, for solutions of sodium, potassium, and lithium chlorides, show minima, and the vapour pressure–concentration curves show points of inflexion, have been calculated by Harned's equation (A., 1920, ii, 664). The values are not in agreement with those found experimentally by various investigators. M. S. BURR.

Intermetallic compounds. VI. Reaction between solid magnesium and liquid tin. W. HUME-ROTHERY (J. Inst. Metals, Sept., 1927, advance copy, 5 pp.; cf. A., 1926, 356).—The reaction between solid magnesium and liquid tin has been investigated between 250° and 350° in order to see whether reactions of the type primary solid X+liquid→secondary solid Y can proceed when the solid phases concerned do not form solid solutions. According to the equilibrium diagram, when a rod of magnesium is suspended in a limited amount of molten tin, the magnesium should dissolve until the liquid has the equilibrium composition, after which a slow reaction of the type solid magnesium+liquid ⟶ magnesium stannide (Mg_2Sn or Mg_4Sn_2) should take place. Actually when sufficient magnesium has dissolved to give the equilibrium composition, all further direct action is stopped by a thin film of magnesium stannide which shows no thickening even after 3 weeks at the above temperatures. A few large crystals of magnesium stannide are, however, sometimes formed by a slow reaction, which is probably analogous to crystal growth due to surface energy effects, since the thin surface film has a high surface energy and so tends to form a more compact mass, but since dissolution at any point exposes more magnesium to the liquid, the action proceeds slowly in spite of the absence of solid solutions. W. Hume-Rothery.

Method of measuring variations of electrical resistance for the determination of the thermal equilibrium diagram of an intermetallic system. F. H. Jeffery (Trans. Faraday Soc., 1927, 23, 563—570).—Two continuous methods are described for measuring the change of electrical resistance of alloys with change in temperature, as determined by a chromel–alumel couple. The first is a null method, using Callendar records, and the second involves a "back *E.M.F.*" method of measuring temperature and the measurement of variations of resistance by means of the current through an Ayrton–Mather galvanometer. The accuracy of the second method has been tested by application to copper–tin alloys containing from 40 to 98 atoms per cent. of tin. The results are in almost complete agreement with those of Heycock and Neville, but deviate from those of Isihara (J. Inst. Metals, 1924, 1, 315) and of Haughton (*ibid.*, 321). The higher transition point of tin, as determined by this method, is 162°. This electrical resistance method, with slow cooling, is very sensitive to the formation of a new phase, but for accurate work there is an upper limit to the rate of cooling. This, however, is not necessarily the same for every alloy. Preliminary experiments to fix the solidus, when solid solutions are formed, gave results in agreement with those of micrographic analysis.
M. S. Burr.

System aluminium–thorium. A. Leber (Z. anorg. Chem., 1927, 166, 16—26).—The equilibrium diagram for concentrations up to 56% of thorium has been obtained. In addition to the compound Al_3Th (Hönigschmid, A., 1906, ii, 173) it would seem that a compound richer in thorium is formed, or that mixed crystals separate from the more concentrated solutions.
R. Cuthill.

System phenol–water. E. R. Jones (J. Physical Chem., 1927, 31, 1316—1321).—The system phenol–water at temperatures below 13° has been studied, and the phase diagram established. Two eutectic points, phenol hydrate, solution, ice, and solid phenol, solution, and ice, respectively, have been observed at respective temperatures and concentrations of −0·843° and 4·607 g. phenol/100 g. solution, and −1·174° and 6·839 g. phenol/100 g. solution. An unstable invariant point (ice and two liquid phases) has also been observed at −1·252°. Solubility measurements are given, and the f. p. of pure phenol is found to be 40·71°. L. S. Theobald.

Gold–palladium–nickel alloys. W. Fraenkel and A. Stern (Z. anorg. Chem., 1927, 166, 161—169; cf. A., 1926, 344).—The solidus curve for alloys of gold and nickel cannot be determined from cooling curves in the usual way, since with the normal rate of cooling the mixed crystals do not reach equilibrium with the liquid. It was therefore necessary to trace the curve by observation of the heating curves of alloys rendered homogeneous by annealing, and in the course of these experiments the existence of a miscibility gap in the solid state was revealed. The solidus and liquidus curves for the system palladium–nickel pass through a minimum at a point corresponding with 60% of palladium, and here also there is a miscibility gap in the solid state. Determination of the freezing surface for the system gold–palladium–nickel shows that the minima exhibited by the binary systems gold–nickel and nickel–palladium become one in the ternary system. R. Cuthill.

Systems sodium chloride–lead chloride–water and lithium chloride–lead chloride–water. G. E. R. Deacon (J.C.S., 1927, 2063—2065).—The equilibrium relations at 25° afford no evidence of double compounds. F. S. Hawkins.

Electrometric study of the system potassium chloride–lead chloride–water at 25°. A. J. Allmand and L. J. Burrage (Trans. Faraday Soc., 1927, 23, 470—477).—In the above system a detailed study has been made of the activity of the lead chloride by measurements on the cell Pb(amalgamated)|solution, AgCl(solid)|Ag. If N_1, N_2, and N_3 are the molar fractions of lead chloride, potassium chloride, and water, respectively, then continuous addition of potassium chloride to a solution of constant N_1/N_2 ratio causes first an increase in the activity of lead chloride and then a decrease. By making certain assumptions, based on the published data for the vapour pressure of potassium chloride solutions, it is shown that the addition of lead chloride to a solution of constant N_2/N_3 ratio causes a decrease of the activity of potassium chloride if N_2/N_3 is small. This becomes less pronounced, and is finally converted into an increase, as N_2/N_3 becomes larger, but the increase also becomes less marked as saturation with potassium chloride is approached.
M. S. Burr.

Systems boron trioxide–sulphur trioxide–water and boron trioxide–phosphorus pentoxide–water. M. Levi and L. F. Gilbert (J.C.S., 1927, 2117—2124).—The equilibrium relations at 25° and 45° show the formation of $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$; this result is confirmed by direct analysis. Difficulty was experienced owing to the supersaturation and high viscosity of the liquid phase. The data for the second system at 25° indicate that orthoboric acid and boron phosphate (BPO_4) occur as solid phases. Measurements of the viscosity of solutions of orthoboric acid in sulphuric acid are recorded. F. S. Hawkins.

Equilibrium between two liquid phases. IV. System *o*-toluidine–lactic acid–water. M. Angelescu (Bul. Soc. Chim. România, 1927, 9, 19—25).—The isotherms for 20° and 30° and the partition coefficient at 30° have been determined. The miscibility curves for given concentrations of lactic acid indicate the existence of a lower critical solution temperature, but chemical action between the components occurs before the upper critical solution temperature can be realised. F. S. Hawkins.

Equilibria in the reduction, oxidation, and carburation of iron. III. R. Schenck and T.

Dingmann [with J. Bökmann, W. Ebert, W. Kesting, G. Lepetit, J. Müller, and W. Pratje] (Z. anorg. Chem., 1927, **166**, 113—154; cf. this vol., 939).—The equilibria $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$ and $FeO+CO \rightleftharpoons Fe+CO_2$ have been examined between 600° and 1100° by gradually removing the oxygen from ferric oxide by means of carbon monoxide at constant temperature, the composition of the gas phase being ascertained at each stage when equilibrium had been established. The experimental conditions were such that carbide formation was prevented. At a given temperature, with decrease in the amount of oxygen in the solid phase the composition of the gas phase first remains constant, then the carbon dioxide concentration falls rapidly for a time, after which it ultimately becomes steady again, and decreases further only when the solid phase contains less than about 0·5 atom of oxygen per 3 atoms of iron. The first steady state corresponds with the coexistence in equilibrium of ferrosoferric oxide and a solid solution in this oxide of ferrous oxide. During the second period of constancy, the solid phases are solutions of ferrous oxide in metallic iron ("oxoferrite") and of ferrosoferric oxide in ferrous oxide. The two solid solutions of ferrosoferric and ferrous oxides are to be regarded as the extreme portions of a continuous series of mixed crystals of the two oxides, for which the name "wüstite" is proposed. The data obtained permit of the construction of the diagram of state for the system iron–oxygen, which shows that at 560° wüstite, ferrosoferric oxide, and oxoferrite coexist in equilibrium, but below this temperature the first of these breaks up into the other two. At none of the experimental temperatures does ferrous oxide in the pure state appear as a solid phase. All substances which are able to form compounds or solid or liquid solutions with the oxides of iron influence the reduction in the sense that a larger proportion of carbon monoxide must be present in the gaseous phase to effect reduction than when the oxides of iron alone are present, *i.e.*, more carbon must be used in the furnace. The effect of magnesium oxide has been examined in some detail. With a mixture of the composition $Fe_2O_3+11MgO$ the ferric oxide is reduced directly to the ferrous state without passing through ferrosoferric oxide and wüstite, and solid solutions of ferrous oxide and magnesium oxide exist in equilibrium with oxoferrite in the stage corresponding with the second period of constancy of the composition of the gas phase when no foreign substance is present. This mixture of oxides must be regarded as a mixture of a magnesium ferrite, MgO,Fe_2O_3, with an excess of magnesium oxide. If, on the other hand, the ferric oxide is in excess, as in the mixture $2Fe_2O_3+MgO$, ferrosoferric oxide is present along with the magnesium ferrite in the first part of the reduction. R. Cuthill.

Equilibrium in systems the phases of which are separated by a semipermeable membrane. XX. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 401—410).—A mathematical discussion of the influence of pressure on the osmotic relationships of a system consisting of an aqueous solution separated from the vapour phase by a semipermeable membrane. H. F. Gillbe.

Precipitation laws. P. P. von Weimarn (Kolloid-Z., 1927, **43**, 26—30).—The author's three precipitation laws are summarised and discussed. The view is held that the laws are supported by the recent investigations of Odén (cf. A., 1926, 678). L. L. Bircumshaw.

Equation of state of solid substances. IV. Heats and pressures of evaporation, sublimation, and melting in the neighbourhood of absolute zero, and Nernst's so-called heat theorem. J. J. van Laar (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 383—400).—Polemical. The Nernst theory is invalid for all cases except that of the equilibria between two solid phases at very low temperatures. H. F. Gillbe.

Source of error in conductivity measurements. F. A. Smith (J. Amer. Chem. Soc., 1927, **49**, 2167—2171).—Conductivity values determined by the use of cells with differently-disposed electrodes agree only for that range of conductivity which corresponds with that of the potassium chloride solution used to determine the cell constants (cf. Washburn, A., 1917, ii, 10). S. K. Tweedy.

Conductivity of strong electrolytes in dilute solutions. P. Debye (Trans. Faraday Soc., 1927, **23**, 334—340).—Theoretical. The interionic attraction theory offers an adequate explanation of Kohlrausch's square-root law, provided two factors are taken into account. The first is the variation in dissymmetry of the charge density in the ionic atmosphere, as the ion moves under the influence of an electric field, in solutions of different concentration. It may be shown that, as a result of the finite time of relaxation responsible for this dissymmetry, the ion is acted on by a force which tends to decrease its velocity, and that this apparent frictional force increases with increasing velocity. The second factor, which also tends to increase the frictional force on the ion, is a cataphoretic effect, due to the movement of the ion in a solvent containing ions. M. S. Burr.

Ionisation of some typical strong electrolytes. D. A. MacInnes and I. A. Cowperthwaite (Trans. Faraday Soc., 1927, **23**, 400—404).—Transference and conductance measurements have been made on nitrates and chlorides in $0{\cdot}1N$ solutions, and the results indicate that, if the alkali chlorides and hydrochloric acid are completely dissociated, then nitric acid and ammonium nitrate are also of this class. Sodium, potassium, and silver nitrates, however, must be partly associated. M. S. Burr.

Revision of the conductivity theory. L. Onsager (Trans. Faraday Soc., 1927, **23**, 341—349).—The Debye–Hückel theory of the conductivity of strong electrolytes may be modified by taking into consideration the Brownian movement of the ions. A knowledge of the ionic radius then becomes unnecessary and all arbitrary constants are eliminated from the limiting formula. When Λ is plotted against $\sqrt{n\mu}$, where n is the sum of the valencies

of the two ions and μ the concentration, deviations at higher concentrations from the limiting slope at zero concentration probably indicate association.
M. S. Burr.

Mobilities of the elementary ions in methyl alcohol. H. Hartley and H. R. Raikes (Trans. Faraday Soc., 1927, **23**, 393—396).—The mobilities of all the univalent and most of the bivalent ions in methyl alcohol at infinite dilution are tabulated and compared with those in water at 25°. The general relationships are the same in both solvents, although the relative mobility of the ions in the two solvents is not constant. For the bivalent ions the value is approximately unity, as is the case for lithium. Applying Stokes' law, the ionic radii in water and methyl alcohol are compared with one another, and also with the effective ionic radii in the crystal lattice as determined by other investigators. The radii of all ions in methyl alcohol are greater than in water. The fact that the radii in water of several of the alkali and halide ions appear to be smaller than their effective radii in the lattice throws doubt on the absolute values of the ionic radii obtained by these means.
M. S. Burr.

Ionic mobilities in non-aqueous solvents. H. Ulich (Trans. Faraday Soc., 1927, **23**, 388—393).—According to Walden the product of the mobility l of a large ion, which may be regarded as not solvated because of its size, and the viscosity η is a constant and independent of the solvent. This is shown to be true for a number of solvents, including water, in the case of certain large organic ions such as the tetramethyl- and tetraethyl-ammonium ions and the picrate ions. On the assumption that Stokes' law holds, and that solvation is indicated when the product $l\eta$ is not constant, the number of molecules of solvent per ion has been calculated for the alkali and halide ions in different solvents and the results are tabulated.
M. S. Burr.

Debye–Hückel theory. H. Hartley and R. P. Bell (Trans. Faraday Soc., 1927, **23**, 396—400).—Examination of a large number of conductivity data in organic solvents shows that, in general, the Kohlrausch square-root relation is confirmed in dilute solution. This is in accordance with the Debye–Hückel theory. A further test of the latter may be applied by calculating b, the harmonic mean of the ionic radii, from the Debye–Hückel equation, and comparing it with the value calculated on the assumption that, at infinite dilution, the motion of the ions obeys Stokes' law. Divergences between the two values for solvents with dielectric constants less than 20 are rather large, but the approximate agreement among the remainder is regarded as evidence of the essential correctness of the Debye–Hückel theory. The results also show that conformity to the square-root law is no guarantee that the conductivity–concentration curve will be in accordance with Debye's equation. This may arise from incomplete ionisation.
M. S. Burr.

Conductivity of acids and salts in liquid ammonia. F. A. Smith (J. Amer. Chem. Soc., 1927, **49**, 2162—2167).—Solutions of amides, imides, etc., and of their monoalkali derivatives were examined at −33·5° (cf. this vol., 1023). Values of Λ_∞ are calculated by Kraus and Bray's method. Except in the case of succinimide, the salt is always a better conductor than the corresponding acid, although the difference is small for the "strong" acids which probably form ammonium salts. Mercury succinimide has a very low conductivity. The conductivity of ammono-carbonic acids and of their alkali salts increases with de-ammonation of the acid and decreases with polymerisation. Sulphur nitride behaves as a typical binary electrolyte; this compound is the mixed "anammonide" of ammonosulphurous and ammonothiosulphuric acids, and it probably dissociates in ammonia solution into the two anammonous radicals which on ammonation would give these acids.
S. K. Tweedy.

Electrolytic transference of water, true transference numbers, ionic mobilities, and water sheaths of the ions. H. Remy (Trans. Faraday Soc., 1927, **23**, 381—388).—True transference numbers have been calculated from the available data for the electrolytic transference of water in normal aqueous solutions of inorganic electrolytes. A comparison of solutions of homologous types shows that the product of the true mobility of an ion and the viscosity of the solution varies much less from solution to solution than the product of the apparent mobility and the viscosity. This applies similarly to the quotient of the mobility and the coefficient of conductivity. On the assumption that large organic ions do not carry water sheaths (cf. von Hevesy, A., 1916, ii, 594; Lorenz, *ibid.*, 312), values have been deduced for the amount of water carried by chlorine and bromine ions in normal solutions of aniline and *p*-toluidine hydrochloride and hydrobromide. Hence the absolute values for the number of water molecules carried by hydrogen, alkali, and alkaline-earth metals, iodine, and also some small organic ions have been determined and the results tabulated.
M. S. Burr.

Electrolytic conduction of potassium through glass. V. Zworykin (Physical Rev., 1926, [ii], **27**, 813).—Burt's experiments on the introduction of sodium into a thermionic vacuum tube by electrolysis have been extended to potassium. When a soda–potash glass is immersed in potassium nitrate, the metal introduced is primarily sodium; the glass is enriched in potassium and becomes brittle. With potash glass, potassium passes into the tube without corroding or embrittling the glass.
A. A. Eldridge.

Ionic mobilities in mixed crystals and their relationship to those in the pure salts. C. Tubandt, H. Reinhold, and W. Jost (Z. physikal. Chem., 1927, **129**, 69—78).—A quantitative method of expressing the degree of interlocking between the various components in a mixed crystal has been derived by comparing the ionic mobilities of the pure salts with those of the mixed crystals, as calculated from measurements of conductivity and of transport number. From the relationship between the mobilities it is possible to determine the extent to which the diffusion coefficients obtained from diffusion measurements represent the true diffusion coefficients of the pure components.
H. F. Gillbe.

Effect of temperature on diffusion potentials. E. B. R. Prideaux (Trans. Faraday Soc., Sept., 1927, advance proof).—From the ionic mobilities of a series of univalent electrolytes, it is shown that the temperature coefficients of the diffusion potentials are small and possibly zero; this is attributed to the tendency towards equalisation of the mobilities of anion and cation as the temperature is raised. Measurements of the diffusion potentials at 18° and 25° and over the concentration range from 0·1 to 0·01N, using a flowing junction, are in agreement with this view. For univalent electrolytes of varying character the observed change in diffusion potential is less than 0·5 millivolt. For acetic acid, the increase in the diffusion potential with the temperature is larger, amounting to 0·7 millivolt between 18° and 25°. G. A. Elliott.

Cells of the standard-cell type with low *E.M.F.* W. C. Vosburgh (J. Amer. Chem. Soc., 1927, 49, 2222—2229).—The *E.M.F.* of the cells $(Cd+Pb)Hg|CdCl_2,2{\cdot}5H_2O$ (sat. soln.)$|CdCl_2,2{\cdot}5H_2O+PbCl_2$ (sat. soln.)$|Hg(Pb)$ and $(Cd+Pb)Hg|CdI_2$ (sat. soln.)$|CdI_2+PbI_2$ (sat. soln.)$|Hg(Pb)$ were measured at 5° intervals between 15° and 40° over a period of several months. The former cell is the more reproducible, but exhibits a transition point at 26·2°. The *E.M.F.* of the corresponding cells containing pure cadmium amalgam are given by $E=0{\cdot}13759-0{\cdot}000193(t-25)-0{\cdot}0000012(t-25)^2$ and $E=0{\cdot}0996+0{\cdot}000235(t-25)-0{\cdot}0000002(t-25)^2$, respectively. The former equation gives values in slight disagreement with those of Obata (Proc. Phys. Math. Soc. Japan, 1921, [iii], 3, 64, 136) and of Taylor and Perrott (A., 1921, ii, 303). The *E.M.F.* of the corresponding cells with pure metal electrodes are given by $E=0{\cdot}1824-0{\cdot}000453(t-25)-0{\cdot}0000012(t-25)^2$ and $E=0{\cdot}1444-0{\cdot}000025(t-25)+0{\cdot}0000002(t-25)^2$, whence for the reaction $Cd+PbCl_2+2{\cdot}5H_2O$ (in sat. soln.)$=CdCl_2,2{\cdot}5H_2O+Pb$, $\Delta F=-8417$ g.-cal., $\Delta S=-20{\cdot}9$ g.-cal./degree, and $\Delta H=-14{,}650$ g.-cal. at 25°, and for the reaction $Cd+PbI_2=CdI_2+Pb$, $\Delta F=-6664$ g.-cal., $\Delta S=-1{\cdot}15$ g.-cal./degree, and $\Delta H=-7008$ g.-cal. These values agree with the thermochemical data. None of these cells is suitable as a standard cell; their temperature coefficients are large and the iodide cells exhibit persistent hysteresis. S. K. Tweedy.

Electrical action due to the atomisation of a solution of a univalent electrolyte. A. Bühl (Ann. Physik, 1927, [iv], 83, 1207—1224).—The effects produced by the air spraying of solutions of electrolytes and the charged particles resulting thereby have been investigated. The number of charged particles depends on the concentration of the solution and the velocity of the air stream. The results are discussed in terms of Lenard's conception of the structure of the surface layers of liquids. W. E. Downey.

Dissolution velocity and the electrolytic solution pressure of lead and of bismuth. J. Gróh (Z. physikal. Chem., 1927, 128, 449—458).—The rate of exchange of lead between lead amalgams and aqueous solutions of lead nitrate has been measured by an electroscopic method. The rate of dissolution of lead from the amalgam increases with increase of the concentration of the lead nitrate solution: change of concentration from 0·01 to 0·1M increases the velocity about one hundredfold, but at higher concentrations the rate of increase diminishes. A method is described for measuring the velocity when the time of contact between the amalgam and the solution is a minimum. The mean velocity at 18°, calculated for a saturated amalgam, is 0·0051 g./cm.^{2}/sec. Qualitative observations with bismuth indicate that the velocity is greater than $1{\cdot}5\times10^{-5}$. H. F. Gillbe.

Electrochemical studies of titanium. E. D. Botts and F. C. Krauskopf (J. Physical Chem., 1927, 31, 1404—1419).—The preparation of titanium, its single potential, and its power of replacing other metals from salt solutions have been studied. The method of Nilson and Pettersson, as modified by Hunter (A., 1910, ii, 302), yielded crystalline titanium of 99·6—99·9% purity in pieces varying in size up to 5 g. The optimum conditions are described, and sodium is shown to be preferable to potassium, or to a mixture of both, as the reducing agent. Single potential measurements of titanium in 0·25M solutions of the trichloride and of the corresponding sulphate gave average values of 0·23 and 0·18 volt, respectively. The presence of hydrofluoric acid in the titanous solution increased the single potential by 0·22 volt, but additions of hydrochloric and sulphuric acids to the corresponding salt solution lowered it. Alkali salts having an ion in common with the titanium salt caused a slight increase. Replacement experiments do not agree with these measurements except in solutions of the fluorides, copper, silver, lead, and cadmium, but not cobalt, nickel, zinc, or iron, being replaced by titanium only from a solution of the respective fluoride. L. S. Theobald.

Helmholtz double layer related to ions and charged particles. E. F. Burton (Fourth Colloid Symposium Monograph, 1926, 132—144).—There appears to be mutual action of charged particles, and interaction of colloid particles and ions in solution; this opposes the view that within molecular distance of the surface there exists an electrically equivalent layer of opposite charge. Gouy's equations indicate that the thickness of the outer Helmholtz double layer decreases as the concentration of the electrolyte increases, the decrease for electrolytes of the same molar concentration being the greater the higher is the valency of the ions; if the ions have the same valency their concentrations remain proportional, but if they differ in valency their concentrations in the neighbourhood of the surface differ. Chemical Abstracts.

Thermodynamic *P.D.* at the boundary between two liquid phases. V. S. Vosnessenski and K. Astachov (Z. physikal. Chem., 1927, 128, 362—368).—A method is described for measuring the *P.D.* at the interface between two liquid phases in which various electrolytes are dissolved. If the partition coefficient of the electrolyte be constant, the *P.D.* is constant at moderate concentrations. At concentrations above about 0·5N the *P.D.* remains constant, even although the partition coefficient undergoes change. The partition of the cations sodium, potassium, and hydrogen is in the same order as that of their degree of hydration, and a similar relation probably obtains for the commoner anions.

H. F. Gillbe.

Experimental investigation of the theory of local currents. M. Centnerszwer and M. Straumanis (Z. physikal. Chem., 1927, 128, 369—393).—Simultaneous measurements have been made of the electrode potential, current strength, and internal resistance of typical polarisable cells. The logarithm of the current strength at constant anode potential decreases in direct proportion to the time, a conclusion which follows from Boguski's law. With the cell short-circuited, rise of temperature produces a logarithmic increase of the current strength. On anodic dissolution of a metal in acid its potential increases; increase of external resistance causes the anode to become more negative, whilst increase of internal resistance has the reverse influence. With increase of current strength the potential of the anode increases up to a limiting value dependent on the electrolyte. The velocity of dissolution of an anode in different acids or in the same acid at different concentrations increases as the equivalent conductivity of the solution increases and is the greater the smaller the overvoltage at the cathode. The properties of tin, cadmium, and iron anodes are very similar to those of zinc. H. F. Gillbe.

Passivation of metals by anodic polarisation. G. Grube (Z. Elektrochem., 1927, 33, 389—399).—Theories of passivity are briefly reviewed and recent work, mainly by the author and his collaborators, on the anodic passivation of metals in alkaline solutions is discussed (cf. A., 1921, ii, 49; 1922, ii, 570; 1923, ii, 118; 1926, 362, 687; B., 1923, 233). At low current densities iron, cobalt, manganese, and lead dissolve anodically in bivalent form in solutions of sodium or potassium hydroxides, but with increasing current density the polarisation eventually increases sufficiently to permit oxidation of the bivalent ions to the tervalent or quadrivalent stages. Relatively insoluble intermediate oxides, such as Fe_3O_4, Co_3O_4, and Mn_3O_4, can then be deposited as a film on the anode. Passivity then ensues, the polarisation increasing rapidly and higher oxides being formed, which may decompose, giving oxygen evolution, or, at least in part, dissolve in the electrolyte as in the formation of ferrates and manganates. The behaviour of chromium is similar, but passivation occurs at an exceptionally low current density. Anodic passivity in acid solutions, however, does not seem to be of this mechanical type. An anomaly in the behaviour of chromium in acid solutions is discussed. H. J. T. Ellingham.

Corrosion of metals as an electrochemical problem. A. Thiel [with J. Eckell] (Z. Elektrochem., 1927, 33, 370—386).—One side of a disc of specially purified zinc was exposed to 0·5*N*-hydrochloric acid, which was vigorously stirred, and, when the rate of dissolution of the metal had become practically constant, the disc was connected through an external variable resistance with a plate of a nobler metal (platinum, copper, lead, tantalum, or silver) dipping into the same solution. The current passing through the system, of which the zinc forms the anode, was measured under various conditions, and changes in the rate of dissolution of the zinc could be followed from measurements of the rate of hydrogen evolution from the complete cell. In accordance with the "local element" theory of corrosion, it was found that with given external resistance lower currents were obtained when cathode metals of higher hydrogen overvoltage were used. Also the single potentials of the various cathode metals combined with the zinc are of the order of magnitude to be expected from known overvoltage data. If v_0 is the rate of dissolution of the zinc before connexion with the other metal and v the velocity when so connected, then if v_e is the rate of "enforced" dissolution which corresponds with the current passing under the latter conditions, it is found that $v_0+v_e=v+\Delta$, where Δ is a positive quantity named the "difference effect." Provided that v_0 exceeds a certain critical value, $\Delta=kI$, where I is the current and k is a constant independent of the nature of the cathode metal. For low values of v_0, however which can be obtained by using a polished zinc surface, k is no longer constant, but falls towards zero as v_0 is diminished. Experiments with aluminium in *N*-sodium hydroxide solution yielded similar results, but the value of k is notably greater in this case. A negative value of Δ for aluminium in dilute hydrochloric acid is being further investigated. The results described give strong support to the local element theory of corrosion of metals, but it is pointed out that, when conditions are such that hydrogen evolution from the surface of the dissolving metal is very rapid, the rate of diffusion of hydrogen ions towards that surface can become a determining factor, so that eventually the phenomenon passes over into that described by Nernst and Brunner (1904) for the dissolution of other solid substances in acids. The difference effect is attributed to the retardation of diffusion of hydrogen ions towards the metal surface caused by accumulation of salts of the dissolving metal in that region. Provided that v_0 is high enough for diffusion to be the ruling factor, Δ may be expected to be proportional to I which determines v_e and hence the extent of this accumulation of metallic salt. Measurements of the single potential of zinc when combined with a platinum cathode in 0·5*N*-hydrochloric acid show an increasing ennoblement as the current increases, which corresponds with an increasing concentration of zinc ions at the metal surface. Wide variations in the values of v_0 observed with discs of zinc cut from the same rod are found to be accompanied by corresponding variations in the microscopic appearance of the metal after corrosion. An exceptionally pure sample of zinc showed no corrosion during 2 hrs. in 0·5*N*-hydrochloric acid, but scratching with a diamond led to formation of hydrogen bubbles along the crevice, a result which is attributed to decreased hydrogen overvoltage at an irregular surface. Palmaer's view (B., 1926, 589) that the increased rate of dissolution of iron containing graphite can be attributed to a low overvoltage of the latter is disputed and conclusions of Centnerszwer and Zablocki (A., 1926, 1010) as to the mechanism of the dissolution of aluminium in acids are criticised. H. J. T. ELLINGHAM.

Photo-voltaic cells. C. W. TUCKER (J. Physical Chem., 1927, **31**, 1357—1380; cf. Case, B., 1917, 1102; Garrison, A., 1923, ii, 728; 1924, ii, 339, 401).—The cuprous oxide and silver halide photo-voltaic systems have been studied in cells of the type—illuminated metal|oxide or halide–solution–oxide or halide|metal. Illuminated electrodes of cuprous oxide deposited in the meshes of platinum gauze gave small but definite photo-voltages. In reducing solutions, photochemical reduction of cuprous oxide tends to occur, and oxidation in oxidising solutions. Substitution of copper for platinum has a specific influence on the behaviour of the copper–cuprous oxide electrode, and cells with copper in the form of gauze show the so-called "Minchin effect," *i.e.*, the illuminated electrode is at first anodic, changing to cathodic on continued illumination. The initial anodic effect is more permanent with an oxidising than with a reducing solution in the cell. Removal of the light results in an increase in cathodic tendency and the *P.D.* between the two cell electrodes slowly returns to zero. When the gauze is replaced by sheet copper, the anodic effect is magnified as the local cell formation is decreased, but the voltage maximum indicates that local cell action is still appreciable and that sign reversal of the electrodes would still occur with continued illumination. The anodic effect is now greatest in reducing solutions. The general form of time–voltage curve is independent of the solution used. The behaviour of platinum|silver halide electrodes closely resembles that of the copper|cuprous oxide electrodes, and the photo-voltage with silver chloride is, in general, greater than that with the bromide, which, in turn, is greater than that with the iodide. The silver|silver halide electrodes have also been examined. The above results are explained in terms of local cell formation, which will be at a minimum on the illuminated surface when the photosensitive substance on this surface is present as a uniform layer; in these circumstances the exposed electrode is the anode. On the other hand, when the layer is non-uniform, local cells are set up in the illuminated electrode, which becomes the cathode on continued illumination. When the local cells are completely reversible, the behaviour of the electrode is determined by the oxidising or reducing nature of the cell solution; it is a cathode in the former and in a neutral solution, and an anode in a reducing solution.

The work of previous investigators is summarised and discussed. L. S. THEOBALD.

Velocity of coupled reactions. J. A. CHRISTIANSEN (Z. physikal. Chem., 1927, **128**, 430—438).—The method of instantaneous velocities is shown to be applicable to the kinetics of reaction. For the velocity of a series of consecutive reactions, without side reactions, an expression has been derived which is in agreement with thermodynamic considerations if with Brönsted the assumption be made that the probability of reaction is proportional to the product of the activity coefficients of the reactants and a divisor f_x which is common to the two opposing reactions. For a special case of consecutive reactions accompanied by side reactions an expression for the velocity has been deduced, and is discussed in its application to the reactions between hydrogen peroxide and the bromine ion and molecule.

H. F. GILLBE.

Thermal decomposition of hydrogen peroxide vapour. L. W. ELDER, jun., and E. K. RIDEAL (Trans. Faraday Soc., 1927, **23**, 545—552; cf. Hinshelwood and Prichard, J.C.S., 1923, **123**, 2726).—An apparatus for the measurement of the rate of decomposition of hydrogen peroxide vapour at constant volume is described. By comparison of the vapour pressure of the original mixture, obtained from a hydrogen peroxide preparation of approximately 60%, with that of the resulting water vapour, it has been shown that hydrogen peroxide vapour, under about 85 mm. pressure at 85°, consists of simple unhydrated molecules. The decomposition bulb was made of quartz, since glass gives no reproducible results. The thermal decomposition at 85° is a reaction of zero order, inhibited by molecular oxygen, which brings the reaction to an end when only about 20% of the hydrogen peroxide is decomposed. The inhibiting reaction is stronger still at 95°. On a platinum surface the reaction is apparently unimolecular, and is probably determined by the rate of diffusion through an adsorbed or dissolved layer of oxygen. The reaction on a mercury surface consists of a preliminary direct oxidation of mercury to mercurous oxide, followed by oxidation of the latter to mercuric oxide, with simultaneous liberation of an equivalent amount of atomic oxygen which oxidises a further quantity of hydrogen peroxide. The mercuric oxide is not reduced by hydrogen peroxide vapour. A method is described for the preparation of pure concentrated hydrogen peroxide from "Hyperol."

M. S. BURR.

Thermal decomposition of hydrogen peroxide. F. O. RICE and O. M. REIFF (J. Physical Chem., 1927, **31**, 1352—1356).—The decomposition of pure aqueous solutions of hydrogen peroxide, prepared by the method of Kilpatrick, Reiff, and Rice (this vol., 120), and of commercial solutions at 80·2° has been studied. The rate of decomposition of the former, freed from suspended matter and heated in vessels with smooth walls, is very slow. Pure, aqueous solutions, free from inhibitors but not from dust, give a linear decomposition curve; addition of chlorides, alkalis, and inhibitors gives curves which are often unimolecular in type. Merck's perhydrol, and pure solutions to which were added inhibitors such as barbituric or uric acid, or benzamide, show an initial induction period on the decomposition curves. The catalysis of hydrogen peroxide by the iodine–iodic acid couple (Bray, A., 1921, ii, 629) appears to be a heterogeneous reaction occurring on the surface of dust particles. The ordinary decomposition of hydrogen peroxide also takes place on these surfaces and on the walls of the vessel, and an inhibitor evidently acts by poisoning the surface.

L. S. THEOBALD.

Thermal dissociation of carbonyl chloride. H. INGLESON (J.C.S., 1927, 2244—2254).—The thermal dissociation of carbonyl chloride has been investigated between 357° and 480° in quartz vessels. Trustworthy results could not be obtained in glass, as it is attacked by the chlorine produced. The heat of reaction at constant volume is 25,500 g.-cal. at a mean temperature of 416°. A linear relation is found between the reciprocal of the absolute temperature and the logarithm of the reaction velocity constant. Christiansen's view that the decomposition is accelerated by the products (A., 1923, ii, 62) is supported qualitatively (cf. Atkinson, Heycock, and Pope, J.C.S., 1920, **117**, 1410). C. W. Gibby.

Oxygen required for the propagation of hydrogen, carbon monoxide, and methane flames. G. W. Jones and G. St. J. Perrott (Ind. Eng. Chem., 1927, **19**, 985—989).—The minimum proportion of oxygen necessary to propagate the flames of methane, hydrogen, and carbon monoxide in admixture with varying proportions of nitrogen was determined. With less than 12% of oxygen no methane–nitrogen mixture was combustible, but for sufficiently high proportions of hydrogen and carbon monoxide (4% and 14%, respectively) the minimum oxygen concentration is 5—6%. The presence of carbon dioxide raises the oxygen concentration necessary. Helium has a similar effect on the combustion of hydrogen. C. Irwin.

Inflammation of mixtures of the paraffins and air in a closed spherical vessel. G. B. Maxwell and R. V. Wheeler (J.C.S., 1927, 2069—2080).—The pressures in mixtures of air with the first five members of the paraffin series developed on ignition centrally in a spherical bulb have been measured, and are compared with the calculated values. Discrepancies are probably due to errors in specific heat and equilibrium data. The mean temperature of the explosion is the main factor in determining the mean rate of development of pressure. C. W. Gibby.

Influence of hydrogen on two homogeneous reactions. C. N. Hinshelwood and P. J. Askey (Proc. Roy. Soc., 1927, A, **116**, 163—170; cf. this vol., 26, 212).—If a molecule in a gaseous reaction is activated by collision, transformation may follow immediately, or it may be delayed until the molecule passes through a suitable internal phase. If the transformation is immediate, the reaction is kinetically bimolecular, but if there is a time lag, then, as Lindemann has indicated (Trans. Faraday Soc., 1922, **17**, 599), the reaction appears to be unimolecular. The time lag after activation is considered to be most probable when the structure is complex and the energy distributed among a number of degrees of freedom, whilst its absence is to be expected when the mechanism of activation is very simple. The reactions involved in the decomposition of propaldehyde and dimethyl and diethyl ether are unimolecular at higher pressures, but betray their dependence on molecular collisions by decreasing in rate when the pressure of the reacting gas is reduced below a certain limit. In the case of the two ethers, it has been found (*loc. cit.*) that the rate of decomposition maintains its unimolecular character at low pressures if sufficient hydrogen is present, and it is now shown that the decomposition of propaldehyde is similar, but that the bimolecular decomposition of acetaldehyde is influenced less, and in a different way, by hydrogen. These results are consistent with the assumption that the activation of acetaldehyde involves only a few degrees of freedom, whilst that of propaldehyde is a more complex process, and that in the propaldehyde process a time lag exists between activation and transformation. L. L. Bircumshaw.

Esterification in mixed solvents. B. W. Bhide and H. E. Watson (J.C.S., 1927, 2101—2107).—The velocities of esterification of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene or petroleum have been measured in the presence of hydrochloric acid as catalyst. The velocity coefficients given by the formula of Goldschmidt and Udby (A., 1907, ii, 852), $kt=(r-a)\log a/(a-x)-x$, are satisfactory and increase on dilution of the alcohol in an approximately hyperbolic relation with the composition of the solution. Conductivity and viscosity measurements show that ionisation of the catalyst has no influence on the velocity, and it is suggested that the latter depends on the molecular ratio of catalyst to alcohol. C. W. Gibby.

Coefficient of hydrolysis of ethyl acetate by sodium hydroxide. (Miss) E. M. Terry and J. Stieglitz (J. Amer. Chem. Soc., 1927, **49**, 2216—2222).—The experiments were carried out in approximately 0·01*N*-sodium hydroxide solution, the apparatus being an improvement of that described by Reicher (A., 1885, 1034). The coefficient is 6·76 (±0·75%) at 25° (concentrations in mol./litre) and increases 0·045 per 0·1°. Improved experimental technique is described in detail. S. K. Tweedy.

Hydrolysis of ethyl acetate. W. T. Gooch (J. Amer. Chem. Soc., 1927, **49**, 2257).—Intensity variations of diffused daylight do not influence the rate of hydrolysis of ethyl acetate in aqueous sodium hydroxide at 25°. S. K. Tweedy.

Kinetics of the hydrolysis of glyoxal tetra-acetate. A. Skrabal and E. Gitschthaler (Z. physikal. Chem., 1927, **128**, 459—471).—The hydrolysis constants of the hydrolysis of glyoxal tetra-acetate in neutral, acid, and alkaline solution are for the first stage 0·000138, 0·01640, and 2740, and for the second stage 0·000069, 0·00820, and 1370, respectively. The relationship between the constitution of a number of esters of acetic acid and their rates of hydrolysis is discussed. H. F. Gillbe.

Kinetics of oxime formation. A. Ölander (Z. physikal. Chem., 1927, **129**, 1—32).—The quantity of iodine reduced in the iodometric determination of hydroxylamine is not directly proportional to the amount of the latter. The relation between them has been ascertained for quantities of hydroxylamine up to 5·5 mg. The dissociation constant of hydroxylamine at 20° is $1{\cdot}07\times10^{-8}$, and that of dibromocresolsulphonephthalein in presence of 0·1*M*-phosphate is $7{\cdot}4\times10^{-7}$. Free hydroxylamine reacts slowly with acetone, but the hydroxylammonium ion reacts comparatively quickly and reversibly; for the reaction between the ion and acetone the bimolecular velocity coefficient is 84. The additive reaction product decomposes reversibly with the formation of acetoxime and water; the unimolecular velocity constant of the reverse reaction is 0·07. The optimum p_H, at 20° and 0·003*M* solution, is 4·5 for the formation of the oxime and 2·3 for its decomposition; the forward reaction is complete only at $p_H > 7$. The velocity and degree of completeness of the reaction have been determined in 0·003*M* solution in presence of acid at various concentrations. H. F. Gillbe.

Reactions in the solid state at high temperatures. II. Reaction velocity of exothermic changes. W. Jander (Z. anorg. Chem., 1927, **166**, 31—52).—Extension of the theory that reactions in binary mixtures of solids are governed by the ordinary laws of diffusion (this vol., 736) to solids between which an exothermic reaction occurs shows that the percentage reaction, x, is related to the time, t, by the formula $1-[(100-x)/100]^{1/3}=2{\cdot}3\{\log t+\log b'-2\log[1-\sqrt[3]{(100-x)/100}]\}/c$. Here b' measures the diffusivity at the start of the reaction, and c is a function of x and the temperature, T. This equation is in good agreement with the experimental results for mixtures of barium carbonate and tungstic anhydride and of silver sulphate and lead monoxide. Both b' and the velocity coefficient at the final stage of the reaction are related to the temperature by an exponential expression. R. Cuthill.

Application of Tammann's method of thermal analysis to reactions between solid phases. J. Guillissen (Bull. Acad. roy. Belg., 1927, [v], **13**, 233—238).—The application of Tammann's method (A., 1926, 921), *i.e.*, comparison of temperature–time curves of the initial reaction mixture and of the reaction product, to the study of the formation of certain ferrites not yielding a trustworthy indication of the temperature of commencement of reaction, an attempt has been made to increase the sensitivity of the method by using a Le Chatelier–Saladin differential galvanometer and constructing a temperature–temperature difference curve.

The reaction between barium carbonate and ferric oxide commences at about 800°. An equimolar mixture, when heated for 3 hrs. at 830° in a slow current of air, undergoes a change in weight corresponding with the formation of 87·5% of barium ferrite. The direct addition of barium oxide to ferric oxide occurs at about 300°. Owing to secondary disturbances no definite indication of the temperature of reaction between calcium carbonate and ferric oxide could be obtained. The reaction certainly occurs at relatively low temperatures.

J. S. Carter.

Temperature of formation of zinc ferrite from the solid constituents. J. Guillissen and Richard (Bull. Acad. roy. Belg., 1927, [v], **13**, 238—240; cf. preceding abstract).—Interaction between zinc and ferric oxides commences at 620—650°. On account of the stability of zinc ferrite towards dilute acids the importance of considering its probable formation during the roasting of zinc blendes preparatory to an electrolytic process is emphasised. After being heated at 890° a mixture containing 34% of zinc oxide yielded only 8% of zinc oxide to an ammoniacal solution of ammonium chloride.

J. S. Carter.

Influence of diffusion of oxygen on the rate of combustion of solid carbon. J. T. Ward and J. B. Hamblen (Ind. Eng. Chem., 1927, **19**, 1025—1027).—A carbon block was burned in air and by very slow sampling the gas was drawn off from the carbon side of the gas film by a quartz capillary sealed into the end of the block. The analyses showed an average ratio of 28·07 mols. of oxygen to 100 mols. of nitrogen, carbon dioxide and carbon monoxide being returned as oxygen, as against an air ratio of 26·58. This is in accordance with the theory that the rate of the reaction $C+O_2=CO_2$ is limited by the rate of diffusion of oxygen through the gas film surrounding each particle of carbon. C. Irwin.

Corrosion of non-ferrous metals and alloys. T. S. Fuller (Proc. Amer. Soc. Testing Materials, [advance copy], 1927, No. 19, 1—18).—Modified procedures are given for the total immersion and alternate immersion tests. The spray test and the electrolytic test do not appear to be generally applicable.

Chemical Abstracts.

Corrosion fatigue of non-ferrous metals. D. J. McAdam, jun. (Proc. Amer. Soc. Testing Materials, [advance copy], 1927, No. 36, 1—26).—An examination of 18 non-ferrous metals and alloys with fresh and salt water. For nickel and Monel metal, the fully annealed and strain-hardened metal have the same "corrosion-fatigue limits," but this is not the case for copper–nickel alloys. The corrosion-fatigue limits of these alloys may depend chiefly on their electrode potentials. The stress-cycle curves for aluminium and for aluminium–manganese alloys give a corrosion-fatigue limit far below the endurance limit in air. Each metal and alloy appears to have an intrinsic corrosion-fatigue limit depending chiefly on the corrosion agent and the corrosion resistance of the metal. Possibly this limit depends on the ease of removal of atoms from the space lattice under the combined influence of electrolytic solution pressure and cyclic strain of the lattice.

Chemical Abstracts.

Passivity of iron mirrors. H. Freundlich, G. Patscheke, and H. Zocher (Z. physikal. Chem., 1927, **128**, 321—344).—The physical and chemical properties of iron mirrors on glass, produced by the thermal decomposition of iron pentacarbonyl, have been studied in their relationship to the problem of passivity. The mirrors are rendered passive by treatment with concentrated nitric acid, and are then in the same condition as ordinary passive iron. Mirrors maintained out of contact with air are considerably more active than those to which air has access, being readily dissolved by nitric acid; this activity is unaffected by carbon dioxide, nitrogen, or water. The passivity produced by contact with the atmosphere cannot be destroyed by placing the mirror in a vacuum, although in certain cases heating the mirror in a vacuum restores its activity. Similar conditions obtain for mirrors rendered passive by acids. Considerations of "vacuum activity" and "air passivity," together with observations of the brown film of insoluble matter which remains when an iron mirror is dissolved in acid, lead to a simple oxidation theory of the passive state. H. F. Gillbe.

Catalysis in homogeneous gas reactions. A. von Kiss (Chem. Weekblad, 1927, **24**, 466—471).—The modern theories of the relations between kinetic and internal energies of molecules and frequencies of molecular collisions and reaction velocities are considered in the discussion of the mechanism of catalysed reactions. If an unalterable energy of activation be postulated, it becomes impossible to understand the action of a "physical" catalyst, *i.e.*, of one which takes no part in the reaction; the effect of a chemical catalyst, on the other hand, is readily explained by the theory. S. I. Levy.

Acid and salt effects in catalysed reactions. X. Hydrolysis of ethyl acetate with acetic acid as catalyst. H. M. Dawson and W. Lowson (J.C.S., 1927, 2107—2114).—If the effect of the reverse reaction is neglected in the calculation of the true velocity coefficient for ester hydrolysis, correct values are obtained only at low concentrations of the ester.

The rate of hydrolysis of ethyl acetate in the presence of acetic acid has been measured and the velocity at various stages compared with the theoretical values. The catalytic coefficient for the hydrogen ion is calculated to be $1{\cdot}14\times10^{-4}$ at 25°. C. W. Gibby.

Significance of iso-catalytic data and the so-called protion theory of chemical reactivity. H. M. Dawson (J. Physical Chem., 1927, **31**, 1400—1403).—A reply to Bergstein and Kilpatrick (this vol., 214) and a criticism of their conclusions on the catalytic minimum point. The interpretation of observations on the reaction between acetone and iodine is also discussed (cf. Dawson, this vol., 320) and the factors determining minimum reaction velocity are considered in relation to the catalytic catenary. Further, it is shown that Rice's protion theory is at variance with established facts. L. S. Theobald.

Catalytic properties of mineral waters. II. The benzidine reaction of the Wiesbaden hot spring. L. Fresenius and H. Lederer (Z. anorg. Chem., 1927, **166**, 99—109; cf. this vol., 320).—Artificially prepared solutions containing no iron, but otherwise similar in composition to the water of the Wiesbaden hot spring, do not give the benzidine reaction unless ferrous hydrogen carbonate is added, or unless manganese is present and the water is made alkaline, in which case part of the manganese passes into a higher state of oxidation. Since the natural water is acid in reaction, its activity must therefore depend on the presence of iron. It is found, further, that the gradual loss of the ability to give the benzidine reaction which occurs on keeping the natural water runs parallel with an increase in the amount of ferric iron present, and a decrease to zero of that of the ferrous iron, and that the rate at which the activity is lost depends on the rate at which the dissolved carbon dioxide escapes. The disappearance of the activity must consequently be attributed to the oxidation of ferrous hydrogen carbonate with subsequent precipitation of the product. If there is present an acid which is able to form some ferric ions before settling out is complete, *e.g.*, hydrochloric acid when benzidine hydrochloride is used for the test, a positive reaction may be obtained in absence of any ferrous salt, unless there is also present some acid, such as tartaric acid, which forms a very stable complex with the ferric ion. Light exerts no appreciable effect on the loss of activity of the water, except in so far as it influences the rate at which carbon dioxide escapes. The present results thus confirm those of Simon and Kötschau (this vol., 843). R. Cuthill.

Activity of hydrogen. C. F. Holmboe (Z. komp. fluss. Gase, 1927, **26**, 17—19).—Hydrogen prepared from steam and iron is less efficient in catalytic hydrogenation than electrolytic hydrogen; possibly the latter is "activated." Chemical Abstracts.

Active nitrogen. III. Active nitrogen and the metals. E. J. B. Willey (J.C.S., 1927, 2188—2196).—The relative catalytic efficiencies of various metals for the destruction of active nitrogen have been determined by measuring the rise in temperature produced when the gas is passed over filaments of the metals. With platinum, iron, silver, zinc, tungsten, and molybdenum a linear relation was found between the rise in temperature and the rate of flow, but in the case of copper the rise in temperature was much greater. The decay process is bimolecular with respect to the active nitrogen, and the energy of active nitrogen is calculated to be 46,000 g.-cal. per g.-mol. It is considered that the mechanism of the process is the alternate formation and decomposition of the nitrides of the metals. C. W. Gibby.

Catalytic activity of metallised silica gels. V. N. Morris and L. H. Reyerson (J. Physical Chem., 1927, **31**, 1332—1337).—The hydrogenation of acetylene using silica gels metallised with platinum, palladium, and copper has been studied by the method employed in the case of ethylene (this vol., 839). Ethylene and ethane are both produced, the palladium-silica gel becoming active at 50°, the platinum gel at 100°, and the copper gel at 200°. Palladium is the better catalyst for the production of ethylene, regardless of the original mixtures used, whilst platinum favours the production of ethane. Further, as the ratio of acetylene to hydrogen increases from 1 : 10 to 3 : 1, the production of ethylene passes through a maximum. It is probable that the combined adsorptions of gel and metal produce a more satisfactory condition for the catalysis of ethylene formation than does the adsorption of either alone. The ready production of ethylene is noteworthy, especially in view of the work of Ross, Culbertson, and Parsons (A., 1921, i, 761). L. S. Theobald.

Adsorption of hydrogen and ethylene on a copper catalyst poisoned with carbon monoxide. C. W. Griffin (J. Amer. Chem. Soc., 1927, **49**, 2136—2145).—The above adsorption was investigated at 0° and 20° in the manner previously described (cf. A., 1923, ii, 842, 862). An increase of poison causes progressive decrease of adsorption at higher pressures, and an increase of adsorption at lower pressures, which, however, persists at higher pressures in the case of hydrogen than of ethylene. For either gas the smallest amount of poison causes the greatest increase or decrease of adsorption. The results possibly indicate that each poison molecule is adsorbed on a very active centre and thereafter takes up hydrogen or ethylene molecules to such an extent that the total adsorption at low pressures is greater than on the unpoisoned catalyst. The poison, however, prevents dissolution of the hydrogen in the copper, so that at higher pressures the adsorption appears to decrease when the catalyst is poisoned. This explanation is not readily deduced in the case of ethylene. The extra sorption at low pressures does not leave the gases activated.

S. K. Tweedy.

Catalytic combustion of ammonia in presence of alkaline surfaces. L. Andrussov (Z. anorg. Chem., 1927, **166**, 60—62).—The fact that the presence of alkaline surfaces in the catalytic oxidation of ammonia causes a quantitative yield of nitrites and nitrates, no nitrogen being produced, is readily explained by supposing that the nitroxyl formed as an intermediate stage in the oxidation (cf. B., 1927, 217) combines with the alkali, and is then oxidised to nitrite and nitrate, instead of breaking down with liberation of nitrogen. R. Cuthill.

Rapid catalytic processes in currents of gases and the oxidation of ammonia. V. L. Andrussov (Ber., 1927, 60, [*B*], 2005—2018; cf. B., 1926, 318).—The interaction of ammonia and oxygen when passed through heated platinum capillary tubes of varying length at 1100°±100° has been investigated. Even with very rapid currents of gas only traces of ammonia are present at the end of a sufficiently long capillary. If the capillary is sufficiently shortened, the great bulk of the ammonia is burnt immediately at the end of the capillary to nitrogen. A flame cone is then formed which, under certain conditions, can have a very unstable existence within the capillary. Under favourable conditions the cone is very stable and cannot be destroyed by great increase in the velocity of the gas. If oxygen is deficient, it does not appear. Nitric oxide is comparatively stable in the cone, but possible decomposition to the extent of 10% must be assumed, so that the actual change at the wall of the capillary is certainly 10—20% greater than is indicated by the yield of nitric oxide. The dependence of concentration distribution on the velocity of the gas current is examined in detail. The quantity of undecomposed ammonia increases very little with increasing velocity and considerable quantities of ammonia escape combustion on the explosion zone only with short capillaries. With excess of oxygen (more than 1·5—1·7 mols. O_2 to 1 mol. NH_3) the production of nitric oxide is little influenced by the initial concentration. At very great dilution ($O_2/NH_3>5$) slight diminution of the yield is observed, corresponding with a broadening of the reaction zone, but, in such cases, the mean temperature of the mixture is considerably lowered by the cooling effect of the excess of gas. With mixtures poor in oxygen the production of free nitrogen is still considerable, and undecomposed ammonia is first observed with an initial gas ratio $O_2/NH_3=1{\cdot}3$. The thermal decomposition achieves increased importance and becomes more comparable with the actual combustion. The co-existence of free hydrogen and oxygen if the initial gases are in the ratio $O_2/NH_3<0{\cdot}8$ is remarkable. H. Wren.

Decomposition of ammonia on iron catalysts. C. H. Kunsman (Science, 1927, 65, 527—528).—The catalytic activity of iron catalysts (unpromoted iron catalyst, iron catalyst promoted with aluminium and potassium oxides, catalyst poisoned by tin) used in the synthesis of ammonia was investigated by the decomposition of ammonia on specially prepared surfaces. Values of E in Arrhenius' expression $Ae^{-E/RT}$ for the rate of chemical change are 38,000—42,000 g.-cal. per g.-mol. for the various catalysts, although the ratio in catalytic activity was 18·1. It is concluded that the primary effect of promoters on the iron catalysts is to increase the number of atoms on which decomposition takes place; that the effect of heat-treatment and poisoning is to decrease that number; and that poisoning, heat-treatment, or promoter action does not sufficiently alter the quality or nature of the atoms on which the reaction takes place to cause an appreciable change in the heat of activation.

A. A. Eldridge.

Low-temperature oxidation at charcoal surfaces. IV. Active areas for different acids and relative rates of oxidation. W. M. Wright (J.C.S., 1927, 2323—2330; cf. A., 1925, ii, 806; 1926, 582).—The rates of oxidation of formic, oxalic, malonic, and aminoacetic acids on charcoal surfaces, and the effect of poisoning by hexoic acid have been determined. Identical amounts of poison are required to inhibit the oxidation of all the acids, and the effective area is 4—8% of the total area. All except malonic acid are oxidised more rapidly on promoted charcoal prepared from sugar, carbamide, and ferric chloride. The depolarising capacities of the acids were measured, and follow the same order as the velocities of the reactions. C. W. Gibby.

Chemical effect of electric discharge in ethane. S. C. Lind and G. Glockler (Amer. Electrochem. Soc., Sept., 1927, advance copy, 9 pp.).—Ethane was submitted to a silent discharge in a Siemens ozoniser through which it was circulated continuously by means of an all-glass magnetic pump. Most of the ethane is decomposed in 3 hrs., yielding a gas consisting mainly of hydrogen, methane, and propane with smaller amounts of higher homologues, but as much as 45—55% of the ethane is converted into a very viscous, reddish-yellow oil, d 0·862, n^{20} 1·490. This oil has the composition C 85·48%, H 13·09%, and its apparent mol. wt. from f.-p. depression of benzene is 467. It readily forms substitution products with bromine. The production of 5 g. of oil requires about 10 kw.-hrs. The action of the silent discharge on ethane is compared with that caused by α-particles from radon (cf. A., 1926, 1077).

H. J. T. Ellingham.

Nature of the activating radiation in photochemical action. W. Taylor and A. Elliot (Trans. Faraday Soc., 1927, 23, 583—592; cf. this vol., . 216).—Actinic extinction curves have been obtained by allowing light filtered through various concentrations of chlorine to activate a mixture of hydrogen and chlorine. The results can be accounted for on the assumption that the efficiency is independent of the frequency throughout the range 3500—5500, and that, for a given frequency, the activation is directly proportional to the light intensity. There is thus no evidence that there are two different types of absorption, "actinic" and "thermal," nor that activation is due to a few superposed bands, rather than to the whole general absorption band. This latter may account for the failure to separate isotopes of chlorine by photochemical methods, since the general absorption is continuous. The chlorine molecule absorbs the same actinic radiation when in the gaseous state as when dissolved in carbon tetrachloride. M. S. Burr.

Action of light on chlorine. G. B. Kistiakowsky (J. Amer. Chem. Soc., 1927, **49**, 2194—2200).—Intensive drying of chlorine has no appreciable influence on the structure of its absorption spectrum or on the total amount of light energy absorbed. Less than 5% of the latter is re-emitted as fluorescence. It is difficult to reconcile these data with those theories requiring the presence of foreign molecules for the primary photochemical process in chlorine. It is suggested that chlorine is dissociated into atoms on absorption of light energy in the region of continuous absorption independently of its degree of purity; water is assumed to have a catalytic influence on the rate of recombination of the atoms and, therefore, also on the rate of thermal dissociation of chlorine molecules. S. K. Tweedy.

Function of water vapour in the photosynthesis of hydrogen chloride. B. Lewis (Nature, 1927, **120**, 473—474).—The Nernst atomic chain provides the most plausible mechanism for the photochemical union of hydrogen and chlorine. The chain cannot be initiated in the absence of water vapour, but there is no evidence that water vapour functions in the chain itself. Two mechanisms for the interaction of moist hydrogen and chlorine in visible light, and of dry hydrogen and chlorine in ultra-violet light are considered. The mechanism of the moist reaction is considered as involving a primary dissociation of the chlorine molecules under the influence of water vapour, followed by an atom chain—that of Nernst or of Thon. The dry reaction is regarded as involving activation of a chlorine molecule and its interaction with hydrogen molecules to form 2 mols. of hydrogen chloride. If water has a rôle in the chain mechanism, no chains should be propagated when a dry mixture of hydrogen and chlorine is exposed to α-radiation. A. A. Eldridge.

Photosynthesis with ammonia. D. Burk (J. Physical Chem., 1927, **31**, 1338—1351).—Possible photochemical reactions between ammonia and various carbon compounds, including carbon dioxide, formic acid, formaldehyde, and dextrose, have been investigated. Sunlight condensed through 30 cm. lenses in combination with coloured inorganic catalysts was used, the exposures being made in very thin glass vessels. Some 500 experiments were made, but the results were generally negative, only one type of reaction being observed. This was the oxidation of ammonia, in the presence of ferric chloride, to nitrates, and in the presence of zinc or mercuric oxide, to nitrites and nitrates. Hydroxylamine and hydrogen peroxide were never produced. The zinc oxide to be effective must be in the solid state, and its previous exposure to sunlight enables the oxidation of aqueous ammonium salts to be accomplished in the absence of light. Photochemical reduction of carbon dioxide was not observed, and no complex nitrogen compounds could be produced from ammonia and carbon compounds. The positive photosynthesis claimed by Moore ("Biochemistry," 1921), by Dhar and Sanyal (A., 1925, ii, 884), and other workers is challenged. L. S. Theobald.

Photochemical oxidation of alcohols by the dichromate ion. E. J. Bowen and C. W. Bunn (J.C.S., 1927, 2353—2358).—The photochemical oxidation of methyl, ethyl, *n*-propyl, and *iso*propyl alcohols by the dichromate ion has been investigated. The quantum efficiency is independent of the light intensity over a range of 1 : 80, of added acid above a certain limit, of dichromate-ion concentration between $0{\cdot}1N$ and $0{\cdot}01N$, and of temperature between 15° and 50°. The reaction rate diminishes regularly with decreasing acid concentration. In acid solution aldehyde is formed without the production of any precipitate. In neutral and alkaline solutions the chromate ion is photochemically insensitive towards alcohols, and in neutral solution a precipitate of uncertain composition is formed. The mechanism of the reaction is discussed. C. W. Gibby.

Photosynthesis of naturally occurring compounds. I. Action of ultra-violet light on carbonic acid. E. C. C. Baly, J. B. Davies, M. R. Johnson, and H. Shanassy (Proc. Roy. Soc., 1927, A, **116**, 197—211).—When carbonic acid in aqueous solution is illuminated with ultra-violet light, a photostationary state is established, involving as one of the components a complex aldehyde. In an attempt to effect the photosynthesis of carbohydrates by the addition of a reducing agent to the carbonic acid solution, it was found that ferrous hydrogen carbonate in aqueous solution is converted by ultra-violet light in absence of oxygen into ferric hydroxide, organic compounds with reducing properties being formed simultaneously. This reaction appears to take place chiefly on the surface of the quartz tubes containing the solution, and also on the iron rods used. Complex organic compounds may be synthesised by the action of ultra-violet light on suspensions of various insoluble powders (aluminium powder, barium sulphate, freshly-precipitated aluminium hydroxide, and the basic carbonates of aluminium, magnesium, and zinc) in water through which a stream of carbon dioxide is maintained. Aluminium hydroxide which has been in contact with water for some hours loses its efficacy, due to the fact that it then has no affinity for carbonic acid. The organic compounds thus produced may be recovered by evaporation of the solution after removal of the insoluble powder, and appear to be of the nature of complex carbohydrates. Photosynthesis of complex organic compounds containing nitrogen takes place in presence of ammonium hydrogen carbonate or a soluble nitrite. Rigid proof is given that the carbon dioxide and other materials used were free from all organic impurity, and negative results were obtained in control experiments in which powders incapable of adsorbing carbon dioxide were employed.

L. L. Bircumshaw.

Photosynthesis of naturally occurring compounds. II. Photosynthesis of carbohydrates from carbonic acid by means of visible light. E. C. C. Baly, W. E. Stephen, and N. R. Hood (Proc. Roy. Soc., 1927, **A**, **116**, 212—219).—Photosynthesis of organic compounds occurs when carbon dioxide, rigidly free from organic impurities, adsorbed on the surface of a fine coloured powder (nickel or cobalt carbonate) suspended in water, is exposed to visible light. The carbonates must be free from alkali, nitrate, chloride, and sulphate. One of the products of the photosynthesis is a carbohydrate which reduces Benedict's solution, gives well-marked Molisch and Rubner reactions, and forms a solid osazone. The reducing power of the photosynthesised compounds is materially increased by hydrolysis with hydrochloric acid. The total quantity of material photosynthesised by means of a coloured surface in visible light, and also the percentage reducing power, is greater than with a white surface in ultra-violet light (cf. preceding abstract). In this case, the products are not so liable to undergo photochemical decomposition. When moist nickel and cobalt carbonates are exposed to visible light in presence of carbon dioxide, a surface film of nickel and cobalt oxide, respectively, is formed, and it is found that the oxygen set free during the photosynthesis tends to poison the surface. Increased yields of the carbohydrates are obtained with unit quantity of light when the intensity of illumination is decreased, owing to the fact that the poisoned surface slowly recovers under water. When the surface has become completely poisoned the photosynthetic process ceases, and then with intense illumination the carbohydrates previously formed are photochemically decomposed. Complex nitrogen compounds may be photosynthesised by exposing to visible light ammonium hydrogen carbonate solution containing nickel or cobalt carbonate in suspension.

L. L. Bircumshaw.

Photosynthesis of naturally occurring compounds. III. Photosynthesis *in vivo* and *in vitro*. E. C. C. Baly and J. B. Davies (Proc. Roy. Soc., 1927, **A**, **116**, 219—226).—A marked similarity is shown to exist between the laboratory photosynthesis of complex carbohydrates in a single operation from carbonic acid (cf. preceding abstracts) and the natural process of photosynthesis in the living leaf. In neither case does ordinary formaldehyde take part in the reaction. The photosynthesis *in vitro* has been achieved by the action of light on carbonic acid adsorbed on a surface, and there are strong indications that a limiting surface exists in the chloroplast and is necessary for the occurrence of the normal photosynthesis. In each case a visibly coloured surface and visible light are involved. The fatigue effect observed when the living leaf is exposed to too long and intense illumination may be compared with the fatigue effect observed in the laboratory, due to poisoning of the surface by oxygen. In both processes there is a slow recovery reaction, and it appears that in both, the rate of photosynthesis must not exceed the rate of this slow reaction. It appears that the yield of carbohydrates photosynthesised *in vitro* per hr. per $cm.^2$ of surface is not greatly at variance with that observed in nature. It is suggested that the constant ratio of chlorophyll-*A* to chlorophyll-*B*, observed by Willstätter and Stoll in the living leaf, is maintained by the carotin, which becomes oxidised to xanthophyll, and that, since the xanthophyll : carotin ratio tends to increase during photosynthesis, the slow recovery process present in the leaf is that in which the xanthophyll is reduced again to carotin.

L. L. Bircumshaw.

Photochemical rearrangement of acetylchloroaminobenzene. C. W. Porter and P. Wilbur (J. Amer. Chem. Soc., 1927, 49, 2145—2149).—The ultra-violet absorption spectra of acetylchloroaminobenzene and its isomeride, *p*-chloroacetanilide, are recorded. Conversion into the isomeride occurs in the solid state in the radiation of a mercury vapour lamp, and also at 100°. The change is rapid above the m. p. Mechanisms involving intermediate products cannot apply to the reaction in the solid phase.

S. K. Tweedy.

Optical sensitisation with dyes. K. Burgherr (Z. wiss. Phot., 1927, 24, 393—408).—When a molecule of sensitiser absorbs a quantum of light and enters the phototropic state, it acquires an electrical polarisation designated $E\{^{+}_{-}$ and the positive and negative poles in the molecule act as cathode and anode in a kind of molecular electrolysis. The idea is illustrated in the photolysis of a solution of ammonium oxalate and mercuric chloride in the presence of eosin,

$$E\left\{\begin{array}{l} ^{+}\ +0{\cdot}5\mathrm{C_2O_4}'' \longrightarrow \mathrm{CO_2} \\ ^{-}\ +\mathrm{HgCl_2} \longrightarrow \mathrm{HgCl}+\mathrm{Cl}'. \end{array}\right.$$

Using silver nitrate and sucrose, glycine, or glycerol as cathodic and anodic depolarisers, respectively, the sensitising action of the following dyes has been studied: rhodamine-*B*, eosin, safranine-*G*, phenosafranine, fluorescein, methyl-violet, chromotrope-2*R*. The photolysis results in the separation of silver (which can be determined by means of ammonium thiocyanate) and the concomitant formation of oxidation products. Some silver was liberated in the binary systems silver nitrate–dye, silver nitrate–sucrose, but a larger amount was set free in the ternary systems composed of dye and depolarisers.

The sensitised photolysis very soon reaches a stationary state, apparently owing to the formation of a new anodic depolariser which begins to compete with the existing depolariser. Experiments carried out with air-containing and air-free solutions show that the most likely agent for this effect is the finely-divided silver, *i.e.*, $E\left\{\begin{array}{l} ^{+}\ +\mathrm{Ag} \longrightarrow \mathrm{Ag}^{\cdot} \\ ^{-}\ +\mathrm{Ag}^{\cdot} \longrightarrow \mathrm{Ag} \end{array}\right.$

The experiments with glycine and glycerol show that these substances can be further oxidised, so that it is not possible to ascribe the stationary state to their appearance as the first decomposition products of sucrose. The investigation lends support to the inner polarisation mechanism for sensitisation.

R. A. Morton.

Light sensitivity of guaiacum resin and its possible application in photography. C.

Schweckendiek (Diss., Giessen, 1927).—Guaiaconic acid, like guaiaretic acid, is sensitive to light, the sensitivity being increased by the addition of collodion, Zapon lacquer, or a solution of sulphur in carbon disulphide. The green image is fixed with a mixture of ammonium acetate and benzene. The insolubilising action of light on guaiaretic acid is an oxidation process. Chemical Abstracts.

Mechanism of formation of the latent photographic image. F. C. Toy (Nature, 1927, **120**, 441).—Although the formation of the latent photographic image does not appear to be due to a complete liberation of electrons from silver bromide crystals, it appears to be closely connected with the photo-conductivity effect. Experimental evidence is adduced in support of the view that the formation of the latent image involves the transfer of valency electrons from bromide ions to silver ions, resulting in the production of metallic silver and free bromine. The observed decrease in photo-conductivity in the violet and its absence in the ultra-violet portion of the spectrum are due to the thickness of the film employed. A. A. Eldridge.

Chemical reactions in the gaseous phase in electromagnetic fields of high frequency. R. Moens and A. Juliard (Bull. Acad. roy. Belg., 1927, [v], **13**, 201—205; cf. *ibid.*, 72).—In an attempt to investigate the chemical behaviour of gases in electromagnetic fields of high frequency, the changes produced in certain gases and gaseous mixtures by the passage of an electrodeless discharge were followed manometrically. The discharge usually appears at pressures of the order of 1 cm. and in the case of simple gases, *e.g.*, hydrogen, oxygen, nitrogen, is accompanied by an increase of pressure. On interruption of the discharge the pressure falls instantly to a value indicative of a contraction or an expansion depending on the nature of the gas and the duration and intensity of the discharge. A mixture of 2 vols. of hydrogen and 1 vol. of oxygen shows a contraction corresponding with complete conversion into water vapour. Although a mixture of 3 vols. of hydrogen and 1 vol. of nitrogen shows a slight expansion, in presence of sulphuric acid the pressure falls almost to zero. A mixture of hydrogen and carbon di(?)oxide shows a slight expansion, but returns to the initial pressure after the passage of the discharge even in presence of concentrated sulphuric acid. Mixtures of nitrogen and oxygen undergo an appreciable expansion, the pressure, however, returning to its original value on interruption of the discharge. Acetylene and benzene yield solid deposits, the pressure falling to almost zero. Ethyl ether and ethyl and amyl alcohols are decomposed and the volume is increased almost threefold. With carbon disulphide and carbon tetrachloride the discharge appears only at pressures of the order of 1 mm. J. S. Carter.

Hydrates of lithium chlorate. L. Berg (Z. anorg. Chem., 1927, **166**, 231—236).—A *monohydrate* of lithium chlorate, $LiClO_3,H_2O$, may be prepared by cooling a solution of composition corresponding with the formula to below −25° and adding a few crystals of the hydrate $3LiClO_3,H_2O$ (A., 1926, 1014). A *trihydrate*, $LiClO_3,3H_2O$, separates from the corresponding solution at −20°. R. Cuthill.

Phosphates. V. Hydration of sodium monometaphosphate in alkaline solution at 75°. S. J. Kiehl and H. P. Coats (J. Amer. Chem. Soc., 1927, **49**, 2180—2193; cf. this vol., 312).—The hydration of sodium monometaphosphate (for which crystallographic data are recorded) in sodium hydroxide solution was investigated at 75° in silver vessels. Both pyro- and ortho-phosphate in equimolecular quantities are end-products of the hydration: $3NaPO_3+2H_2O=Na_2H_2P_2O_7+NaH_2PO_4$. The rate of hydration increases with increase in the sodium hydroxide concentration. Pyrophosphate is precipitated in presence of orthophosphate by adjusting the hydrogen-ion concentration of the solution to 5×10^{-4} mol./litre (by addition of acetic acid) and adding zinc acetate solution of the same hydrogen-ion concentration. Orthophosphate may be determined in the filtrate. S. K. Tweedy.

Influence of the concentration of hydrogen ions on the displacement of copper from its solutions at high pressures and temperatures. V. Ipatiev and V. Ipatiev, jun. (Ber., 1927, **60**, [*B*], 1982—1986).—The action of hydrogen on solutions of copper formate and acetate between 90° and 180° at pressures between 0 and 150 atm. and at acidities between 0 and 12·5*N* has been investigated. In neutral solution at 100° hydrolysis occurs with consequent separation of copper oxide, which is only with difficulty reduced by hydrogen. In the presence of acid, this hydrolysis is repressed and the dissolved cupric salt is reduced to the corresponding cuprous salt. If the hydrogen-ion concentration is insufficient, the cuprous salt is hydrolysed and crystalline cuprous oxide separates from the solution. If, however, the hydrogen-ion concentration is sufficient to inhibit hydrolysis, an actual displacement of copper from the cuprous salt occurs. At a sufficiently high temperature (130—180°), the anions of formic and acetic acids become decomposed with production of hydrogen, which, according to the degree of acidity of the solution, causes separation of cuprous oxide or metallic copper. H. Wren.

Reduction of copper sulphate by sodium hypophosphite. S. Ramachandran (Chem. News, 1927, **135**, 214—216).—Copper sulphate is reduced by sodium hypophosphite in aqueous solution only when acidified to a definite extent. The temperature required is the higher the greater is the proportion of hypophosphite present. C. W. Gibby.

Composition and behaviour of precipitated copper and iron sulphides. F. Feigl [with E. Bäcker and L. Rosenberg] (Z. anal. Chem., 1927, **72**, 32—43).—Copper sulphide, freshly precipitated by hydrogen sulphide, consists chiefly of cupric sulphide with small quantities of cuprous sulphide and sulphur, but on keeping, the cupric sulphide continues to decompose into cuprous sulphide and sulphur. The extent of the decomposition was determined by replacing the copper by mercury, boiling with sodium sulphite solution, and determining with iodine the thiosulphate formed. The precipitate obtained in an alkaline solution is a mixture of the two sulphides, but, as before, the composition of the fresh precipitate is dependent on the conditions of precipitation. The precipitate obtained by mixing a ferric salt and ammonium sulphide, of empirical formula Fe_2S_3, was treated with mercuric chloride solution. Ferrous chloride was formed and free sulphur was found in the precipitate. This indicates that the compound has the formula FeS,FeS_2, as the possible reactions with mercuric chloride are $Fe_2S_3+3HgCl_2=3HgS+2FeCl_3$, and $FeS,FeS_2+2HgCl_2=2HgS+S+2FeCl_2$. F. S. HAWKINS.

Crystallisation of some hydroxides. R. FRICKE [with C. GOTTFRIED, W. SKALIKS, A. MÜNCHMEYER, and F. ENGELHARDT] (Z. anorg. Chem., 1927, **166**, 244—256).—The conditions for the production of various hydroxides in the crystalline state have been investigated. Varieties of beryllium hydroxide which give the same *X*-ray diagram but differ in crystalline form may be obtained by slow hydrolysis of sodium beryllate in aqueous solution, and by allowing a 40% solution of sodium hydroxide saturated with amorphous beryllium hydroxide at the b. p. to cool slowly. Beryllium hydroxide aged with ammonia (Haber and van Oordt, A., 1904, ii, 257) has a quite different crystal structure. The solubility in sodium hydroxide solutions at 30° of the form obtained by hydrolysis of sodium beryllate in the cold is maximal for solutions containing about 33% of sodium hydroxide; for lower concentrations the solid phase is beryllium hydroxide, whereas for higher concentrations it is sodium beryllate. One form of crystalline zinc hydroxide may be obtained by slow hydrolysis of alkali zincate solutions at the ordinary temperature, or by ageing the amorphous hydroxide under weak acids such as phenol. A metastable variety differing both in crystalline form and structure is produced by diluting zincate solutions very considerably. Zinc hydroxide precipitated with a slight excess of sodium hydroxide from a solution of a zinc salt represents a third modification. Slow hydrolysis of alkali aluminate solutions gives a form of aluminium hydroxide which at first has the crystalline structure of hydrargillite, but after keeping for some years gives an *X*-ray diagram which belongs neither to hydrargillite nor to bauxite. Specimens of magnesium hydroxide obtained by precipitating magnesium sulphate with sodium hydroxide in the cold, or by precipitating the chloride with ammonia in the cold, or by precipitating a mixed solution of magnesium and ammonium chlorides with ammonia at 60° and ageing the precipitate in contact with the supernatant liquor at 30° all have the same crystalline structure, and there seems to be no evidence for the existence of two allotropic forms as suggested by Gjaldback (A., 1925, ii, 652). R. CUTHILL.

Boric acids and alkali borates. III. Solid alkali mono- and poly-borates. H. MENZEL [with J. MECKWITZ] (Z. anorg. Chem., 1927, **166**, 63—98; cf. this vol., 937).—The literature relating to those borates of the alkali metals which can be crystallised from aqueous solution is critically reviewed, and supplemented in some cases with solubility determinations at 18° and 25° and with isothermal dehydration experiments with the hydrates. *X*-Ray diagrams and dehydration experiments show that the removal of the last molecule of water from the hydrates of sodium monoborate is accompanied by a change in the structure of the crystal. With the diborate it is apparently the last three water molecules which are of structural importance, but the pentahydrate stable above 60° appears to occupy an exceptional position. The pentahydrate of potassium pentaborate reported by Hermans (A., 1925, i, 500) seems to have been the tetrahydrate. Attempts to prepare an ammonium monoborate by treating the tetrahydrate of the diborate with ammonia have been fruitless, although it is apparently possible in this way to replace 1 mol. of the water of crystallisation with an ammonia molecule. The structure of the polyborates has been worked out with the aid of Hermans' theory of the constitution of boric acid (A., 1925, ii, 697). R. CUTHILL.

Reduction of refractory oxides by tungsten at high temperatures. H. VON WARTENBERG and H. MOEHL (Z. physikal. Chem., 1927, **128**, 439—444).—Oxides such as those of aluminium, zirconium. and thorium are reduced by metallic tungsten at 2000° in an atmosphere of nitrogen, volatile tungsten dioxide being produced. H. F. GILLBE.

Aluminium sulphate and its hydrates. Double sulphates and their components. II. F. KRAUSS and A. FRICKE (Z. anorg. Chem., 1927, **166**, 170—176).—Dehydration of the hydrate $Al_2(SO_4)_3,27H_2O$ in the tensi-eudiometer points to the existence of hydrates with 27, 18, 16, 10, and 6 mols. of water. The anhydrous salt commences to lose sulphur trioxide at 605°. R. CUTHILL.

Displacement of metals or their oxides from solutions by hydrogen under pressure. Separation of crystalline hydroxides of aluminium and chromium from solutions of their salts at high temperatures and under high pressures. V. IPATIEV and B. MOUROMTSEV (Ber., 1927, **60**, [*B*], 1980—1982).—For the separation of crystalline hydroxides of aluminium and chromium the acidity of the solution is of primary importance. A solution of the requisite nitrate, acidified with nitric acid, is placed in a golden tube (or silica tube if the temperature does not exceed 330°) and brought under pressure of hydrogen or air in the high-pressure apparatus. The temperature is varied between 320° and 360°, pressure between 200 and 370 atm., and duration between 12 and 24 hrs., although the change is complete in 12 hrs. At lower pressures amorphous products separate. Aluminium nitrate or acetate in the presence of nitric or acetic acid and hydrogen or air gives the monohydrated oxide with all the properties of the mineral diaspore. Neutral aluminium nitrate in presence of air gives a scarcely crystalline precipitate. Chromium nitrate in nitric acid solution under the influence of hydrogen gives monohydrated chromium oxide closely resembling chrome ochre. If air is used in place of hydrogen, smaller crystals are obtained and the separation is not quantitative, a portion of the oxide being converted into chromic acid. Small amounts of dark red crystals are also occasionally obtained. H. WREN.

Azidodithiocarbonic acid. IV. Ammonium and tetramethylammonium azidodithiocarbonates; tetramethylammonium thiocyanate. L. F. Audrieth, G. B. L. Smith, and A. W. Browne [with C. W. Mason] (J. Amer. Chem. Soc., 1927, 49, 2129—2133).—*Ammonium azidodithiocarbonate*, NH_4SCSN_3, is obtained by neutralising azidodithiocarbonic acid with aqueous ammonia or, preferably, in ethereal solution, with gaseous ammonia. It is also formed by the prolonged action of carbon disulphide on aqueous ammonium azide solution (cf. Browne and Hoel, A., 1922, ii, 848). It forms white, non-deliquescent, orthorhombic plates, soluble in water, alcohol, and acetone, but insoluble in benzene; m. p. 120° (decomp.): $NH_4SCSN_3=NH_4SCN+S+N_2$. The salt becomes orange when heated at 90° or on illumination, the change in the latter case being partly reversible. *Tetramethylammonium azidodithiocarbonate* is best prepared by digesting an aqueous solution of tetramethylammonium azide with a slight excess of carbon disulphide ($NMe_4N_3+CS_2=NMe_4SCSN_3$). Its properties are similar to those of the ammonium compound; m. p. 95—98° (decomp.). Tetramethylammonium thiocyanate is conveniently prepared by boiling under reflux an alcoholic solution of tetramethylammonium azide with carbon disulphide. It does not undergo molecular rearrangement into tetramethylthiocarbamide. Crystallographic data are recorded for each of the above compounds.

S. K. Tweedy.

Formation of crystalline silicates in an aqueous medium under pressures and at high temperatures. V. Ipatiev and B. Mouromtsev (Compt. rend., 1927, **185**, 647—649; cf. A., 1926, 1219).—Silicic acid or silicate gels obtained by a double decomposition reaction may be converted into crystalline forms by heating at a constant temperature for 2—3 days in a silver tube containing hydrogen or carbon dioxide under pressure. Any oxides formed are removed by means of hydrochloric acid. The product obtained depends on the conditions, and on the presence or absence of small amounts of impurities. Thus, crystalline SiO_2 and $5SiO_2,2H_2O$ are produced using hydrogen and carbon dioxide, respectively, and silicates of magnesium, calcium, manganese, aluminium, zinc, and iron of varying compositions have also been obtained. The crystalline compound $5SiO_2,3H_2O$ was obtained from a manganese silicate gel free from any soluble manganese salt. J. Grant.

Action of stannous chloride on silver mirror formation. O. Macchia (Chem. News, 1927, 135, 197—200).—The formation of a silver mirror and its adherence to a glass plate are greatly facilitated by previous immersion (10 sec.) of the plate in a dilute solution (preferably 1 in 2000) of stannous chloride. The effect is attributed to the deposition of a very adherent film of gelatinous stannous hydroxide, formed by the hydrolysis of the stannous chloride, and was observed for plates of glass, cellulose, wood, and galatite. G. A. Elliott.

Chromium carbonyl. A. Job and A. Cassal (Bull. Soc. chim., 1927, [iv], 41, 1041—1046).—The solution obtained by the action of carbon monoxide on magnesium ethyl or phenyl bromide (this vol., 865) is hydrolysed with sulphuric acid at 0°, and the ethereal layer is separated, neutralised, and dried, after which the ether is evaporated. When magnesium ethyl bromide is used, crystals of *chromium carbonyl*, $Cr(CO)_6$, separate during the evaporation; otherwise, the residue has to be sublimed under reduced pressure. By grinding the product under benzene and resubliming at 160°, the pure carbonyl is obtained as colourless, orthorhombic crystals, d^{18} 1·77, slightly soluble in benzene and ether, but more soluble (2%) in chloroform and carbon tetrachloride, the solutions being stable only in the dark. The crystals decompose rapidly at 210° into chromic oxide; in a sealed tube they melt at 149—150° and irreversibly deposit a chromium mirror at 230°. The carbonyl is unattacked by dilute acids, bromine, and iodine; fuming nitric acid converts it into chromic nitrate and free carbon. S. K. Tweedy.

Co-ordination compounds of quinquevalent molybdenum. R. G. James and W. Wardlaw (J.C.S., 1927, 2145—2156).—Physical and chemical properties of salts of the type $R_2[MoOCl_5]$ have been investigated, and a scheme of their hydrolysis and ionisation is outlined. The preparation of *diquinolinium molybdenyl pentachloride*, $(C_9H_8N)_2MoOCl_5,H_2O$, *monotrimethylammonium molybdenyl tetrachloride*, $NHMe_3MoOCl_4,H_2O$, and *dimolybdenum tetraoxyhydroxychloride*, $Mo_2O_4(OH)Cl,35H_2O$ is described.

C. W. Gibby.

Oxygen compound of fluorine. P. Lebeau and A. Damiens (Compt. rend., 1927, **185**, 652—654).—In the presence of water the method for the preparation of fluorine by electrolysis of molten acid potassium fluorides below 100° results also in the production of a gaseous oxygen compound of fluorine. The compound is less active chemically than fluorine, and studies of its mixtures with oxygen point to the formula F_2O. Such mixtures have the odour of fluorine, but are stable in the presence of water and of glass even at high temperatures. The gas, which was not isolated in the pure state, liberates iodine from potassium iodide, is soluble in alkali, but only sparingly soluble in water. J. Grant.

Chloro-acids. R. Schwarz and G. Meyer (Z. anorg. Chem., 1927, **166**, 190—212).—Attempts have been made to detect the combination of hydrogen chloride with various chlorides by determining pressure isotherms with the aid of the tensi-eudiometer. In no instance does any combination occur in absence of water, and in the case of the tetrachlorides of silicon and titanium no chloro-acid is formed owing to hydrolysis. With ferric chloride, it is probable that the compounds $Fe_2Cl_6,3HCl,9H_2O$, $Fe_2Cl_6,4HCl,11H_2O$, $Fe_2Cl_6,5HCl,12H_2O$ and $FeCl_3,3HCl,7H_2O$ are capable of existence. Hexa-aquochromic chloride forms no compounds, but dichlorotetra-aquochromic chloride dihydrate apparently gives rise to the compounds $CrCl_3,HCl,6{\cdot}5H_2O$, $CrCl_3,2HCl,8{\cdot}5H_2O$, and $CrCl_3,3HCl,10{\cdot}5H_2O$. Aluminium chloride forms no compounds.

R. Cuthill.

Manganese molybdates. F. Zambonini and V. Caglioti (Rend. Accad. Sci. fis. mat. Napoli, 1927,

[iii], **33**, 181—203).—Irrespective of variations in the method of preparation, a single compound having the formula $4(NH_4)_2O,Mn_2O_3,13MoO_3,9H_2O$, is obtained. This is identical with that described by Struve (J. pr. Chem., 1854, **61**, 449), Friedheim and Samelson (A., 1900, ii, 547), and Friedheim and Alleman (Mitt. naturf. Ges. Bern, 1904, 23). As appears from the ratio $Mn_2O_3 : MoO_3$ the manganese is to be considered present in the bi- and quadri-valent states, the formula being $[Mn^{\cdot\cdot\cdot\cdot}(Mo_2O_7)_6](NH_4)_8,Mn^{\cdot\cdot}MoO_4,9H_2O$. This confirms Struve's result that manganese in the form of Mn_2O_3 may be considered to be MnO and MnO_2, and also Péchard's suggestion that the ratio $MnO_2 : MoO_3$ is 1 : 12 in analogy to the silicomolybdates. M. Carlton.

Sublimation of iron in a vacuum. E. Botolfsen (Compt. rend., 1927, **185**, 649—650).—Iron may be sublimed in a high vacuum at temperatures below its m. p. The effect is independent of the origin of the iron and of the presence of certain substances likely to act as catalysts, and at 1300° its rate is of the order of 0·07% per hr. The sublimate takes the form of a thick deposit of metallic crystals, and is almost pure. J. Grant.

Ferric thiocyanate. K. C. Bailey (J.C.S., 1927, 2065—2069).—The red compound produced by dissolving ferric hydroxide in thiocyanic acid is found, by a repetition of the work of Tarugi (A., 1905, i, 176; 1926, 259), to be ferric thiocyanate. No evidence is obtained in favour of his formula $FeHC_3N_3S_3O_3$. C. W. Gibby.

Preparation of low-conductivity water. G. D. Bengough, J. M. Stuart, and A. R. Lee (J.C.S., 1927, 2156—2161).—Improvements in Bourdillon's still (J.C.S., 1913, **103**, 791) are described. About 4 litres of water per day can be produced, with a conductivity of 0·065 gemmho. C. W. Gibby.

Germanium. XX. Preparation of fused germanium directly from germanium dioxide. (Miss) K. M. Tressler and L. M. Dennis (J. Physical Chem., 1927, **31**, 1429—1432).—Fused, metallic germanium has been prepared by reduction of the dioxide with carbon under a flux of sodium chloride in a graphite crucible heated in an induction furnace. A 90% yield of the metal, containing approximately 1% of dioxide and other impurities in amount not greater than 0·01%, was obtained. Of the germanium lost, 70% can be recovered. Slight modifications in the method should make this loss negligible. Preparation of germanium by electrolysis of the dioxide dissolved in molten cryolite, or molten potassium fluogermanate, and by reduction of the dioxide with aluminium resulted in heavy losses of germanium as germanous oxide. L. S. Theobald.

Precautions [against explosion] in preparing lead bromate. Victor (Z. angew. Chem., 1927, **40**, 841).—Fatal explosions have occurred when lead bromate, prepared by interaction of lead acetate and potassium bromate (cf. Gmelin-Kraut's "Handbuch," IV, 376) has been pulverised. The sensitivity to shock is due to the presence of diacetodiplumbous bromate (Günzel and Marcus, A., 1925, ii, 1086). W. A. Silvester.

Elementary method of qualitative analysis without the use of hydrogen sulphide, thioacetic acid, or sulphides. O. Macchia (Notiz. chim.-ind., 1927, 2, 191—196).—A detailed scheme is presented. Chemical Abstracts.

Continuous electro-conductivity titration. E. Butterworth (Mem. Manchester Phil. Soc., 1926—1927, 71, 53—62).—A new continuous-reading method of electro-conductivity titration is described, giving an accuracy of 0·2—0·3%. The sensitivity is easily controlled within wide limits. C. W. Gibby.

[Absolute] potentiometric titration. B. Cavanagh (J.C.S., 1927, 2207—2216).—A new absolute method of potentiometric titration is described for strong acids and halides, in which no potentiometer, standard cell, or normal electrode is required. It can be used for very dilute solutions and with very small quantities of liquids, and a high degree of accuracy is obtained. C. W. Gibby.

Effect of sodium hydrogen carbonate on the titration of iodine with thiosulphate. O. E. Schupp, jun. (Science, 1927, **65**, 284).—Low values, due to the formation of hypoiodite and iodide, and oxidation of the thiosulphate to sulphate, are obtained if the iodine solution is initially neutral and sodium hydrogen carbonate is added. The results for an initially acid solution containing less than *N*-sodium hydrogen carbonate are as accurate as those for a neutral solution of iodine. A. A. Eldridge.

Determination of sulphuric acid in water analysis by means of benzidine. L. W. Haase.—See B., 1927, 798.

Analysis of polythionate solutions. A. Kurtenacker and E. Goldbach (Z. anorg. Chem., 1927, **166**, 177—189).—Billeter and Wavre's sulphide method of determining trithionate (A., 1918, ii, 330), depending on the reaction $S_3O_6''+S''=2S_2O_3''$, has been extended to tetra- and penta-thionates, both together and separately, and to mixtures of these with trithionate, the reactions being $S_4O_6''+S''=2S_2O_3''+S$, and $S_5O_6''+S''=2S_2O_3''+2S$. Sulphite present along with trithionate only does not interfere with the determination if it is first caused to combine with formaldehyde, but if tetra- or penta-thionate is also present the sulphite combines with the sulphur produced in the above reactions to form thiosulphate. This difficulty may be overcome by first titrating the sulphite with iodine, or as follows. The solution for analysis is heated for 10 min. at a temperature near the b. p. with 20 c.c. of 0·4*N*-sodium sulphide and 20 c.c. of 0·4*N*-sodium sulphite, and the excess of sulphide then precipitated with zinc acetate or carbonate. An aliquot portion of the filtrate is mixed with 5 c.c. of 40% formaldehyde, acidified with 10 c.c. of 20% acetic acid, and titrated with iodine. In this case, the tetra- and penta-thionate radicals react according to the equations $S_4O_6''+S''+SO_3''=3S_2O_3''$ and $S_5O_6''+S''+2SO_3''=4S_2O_3''$. By means of this method and those previously published (A., 1924, ii, 497, 564; 1925, ii, 239, 434, 1189; this vol., 534, 638) a mixture of tri-, tetra-, and penta-thionates, thiosulphate, hydrogen sulphite, and hydrogen sulphide can be analysed. R. Cuthill.

Volumetric determination of azoimide by oxidation with ceric sulphate in acid solution. J. Martin (J. Amer. Chem. Soc., 1927, **49**, 2133—2136).—The nitrometer method of determining azoimide (Sommer and Pincas, A., 1916, ii, 97) : $2Ce^{\cdot\cdot\cdot\cdot}+2HN_3=3N_2+2H^{\cdot}+2Ce^{\cdot\cdot\cdot}$, may be applied iodometrically; the reaction is carried out with the exclusion of air in a closed vessel, excess of potassium iodide is added, and the liberated iodine titrated with standard thiosulphate. Hydrazine must be absent (azoimide may be separated from it by distillation), but the ammonium ion may be present. The acid concentration must be kept low. S. K. Tweedy.

Colorimetric determination of carbon monoxide with ammoniacal silver solution. H. Kast and A. Schmidt.—See B., 1927, 748.

Conversion of alkali chlorides into carbonates by means of oxalic acid. L. N. Muravlev (Z. anal. Chem., 1927, 72, 15—19).—The reactions involved are not quantitative. The conversion of chloride into oxalate is not complete, and the formation of carbonate from oxalate is finished only at temperatures high enough to cause loss by volatilisation. The smallest error was 0·48%. F. S. Hawkins.

Volumetric determination of potassium. G. Jander and O. Pfundt (Z. anal. Chem., 1927, **71**, 417—434).—Potassium may be determined by conductometric titration with sodium perchlorate if the solution used is at least 0·3*N* with respect to potassium and the perchlorate solution is 5—6*N*. To reduce the solubility of the precipitated potassium perchlorate to a minimum the titration is carried out in a vessel cooled with ice; under these conditions the supernatant liquid above the precipitate at the end of the titration is 0·01*N* with respect to potassium. The presence of magnesium sulphate, sodium chloride, and calcium chloride is without effect on the results, so that the process is applicable to the control of liquors obtained in the potash industry. The end-point is sharp and the results are good when the solution is standardised against a potassium solution containing the same quantity of the metal as the trial. A. R. Powell.

Determination of potassium and sodium in the presence of each other. A. Meyer (Chem.-Ztg., 1927, **51**, 778).—The metals are first weighed as chloride (or sulphate), the mixed salts dissolved, and either the chlorine is determined titrimetrically, or the sulphuric acid gravimetrically. In the latter case, to prevent the presence of traces of hydrogen sulphate, the salts should first be evaporated with ammonium carbonate. The proportions determined algebraically in the usual way are subject to a smaller error than those obtained by weighing the chlorides and sulphates. B. P. Ridge.

Determination of sodium. D. I. Perieteanu (Bul. Soc. chim. România, 1927, 9, 17—18).—Sodium is determined as the salt $3UO(C_2H_3O_2)_2,Mg(C_2H_3O_2)_2,Na(C_2H_3O_2)$ by precipitation with an acetic acid solution of magnesium and uranium acetates. After ½ hr., the precipitate is collected in a Gooch crucible, washed three times with the reacting liquid, three times with 95% alcohol, and dried for 30 min. at 105°. Only phosphates interfere with the reaction, and small quantities of sodium can be determined. F. S. Hawkins.

Microchemical reactions of beryllium. V. Caglioti (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 177—180).—The usual microchemical methods of determining beryllium by means of the double oxalate of potassium and beryllium and of the chloroplatinate and sulphate are not entirely satisfactory. The most satisfactory results are obtained by Streng's reaction involving the formation of uranyl sodium beryllium acetate, $(UO_2)_3BeNa(OAc)_9,9H_2O$, as pale yellow, rhombohedral crystals. The presence of aluminium does not affect the reaction, but iron must be carefully removed.

For microchemical research the most satisfactory method of determining beryllium is by formation of beryllium acetylacetonate (cf. Jaeger, A., 1914, i, 797) as clear, colourless, monoclinic prisms which on examination under the microscope show very characteristic interference figures. M. Carlton.

Application of Kolthoff's reaction for magnesium in plant microchemistry. H. Eilers (Chem. Weekblad, 1927, **24**, 448—450; cf. Kolthoff, this vol., 639).—The reaction with titan-yellow is not specific for magnesium in plant tissue, but may be employed if the test is carried out after removal of oils, fats, and resins on tissue before and after treatment with dilute acid, and the colorations obtained in the two cases are compared. S. I. Levy.

Diphenylamine [acetate] as a qualitative reagent for zinc. W. H. Cone and L. C. Cady (J. Amer. Chem. Soc., 1927, **49**, 2214—2215).—The group filtrate containing chromium and zinc is acidified with acetic acid and chromium is tested for on one portion. To the remainder 5 drops of a solution of 1 g. of diphenylamine (or diphenylbenzidine) in 100 c.c. of glacial acetic acid and 5 c.c. of 0·5% aqueous potassium ferricyanide solution are added. The presence of zinc is indicated by a turbidity, the darkness of which increases with the amount of zinc present. Unless its concentration exceeds 10 mg./c.c., potassium dichromate does not influence the test. Contrary to the statement of Knop (A., 1924, ii, 351), diphenylamine sulphate immediately produces a blue coloration with potassium dichromate at concentrations greater than 0·05 mg./c.c. S. K. Tweedy.

Rapid separation of lead and silver by a potentiometric method. E. Müller and H. Hentschel (Z. anal. Chem., 1927, 72, 1—5).—The metals are determined by titrating the solution first with sodium chloride, and observing the potentials with a silver electrode, and then with potassium ferrocyanide, using a platinum electrode. The potentials measured against a normal calomel electrode at which the titrations are finished are 0·23 volt and 0·36 volt, respectively; and the titration is carried out by applying these voltages to the cell, and titrating until no current flows. Accurate titration of the silver with potassium iodide is prevented by adsorption phenomena and the separation of lead iodide. F. S. Hawkins.

Determination of lead in bismuth by spectrum analysis. III. E. Schweitzer (Z. anorg. Chem., 1927, **165**, 364—370).—The spectrum of bismuth containing lead is coupled with that of tin containing lead by making the times of exposure of the photographic plate such that a selected line in the bismuth spectrum appears of the same intensity as a selected line in the tin spectrum. This pair of lines is chosen by photographing the spectra of tin and bismuth each containing the same relative number of atoms of lead under such conditions that the lead lines in one spectrum have the same intensity as those in the other spectrum. If the two spectra are related in this way, corresponding lead lines are always equally intense whenever the lead concentrations in the main metal are the same. The lead in a sample of bismuth may therefore be determined by coupling its spectrum with that of pure tin, and searching for a lead line and a tin line of equal intensity, as previously described (this vol., 845). R. CUTHILL.

Use of titanous chloride in the volumetric determination of copper and iron. W. G. EMMETT (J.C.S., 1927, 2059—2062).—In determining cupric or ferric salts by titration with titanous chloride in presence of potassium thiocyanate as an indicator, error may be introduced by the decomposition of ferric and cupric thiocyanates. By carrying out the titration in cold acid solution immediately after adding the thiocyanate the error may be reduced below 0·2%. The preparation of a standard copper solution by dissolving electrolytic copper in a solution of sodium peroxide in hydrochloric acid is recommended.

C. W. GIBBY.

Sensitive reaction for aluminium and colorimetric determination of this element. I. M. KOLTHOFF (Chem. Weekblad, 1927, **24**, 447—448).—1 : 2 : 5 : 8-Tetrahydroxyanthraquinone gives an intense violet coloration with aluminium compounds in faintly acid solution. The reagent is very suitable for the determination of small quantities of aluminium, especially within the limits 0·02—0·5 mg. per litre. Of the metals which interfere, copper is removed by thiosulphate, and tin, antimony, and bismuth are rendered inactive by addition of sodium tartrate; iron must be precipitated (cf. A., 1924, ii, 785).

S. I. LEVY.

Determination of manganese and magnesium in aluminium alloys. F. MUGRAUER.—See B., 1927, 783.

Potentiometric titration of iron and aluminium with bases. P. DROSSBACH (Z. anorg. Chem., 1927, **166**, 225—230).—If pure solutions of ferric or aluminium chloride lying within a certain concentration range are titrated with sodium hydroxide, the potential of a hydrogen electrode dipping into the solution changes suddenly at the equivalence point. The p_H at this point is 6·8—7·0, and the titration of ferric chloride may actually be effected with bromothymol-blue as indicator. If the chloride solutions contain free acid, the second sudden change in potential corresponds with the complete reaction of the hydroxide with both chloride and free acid. The amount of free acid in aluminium chloride solutions may be determined by direct titration, using bromothymol-blue as indicator, if the aluminium is first converted into the cryolite complex by addition of potassium fluoride, excess being avoided, and if no considerable amounts of alkali chlorides are present.

R. CUTHILL.

Analysis of iron and steel. Determination of silicon, phosphorus, sulphur, and manganese. M. MARQUEYROL and L. TOQUET.—See B., 1927, 751.

Rapid determination of nickel. G. SPACU and J. DICK (Z. anal. Chem., 1927, **71**, 442—446).—The nickel solution is diluted to 100 c.c., treated with 0·5 g. of ammonium thiocyanate for every 0·1 g. of nickel present, heated to boiling, and treated drop by drop with 1—2 c.c. of pyridine. After cooling completely, the precipitate of glistening, sky-blue prisms is collected on a filtering crucible and washed successively with water containing 4 g. of ammonium thiocyanate and 6 c.c. of pyridine per litre, 35% alcohol containing 15 c.c. of pyridine and 1 g. of ammonium thiocyanate per litre, absolute alcohol containing 5 c.c. of pyridine per 100 c.c., and ether, to 20 c.c. of which are added 2 drops of pyridine. The crucible and contents are dried in a vacuum desiccator for 10 min. and weighed. The compound, $Ni(SCN)_2,4C_5H_5N$, contains 11·95% Ni.

A. R. POWELL.

Analytical chemistry of tantalum, niobium, and their mineral associates. VII. Precipitation of tungstic acid by tannin. VIII. Separation of tungsten from tantalum and niobium. W. R. SCHOELLER and C. JAHN (Analyst, 1927, **52**, 504—514).—VII. To obtain total precipitation of tungstic acid in one operation 100—150 c.c. of the alkaline tungstate solution containing alkali chloride are neutralised with dilute hydrochloric acid to the hydrogen carbonate stage, treated with a freshly-made solution of 0·5 g. of tannin, part of which flocculates as a white precipitate if the chloride-ion concentration is high, and dilute acid is added until the solution is acid to litmus, when the brown turbidity due to the tungsten complex appears. On boiling, the precipitate becomes dark brown and flocculent, and a 5% solution of cinchonine hydrochloride (5 c.c. diluted with water) is added, boiling continued for 5 min., and after keeping in the cold for 6 hrs. the clear liquid is decanted, the precipitate mixed with pulped filter fibre, washed on the filter with 5% ammonium chloride solution containing a little tannin, dried, ignited, and weighed as WO_3.

VIII. Tungsten may be separated from tantalum and niobium, since sodium tungstate is freely soluble, whilst the tantalate and niobate are nearly insoluble in solutions of high sodium-ion concentration. Small quantities of tungsten may be separated from large quantities of earth acids by the method previously described (this vol., 32). To separate small quantities of earth acids from large quantities of tungstic acid the solution should be free from potassium ions; fusion is effected with sodium hydroxide in a nickel crucible, and the fused mass extracted with half-saturated sodium chloride solution. Sodium tantalate and niobate remain undissolved and tungstic oxide is determined by difference. Satisfactory results were obtained by both methods. D. G. HEWER.

Potentiometric method for separation of tin and antimony. H. BRINTZINGER and F. RODIS

(Z. anorg. Chem., 1927, **166**, 53—59).—If a mixed solution of stannic and antimonic chlorides containing in 100 c.c. 30 g. of crystallised calcium chloride and 20 c.c. of concentrated hydrochloric acid and free from dissolved oxygen is titrated at 90—100° with chromous chloride solution, the first sudden change in the potential of a platinum electrode immersed in the solution indicates the complete reduction of the antimony salt to the tervalent state, and the second, which is relatively small, that of the tin salt to the stannous state. The addition of chromous chloride should be spread over 30—40 min., and, especially near the end-points, sufficient time should be allowed for the potential to become steady before a reading is made. R. Cuthill.

Separation of vanadium from tungsten. S. G. Clarke.—See B., 1927, 752.

Separation of vanadium from tungsten. S. G. Clarke (Analyst, 1927, **52**, 527).—Small amounts of vanadium may be separated from an impure tungstic oxide in steel analysis in the same way as larger amounts (B., 1927, 752), except that 50 g. of ammonium chloride should be dissolved in the solution before adding the cupferron to assist separation of the precipitate, which is collected, washed, ignited, and the residue fused with fusion mixture. The vanadium is then determined colorimetrically in the aqueous extract by the hydrogen peroxide method of Meyer and Pawletta (A., 1926, 1020). H. G. Hewer.

Sensitive test for bismuth. H. Kubina and J. Plichta (Z. anal. Chem., 1927, **72**, 11—14).—If dimethylglyoxime and sufficient ammonia are added to a hot very dilute bismuth nitrate or chloride solution, an intense yellow colour is developed, and in more concentrated solutions a precipitate is formed. The colour is developed with a bismuth concentration of 1 in 7×10^4. No colour is obtained with bismuth sulphate solution until a chloride is added, and arsenic, antimony, zinc, cobalt, manganese, and ferric salts interfere with the reaction. Bismuth cannot be determined by this method owing to the occlusion of salts. F. S. Hawkins.

Volumetric determination of bismuth. W. Strecker and A. Herrmann (Z. anal. Chem., 1927, **72**, 5—11).—The bismuth solution is added drop by drop, when boiling, to a standard solution of disodium hydrogen phosphate; the liquid is filtered when cold, neutralised with sodium hydroxide, and mixed with an excess of sodium acetate and standard silver nitrate solution. After dilution the excess of silver in an aliquot portion is titrated with ammonium thiocyanate. In a second method of determination, the bismuth solution is neutralised with ammonia until a slight turbidity appears, dilute hydrochloric acid is added, the boiling solution cleared with hydrochloric acid or ammonium chloride, and the oxychloride is precipitated with hot water. The oxychloride is dissolved in nitric acid, and the chloride determined by Volhard's method. A third method of determination consists in reducing the hot bismuth solution with magnesium, adding ammonium sulphate solution, and heating until the ammonia is removed. The reduced bismuth is then dissolved in ferric chloride solution in an atmosphere of carbon dioxide, and titrated with permanganate. Bismuth can also be determined by reducing with alkaline formaldehyde solution and titrating the excess with iodine. F. S. Hawkins.

Thermostat heater. I. A. Cowperthwaite (J. Amer. Chem. Soc., 1927, **49**, 2255).—The usual lamp is replaced by a resistance of graphite flakes packed in a U-tube of pyrex glass. S. K. Tweedy.

Micropyrometer. H. von Wartenberg and H. Moehl (Z. physikal. Chem., 1927, **128**, 445—448).—A micropyrometer is described which may be employed at any distance above 8 cm. from the heated body and gives a sufficiently large image of such an object as the filament of an electric lamp. Its applications to the measurement of high m. p. and to the determination of the relationship between the current through an electric lamp filament and the temperature are described. H. F. Gillbe.

Apparatus for the determination of melting temperature. G. Lynn (J. Physical Chem., 1927, **31**, 1381—1382).—The apparatus described by Washburn (A., 1924, ii, 344) has been modified by the addition of an electric heating coil and of removable sampling tubes. The present form may be used from temperatures below 0° to 400°; 1 c.c. of recoverable material is required, and the heating and cooling curves obtained give for the m. p. a value which is more trustworthy than that obtained by the capillary tube method, which may be up to 3° too high (Andrews, Lynn, and Johnston, A., 1926, 668). L. S. Theobald.

Simple automatic pipette. F. Friedrichs (Chem.-Ztg., 1927, **51**, 688).—A rubber bulb supplies the suction and an overflow regulates the quantity as in other automatic pipettes, but the expansion of the bulb is regulated by a rod and pressure disc, permitting accurate regulation. A side tube is provided for the eventual removal of the overflowed liquid. C. Irwin.

Laboratory hydrogen and oxygen generator. C. G. Fink and C. L. Mantell (Amer. Electrochem. Soc., Sept., 1927, advance copy, 5 pp.).—An apparatus is described for furnishing a continuous supply of hydrogen at constant pressure for long periods, the hydrogen being generated by electrolysis of 30% sodium hydroxide solution using nickel electrodes. H. J. T. Ellingham.

Rubber stopcock lubricants for high-vacuum and other uses. M. Shepherd and P. G. Ledig (Ind. Eng. Chem., 1927, **19**, 1059—1061).—Lubricants compounded of rubber, "vaseline," and paraffin wax were studied. Pale crêpe and smoked sheet rubber gave the best results. Good results were obtained with paraffin wax of m. p. 30—40°. For high-vacuum work a mixture of pale crêpe rubber (31 parts), white "vaseline" (24 parts), and paraffin wax (5 parts) is recommended. It should be stirred for 190 hrs. at 155°, and then quickly cooled. For lighter lubricants the proportion of rubber should be less. There is evidence of chemical reaction and the time and temperature conditions stated should be precisely followed. The lubricant retains a satisfactory consistency for 12—24 months. C. Irwin.

Equations for design of fractionating columns. L. H. Shirk and R. E. Montonna.—See B., 1927, 735.

Rapid [method of] extraction. A. G. Kuhlmann (Z. anal. Chem., 1927, **72**, 20—27).—The substance to be extracted is contained in a glass weighing bottle with a perforated bottom, which can be covered by a glass cap. The bottle rests in a constriction in the neck of a flask, which is fitted with a condenser, and contains the extracting liquid. On boiling, the vapour rises through and around the sides of the bottle, and the condensed liquid drops back into it. The extraction is rapid and quantitative, and the all-glass construction allows of the use of strong acids as extracting liquids. For a series of extractions at the temperature of the condensed liquid, a large Soxhlet apparatus can be used to hold a number of the glass bottles. Determinations of the soluble matter in linseed-oil cake and wheat flour showed good agreement with the usual Soxhlet method. F. S. Hawkins.

One-way safety valves for vacuum pumps and gas generating apparatus. F. Hein (Z. angew. Chem., 1927, **40**, 864—865).—The valve, of which various applications are described and figured, consists of a pipette-like vessel containing a diaphragm of sintered glass (a Jena glass filter-plate). The pores in the diaphragm are small enough to retain mercury under the pressure likely to prevail in the apparatus. The diaphragm is covered by a layer of mercury 3—4 mm. deep. W. A. Silvester.

Direct-reading hydrogen-ion meter. C. G. Pope and F. W. Gowlett (J. Sci. Instr., 1927, **4**, 380—387).—An apparatus is described for obtaining direct readings of $p_{\rm H}$ values. A four-electrode valve and a potentiometer circuit are used. With a hydrogen electrode the maximum error in $p_{\rm H}$ is 0·09 and with a quinhydrone electrode 0·10. C. W. Gibby.

Sodium voltameter. R. C. Burt (Physical Rev., 1926, [ii], **27**, 813).—The sodium voltameter, in which sodium passes through glass by electrolysis, yields results correct to 1 in 2×10^3, and probably correct to 1 in 6×10^3. A. A. Eldridge.

Measurements with an absorptiometer of objective type. W. Tschudi (Helv. Chim. Acta, 1927, **10**, 614—619).—The absorptive powers of liquids are measured by comparing the effects recorded by a thermopile when cells containing the liquids under examination are placed between the thermopile and a constant light source. The intensity of the light transmitted by an aqueous solution of a coloured substance does not decrease with increasing concentration according to the requirements of a formula of an exponential type. Examination of the variation of the absorptive power of dilute "solutions" of silver chloride with time shows that as aggregation of the particles proceeds the absorptive power of the "solution" increases. J. S. Carter.

Polishing and etching lead, tin, and some of their alloys for microscopical examination. J. R. Vilella and D. Beregekoff (Ind. Eng. Chem., 1927, **19**, 1049—1052).—The sample is cut with a sharp, oiled hacksaw and then ground with a series of emery papers of increasing fineness smeared with a concentrated solution of paraffin wax in kerosene. Wet polishing is carried out on soaped broadcloth with the finest levigated alumina. For etching lead and lead–antimony alloys a mixture of concentrated nitric acid (1 vol.), glacial acetic acid (1 vol.), and glycerol (4 vols.) is suitable. For lead–tin alloys twice as much glycerol is necessary. The structure is best developed by alternate polishing and etching, the etching being conducted for only a few seconds at a time. C. Irwin.

[Diagrammatic] representation of the elements for instruction. A. Piutti (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], **31**, 142—143).—A new spiral chart of the elements (cf. Oddo, A., 1925, ii, 623) is reproduced and described. E. W. Wignall.

Mosandrum. R. C. Wells (J. Washington Acad. Sci., 1927, **17**, 385—388).—Mosandrum, claimed by Smith (Compt. rend., 1878, **87**, 146) as a new element, was a mixture of at least two elements—samarium and gadolinium. The history of the subject is sketched. C. W. Gibby.

Early experiments on ultra-filtration. E. Hatschek (Nature, 1927, **120**, 515).—Schmidt's observation (Ann. Phys. Chem., 1856, **99**, 337) that an animal membrane is less permeable to colloids than to sugar or salts antedates Graham's papers on dialysis. A. A. Eldridge.

Mineralogical Chemistry.

Distribution and transportation of chlorides in the atmosphere. F. Bordas and A. Desfemmes (Compt. rend., 1927, **185**, 603—605).—The chlorine contents of samples of rain-water may be considered to be an indication of the salt content of air in the neighbourhood of the sea. At Cette (Midi) the highest normal value recorded (for the dust) was 3·4% of sodium chloride, and at 35 km. from the sea 0·00267 g. per litre of water. The results depend largely on the atmospheric conditions; thus, after a dust-storm 8·41 g. per m.² of sodium chloride were registered, and after a fall of snow 0·0346 g. per litre. There is no exact relationship between the number of solid particles in the air and its salt content. J. Grant.

Chemical analysis of mud collected on the upper terrace of the Musée Océanographique at Monaco, after the storm on October 31, 1926. H. Marcelet (Compt. rend., 1927, **185**, 662—663).—The dried mud was chestnut-brown in colour, and 97·3% passed a sieve having 4900 meshes/cm.², and the remainder a sieve of 2700 meshes. It contained :

SiO_2 46·56, Al_2O_3 10·69, Fe_2O_3 6·01, CaO 18·09, MgO 2·09, SO_3 0·47, CO_2 (by difference) 16·09%. Assuming the existence of free silica, alumina, and ferric oxide, the remaining elements may be grouped as $CaCO_3$ 31·67, $CaSO_4$ 0·71, and $MgCO_3$ 4·36%.

J. GRANT.

Temperature and salinity observations in the Gulf of Aden. D. J. MATTHEWS (Nature, 1927, **120**, 512).—The phosphorus content of the water in and off the Gulf of Aden is 0·03 mg. P_2O_5 per litre in the upper 50 m., increasing from 200 m. downwards to 0·143 mg. at 1750 m. The arsenic content is 0·005 mg. As_2O_3 per litre at 500—1750 m., but less than 0·001 mg. in the upper 50 m. It is probable that arsenic is removed by plankton organisms much as phosphorus is. A. A. ELDRIDGE.

Chemical composition of the earth, of meteorites, and of the atmosphere of the sun. H. S. WASHINGTON (Bull. Nat. Res. Council, 1926, **2**, II, 30—32).—The earth is considered to possess a central core of iron or iron and nickel, surrounded by a "lithosporic" shell, in which silicates are included sporadically in the metal, then by a "ferrosporic" shell in which iron occurs sporadically in silicate rock, next by a shell of peridotite, and then by the crust. The composition of the earth is given as: Fe (metal) 31·82, Ni (metal) 3·16, Co (metal) 0·23, O 27·71, Si 14·53, Mg, 8·69, Fe (silicate) 7·94, Ca 2·52, Al 1·79, S 0·64, Na 0·39, Cr 0·20, K 0·14, P 0·11, Mn 0·07, C 0·04, Ti 0·02%. Of the 11 most abundant elements in the earth, 9 are among the 11 most abundant elements in the atmosphere of the sun.

CHEMICAL ABSTRACTS.

Crystalline nature of the chief constituent of ordinary coal. C. S. FOX (Nature, 1927, **120**, 547).—When thin sections of coal are examined in ordinary transmitted light, practically all of the bright coal and much of the dull coal layers appear to consist of a madder-red, somewhat granular, translucent substance ("coal substance"); in very thin sections or with strong sunlight it is golden-yellow. Pleochroism is absent, but the substance is isotropic. Sections cut perpendicularly to the planes of lamination show that the substance has the crystalline character of a uniaxial crystal. The presence of three types of minor constituents of coal: resinous substances, amorphous "mineral charcoal," and inorganic matter, is revealed. The nomenclature of the constituents of coal is discussed. A. A. ELDRIDGE.

Zeolites from the leucites near Rome. Gismondite from Capo di Bove and pseudophillipsite from Acquacetosa. V. CAGLIOTI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 163—177).—A carefully selected sample of pure gismondite, d^{18} 2·277—2·279, contained SiO_2 33·89, Al_2O_3 28·14, Fe_2O_3 0·0044, CaO 13·96, BaO 0·27, SrO 0·025, K_2O 2·86, H_2O 20·76, total 99·91%, corresponding with the formula $(Ca,Ba,Sr,K_2)Al_2Si_2O_8,4H_2O$ in agreement with Zambonini and others. It is also in accord with Clark's view that gismondite is similar to hydrated anorthite.

Pseudophillipsite, d^{18} 2·257—2·259, contained SiO_2 37·35, Al_2O_3 26·27, Fe_2O_3 0·0037, CaO 12·65, BaO 0·21, SrO 0·019, K_2O 3·00, H_2O 20·32, total 100·022%, corresponding with the formula $R_2Al_4Si_5O_{18},9H_2O$. Dehydration was effected over sulphuric acid and then by heating in a current of air. On dehydration over sulphuric acid, gismondite attained equilibrium after 900 hrs. and pseudophillipsite after 450 hrs. Dehydration proceeds rapidly in the first few hours, then continues very slowly; there is no sudden break in the curve, indicating the absence of a definite hydrate. On exposure to moist air at 18·3° the lost water was reabsorbed much more rapidly than it was emitted.

On heating the minerals in dry air up to 700° the curves obtained for both minerals are continuous, showing that the water is dissolved or absorbed. After exposure to moist air for 19 hrs. at different temperatures, the amount of water reabsorbed is not in complete agreement with that evolved. Moreover there is a notable variation in the rate of absorption between 270° and 310°. Samples which have been completely dehydrated do not reabsorb water.

M. CARLTON.

Chemical composition of herschellite from Acicastello. V. CAGLIOTI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 156—163).—The results of previous analyses of the mineral herschellite are not concordant and it is doubtful whether the samples analysed were pure. The greatest discrepancies arise in the values obtained for calcium and sodium and potassium; these, however, may be due to the fact that the herschellite obtained from Acicastello is accompanied by phillipsite and analcime and the separation of these latter from herschellite is difficult. The mineral contains: SiO_2 44·73, Al_2O_3 21·18, Fe_2O_3 0·00126, CaO 1·65, K_2O 4·53, Na_2O 8·04, H_2O 20·11, total 100·24%. Neither barium nor strontium could be detected spectroscopically. The formula deduced from these results is $R_2Al_4Si_7O_{18},11H_2O$.

Loss of water from the mineral over sulphuric acid was 6·27%, equilibrium being attained after about 358 hrs.; the curve obtained is smooth as with other zeolites. Reabsorption of the lost water was complete after 6 hrs.' exposure to air saturated with water vapour, *i.e.*, in about 1/60 of the time required for its emission.

A sample of the mineral heated at 182° lost 11·20% of water and reabsorbed it again from a moist atmosphere in about 20 hrs. at 22°, the amount reabsorbed exceeding that emitted by 0·062%. Again the curve is characteristic of other zeolites. M. CARLTON.

Sericite–lazulite pseudomorphs after orthoclase from Bolivia. E. V. SHANNON (J. Washington Acad. Sci., 1927, **17**, 388—390).—A description of certain specimens in the U.S. National Museum.

C. W. GIBBY.

Ferrimolybdite from Bivongi (Calabria). G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 53—57).—The yellow mineral accompanying Bivongi molybdite is ferrimolybdite (cf. Pilipenko, Festsch. Vernadsky, Moscow; Neues Jahrb. Min. Ref., 1915, 191), for which the formula $4Fe_2O_3,13MoO_3,44H_2O$ is found. E. W. WIGNALL.

Organic Chemistry.

Mechanism of molecular rearrangements. (Mme.) Ramart-Lucas (Compt. rend., 1927, 185, 561—563).—A theoretical explanation of common examples of molecular rearrangements involving the movement of single electron linkings.

H. Burton.

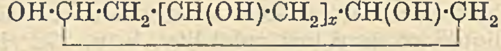
Carbon monoxide and bivalent carbon. H. Scheibler (Z. angew. Chem., 1927, 40, 1072—1081).—A review of recent work.

Synthesis of hydrocarbons of the allene series. M. Bouis (Bull. Soc. chim., 1927, [iv], 41, 1160—1165).—Alkyl derivatives of allyl alcohol of the type $OH\cdot CHR\cdot CH:CH_2$ when treated with phosphorus tribromide (in presence of pyridine to prevent addition of hydrogen bromide to the double linking) yield α- and not γ-brominated derivatives, $CHR:CH\cdot CH_2Br$, in excellent yield. These substances are readily converted by bromine into alkylated glycerol tribromohydrins, which with solid potassium hydroxide yield epidibromohydrins, $CHRBr\cdot CBr:CH_2$, and from these, on treatment with zinc powder in presence of alcohol, allene derivatives may be prepared in 70—75% yield. The following substances were prepared: *α-bromo-Δ^{β}-pentene*, b. p. 123—124°/760 mm., d^{20} 1·2545, n_D^{20} 1·4731; *α-bromo-Δ^{β}-hexene*, b. p. 42—44°/10 mm., d^{16} 1·2119, n_D^{16} 1·4778; *α-bromo-Δ^{β}-heptene*, b. p. 62—64°/10 mm., d^{17} 1·1682, n_D^{17} 1·4760. The foregoing substances were characterised by conversion into the corresponding acetates and alcohols, viz., *Δ^{β}-pentenyl acetate*, b. p. 149—151°, d^{22} 0·9019, n_D^{22} 1·4219; *Δ^{β}-hexenyl acetate*, b. p. 171—173°, d^{18} 0·8976, n_D^{18} 1·4282; *Δ^{β}-heptenyl acetate*, b. p. 192—194° (corr.), d^{13} 0·8915, n_D^{13} 1·4314; *Δ^{β}-penten-α-ol*, b. p. 138—139°, d^{23} 0·8444, n_D^{23} 1·4359; *Δ^{β}-hexen-α-ol*, b. p. 158—160°, d^{16} 0·8490, n_D^{16} 1·4403; *Δ^{β}-hepten-α-ol*, b. p. 177—179° (corr.), d^{20} 0·8421, n_D^{20} 1·4410: the tribromohydrins prepared were *αβγ-tribromopentane*, b. p. 122—124°/18 mm., d^{19} 2·0714, n_D^{19} 1·5580; *αβγ-tribromohexane*, b. p. 127—129°/11 mm., d^{16} 1·9429, n_D^{16} 1·5506; *αβγ-tribromoheptane*, b. p. 142—143°/12 mm., d^{17} 1·8112, n_D^{17} 1·5393: epitribromohydrins, *βγ-dibromo-Δ^{α}-pentene*, b. p. 173°/760 mm., d^{19} 1·7442, n_D^{19} 1·5316; *βγ-dibromo-Δ^{α}-hexene*, b. p. 83—85°/9 mm., d^{14} 1·6381, n_D^{14} 1·5248; *βγ-dibromo-Δ^{α}-heptene*, b. p. 108—110°/12 mm., d^{18} 1·5595, n_D^{18} 1·5200: allene derivatives, *$\Delta^{\alpha\beta}$-pentadiene*, b. p. 44—45°, d^{20} 0·6890, n_D^{20} 1·4149; *$\Delta^{\alpha\beta}$-hexadiene*, b. p. 78—79°, d^{17} 0·7198, n_D^{17} 1·4298; *$\Delta^{\alpha\beta}$-heptadiene*, b. p. 105—106° (corr.), d^{18} 0·7410, n_D^{18} 1·4376. These allene derivatives do not precipitate ammoniacal solutions of cuprous chloride, but, like their acetylenic isomerides, they give white precipitates with mercuric chloride solutions. The action of bromine yields *αββγ-tetrabromopentane*, b. p. about 120°/3 mm., d^{22} 2·2839, n_D^{22} 1·5916, *αββγ-tetrabromohexane*, b. p. about 130°/3 mm., d^{15} 2·1873, n_D^{15} 1·5850, and *αββγ-tetrabromoheptane*, b. p. about 140°/3 mm., d^{20} 2·0675, n_D^{20} 1·5718. During attempts to prepare arylallene derivatives by the same synthetic method, γ-phenyl-Δ^{α}-propen-γ-ol, $OH\cdot CHPh\cdot CH:CH_2$, yielded, with phosphorus tribromide, cinnamyl bromide, a molecular transposition again taking place, and the latter was readily converted into αβγ-tribromo-α-phenylpropane, but the treatment of this substance with solid potassium hydroxide or sodium ethoxide yielded no definite product. W. J. Powell.

Hydrogenation of squalene. M. Tsujimoto (Chem. Umschau, 1927, 34, 256—258; cf. A., 1916, i, 786; Heilbron, Hilditch, and Kamm, this vol., 130).—Kurozame oil (from the liver of the black shark, mainly of the genus *Zameus*) on hydrogenation in the presence of a nickel catalyst yields a product, m. p. 46—47°, acid value 3·2, saponification value 82·8, iodine value 1·2, unsaponifiable matter 51·43%. The unsaponifiable portion contains dodecahydrosqualene (for which the name squalane is suggested), batyl alcohol, derived chiefly from selachyl alcohol (cf. A., 1922, i, 297), and probably hydrogenated cholesterol. Dodecahydrosqualene as isolated from the crude hydrogenated product by distillation is a colourless liquid of very low volatility, b. p. 272°/15 mm., d_4^{20} 0·8084; n_D^{20} 1·4515; flash point (Pensky–Martens apparatus) 190°. It is unchanged by treatment with sulphuric acid at 70°. W. J. Powell.

Action of cyanogen bromide on dimagnesium acetylene dibromide. A. S. Nekrassov (Ber., 1927, 60, [*B*], 1756—1758).—Dibromoacetylidene, $CBr_2:C$, b. p. 76—76·5°, is prepared by the action of cyanogen bromide on dimagnesium acetylene dibromide (cf. Lawrie, A., 1907, i, 3). H. Wren.

Action of trichloroethylene, ααβ-trichloroethane, and αααβ-tetrachloroethane on magnesium phenyl bromide. L. Bert (Bull. Soc. chim., 1927, [iv], 41, 1173—1174).—The chloro-derivatives mentioned undergo no reaction when 1 mol. of each is added to a solution of 1 mol. of magnesium phenyl bromide in anhydrous ether, even after prolonged boiling. If the ether is replaced by dry toluene and the mixture heated on the water-bath, neither trichloroethylene nor ααβ-trichloroethane reacts, but αααβ-tetrachloroethane yields a crystalline precipitate, which is not the expected ααα-trichloro-β-phenylethane. W. J. Powell.

Highly-polymerised compounds. IX. Polyvinyl acetate and polyvinyl alcohol. H. Staudinger, K. Frey, and W. Starck (Ber., 1927, 60, [*B*], 1782—1792; cf. A., 1926, 719).—Polymerisation of monomeric vinyl acetate at low temperatures yields a viscous resin which gives highly viscous solutions and has a greater mean mol. wt. than the brittle resins which are prepared at higher temperature and give less viscous solutions. The material is thus analogous with styrene (cf. Brunner and Wehrli, Diss., Zürich, 1926). The polyvinyl acetate can be separated into fractions of greater and less solubility by suitable treatment with solvents. The more soluble portions have lower mean mol. wt. and yield less viscous solutions than the less soluble fractions. A material of mean mol. wt. 5500 has been separated into fractions of mean mol. wt. 3000, 4500, and 9000. Hydrolysis of polyvinyl acetate affords polyvinyl alcohol which resembles starch in its insolubility in organic media and (colloidal) solubility in water or formamide. Polyvinyl acetates which give highly viscous solutions yield polyvinyl alcohols with similar properties, whereas alcohols giving less viscous solutions are derived from acetates of lower mean mol. wt. It appears, therefore, that the mean mol. wt. does not undergo change during the hydrolysis. In the polyvinyl alcohols there must therefore be present mixtures of substances in which 40—100 monomerides are united to highly-polymerised molecules. Isolation of individuals is regarded as impossible, since the physical properties of the polymerides do not differ appreciably from one another. The occurrence of materials with differing degrees of polymerisation and variation in properties which are transmitted to their derivatives contradicts the frequent assumption that association products of relatively simple compounds are present in such highly complex compounds. Polymerisation is regarded as consisting in the chemical union of the single unit molecules; thus polyvinyl alcohol is represented as  $OH{\cdot}CH{\cdot}CH_2{\cdot}[CH(OH){\cdot}CH_2]_x{\cdot}CH(OH){\cdot}CH_2$ ($x = 40$—100). It remains uncertain in what manner the terminal valencies are satisfied, but the presence of many-membered rings is probable.

Oxidation of polyvinyl alcohol or acetate with concentrated nitric acid affords oxalic acid. The alcohol can be acetylated, but the impossibility of carrying the process to completion renders fruitless the attempt to decide whether hydrolysis of a given acetate followed by acetylation of the alcohol yields a product identical with the original material. Similar difficulties are experienced in the preparation of the *benzoate*. The *nitrate* and the *methyl ether* are described; the latter resembles methylated starch in its solubility in water and alcohol. In general, a close analogy appears to exist between polyvinyl alcohol and starch, the essential difference being the greater stability of the former and its inability to give monomeric fragments by simple processes, whereas starch readily affords dextrose or its derivatives. This is attributed to the C–C union in the alcohol and the attachment of the dextrose anhydride residues in starch in some unknown manner.

Reduction of polyvinyl alcohol by hydriodic acid gives a dark, highly-polymerised hydrocarbon which certainly is not a simple paraffin; probably ring formation has occurred. Reduction of polyvinyl bromide leads to a complex paraffin.

Attempts to prepare polyvinyl alcohol directly from acetaldehyde have not been successful, but it appears to be present in small amount in aldehyde resin.

H. WREN.

***iso*Propylacetylenylcarbinol and two stereoisomeric forms of di*iso*propylbutinediol.** W. KRESTINSKI and W. MARJIN (Ber., 1927, **60**, [*B*], 1866—1869).—The action of *iso*butaldehyde on the product of the action of acetylene on magnesium ethyl bromide gives *βη-dimethyl-Δ^δ-octinene-γζ-diol*, $CHMe_2{\cdot}CH(OH){\cdot}C{:}C{\cdot}CH(OH){\cdot}CHMe_2$, m. p. 107—108° (*acetate*, b. p. 257—258°; *dibromide*, m. p. 145—146°), and its stereoisomeride, m. p. 69—70° (*acetate*, b. p. 253—256°; *dibromide*, m. p. 156—157°). As by-product, *δ-methyl-Δ^α-pentinen-γ-ol*, b. p. 131—132°, d_4^{20} 0·8779, n_D^{20} 1·43569 (*silver* compound), is formed. The simultaneous production of mono- and dihydroxy-compounds is attributed to the equilibrium $MgBr{\cdot}C{:}C{\cdot}MgBr + C_2H_2 \rightleftharpoons 2CH{:}C{\cdot}MgBr$ in the Grignard solution, the formation of the monohydric alcohol being therefore favoured by the presence of an excess of acetylene. H. WREN.

Attempted application of Merling's reaction to aldehydes. Synthesis of *iso*propylacetylenylcarbinol. W. KRESTINSKI and F. SOLODKI (Ber., 1927, **60**, [*B*], 1869—1873).—δ-Methyl-Δ^α-pentinen-γ-ol, b. p. 131—131·5°, d_4^{20} 0·8778, n_D^{20} 1·43539 (cf. preceding abstract), is obtained in modest yield by the action of sodamide and acetylene on *iso*butaldehyde in ether, thus establishing the enolisation of the aldehyde, $CHMe_2{\cdot}CHO \longrightarrow CMe_2{:}CH{\cdot}OH$. The main products of the change are ββδ-trimethylpentane-αγ-diol, m. p. 51—52°, and γ-hydroxy-ββδ-trimethylhexaldehyde, b. p. 118—120°/16 mm., which are commonly derived from *iso*butaldehyde under the influence of alkali.

H. WREN.

Condensation of ethylene oxides with alcohols in presence of sulphuric acid as catalyst. II. E. FOURNEAU and I. RIBAS (Bull. Soc. chim., 1927, [iv], 41, 1046—1056; cf. this vol., 131).—Ethylene oxide (1 mol.) condenses with ethylene chlorohydrin (2·5 mols.) in presence of a small amount of sulphuric acid, yielding diethylene dioxide (dioxan), β-chloroethyl β-hydroxyethyl ether, and ββ′-chloroethoxyethyl β-hydroxyethyl ether. *β-Dimethylaminoethyl β-hydroxyethyl ether*, b. p. 95°/15 mm. (*picrate*; *picrolonate*, m. p. 110°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*; *cinnamate hydrochloride*), is prepared from the corresponding chloro-compound and dimethylamine at 120°. *ββ′-Dimethylaminoethoxyethyl β-hydroxyethyl ether*, b. p. 135°/15 mm. (*picrate*, m. p. 45°; *picrolonate*, m. p. 74—75°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*, m. p. 83—84°), is obtained similarly. From epichlorohydrin and ethylene chlorohydrin there is obtained *β-chloroethyl γ-chloro-β-hydroxypropyl ether*, b. p. 123—125°/18 mm. (yield, 70%), which with dimethylamine furnishes *β-dimethylaminoethyl γ-dimethylamino-β-hydroxypropyl ether*, b. p. 120°/18 mm. (*dihydrochloride*, m. p. 210°). Ethylene chlorohydrin and *as*-methylethylethylene oxide in presence of sulphuric acid give only methylethylacetaldehyde(?), and a substance, b. p. 75°/18 mm., probably a substituted dioxan. In the absence of acid, at 100° for 4—8 days, there is produced a condensation product which on treatment with dimethylamine furnishes *β-dimethylaminoethyl β-hydroxy-β-methyl*-n-*butyl ether*, b. p. 115°/20 mm. (*picrate*, m. p. 75°; *benzoate hydrochloride*; m-*nitrobenzoate hydrochloride*, m. p. 96°; *cinnamate hydrochloride*). Several of the above hydrochlorides are local anæsthetics. H. BURTON.

Infra-red absorption spectra of organic compounds of sulphur. I. Aliphatic mercaptans and sulphides. F. K. BELL (Ber., 1927, **60**, [*B*], 1749—1756).—Measurements are recorded of the infra-red absorption spectra between 1·0 and 12·0 μ of *n*-propyl, *n*-butyl, and *iso*amyl mercaptan and the corresponding sulphides. Four sharply-defined absorption bands which are present in the spectra of all these mercaptans suffer uniform displacement towards the region of greater wave-length by passage from the mercaptan to the corresponding sulphide. The occurrence of a sharp band at 3·8 μ in the absorption spectra of the mercaptans which is not present in those of the sulphides affords a qualitative method for the discrimination between aliphatic mercaptans and sulphides; the origin of the band cannot be satisfactorily explained. H. Wren.

Preparation and hydrolysis of esters by the distillation method. II. Preparation of *iso*amyl acetate. L. Gay, P. Mion, and M. Auméras (Bull. Soc. chim., 1927, [iv], 41, 1027—1040).—Mixtures of acetic acid (0·48 mol.) and *iso*amyl alcohol (0·52 mol.) with a small amount of sulphuric acid on distillation with a Vigreux column give (*a*) a binary mixture of water (0·788) and *iso*amyl acetate (0·212 g.-mol.), practically free from acetic acid and the alcohol, (*b*) a small intermediate fraction which is mainly water, and (*c*) pure *iso*amyl acetate. The binary mixture also passes over first if the acid or alcohol is in excess, but the difficulty of separation of the acetate is increased. The results agree with the theory previously enunciated (this vol., 14). H. Burton.

Hydrogenation of oleic acid with active hydrogen. H. I. Waterman and S. H. Bertram (Chem. Umschau, 1927, 34, 255—256).—The main reaction between electrically activated hydrogen and oleic acid leads to the formation of polymerised products. The work has been repeated using larger quantities of a sample of oleic acid containing only 0·3—0·5% of saturated fatty acids as an impurity. The amount of stearic acid obtained after treatment with activated hydrogen is considerably greater than that present in the original oleic acid, indicating that hydrogenation also takes place to some extent. W. J. Powell.

Formation of lactic acid from sugar by the action of alkalis. [Determination of lactic acid in aqueous solutions.] W. Windisch, P. Kolbach, and H. Ruckdeschel (Woch. Brau., 1927, 44, 405—410, 417—422, 429—434, 441—446; cf. Kiliani, A., 1882, 715, 827; Meisenheimer, A., 1908, i, 319).—A detailed account of the production of lactic acid from invert-sugar, dextrose, and lævulose by the action of various alkalis. The effects of change of temperature, times of heating, alkali and sugar concentrations have been studied. The best yields recorded are of the order of 50—60%, agreeing with the value quoted by Meisenheimer (*loc. cit.*). For the determination of lactic acid in aqueous solution, the acid is first extracted by ether in a Partheil–Rose apparatus, full details of which are given, and then oxidised to acetaldehyde by standard potassium permanganate solution. The method is accurate to ±1% for quantities of 0·04—0·5 g., but is less accurate for smaller amounts. H. Burton.

Configurational relationships of α-hydroxybutyric and lactic acids. P. A. Levene and H. L. Haller (J. Biol. Chem., 1927, 74, 343—350).—*d*-α-Hydroxybutyric acid, $[\alpha]_D^{22}$ +2·3° (*barium* salt, $[\alpha]_D^{22}$ −5·6°), was converted into the *ethyl* ester, $[\alpha]_D^{22}$ −3·8°, which, on reduction, gave l-*butane*-αβ-*diol*, b. p. 94—96°/12 mm., $[\alpha]_D^{22}$ −7·4° in alcohol (*diphenylcarbamate*, m. p. 121—123°, $[\alpha]_D^{22}$ −19·8° in alcohol). d-*Butane*-αβ-*diol*, b. p. 91—91·5°/13 mm., $[\alpha]_D^{22}$ +12·4° in alcohol, prepared by reduction of hydroxymethyl ethyl ketone with fermenting yeast (*diphenylcarbamate*, m. p. 125—127°, $[\alpha]_D^{20}$ +23·7° in alcohol), gave l-α-*bromo*-β-*hydroxybutane*, b. p. 61—63°/12 mm., $[\alpha]_D^{22}$ −11·8°, which, on reduction, yielded d-*methylethylcarbinol*, $[\alpha]_D^{22}$ +13·0° (*phenylcarbamate*, m. p. 61—63°, $[\alpha]_D^{22}$ +26·5° in alcohol). *d*-α-Hydroxybutyric acid is therefore configurationally related to *d*-lactic and *d*-β-hydroxybutyric acids. C. R. Harington.

Condensation of α-hydroxy- and keto-acids under the influence of the combined action of catalysts. V. Ipatiev and G. Razubaiev (Ber., 1927, 60, [*B*], 1971—1973; cf. A., 1926, 1124).—Sodium glycollate when heated under pressure in aqueous solution with hydrogen in the presence of an aluminium oxide–nickel oxide catalyst yields succinic acid by condensation and acetic acid by hydroxyl reduction. The main reaction consists in decomposition of the molecule into carbonate, methane, carbon dioxide, water, succinic and formic acids; this decomposition increases markedly with increasing temperature. An oil with an intense odour and a small quantity of acids of high b. p. are also produced. Pyruvic acid undergoes condensation more readily, but the temperature should not exceed 230°, above which the yield of the main condensation product (methylsuccinic acid) sinks rapidly and products are formed which resinify rapidly when exposed to air. Lactic acid is regarded as primary product of the change (cf. *loc. cit.*). H. Wren.

Unsaturation phenomena of acetylenic acids and esters. I. Constitution of ι-ketoundecoic acid. W. W. Myddleton and A. W. Barrett (J. Amer. Chem. Soc., 1927, 49, 2258—2264; cf. Chuit and others, this vol., 40).—Treatment of dehydroundecenoic acid (cf. Krafft, A., 1896, i, 665) with mercuric acetate in glacial acetic acid affords *mercuric κκκ-triacetoxymercuri-ι-ketoundecoate* (I). Ethyl dehydroundecenoate yields similarly *ethyl κκκ-triacetoxymercuri-ι-ketoundecoate.* Treatment of (I) with concentrated hydrochloric acid affords ι-ketoundecoic acid, m. p. 59·5° (*ethyl* ester, b. p. 169—170°/12 mm.; *semicarbazone*, m. p. 136·5°) (cf. Welander, A., 1895, i, 447). The *oxime* of the acid, m. p. 68—69°, is converted by concentrated sulphuric acid into a mixture, m. p. 65—72°, of the isomerides $NHMe\cdot CO\cdot[CH_2]_8\cdot CO_2H$ and $NHAc\cdot[CH_2]_8\cdot CO_2H$. Treatment of Δ^{θ}-undecinoic acid with mercuric acetate yields a mixture of *mercuric diacetoxymercuriketoundecoates*, which, on hydrolysis with hydrochloric acid, affords the above ι-ketoundecoic acid, together with an isomeride, presumably *θ-ketoundecoic acid*, m. p. 43·5°. Mercuration of the ethyl esters of the above acids proceeds analogously. F. G. Willson.

Unsaturation phenomena of acetylenic acids and esters. II. Reaction between mercuric acetate and some acetylenic acids and esters. W. W. Myddleton, R. G. Berchem, and A. W. Barrett (J. Amer. Chem. Soc., 1927, 49, 2264—2269; cf. preceding abstract).—Treatment of stearolic, ricinoleic, and behenolic acids with mercuric acetate in glacial acetic acid yields, respectively, *mercuric diacetoxymercuriketostearate*, *diacetoxymercurihydroxyketostearate*, and *diacetoxymercuriketobehenate*, which, on treatment with hydrochloric acid, yield θ-ketostearic, ζ-hydroxy-θ-ketostearic, and θ-ketobehenic acids (cf. Baruch, A., 1894, i, 170, 171; Goldsobel, A., 1895, i, 81; Holt, A., 1892, 812). Mercuration of methyl behenolate proceeds analogously, but definite compounds could not be obtained similarly from γ-butinene-αα-dicarboxylic acid and γ-butinene-α-carboxylic acid. F. G. Willson.

Existence and preparation of methyl orthocarbonate. H. von Hartel (Ber., 1927, **60**, [*B*], 1841).—*Methyl orthocarbonate*, m. p. −5·5°, b. p. 114°, $d_{18·5}^{18·5}$ 1·0232, n_D^{16} 1·3864, is readily obtained by the action of trichloronitromethane on sodium methoxide in pure methyl alcohol. It volatilises to a marked extent with methyl alcohol or ether. H. Wren.

Preparation of ethoxalyl chloride. L. Bert (Bull. Soc. chim., 1927, [iv], **41**, 1165—1166; cf. A., 1926, 56; Barré, this vol., 228).—In the preparation of ethoxalyl chloride by the action of phosphorus pentachloride on ethyl oxalate, yields of 80% may be obtained provided that the starting materials are of a high degree of purity. The phosphorus pentachloride is best prepared beforehand from phosphorus trichloride and chlorine in the flask used for the reaction with ethyl oxalate. W. J. Powell.

Lanthanum, cerous, praseodymium, neodymium, and samarium maleates. L. Coniglio (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 80—82).—*Salts* of the general formula $[(\colon CH\cdot CO_2\cdot)_2]_3R_2,10H_2O$, where R is $Ce^{\cdots}$, Pr, Nd, La, or Sm, are prepared, of which the respective solubilities of the anhydrous salts in water at 25° are 8·05, 6·05, 5·64, 4·19, and 1·45 g. per 100 g. of solution. E. W. Wignall.

C_4-Saccharinic acids. IV. Preparation of the two *dl*-αβ-dihydroxybutyric acids. J. W. E. Glattfeld and S. Woodruff (J. Amer. Chem. Soc., 1927, **49**, 2309—2315; cf. A., 1925, i, 881).—The α-chloro-β-hydroxybutyric acid obtained from crotonic acid by a modification of the method of Melikoff and Zelinsky (A., 1888, 1056) yields, when treated as the barium salt in aqueous solution with silver oxide, an αβ-dihydroxybutyric acid, (I), m. p. 81·5°. Oxidation of crotonic acid with permanganate yields an αβ-dihydroxybutyric acid, $(+1H_2O)$ (II), m. p. 73·5—74·5° (cf. Fittig and Kochs, A., 1892, 956), also obtained by the oxidation of crotonic acid with chlorate in presence of osmium tetroxide (cf. Milas and Terry, A., 1925, i, 780). The following derivatives of (I) and (II) respectively were prepared: *phenylhydrazides*, m. p. 103° and 129·5°; *o-tolylhydrazides*, m. p. 103° and 111·5°; and *barium* and *silver* salts. F. G. Willson.

Combined action of catalysts (nickel oxide and aluminium oxide) on solutions of substituted hydroxysuccinic acids under high pressure of hydrogen and at high temperatures. G. Razubaiev (Ber., 1927, **60**, [*B*], 1976—1980).—The behaviour of sodium lactate under the conditions expressed in the title (cf. A., 1926, 1124) has been explained by the scheme: $2OH\cdot CHMe\cdot CO_2H \longrightarrow CO_2Na\cdot CMe(OH)\cdot CHMe\cdot CO_2Na \longrightarrow CO_2Na\cdot CMe\colon CH\cdot CO_2Na \longrightarrow CO_2Na\cdot CHMe\cdot CH_2\cdot CO_2Na$, but α-hydroxy-αβ-dimethylsuccinic acid could not be detected among the products. The sodium salts of α-hydroxy-αβ-dimethylsuccinic, α-hydroxy-α-methylsuccinic, and α-hydroxy-α-methyl-β-ethylsuccinic acids have been subjected to the same treatment. In each case methylsuccinic acid is produced in 25—30% yield. In addition, fission of the molecule occurs with production of methane, carbonate, and a series of monobasic acids. Formic and acetic acids are invariably produced, the yield being highest (45%) with α-hydroxy-α-methylsuccinic acid and lowest (16%) with α-hydroxy-α-methyl-β-ethylsuccinic acid. The yield of higher monobasic acid increases in the inverse order; with α-hydroxy-α-methyl-β-ethylsuccinic acid butyric acid is obtained in 30% yield, due to fission between the α- and β-carbon atoms. In all cases an intensely odorous oil, similar to that derived from sodium lactate (*loc. cit.*), is produced in quantity too small for extended examination. H. Wren.

Reduction of polybasic α-hydroxy-acids under the influence of the combined action of catalysts. V. Ipatiev and G. Razubaiev (Ber., 1927, **60**, [*B*], 1973—1976; cf. A., 1926, 1124, and preceding abstract).—The action of hydrogen under pressure on heated solutions of sodium malate, tartrate, and citrate in the presence of aluminium oxide and nickel oxide is characterised by reduction of the hydroxyl group by hydrogen with production of the corresponding saturated polybasic acid and decomposition of the molecule into monobasic acids. The first change is observed only with malic and tartaric acids, which give succinic acid in 50% yield and very small amount respectively. Decomposition of the acids affords formic and acetic acids, carbon dioxide, and methane. Methylsuccinic acid is obtained from citric acid in rather more than 30% yield. H. Wren.

Catalytic reduction of *d*-gluconic acid to *d*-glucose. J. W. E. Glattfeld and E. H. Shaver (J. Amer. Chem. Soc., 1927, **49**, 2305—2308).—*d*-Gluconic acid was treated in faintly acid aqueous solution at the ordinary temperature with hydrogen under a pressure of 17 lb./sq. in., in presence of platinum oxide. Glucosazone was isolated from the reaction mixtures in amounts corresponding with 14—28% yields of dextrose, the latter also being obtainable in crystalline condition. F. G. Willson.

Behaviour of aldehydeacetals on hydrogenation. Formation of ethers from acetals. F. Sigmund and G. Marchart (Monatsh., 1927, **48**, 267—288).—Hydrogenation of benzaldehydediethylacetal at 180° by the Sabatier and Senderens process yields benzyl ethyl ether (45%), b. p. 185—187°. From phenylacetaldehydedimethylacetal there is produced methyl β-phenylethyl ether (50%), b. p. 189—190°. Similarly, heptaldehydediethylacetal yields ethyl heptyl ether (61%), b. p. 165—167°; *heptaldehydedi-*n*-propylacetal*, b. p. 112·5°/9 mm., affords *n*-propyl heptyl ether (64%), b. p. 182·5—183°; *heptaldehydedi*iso*butylacetal*, b. p. 126·6° (corr.)/10 mm., gives iso*butyl heptyl ether* (64%), b. p. 194—196°; *phenylacetaldehydedi-*n*-propylacetal*, b. p. 136·6° (corr.)/12 mm., furnishes β-*phenylethyl* n-*propyl ether* (80%),

b. p. 225—227° (corr.); and cinnamaldehydediethylacetal yields ethyl γ-phenylpropyl ether, b. p. 220—222°. H. Burton.

α-Bromo- and α-hydroxy-aldehydes. R. Dworzak and P. Pfifferling (Monatsh., 1927, 48, 251—266).—Bromination of parapropaldehyde with 2 atoms of bromine at −10 to −5°, followed by treatment with alcohol, yields the acetal of α-bromopropaldehyde. With 4 atoms of bromine there are produced *αα-dibromopropaldehydeacetal*, b. p. 91°/9 mm., together with a substance, b. p. 130°/2—3 mm., probably *αβγ-tribromo-α-methylvaleraldehyde alcoholate*. Bromination of paraheptaldehyde with 1 mol. of bromine at −6°, with subsequent treatment by alcohol, furnishes *α-bromoheptaldehyde*, b. p. 62°/2 mm., and its *acetal*, b. p. 92°/1 mm.

Hydrolysis of the bromoacetals with water yields the corresponding hydroxyaldehyde. Thus from the acetals of α-bromopropaldehyde, αα-dibromopropaldehyde, and α-bromoheptaldehyde there were obtained α-hydroxypropaldehyde, pyruvaldehyde, and a dimeric form of *α-hydroxyheptaldehyde*. H. Burton.

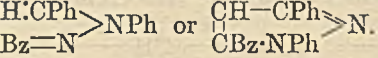
Solvatochromism of the ketones. J. S. P. Blumberger (Chem. Weekblad, 1927, 24, 454—462).—It is proposed to employ the term "solvatochromism" to cover all the phenomena of molecular addition between organic compounds and organic and inorganic compounds, since the term "halochromism," which should be restricted to cases of addition analogous to salt formation, has been hitherto employed very loosely. The theories put forward to account for the various cases of addition are considered and criticised. S. I. Levy.

Stability of acetone to light. K. Wiesler (Z. angew. Chem., 1927, 40, 1023—1024).—One drop of 0·1% potassium permanganate solution per 10 c.c. of acetone was used to test for the presence of oxidisable impurities. Pure acetone, which remained stable to this permanganate for 5 hrs., decolorised it in 6—7 min. after 4 hrs.' exposure to a mercury vapour lamp; on distilling, pure acetone stable to potassium permanganate was obtained as the main distillate, but the last runnings contained a quantity of a viscous substance too small to identify. Exactly similar effects were obtained by repeating the whole experiment with this main distillate, indicating that the sensitivity of acetone to light is due to its actual decomposition, and not to some impurity previously present. S. J. Gregg.

Composition of acetone oil. H. Suida and H. Poll (Monatsh., 1927, 48, 167—192; cf. Wolfes, A., 1891, 819; Pringsheim and Bondi, A., 1925, i, 1072).—Examination of 18 fractions obtained from acetone oil, having b. p. 55—60°/760 mm. to 48—51°/15 mm., shows the following constituents to be present (figures indicate percentage of substance in ketone oil boiling within these temperatures: acetone (2·3), methyl ethyl ketone (5·8), methyl *iso*propyl ketone (2·1), methyl propyl ketone (32·6), methyl butyl ketone (14·5), ethyl propyl ketone (0·6), methyl *iso*butyl ketone (7·6), mesityl oxide (3·8), propyl *iso*propyl ketone (4·6), methyl α-methylpropyl ketone (7·6), methyl α-ethylpropyl ketone (9·0), 3-methyl-Δ^3-hexen-5-one (12·5), and methyl *n*-amyl ketone (4·6). An equimolecular mixture of calcium acetate and calcium butyrate yields on distillation acetone, mesityl oxide, methyl ethyl, methyl propyl, ethyl propyl, and dipropyl ketones. If 4·5 mols. of calcium acetate are used to 1 mol. of calcium butyrate the products are acetone, methyl ethyl and methyl propyl ketones. H. Burton.

Trifluoroacetone. F. Swarts (Bull. Acad. roy. Belg., 1927, [v], 13, 175—180).—Trifluoroacetone, b. p. 21·9°, d^0 1·282 (*hydrogen sulphite*; *monohydrate*, m. p. 51°; *semicarbazone*, m. p. 127°; *oxime*, m. p. −1·5°, b. p. 102·5—103°, $d^{10\cdot5}$ 1·3042, $n_\alpha^{10\cdot5}$ 1·34636, $n_\beta^{10\cdot5}$ 1·3528), may be prepared by boiling ethyl trifluoroacetoacetate (this vol., 646) with 10% sulphuric acid, or more conveniently by decomposing the crude sodium salt of the ester with excess of dilute sulphuric acid. Catalytic reduction with hydrogen yields *trifluoro*iso*propyl alcohol*. The depression of the b. p. consequent on the substitution of three fluorine atoms in a methyl group adjacent to a carbonyl group is always of the order of several degrees, but varies considerably with the nature of the compound considered. J. S. Carter.

Action of amines and ammonia on acetylenic γ-diketones. G. Dupont (Bull. Soc. chim., 1927, [iv], 41, 1167—1169; cf. A., 1914, i, 701; Ruhemann and Cunnington, J.C.S., 1899, 75, 954).—Acetylenic γ-diketones, *e.g.*, dibenzoylacetylene, react readily, not only with secondary amines, but also with the majority of primary amines and even with ammonia to give compounds the analyses of which indicate that addition of 1 mol. of ammonia or amine to the triple linking takes place. The following were prepared: *α-amino-αβ-dibenzoylethylene*, m. p. 142°; *α-amino-αβ-ditoluoylethylene* (?), m. p. 138° (not analysed); *α-amino-αβ-dianisoylethylene*, m. p. 107°: from aniline, *α-anilino-αβ-dibenzoylethylene*, m. p. 131° ($+0\cdot5C_6H_6$, m. p. 121°); *α-anilino-αβ-dianisoylethylene*, m. p. 138°: from *o*-toluidine, *α-o-toluidino-αβ-dibenzoylethylene*, a yellow, crystalline precipitate (m. p. omitted); from piperidine, *α-piperidino-αβ-dibenzoylethylene*, m. p. 181°, *α-piperidino-αβ-dianisoylethylene* (?), m. p. 164—165°. Neither diphenylamine nor hydrazine gave a crystalline derivative with any of the three acetylenic diketones used. With phenylhydrazine and dibenzoylacetylene a *derivative*, m. p. 160°, NHPh·NH·CBz:CHBz or NH_2·NPh·CBz:CHBz, was obtained. This substance loses 1 mol. of water on fusion, yielding a *product*, m. p. 138°, probably



$\begin{array}{l}\text{CH:CPh}\\ |\\ \text{CBz=N}\end{array}\!>\!\text{NPh}$ or $\begin{array}{l}\text{CH—CPh}\\ \|\\ \text{CBz·NPh}\end{array}\!>\!\text{N}$. W. J. Powell.

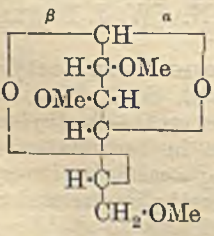
[Action of amines and ammonia on acetylenic γ-diketones.] J. Ballet (Bull. Soc. chim., 1927, [iv], 41, 1170; cf. preceding abstract).—Methylamine reacts with dibenzoylacetylene in benzene solution with evolution of heat, forming *α-methylamino-αβ-dibenzoylethylene*, m. p. 121°; dimethylamine under the same conditions affords *α-dimethylamino-αβ-dibenzoylethylene*, m. p. 144°, in quantitative yield; the *β-naphthylamine* derivative has m. p. 143°. The *product* formed by the interaction of 1 mol. of benzidine with 2 mols. of diketone has m. p. 205—210° (in m. p. tube) and m. p. 169° (Maquenne block), whilst the *pyrrole* derivative has m. p. 175°. *o*-Aminophenol did not appear to react. W. J. POWELL.

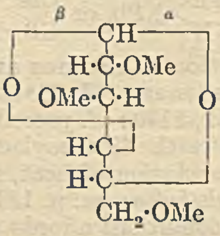
Spectrographic investigations on carbohydrates in the ultra-violet. L. KWIECIŃSKI and L. MARCHLEWSKI (Z. physiol. Chem., 1927, 169, 300; cf. this vol., 291).—The conclusion of Niederhof (this vol., 396) that sugars containing an aldehyde or a ketone grouping have an absorption band at 2800 Å. is refuted. Very pure preparations of dextrose and galactose show a continuous absorption and this band is evident only with less pure preparations. The results are not quite so definite with lævulose, but the absorption band becomes much weaker as the preparation is purified. A. WORMALL.

Percentage formula of pentosans. G. SCHORSCH (Papier-Fabr., 1927, 25, 576—577).—The formula $(C_5H_8O_4)_n$ for the pentosans, due to Tollens, cannot be regarded as definitely established. A critical examination of results given in the literature shows that elementary analysis of amorphous and ash-containing preparations is not conclusive, whilst the C-value given by Tollens and Wheeler is the arithmetic mean of the theoretical C-values of $C_5H_8O_4$ and $C_{10}H_{18}O_9$. That a hexosan formula is improbable is shown by the results of other investigators on the hydrolysis of xylan, no dextrose or other hexose having been found, hence only $C_5H_8O_4$, $C_{10}H_{18}O_9$, or similar anhydride formula need be considered. The hydrolysis of xylan to xylose does not illuminate the problem, since 100% yields of xylose are never obtained. The usual determinations of xylan by its yield of furfuraldehyde phloroglucide show that no 100% value is obtained, calculated on the dry, ash-free substance, in spite of the fact that no other sugars than pentoses can ever be found. The Tollens method for the determination of pentoses in xylose and arabinose was worked out experimentally on crystallised pure products, and the above anomalies are removed only by the use of other calculation factors. With these, together with hydrolysis formulæ, it is shown that all xylan values within the ordinary limits of experimental error give 100%, which points to $(C_{10}H_{18}O_9)_n$ as the composition of the pentosans. B. P. RIDGE.

Oxygen bridges in sugars. III. Anhydrides of βγζ-trimethylglucose. Attempted synthesis of trimethylcellulose. F. MICHEEL and K. HESS (Ber., 1927, 60, [*B*], 1898—1906; cf. A., 1926, 1230; this vol., 43).—If trimethylcellulose is a 2 : 3 : 6-trimethylanhydroglucose it must possess the constitution (I) or (II); the former is almost free from strain, whereas in the latter the strain is very great. The two anhydrides are obtained as follows. 2 : 3 : 6-Trimethylglucose is converted by acetic anhydride and sodium acetate into amylene-oxidic 1 : 4-*diacetyl*-2 : 3 : 6-*trimethyl*-β-*glucose*, m. p. 67—68°, $[\alpha]^{19}$ −8·7° in chloroform, re-converted into 2 : 3 : 6-trimethylglucose by 5% hydrochloric acid. It is converted by hydrogen chloride in the presence of acetyl chloride at −15° to −18° into amylene-oxidic 1-*chloro*-4-*acetyl*-2 : 3 : 6-*trimethyl*-α-*glucose*, b. p. 143—146°/0·04 mm., $[\alpha]_D^{20}$ +146·9° in chloroform, which with alcoholic trimethylamine affords amylene-oxidic 4-*acetyl*-2 : 3 : 6-*trimethylglucosidotrimethylammonium chloride*, $[\alpha]_D^{19}$ −3·7° in chloroform, to which the β-configuration is assigned. If this material is treated with warm barium hydroxide solution ring closure occurs with production of 2 : 3 : 6-trimethylglucose anhydride in 62% yield. The product is a mobile liquid, b. p. 107—108°/0·05—0·07 mm., which shows the expected mol. wt. in solution, does not reduce Fehling's solution, but reacts immediately with cold permanganate. It contains about 75% and 25%, respectively, of the trimethylanhydroglucoses (I) and (II). When treated with 1% methyl-alcoholic hydrogen chloride at the atmospheric temperature it gives 2 : 3 : 6-trimethylmethylglucoside, only one anhydride ring being opened, whilst the other is stable. Separation of the glucoside and unchanged anhydride has not been effected, but the presence of each is established by the methoxyl content of the preparation and the results of further methylation by methyl sulphate and subsequent hydrolysis of the product with 5% aqueous hydrochloric acid to amylene-oxidic 2 : 3 : 4 : 6-tetramethylglucose and amylene-oxidic 2 : 3 : 6-trimethylglucose. It appears certain that neither of the trimethylanhydroglucoses is identical with trimethylcellulose and that either the cryoscopic behaviour of the latter in glacial acetic acid solution must be ignored or that the constitution of trimethylcellulose cannot be based on the production of 2 : 3 : 6-trimethylglucose. H. WREN.

(I.)





(II.)

***d*-Glucose-ζ-chlorohydrin and its derivatives.** B. HELFERICH and H. BREDERECK (Ber., 1927, 60, [*B*], 1995—2001).—The triphenylmethyl ether of acetyl-*d*-glucose or acetyl-α-methylglucoside is converted into triacetyl-α-methylglucoside-6-chlorohydrin in the manner described previously, except that the triphenylmethyl group is removed in the form of its sparingly soluble bromide and is then transformed by aqueous hydrochloric acid into d-*glucose*-ζ-*chlorohydrin*, m. p. 135—136° (corr.), $[\alpha]_D^{10}$ +78·3° to +35·0° in aqueous solution; the *osazone* is described. Similarly, β-*tetra-acetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 114—115° (corr.), $[\alpha]_D^{18}$ +17·6° in chloroform, is prepared by the action of phosphorus pentachloride on β-tetra-acetyl-*d*-glucose 6-triphenylmethyl ether; the mother-liquors obtained in the preparation of the latter compound yield small quantities of a crystalline material, m. p. 120—126°, consisting mainly of the corresponding α-tetra-acetate, which may be converted into α-*tetra-acetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 162—164°, $[\alpha]_D^{20}$ +111·6° in chloroform. β-Tetra-acetyl-*d*-glucose-6-chlorohydrin is transformed by phosphorus pentachloride and aluminium chloride in chloroform into 1 : 6-*dichlorotriacetyl*-d-*glucose*, m. p. 156° (corr.), $[\alpha]_D^{20}$ +196·8° in chloroform, and by hydrogen bromide in glacial acetic acid at 0° into 6-*chloro*-1-*bromotriacetyl*-d-*glucose*, m. p. 165—166° (corr.), $[\alpha]_D^{20}$ +209·0° in chloroform; *tri*-

acetyl-d-*glucose*-6-*chlorohydrin*, m. p. 125° after softening at 118°, $[\alpha]^{19}_{D}$ $+18{\cdot}1°$ in chloroform, and *triacetyl*-β-*methylglucoside*-6-*chlorohydrin*, m. p. 141°, are derived from the bromo-compound by treatment with silver carbonate and acetone or silver oxide and methyl alcohol, respectively. Anhydrous hydrogen fluoride converts β-tetra-acetyl-*d*-glucose-6-chlorohydrin into 1-*fluorotriacetyl*-d-*glucose*-6-*chlorohydrin*, m. p. 151—152° (corr.), $[\alpha]^{20}_{D}$ $+106{\cdot}95°$ in chloroform, from which 1-*fluoroglucose*-6-*chlorohydrin*, decomp. 138° according to the rate of heating, $[\alpha]^{20}_{D}$ $+88{\cdot}8°$ in aqueous solution, is derived. H. WREN.

Synthesis of maltose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1927, **10**, 588—593).—See this vol., 752.

Constitution of the disaccharides. XV. Sucrose. J. AVERY, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1927, 2308—2318).—The adoption of the amylene-oxide formula for normal fructose is justified by the reference of crystalline derivatives of its degradative oxidation products to standard compounds of known constitution. Cautious oxidation of tetramethyl-γ-fructose with nitric acid (*d* 1·42) followed by esterification of the product yields essentially the lactol ethyl ester, $C_{11}H_{20}O_7$, $[\alpha]^{24}_{D}$ $+25{\cdot}8°$ in water, which after methylation yields the amide, $C_{10}H_{19}O_6N$, m. p. 99—100°, identical with that obtained from the corresponding methyl ester (this vol., 859). Oxidation of the lactol ethyl ester with alkaline permanganate followed by esterification of the product with methyl alcohol gives an ester, $C_7H_{14}O_5$, $[\alpha]^{20}_{D}$ $+19°$ in water, from which hydroxydimethoxybutyramide, m. p. 104—105°, $[\alpha]^{19}_{D}$ $+33°$ in water, is obtained. Application of Weerman's reaction to this amide indicates that it is not an α-hydroxy-compound (A., 1917, i, 546). Since the amide is not oxidised by nitric acid as it would be if it were a γ-hydroxy-compound, it is probably the β-hydroxy-compound. The lactol acid, prepared by hydrolysis of the lactol ethyl ester described above, is oxidised in dilute sulphuric acid solution with barium permanganate to give *d*-trimethylarabonolactone, m. p. 32—33°, $[\alpha]_D$ $+44{\cdot}5$ to $+25{\cdot}5°$ in water in 18 days. The m. p. of this substance is identical with and the rotatory power equal and opposite to that of the *l*-isomeride already obtained (this vol., 750). Oxidation of the lactol methyl ester yields the same product. G. A. C. GOUGH.

Transformation of a β-glucoside into an α-glucoside. B. HELFERICH and A. SCHNEIDMÜLLER (Ber., 1927, **60**, [*B*], 2002—2005).—*d*-β-Methylglucoside is converted by successive treatments with triphenylmethyl chloride in pyridine and acetic anhydride into *triacetyl*-β-*methyl*-d-*glucose* 6-*triphenylmethyl ether*, m. p. 126° (corr.), $[\alpha]^{22}_{D}$ $+32{\cdot}0°$ in pyridine. The position of the triphenylmethyl group is established by the conversion of the compound by phosphorus pentabromide (2 mols.) into acetodibromoglucose (yield, 23%) and by phosphorus pentachloride into *triacetyl*-d-β-*methylglucoside*-6-*chlorohydrin*, m. p. 141° (corr.), $[\alpha]^{19}_{D}$ $-9{\cdot}8°$ in pyridine, from which d-β-*methylglucoside*-6-*chlorohydrin*, m. p. 156—157° (corr.), $[\alpha]^{17}_{D}$ $-48{\cdot}7°$ in water, is derived. The constitution of this substance is established by its hydrolysis to *d*-glucose-6-chlorohydrin and the anhydroglucose of Fischer and Zach. It is remarkable that *d*-β-methylglucoside-6-chlorohydrin (like the majority of *d*-β-methylglucosides containing a substituent in the 6-position) is indifferent towards emulsin. Treatment of triacetyl-β-methyl-*d*-glucose 6-triphenylmethyl ether with phosphorus pentabromide (1 mol.) leads unexpectedly to *d*-α-methylglucoside-6-bromohydrin in addition to decomposition products, the yield being 12%. Transformation does not appear to occur when tetra-acetyl-*d*-methylglucoside is melted with phosphorus pentabromide, and isomerisation therefore appears at any rate to be facilitated by simultaneous change at the 6 carbon atom. A somewhat similar instance of transformation under more drastic conditions has been recorded by Irvine (J.C.S., 1905, **87**, 901). H. WREN.

Synthetic glucosides of pyrimidine derivatives. III. A. HAHN and W. LAVES (Z. Biol., 1926, **85**, 280—288).—The *tetra-acetyl*-d-*glucoside* of 2-*methylanilino*-6-*oxypyrimidine* has been isolated as a crystalline compound, m. p. 145°, $[\alpha]^{20}_{D}$ $-45{\cdot}04°$ in toluene, by the action of the silver salt of 2-methylanilino-6-oxypyrimidine on a xylene solution of tetra-acetobromoglucose at 155°. From this substance 2-methylanilino-6-oxypyrimidine-*d*-glucoside, m. p. 116—118° (indef.), $[\alpha]^{18}_{D}$ $-66{\cdot}39°$ in alcohol, has been isolated after deacetylation with methyl-alcoholic ammonia.

The *tetra-acetyl*-d-*glucoside* of 2-*methylanilino*-6-*oxy*-5-*methylpyrimidine*, m. p. 143—145° (indef.), $[\alpha]^{20}_{D}$ $-63{\cdot}9$ in benzene, has been isolated in an analogous manner from the silver salt of 2-methylanilino-6-oxy-5-methylpyrimidine. By deacetylation with methyl-alcoholic ammonia, 2-*methylanilino*-6-*oxy*-5-*methylpyrimidine*-d-*glucoside*, m. p. 135—136°, $[\alpha]^{22}_{D}$ $-57{\cdot}54°$, is formed.

The *picrate*, m. p. 109—110°, of the *tetra-acetylglucoside* of 2-*ethylthiol*-6-*oxypyrimidine* has been prepared by the addition to a saturated aqueous solution of picric acid of a boiling alcoholic solution of the condensation product of tetra-acetobromoglucose and 2-ethylthiol-6-oxypyrimidine. The free *glucoside*, m. p. 103°, $[\alpha]^{22}_{D}$ $-13{\cdot}73°$, is described. Deacetylation of this substance with methyl-alcoholic ammonia produces 2-*ethylthiol*-6-*oxypyrimidine*-d-*glucoside*, m. p. 144—145°, $[\alpha]^{20}_{D}$ $-68{\cdot}47°$; its hydrolysis by emulsin proves it to be a β-glucoside. None of these synthetic glucosides reduces Fehling's solution until after fission with dilute hydrochloric acid except 2-methylanilino-6-oxypyrmidine-*d*-glucoside, which, although stable in alkaline solution, is hydrolysed into its components by keeping in neutral aqueous solution. E. A. LUNT.

Nitrogenous glucosides. K. JOSEPHSON (Ber., 1927, **60**, [*B*], 1822—1826).—Silver phthalimide is conveniently prepared by the gradual addition of alcoholic sodium hydroxide to a hot aqueous-alcoholic solution of silver nitrate and phthalimide. With acetobromoglucose in boiling xylene it yields phthalimide as sole isolable product. *Silver saccharin* and acetobromoglucose afford *tetra-acetylglucosidosaccharin*,  $C_6H_4{<}\begin{smallmatrix}CO\\SO_2\end{smallmatrix}{>}N{\cdot}C_6H_7O_5Ac_4$, m. p. 154° (corr.), $[\alpha]$

—40·2° in chloroform. It is converted by barium hydroxide into *o-glucosidosulphamidobenzoic acid*, $C_6H_{11}O_5\cdot NH\cdot SO_2\cdot C_6H_4\cdot CO_2H$, [α] +2·8° in water (corresponding *sodium* salt, incipient decomp. 119°, [α] —14·9° in water), which readily reduces Fehling's solution. Hydrolysis with methyl-alcoholic ammonia appears to convert tetra-acetylglucosidosaccharin into glucosidosaccharin, which passes readily into *o*-glucosidosulphamidobenzamide. H. Wren.

Amphoteric nature of cellulose. E. Öman (Papir-Journalen, 1927, **15**, 91—96, 107—110, 116—120).—The chemical activity of cellulose is demonstrated by its reduction, by chemical combination, of the acidity or alkalinity of dilute aqueous solutions. The extent to which hydrogen ions are taken up by the cellulose is variable, and dependent on the hydrogen-ion concentration of the water.

Chemical Abstracts.

Cellulose. XXX. Acetolysis of cellulose by hydrogen bromide and acetyl bromide. Degradation to a trihexosan. K. Hess and F. Micheel (Annalen, 1927, **456**, 69—86; cf. Hess, Weltzien, and Kunau, A., 1924, i, 146).—By the action of hydrogen bromide and acetyl bromide cellulose acetate undergoes complete fission into brominated dextrose derivatives in 15 days at 0° or in 10—12 days at 4—6°. The progress of the acetolysis is followed (i) polarimetrically, (ii) by bromine determinations, (iii) by mol. wt. determinations. The bromine content of the final product (above 24%) is greater than required for dextrose monobromide acetate (19·5% Br); more than half this bromine reacts with silver acetate and is thus attached to the C_1 atom of an aldehydic sugar. The mol. wt. of the final product, freed from cellobiose bromide acetate, is 630—380 (disaccharide 700, dextrose 410, as bromide acetate). Cellobiose bromide acetate under similar conditions is practically unattacked by 5% hydrogen bromide in acetyl bromide, but by 7·5% at 15° it is converted after treatment with silver acetate into equal amounts of dextrose penta-acetate and a dextrose bromide acetate.

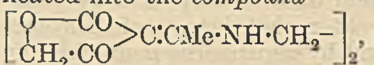
The final product of complete acetolysis of cellulose acetate with 6% hydrogen bromide in acetyl bromide at 5° for 17 days, on acid hydrolysis under special conditions, yields a water-soluble *trihexosan*, $(C_6H_{10}O_5)_3,H_2O$, m. p. 184—189° (decomp.), $[\alpha]_D^{17}$ +90·5° in water, $[\alpha]_D^{19}$ +96·8° in methyl alcohol, which is without reducing action on Fehling's solution. The trihexosan forms crystalline additive products with toluene and xylene and is thus separated from the reducing sugars which accompany it. It is purified by fractional crystallisation of the *acetate*, $C_{36}H_{48}O_{24}$, m. p. 123—126°, $[\alpha]_D^{20}$ +86·6° in chloroform, which is a nona-acetate of a trisaccharide anhydride. Celloglucosan is not present in the products of acid hydrolysis. Methylation of trihexosan with methyl sulphate and alkali gives smoothly the *nonamethyltrihexosan*, m. p. 84—91°, $[\alpha]_D^{19}$ +94·8° in chloroform, which on hydrolysis yields only βγζ-trimethyldextrose. Trihexosan must thus have one of the constitutions assigned by Irvine to cellulose, from which, however, it differs completely.

C. Hollins.

Aminohydroxy-compounds which show the biuret reaction. III. Separation of γ-amino-β-hydroxybutyric acid into optically active components. M. Tomita and Y. Sendju (Z. physiol. Chem., 1927, **169**, 263—277; cf. Tomita and Fukagawa, A., 1926, 1235).—*dl*-γ-Amino-β-hydroxybutyric acid has been resolved into the active components by means of the brucine salts of the benzoyl derivative. The amino-acid is benzoylated and an alcoholic solution of brucine is added. After some days at 0°, *brucine benzoyl*-l-*γ-amino*-β-*hydroxybutyrate*, m. p. 87°, separates as colourless plates, whilst colourless needles of the *brucine benzoyl*-d-*γ-amino*-β-*hydroxybutyrate*, m. p. 41°, are obtained from the mother-liquor. The former brucine salt yields two isomeric l-*γ-benzamido*-β-*hydroxybutyric acids*, m. p. 172°, $[\alpha]_D^{20}$ —7·59° and m. p. 114° and $[\alpha]_D^{20}$ —11·84° (+1H_2O, m. p. 80—81°); the other brucine salt gives two d-*γ-benzamido*-β-*hydroxybutyric acids*, m. p. 178°, $[\alpha]_D^{20}$ +4·08°, m. p. 116° and $[\alpha]_D^{20}$ +10·0° (+1H_2O, m. p. 78—80°). Hydrolysis of the benzoyl compounds with hydrobromic acid yields two l-*γ-amino*-β-*hydroxybutyric acids*, m. p. 213°, $[\alpha]_D^{20}$ —3·40° and m. p. 212°, $[\alpha]_D^{20}$ —21·06°, respectively, and two d-*γ-amino*-β-*hydroxybutyric acids*, m. p. 214°, $[\alpha]_D^{20}$ +3·21° and m. p. 214° (decomp.), $[\alpha]_D^{20}$ +18·30°, respectively. The d- and l-*γ-amino*-β-*hydroxybutyric acids* all give positive biuret reactions. On exhaustive methylation they yield two l-*γ-trimethyl*-β-*hydroxybutyrobetaines*, $[\alpha]_D^{20}$ —7·25° (*gold* salt, m. p. 151—152°, $[\alpha]_D^{20}$ —20·98°, *gold* salt, m. p. 155°, *platinic* salt, m. p. 220°, and *mercury* salt, m. p. 204°, respectively, the second compound being identical with carnitine, and two d-*γ-trimethyl*-β-*hydroxybutyrobetaines*, $[\alpha]_D^{20}$ +8·42°, *gold* salts, m. p. 150—151°, $[\alpha]_D$ +20·20°, and m. p. 155°, respectively. A. Wormall.

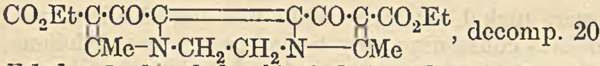
Acylation of derivatives of *NN′*-ethylenebis-β-aminocrotonic acid and similarly constituted substances. E. Benary (Ber., 1927, **60**, [*B*], 1826—1836; cf. A., 1923, i, 37, 201; this vol., 45).—In general, *C*-derivatives cannot be obtained from compounds of αγ-diketones with bases of the type NHR′·CR:CHX by means of acid chlorides, whereas they are prepared from substances in which X represents an ester, nitrile, or acid amide group. From the former compounds the preparation of β-hydroxypyrroles cannot therefore be effected.

Ethyl *NN′*-ethylenebis-β-aminocrotonate is converted by chloroacetyl chloride and pyridine in presence of ether into *ethyl* NN′-*ethylenebis*-β-*amino*-α-*chloroacetylcrotonate*, $[-CH_2\cdot NH\cdot CMe{:}C(CO\cdot CH_2Cl)\cdot CO_2Et]_2$, m. p. 124°, which is transformed by potassium hydrogen sulphide into ethyl 4-hydroxy-2-methylthiophen-3-carboxylate, m. p. 64·5—66° (cf. A., 1915, i, 576), and passes when heated into the *compound*



$$\left[\begin{matrix}O\text{——}CO\\ CH_2\cdot CO\end{matrix}{>}C{:}CMe\cdot NH\cdot CH_2-\right]_2$$, m. p. 290° (decomp.).

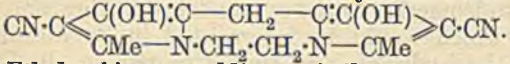
It is transformed by alcoholic ammonia into *ethyl* 1 : 1′-*ethylenebis*-3-*hydroxy*-5-*methylpyrrole*-4-*carboxylate*, decomp. 180—200° after darkening at 160°. The aqueous solution of the latter ester is converted by ferric chloride into the *pyrroline* derivative,



$$\begin{array}{l}\mathrm{CO_2Et{\cdot}C{\cdot}CO{\cdot}C{=\!=\!=\!=}C{\cdot}CO{\cdot}C{\cdot}CO_2Et}\\ \quad\mathrm{CMe{-}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{-\!-}CMe}\end{array}$$

, decomp. 200°. *Ethyl* 1 : 1′-*ethylenebis-2-hydroxylamino-3-keto-5-methylpyrroline-4-carboxylate*, m. p. 168° (decomp.) after darkening at 160°, and *ethyl* 1 : 1′-*ethylenebis*-2-*nitrimino-3-keto-5-methylpyrroline-4-carboxylate* (anhydrous and dihydrate), decomp. about 198°, are described.

Diacetonitrile is readily transformed by ethylenediamine in acetic acid solution into NN′-*ethylenebis-diacetonitrile*, $[\mathrm{CN{\cdot}CH{:}CMe{\cdot}NH{\cdot}CH_2{-}}]_2$, m. p. 194—195°, which, with chloroacetyl chloride and pyridine, affords NN′-*ethylenebis-2-chloroacetyldiacetonitrile*, m. p. 220°; it is transformed by successive treatment with ammonia and formaldehyde into the *compound*,



$$\mathrm{CN{\cdot}C}{<}\begin{array}{l}\mathrm{C(OH){:}C{-\!-}CH_2{-\!-}C{:}C(OH)}\\ \mathrm{CMe{-\!-}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{-\!-}CMe}\end{array}{>}\mathrm{C{\cdot}CN}$$

. NN′-*Ethylenebis-α-acetyldiacetonitrile*, m. p. 230°, is converted by phenylhydrazine into 1-*phenyl*-3 : 5-*dimethylpyrazole-4-nitrile*, m. p. 89—90°, identified by hydrolysis to 1-phenyl-3 : 5-dimethylpyrazole-4-carboxylic acid.

Acetylacetone–ethylenediamine, chloroacetyl chloride, and pyridine afford NN′-*ethylenebis*-N-*chloroacetyl-acetylacetonamine*, $[\mathrm{CHAc{:}CMe{\cdot}N(CO{\cdot}CH_2Cl){\cdot}CH_2{-}}]_2$, m. p. 108°, which is converted by alcoholic alkali hydroxide into NN′-*ethylenebis*-N-*hydroxyacetylacetylacetonamine*, m. p. 275° (decomp.) after darkening at 260°. NN′-*Ethylenebis*-N-*benzoylacetylacetonamine*, m. p. 192°, N-*benzoylbenzoylacetonamine*, m. p. 114°, N-*acetylbenzoylacetonamine*, m. p. 101°, and NN′-*ethylenebisbenzoylacetonamine*, m. p. 183°, are described. Chloroacetylacetylacetonamine is converted by potassium hydrogen sulphide into *thiobis*-N-*acetylacetylacetonamine*, $\mathrm{S[CH_2{\cdot}CO{\cdot}NH{\cdot}CMe{:}CHAc]_2}$, m. p. 123°; it does not appear to give a pyrrole derivative with alcoholic ammonia.

Formylacetonanil and formylacetophenonanil give O-*chloroacetyl* derivatives, m. p. 137·5° and 144°, respectively. *Formylacetophenonanilphenylhydrazone*, m. p. 225—226°, is described. H. Wren.

So-called "diethyl dicyanoglutaconate" and some derivatives. Y. Urushibara (Bull. Chem. Soc. Japan, 1927, 2, 236—241; cf. this vol., 345).—In the condensation of ethyl cyanoacetate with chloroform and sodium ethoxide, excess of the latter two compounds gives an improved yield of ethyl sodio-αγ-dicyanoglutaconate. From the silver derivative of this compound an *ammonium* derivative, $\mathrm{C_{11}H_{12}O_4N_2,NH_3,2H_2O}$, losing 1 mol. of water at 130°, was obtained (cf. Ruhemann and Browning, J.C.S., 1898, 73, 283). An attempt to synthesise the true ethyl dicyanoglutaconate by heating together ethyl cyanoacetate, ethyl orthoformate, and acetic anhydride yielded ethyl sodiodicyanoglutaconate, the desired product possibly having been formed initially. Methyl cyanoacetate and chloroform condensed with sodium methoxide in methyl alcohol, giving *methyl sodio-αγ-dicyanoglutaconate*, $\mathrm{C_9H_7O_4N_2Na,H_2O}$, from an acidified solution of which *methyl αγ-dicyanoglutaconate semihydrate*, $(+0{\cdot}5\mathrm{H_2O})$, m. p. 225°, was precipitated. This compound yielded an indefinite bromine derivative from which *αγ-dicarbomethoxyglutaconamide picrate*, $\mathrm{C_9H_{12}O_6N_2,C_6H_2(NO_2)_3{\cdot}OH}$, was obtained. B. W. Anderson.

New reference compounds in the sugar group. Methylamides of *d*-, *l*-, and *i*-dimethoxysuccinic acids and of *l*-arabo- and *i*-xylo-trimethoxyglutaric acids. W. N. Haworth and D. I. Jones (J.C.S., 1927, 2349—2353).—d-*Dimethoxysuccinomethylamide* has m. p. 205°, $[\alpha]_D^{15}$ +132·6° in water. *Methyl* l-*dimethoxysuccinate*, b. p. 83°/0·07 mm., n_D^{18} 1·4345, $[\alpha]_D^{18}$ −78·8° in methyl alcohol, gives l-*dimethoxysuccinamide*, m. p. 278° (decomp. 294°), and l-*dimethoxysuccinomethylamide*, m. p. 205°, $[\alpha]_D^{17}$ −131·8° in water. i-*Dimethoxysuccinomethylamide* has m. p. 210°. Methyl *i*-trimethoxyglutarate, b. p. 102—104°/0·09 mm., n_D 1·4402, obtained by the cautious oxidation of trimethyl δ-xylonolactone with nitric acid (*d* 1·42) followed by esterification with methyl-alcoholic hydrogen chloride, gives i-*xylo-trimethylglutaramide*, m. p. 195—198° after darkening at 195°, and i-*xylo-trimethoxyglutaromethylamide*, m. p. 167—168°. Trimethyl δ-arabonolactone, m. p. 45°, $[\alpha]_D^{21}$ +179° in water, prepared from trimethyl-β-methylarabinoside, is similarly oxidised to give finally *methyl* l-*arabono-trimethoxyglutarate*, b. p. 105°/0·14 mm., $[\alpha]_D^{20}$ +37·6° in water, +41·2 in methyl alcohol; l-*arabono-trimethoxyglutaramide*, m. p. 230° (decomp.), and l-*arabono-trimethoxyglutaromethylamide*, m. p. 172°, $[\alpha]_D^{18}$ +59·9° in water, are described.
G. A. C. Gough.

Nitroalkylguanidines. T. L. Davis and S. B. Luce (J. Amer. Chem. Soc., 1927, 49, 2303—2305; cf. this vol., 863).—The following nitroalkylguanidines, obtained from nitroguanidine and the corresponding amines in aqueous solution, are described: *nitro-methyl-*, m. p. 160·5—161·0°; *-dimethyl-*, m. p. 193·6—194·5°; -n-*propyl-*, m. p. 98·0—98·5°; -iso*propyl-*, m. p. 154·8—155·6°; -iso*butyl-*, m. p. 121·0—121·5°; -n-*amyl-*, m. p. 98·8—99·3°; -iso*amyl-*, m. p. 145·5 146·2°, and -tert.-*amyl-guanidine*, m. p. 154·8—155·6°.
F. G. Willson.

Methylation with diazomethane. M. Nierenstein (Ber., 1927, 60, [*B*], 1820—1821).—Ethylene glycol does not react with diazomethane. Its monoacetate is readily converted by the reagent into β-methoxyethyl acetate, b. p. 143—144°. The latter substance is hydrolysed by alcoholic ammonia to β-methoxyethyl alcohol, which cannot be methylated by diazomethane. Triphenylmethyl chloride, β-methoxyethyl alcohol, and pyridine afford *triphenylmethyl β-methoxyethyl ether*, m. p. 104°. H. Wren.

Reaction between lithium *n*-butyl and organic halogen compounds. C. S. Marvel, F. D. Hager, and D. D. Coffman (J. Amer. Chem. Soc., 1927, 49, 2323—2328; cf. A., 1926, 1232).—Treatment of lithium *n*-butyl with *n*-heptyl bromide in light petroleum affords *n*-undecane. Methylene iodide yields similarly *n*-nonane, whilst β-bromostyrene affords *α-phenyl-Δ^α^*-n-*hexene*, b. p. 97—100°/8 mm., d_0^{25} 0·9455, n_D^{25} 1·5377, together with *trans-trans*-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene (cf. Rebuffat, A., 1891, 76). The initial deep coloration of the reaction mixture supports the view that the products of the last reaction are derived from intermediately formed free radicals. Lithium *n*-butyl and triphenylmethyl chloride yield mainly ααα-*triphenyl*-n-*pentane*, m. p. 153—154°, b. p. 170—180°/0·01 mm. *o*- and *m*-Bromotoluenes yield similarly toluene, but *p*-bromotoluene affords *p*-butyltoluene in 75% yield. Definite products could not be obtained from lithium *n*-butyl and α-chloropyridine, trimethylene bromide, carbon tetrachloride, *o*-dichlorobenzene, hexabromobenzene, and tetrachloroethylene. F. G. Willson.

Magnesium diethyl and its reaction with acetyl chloride. H. Gilman and F. Schulze (J. Amer. Chem. Soc., 1927, **49**, 2328—2330).—The production of magnesium diethyl from magnesium powder and mercury diethyl at 130° is greatly facilitated by the presence of a small proportion of mercuric chloride (cf. Löhr, A., 1891, 682; Fleck, A., 1893, i, 622). Magnesium diethyl reacts with ethereal acetyl chloride with production of methyldiethylcarbinol (cf. Fleck, *loc. cit.*). F. G. Willson.

Pyrogenic dissociation of certain aromatic compounds under pressure of hydrogen and by the combined action of catalysts. V. Ipatiev and N. Orlov (Ber., 1927, **60**, [*B*], 1963—1971).—The dissociation of a series of substances has been investigated in the presence of a catalyst (aluminium oxide, alone or with addition of oxide of copper or iron) to depress the temperature of dissociation and in an atmosphere of hydrogen to combine with the dissociated fragments. The initial pressure of the hydrogen is about 70 atm. and a minimum temperature of 400° is necessary to ensure a reasonably rapid action. Under these conditions, diphenyl ether is partly decomposed into phenol, traces of benzene, and a non-volatile resin. Phenol affords benzene in 20% yield. *o*-Cresol gives very little resin and about 30% of a mixture of benzene and toluene. Pyrocatechol yields benzene, much phenol, and a brittle resin. Aniline decomposes into benzene, ammonia, and a little diphenylamine; the change appears reversible, since aniline is produced in small amount from benzene and aqueous ammonia. Triphenylmethane gives benzene and a little diphenylmethane; the latter substance is more stable, giving only a small proportion of benzene. Naphthalene and a mixture of hydrocarbons are derived from tetrahydronaphthalene; diphenyl readily yields benzene. Acenaphthene affords naphthalene and liquid hydrocarbons, together with saturated gaseous hydrocarbons. Anthracene is converted almost completely into coke. Mesitylene appears to suffer loss of methyl groups to some extent. The uniform production of substances with simply constructed molecules is noteworthy. Solvent naphtha is converted into benzene, toluene (accompanied by xylenes or ethylbenzene), naphthalene, and small amounts of resin; phenols appear to be formed in very small quantity. Coal-tar heavy oil affords "light petroleum," benzene, toluene, xylene, naphthalene, and, probably, polymerised products. H. Wren.

Pyrogenic dissociation of phenanthrene in the presence of hydrogen under pressure. N. A. Orlov (Ber., 1927, **60**, [*B*], 1950—1956).—Phenanthrene is decomposed when heated at about 500° in the presence of hydrogen under initial pressure of about 75 atm. and aluminium oxide mixed with copper, nickel, or iron oxide yielding disubstituted benzenes containing very little benzene, naphthalene, methylnaphthalene, 2-ethylnaphthalene, dihydrophenanthrene, and unchanged phenanthrene. Dissociation occurs therefore with intermediate production of dihydrophenanthrene and fission of one ring with the formation of naphthalene and alkylnaphthalenes, the process representing the converse of the synthesis of phenanthrene from naphthalene and ethylene. The second possible mode of dissociation, into diphenyl and ethylene, does not appear to be realised in these experiments, as indicated by the almost complete absence of benzene and toluene from the products. Probably the dissociation of phenanthrene into naphthalene is caused by its tendency to isomerise to the symmetrical anthracene, a process which would be interrupted in its initial stages by the hydrogen and thus give rise to alkylnaphthalenes. It is probable that a dynamic isomerism exists between 9 : 10-dihydrophenanthrene and the dihydro-product formed by addition of hydrogen to the neighbouring ring. H. Wren.

Nitration of xylene with dilute nitric acid in presence of mercury. E. I. Orlov (Ukraine Chem. J., 1926, **2**, 370—375).—See A., 1926, 1130.

Nitration of cumene. L. Bert and P. C. Dorier (Bull. Soc. chim., 1927, [iv], **41**, 1170—1171; cf. A., 1926, 56, 285).—The observation of Vavon and Callier (this vol., 455) that nitration of cumene by the Pictet method yields almost exclusively the *p*-nitro-derivative is confirmed. W. J. Powell.

Arylsulphur chlorides and arylsulphuranilides. E. Gebauer-Fülnegg (J. Amer. Chem. Soc., 1927, **49**, 2270—2275).—Treatment of 2 : 5-dichlorothiophenol with chlorine in cold carbon tetrachloride affords 2 : 5-*dichlorochlorothiolbenzene*, b. p. 92°/3 mm., which, on treatment with aniline in chloroform or carbon tetrachloride, yields 2 : 5-*dichlorobenzenesulphenanilide*, m. p. 85°. p-*Chlorochlorothiolbenzene*, b. p. 94°/6 mm., was prepared analogously, and converted by treatment with aminoazobenzene into the corresponding substituted p-*chlorobenzenesulphenamide*, red, m. p. 188°. Treatment of 4-chloro-2-nitrochlorothiolbenzene with methylaniline in absolute ether affords 4-*chloro-2-nitrobenzenesulphenmethylanilide*, non-crystalline, red, and an analogous substituted 4-*chloro-2-nitrobenzenesulphenamide*, brownish-red, was also obtained from 2 : 4-diaminoazobenzene. A study of absorption spectra indicates that 4-chloro-2-nitrochlorothiolbenzene, its anilide, and 4-chloro- and 2 : 5-dichloro-chlorothiolbenzenes have similar structures, whilst 2 : 5-dichlorobenzenesulphenanilide has a structure differing from these. Variations in colour amongst these derivatives are ascribed to "approached quinonoid structures" of the molecules concerned (cf. Lecher and Holschneider, A., 1924, i, 728). F. G. Willson.

Oxidising action of "chloramine-*T*" [sodium *p*-toluenesulphonchloroamide]. G. Schiemann and P. Novak (Z. angew. Chem., 1927, **40**, 1032—1033).—Contrary to Engelfeldt's statement (A., 1923, i, 454), "chloramine-*T*" is stable on boiling a 10% aqueous solution for 3 hrs., and elimination of sodium hypochlorite does not occur. Oxidation by "chloramine-*T*" in acid solution is represented by the equations $2C_6H_4Me{\cdot}SO_2NaNCl+2H^{\cdot}=C_6H_4Me{\cdot}SO_2{\cdot}NH_2+C_6H_4Me{\cdot}SO_2{\cdot}NCl_2+2Na^{\cdot}$; $C_6H_4Me{\cdot}SO_2{\cdot}NCl_2+2H_2O=C_6H_4Me{\cdot}SO_2{\cdot}NH_2+HOCl$, whilst in neutral solution it follows the equation, $C_6H_4Me{\cdot}SO_2NaNCl+H_2O=C_6H_4Me{\cdot}SO_2{\cdot}NH_2+NaCl+O$. In alkaline solution only does elimination of sodium hypochlorite occur. In agreement with Chattaway (J.C.S., 1905, **87**, 145) and Engelfeldt (*loc. cit.*) the constitution of "chloramine-*T*" is given as $C_6H_4Me{\cdot}SO(\colon NCl){\cdot}ONa,3H_2O$.

S. J. Gregg.

Bivalency of carbon. I. Displacement of chlorine from diphenylchloromethane. *s*-Tetraphenyldimethyl ether. A. M. Ward (J.C.S., 1927, 2285—2295).—The chlorine group in diphenylchloromethane is displaced by ethyl alcohol or aqueous ethyl alcohol, both alone and in the presence of sodium hydroxide, to give mainly benzhydryl ethyl ether together with benzhydrol. The velocity coefficients of the reactions at 25° and at 35° under each of the above conditions and also in an experiment where alcoholic sodium ethoxide was used are those of a unimolecular reaction. Thus the sodium compounds, which merely accelerate the reaction, play no direct part in the displacement. It is suggested that the slowest reaction is the ionisation of the diphenylchloromethane, which is followed by the rapid reactions of the diphenylmethyl ion with hydroxyl and ethoxyl ions to give benzhydrol and benzhydryl ethyl ether (cf. Nef, A., 1898, i, 102). Benzhydrol gives *s*-tetraphenyldimethyl ether on boiling with dilute hydrochloric acid; on raising the concentration of the acid the yield of this product falls and diphenylchloromethane finally becomes the principal product. Boiling 2*N*-hydrochloric acid is without action on *s*-tetraphenyldimethyl ether, but the concentrated acid, or better ethereal hydrogen chloride, converts it into diphenylchloromethane.

G. A. C. Gough.

Reduction of 2-nitrofluorene. F. E. Cislak, I. M. Eastman, and J. K. Senior (J. Amer. Chem. Soc., 1927, **49**, 2318—2322).—Reduction of 2-nitrofluorene with zinc dust and calcium chloride in boiling aqueous alcohol affords 2 : 2′-azoxyfluorene, orange-yellow, m. p. 279° (decomp.). Owing to its insolubility, the latter can be reduced to 2-aminofluorene only by zinc dust and hydrochloric acid in phenol solution. If this reduction is carried out with glacial acetic acid instead of hydrochloric acid, at below 40°, the product appears to be the result of an *o*-semidine rearrangement of the corresponding hydrazo-derivative. It is colourless, has m. p. 257—258° (decomp.) after becoming red at 240—245°, and is considered to be either 2′-*amino*-2 : 3′-*difluorenylamine* or 2-*amino*-1 : 2′-*difluorenylamine*. When boiled with acetic anhydride, it yields an oxygen-free compound, m. p. 179°, to which the corresponding alternative constitutions, 3-(2-*fluorenyl*)-2-*methyl*-2 : 3-*fluoreniminazole* and 1-(2-*fluorenyl*)-2-*methyl*-1 : 2-*fluoreniminazole*, are ascribed.

F. G. Willson.

Preparation and constants of phenylpropinene and certain of its homologues. L. Bert and P. C. Dorier (Bull. Soc. chim., 1927, [iv], **41**, 1171—1173).—A reply to Bourguel's criticisms (this vol., 337) of the authors' work on this subject (A., 1925, i, 803, 1373; 1926, 391).

W. J. Powell.

System acetanilide–propionanilide. E. C. Gilbert and L. Clarke (J. Amer. Chem. Soc., 1927, **49**, 2296—2299).—The f.-p. curve of mixtures of acetanilide and propionanilide shows that a compound, m. p. 79·2—79·4°, almost completely dissociated in the liquid state, is formed between the two substances, but the shape of the curve does not permit the composition of this compound to be determined (cf. Hurd, A., 1924, i, 140).

F. G. Willson.

Tautomerism of the amidines. VII. Methylation of benzenyl-*p*-nitrodiphenylamidine [*N*-phenyl-*N′*-*p*-nitrophenylbenzamidine]. C. Chew and F. L. Pyman (J.C.S., 1927, 2318—2323).—N-*Phenyl*-N′-p-*nitrophenylbenzamidine*, m. p. 184° (corr.; *hydrochloride*, m. p. 261°), prepared by an application of the method of Hill and Cox (this vol., 144), and methyl iodide give a 28·8% yield of *N*-phenyl-*N′*-*p*-nitrophenyl-*N*-methylbenzamidine, and 24·9% of the *N′*-methyl isomeride. These results confirm the suggestion (Pyman, J.C.S., 1923, **123**, 3359; A., 1926, 1156) that the preferential alkylation of the nitrogen atom attached to an aryl group of *N*-aryl-*N′*-alkylbenzamidines is due to the tendency of the aryl group to attract the double linking into the αβ-position. If the difference in basicity of the two nitrogen atoms (which must be considerable in the present case) determined the proportion of the isomerides in the methylation product, a large preponderance of one isomeride would be expected. N-*Phenyl*-N′-p-*nitrophenyl*-N-*methylbenzamidine*, m. p. 138° [corr.; *picrate*, m. p. 206° (corr.)], prepared by the interaction of *p*-nitrobenzanilide-iminochloride (free from traces of hydrogen chloride) and methylaniline in dry ethereal solution, could not be prepared by the method of Hill and Cox. N-*Phenyl*-N′-p-*nitrophenyl*-N′-*methylbenzamidine* [oil; *hydrochloride* +EtOH, m. p. 226° (corr.; with effervescence); *hydriodide*, m. p. 225° (corr.); *picrate*, m. p. 194° (corr.)], was obtained by the method of Hill and Cox, but could not be isolated from the products of the interaction of benzanilide-iminochloride and *p*-nitromethylaniline.

G. A. C. Gough.

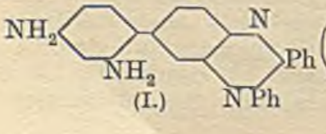
Crystalline products formed by the action of aromatic amines on thiosemicarbazide and its derivatives. H. Macurevitsch (Bull. Soc. chim., 1927, [iv], **41**, 1065—1074).—The mol. wt. of the crystalline substances of high m. p. obtained by the action of aniline, *o*-, *m*-, and *p*-toluidines on hydrazodithiodicarbonamide, and of *o*-toluidine on phenylhydrazodithiodicarboxylamide (this vol., 777), have been determined in various solvents, and the values obtained show that the formulæ previously assigned to them should be halved. On heating with benzophenone chloride these compounds do not give blue colorations (see Tschugaev, A., 1902, i, 630), and it is concluded that the groupings $\cdot CS{\cdot}NH_2$ and $\cdot CS{\cdot}NH{\cdot}$ are not present in their molecules. The suggestion that these compounds are substituted tetrazines is abandoned, and they are formulated as thio-1 : 2 : 4-triazoles, formed by elimination of 1 mol. of hydrogen sulphide from the intermediate

substance $NH_2 \cdot CS \cdot NH \cdot NH \cdot CS \cdot NHR$, which is obtained from 1 mol. of the amine and 1 mol. of hydrazodithiodicarboxylamide, by elimination of ammonia.
H. Burton.

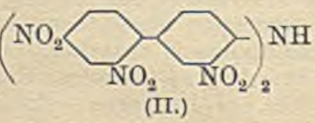
Determination of the amino-group in nitroarylamines. I. Determination of nitroaniline and nitroacetanilide. N. Semiganovsky (Z. anal. Chem., 1927, 72, 27—30).—The amine is refluxed with sodium hydroxide solution, which, throughout the analysis, is never more concentrated than 25%, and the ammonia evolved is collected and titrated with standard acid. When the amine is completely decomposed, the water-jacket of the reflux condenser is disconnected, the ammonia being distilled over through a second condenser. The results obtained agree within 0·2%.
F. S. Hawkins.

Determination of secondary nitrosoamine groups. K. Lehmstedt (Ber., 1927, 60, [*B*], 1910—1912).—Reduction of nitrosoamines by mercury and concentrated sulphuric acid does not generally proceed quantitatively, since the acid frequently causes partial conversion into the *C*-nitroso-compound. Reduction may, however, be effected with ferrous chloride and hydrochloric acid in boiling solution: $NR'R'' \cdot NO + HCl + FeCl_2 = NHR'R'' + FeCl_3 + NO$. The liberated nitric oxide is measured. The results are generally somewhat low, since reduction to ammonia occurs to some extent and a little nitric oxide usually remains in the evolution flask. *C*-Nitroso- and *C*-nitro-groups do not cause complication. Analyses of di*iso*butyl-, phenylmethyl-, diphenyl-, piperidyl-, and acetylphenylnitrosoamines are recorded.
H. Wren.

Orientation effects in the diphenyl series. IV. Reduction of Bandrowski's and of Strakosch's dinitrobenzidines, and condensation of the products with benzil. Nitration of 2-nitrodiacetylbenzidine and of 4 : 4'-dibromodiphenyl. R. J. W. Le Fèvre, D. D. Moir, and E. E. Turner (J.C.S., 1927, 2330—2339).—The observation of Brady and McHugh (*ibid.*, 1923, **123**, 2047) that Bandrowski's dinitrobenzidine, m. p. 233° (originally supposed to be 3 : 3'-dinitrobenzidine, but recently shown to be the 2 : 3'-derivative, m. p. 236—237°; Le Fèvre and Turner, A., 1926, 946), yields the same quinoxaline, m. p. 313° (corr.), as 3 : 3'-dinitrobenzidine (Strakosch's dinitrobenzidine) when reduced and subsequently treated with benzil has been verified, but the yield from Bandrowski's dinitrobenzidine is small. The latter is very difficult to purify, and it is shown by examining artificial mixtures that any sample of m. p. 233° or lower contains 2% or more of Strakosch's dinitrobenzidine, which is sufficient to account for the quinoxaline formed. Samples of Bandrowski's dinitrobenzidine, m. p. 237° (uncorr.), yield no quinoxaline. By analogy with the benzidine–benzil condensation product, this quinoxaline should have the structure I, and should condense further with benzil at higher temperatures.



(I.)



(II.)

Actually, when heated in the solution in which it is formed, it undergoes further condensation with production of what is evidently a mixture (m. p. range about 30°).

4-Bromo-4'-nitrodiphenyl was nitrated to give 4-*bromo*-3 : 4'-*dinitrodiphenyl*, m. p. 135°, which on further nitration yielded 4-bromo-2' : 3 : 4'-trinitrodiphenyl (Le Fèvre and Turner, A., 1926, 1029). Small quantities of the latter compound were readily converted into 2' : 3 : 4'-*trinitro*-4-*aminodiphenyl* (m. p. 192—193°) on heating in a sealed tube with alcoholic ammonia, but the large-scale conversion proved unsatisfactory. On dissolving 4-bromo-2' : 3 : 4'-trinitrodiphenyl in boiling nitrobenzene and passing in dry ammonia, 4 : 4'-*bis*-op-*dinitrophenyl*-2 : 2'-*dinitrodiphenylamine* (II), m. p. 256—257°, was obtained. Under the same conditions, picryl chloride yielded trinitroaniline, 1-chloro-2 : 4-dinitrobenzene gave 2 : 4-dinitroaniline, 2 : 5-dichloronitrobenzene was unaffected, and 4 : 4'-dibromo-2 : 3'-dinitrodiphenyl was partly converted into the corresponding bromo-amino-compound.

From the nitration product of 2-nitrodiacetylbenzidine, which is mainly 2 : 3'-dinitrodiacetylbenzidine (Le Fèvre and Turner, *loc. cit.*), 2 : 5 : 3'-*trinitrobenzidine*, dark red, m. p. 276° (*diacetyl* derivative, m. p. above 300°), was obtained in the form of the sparingly soluble *sulphate*. The constitution of this base was proved by its conversion by the perbromide method into 4 : 4'-*dibromo*-2 : 5 : 3'-*trinitrodiphenyl*, m. p. 251—252°, which reacted readily with piperidine to give 2 : 5 : 3'-*trinitro*-4 : 4'-*dipiperidinodiphenyl*, m. p. 160°. The occurrence of this trinitrobenzidine shows that some 2 : 5-dinitrodiacetylbenzidine must be formed in the nitration of 2-nitrodiacetylbenzidine, since the 2 : 3'-compound is unaffected by even more drastic nitrating conditions than those used. Nitration of 4 : 4'-dibromo-2 : 3'-dinitrodiphenyl yielded 4 : 4'-*dibromo*-2 : 3' : 5'-*trinitrodiphenyl*, m. p. 176—177°, which with piperidine afforded 4-*bromo*-2 : 3' : 5'-*trinitro*-4'-*piperidinodiphenyl*, m. p. 194° (cf. Lellmann, A., 1883, 343). 3 : 4'-*Dinitro*-4-*anilinodiphenyl* has m. p. 155—156°, 3 : 2' : 4'-*trinitro*-4-*anilinodiphenyl*, m. p. 190—191°, and 3 : 2' : 4'-*trinitro*-4-*methylanilinodiphenyl*, m. p. 212°.
W. J. Powell.

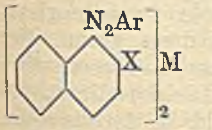
Compounds of aromatic *p*-diamines with sulphur dioxide. I. G. Farbenind. A.-G.—See B., 1927, 742.

The two *p*-nitroazoxybenzenes. A. Angeli and D. Bigiavi (Atti R. Accad. Lincei, 1927, [vi], 5, 819—823).—When treated with excess of bromine in presence of a very small quantity of iron filings, *p*-nitroazoxybenzene (*a*), m. p. 148° (cf. Angeli and Alessandri, A., 1911, i, 1045), yields (1) the *tribromo*-derivative, $C_6H_2Br_3 \cdot N \colon NO \cdot C_6H_4 \cdot NO_2$, m. p. 206—208°, which is obtained also on brominating monobromonitroazoxybenzene, m. p. 203°, in the cold, and (2) the isomeric *p*-nitroazoxybenzene (*b*). Under similar treatment, the latter yields a monobromo-compound, $C_{12}H_8O_3N_3Br$, m. p. 135—137°, which may be identical with the compound, m. p. 127°, described by Valori (Atti R. Accad. Lincei, 1912, [v], **21**, i, 794).
T. H. Pope.

Reduction of nitro-compounds by aromatic ketols. I. Some *p*-azoxy-compounds. H. B. Nisbet (J.C.S., 1927, 2081—2086).—Hot alcoholic solutions of benzoin, anisoin, or furoin reduce aromatic nitro-compounds to the corresponding azoxy-compounds in the presence of a trace of sodium methoxide or ethoxide. The ketols are oxidised to the 1 : 2-diketones. In this way the following azoxy-compounds are prepared: p-*azoxybenzylideneaniline*, decomp. 226° (sintering at 185°); p-*azoxybenzylidene*-p-*toluidine*, m. p. 217° (decomp.; sintering at 189—190°); p-*azoxybenzylidene*-p-*aminoacetophenone*, m. p. 217° (decomp.; sintering at 187°); p-*azoxybenzonitrile*, m. p. 221°; p-*azoxystilbene*, m. p. 271—272° (decomp.; sintering at 259°); p-*azoxy*-2-*nitrostilbene*, m. p. 208—210°; p-*azoxy*-2 : 3′-*dinitrostilbene*, m. p. 212°; p-*azoxy*-2 : 6-*dinitrostilbene*, m. p. 270°; p-*azoxy*-2-*nitro*-4′-*methoxystilbene*, m. p. 208°; p-*azoxy*-2-*nitro*-3′ : 4′-*methylenedioxystilbene*, m. p. 230°; p-*azoxy*-2 : 6-*dinitro*-4′-*methoxystilbene*, m. p. 297° (decomp.); p-*azoxy*-2-*nitro*-4′-*dimethylaminostilbene*, unmelted at 305°. Methyl and ethyl *p*-azoxycinnamates may conveniently be prepared by this method. The nitrostilbenes were prepared by a modification of Bishop and Brady's method (J.C.S., 1922, 121, 2367; cf. A., 1916, i, 24) and of them the following are new: 2 : 4 : 4′-*trinitrostilbene*, m. p. 234—235°; 2 : 4-*dinitro*-3′ : 4′-*methylenedioxystilbene*, m. p. 178—180°; 2 : 4 : 6-*trinitro*-4′-*methoxystilbene*, m. p. 167—168°; 2 : 4-*dinitro*-4′-*dimethylaminostilbene*, m. p. 181° (*chloroplatinate*, m. p. 211°).

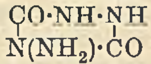
G. A. C. Gough.

Metallic derivatives of azo-compounds. G. B. Crippa (Gazzetta, 1927, 57, 497—504).—The metallic complexes formed by the union of an atom of copper, nickel, or cobalt with 2 mols. of arylazo-β-naphthylamine or arylazo-β-naphthol and obtained either by the action of the metal ammonium sulphate on the amino- or hydroxy-azo-derivatives in alcoholic suspension or by boiling solutions of the aminoazo-derivatives in aniline or nitrobenzene with powdered nickel or cobalt exhibit properties which suggest for these complexes formulæ of the type annexed, where X=NH_2 or OH. These complexes yield the azo-derivative when treated with dilute mineral acid or acetic acid, sometimes in the cold; but they remain unchanged when boiled in a strongly alkaline medium. Neither the complexes derived from the benzeneazonaphthols nor the aminocupric complexes are obtainable by the latter of the two methods mentioned, but are readily formed by the former method.



[With U. Martegani.]—*Cupridi*-p-*anisylazo*-β-*naphthol*, $C_{34}H_{28}O_4N_4Cu$, forms burnt-sepia needles, m. p. 271°; the corresponding *nickel* and *cobalt* complexes have m. p. 279° and 265°, respectively. *Cupri*-, *nickelo*-, and *cobalto-di*-o-*anisoleazo*-β-*naphthols* have m. p. 225°, 300° (decomp.), and 254° (decomp.), respectively. *Cupri*-, *nickelo*-, and *cobalto-di*-p-*phenetoleazo*-β-*naphthols* have m. p. 267°, 265°, and 224°, respectively. The corresponding *complexes* from o-*phenetoleazo*-β-*naphthol* have m. p. 219°, 295°, and 253°; from *p*-anisoleazo-β-naphthylamine, 157°, 257°, and 236°; from *o*-anisoleazo-β-naphthylamine, 170°, 226—228°, and 167°, and from *p*-phenetoleazo-β-naphthylamine, 186°, 267°, and 212°. T. H. Pope.

Action of hydrazines on semicarbazones. III. W. Baird and F. J. Wilson (J.C.S., 1927, 2114—2117; cf. A., 1926, 1141).—That the thermal decomposition of acetone-δ-anilinosemicarbazone to give acetone-phenylhydrazone and 4-aminourazole,



$$\begin{array}{l}CO\cdot NH\cdot NH\\ |\qquad\qquad\ \ |\\ N(NH_2)\cdot CO\end{array}$$

(previously described in error as 1-aminourazole), proceeds through the intermediate formation of acetonecarbohydrazone and diphenylcarbohydrazide, is confirmed by the formation of the same final products by the interaction of the hypothetical intermediates. Some dimethylketazine is formed in both reactions probably by the decomposition of the carbohydrazone. In a similar way pinacolin-δ-anilinosemicarbazone affords pinacolinphenylhydrazone, pinacolinazine, and 4-aminourazole; benzylidene-δ-anilinosemicarbazone affords benzaldehydephenylhydrazone and 4-aminourazole; acetone-δ-diphenylaminosemicarbazone affords acetonediphenylhydrazone, dimethylketazine, and 4-aminourazole. In the last decomposition some of the intermediate compound, tetraphenylcarbohydrazide (Acree, A., 1903, i, 861), was actually isolated. *Pinacolinazine*, b. p. 213—216°/17 mm., was identified by comparison with the synthetic product obtained by the interaction of alcoholic solutions of hydrazine hydrate and pinacolin. Attempts to prepare δ-anilinothiosemicarbazones by the interaction of the thiosemicarbazones of acetone, acetophenone, and dibenzyl ketone with phenylhydrazine resulted in the formation of thiosemicarbazide and the ketonephenylhydrazones. *Dibenzyl ketone thiosemicarbazide*, m. p. 165—166°, and *methyl ethyl ketone* δ-*anilinosemicarbazide*, m. p. 137°, are also described. G. A. C. Gough.

Azides. A. Angeli (Atti R. Accad. Lincei, 1927, [vi], 5, 732—736).—The molecular structure of the azides is discussed. The fact that the presence of a small proportion of acid effects the isomerisation of the nitroso-derivative obtained from benzylmethylhydrazine, $CH_2Ph\cdot N(NO)\cdot NHMe \longrightarrow CH_2Ph\cdot NH\cdot NMe\cdot NO$, renders it possible that the formation of phenyl azide by the action of an acid on nitrosophenylhydrazine is accompanied by a similar change: $NO\cdot NPh\cdot NH_2 \longrightarrow NHPh\cdot NH\cdot NO \longrightarrow NPh{:}N{:}N$. An analogous transformation is possible in the conversion of the sodium derivative of nitrosophenylhydrazine into *iso*diazo-oxides and nitrous oxide by the action of alcoholic nitrite solution: $NH{:}NPh{:}N\cdot OH \longrightarrow NO\cdot N{:}NPh{:}N\cdot OH \longrightarrow NPh{:}N\cdot OH + N_2O$. It appears likely that the tautomeric form of nitrosophenylhydrazine belongs to a group of compounds which contain a quinquevalent nitrogen atom united to the aromatic nucleus, such as $O{:}NPh{:}O$, $O{:}NH_2Ph$, $O{:}NPh{:}NH$, $O{:}NPh{:}N\cdot OH$.

T. H. Pope.

Diazo hydroxides. L. Cambi (Atti R. Accad. Lincei, 1927, [vi], 5, 837—840).—Our knowledge of the structure of the alkali salts of the normal diazohydroxides is in agreement with the structural formula ascribed by Angeli to these hydroxides themselves (A., 1926, 947). Hantzsch's views on this question are refuted. T. H. Pope.

Organic compounds of quinquevalent bismuth. G. Charrier (Atti R. Accad. Lincei, 1927, [vi], 5, 889—892).—In hydrochloric acid solution, bismuth trichloride reacts with aryldiazonium chlorides giving stable crystalline compounds containing quinquevalent bismuth: $BiCl_3+ArN_2Cl \longrightarrow ArN_2BiCl_4$. The chlorine atoms in these chlorobismuthates are readily replaceable by sulphuric or nitric residues. *Benzenediazonium chlorobismuthate*, $N_2Ph{\cdot}BiCl_4$, has m. p. 85—87° (decomp.); the *toluene*-o-*diazonium* compound, m. p. 115—120° (decomp.); *toluene*-m-*diazonium*, m. p. 120° (decomp.); *toluene*-p-*diazonium*, m. p. 120° (decomp.); p-*methoxybenzenediazonium*, m. p. 145—147° (decomp.); p-*chlorobenzenediazonium*, m. p. 105—107° (decomp.); p-*bromobenzenediazonium*, m. p. 135—140° (decomp.). T. H. Pope.

Halogenated tertiary amines. C. S. Marvel, W. H. Zartman, and O. D. Bluthardt (J. Amer. Chem. Soc., 1927, 49, 2299—2303).—Treatment of boiling diethylamine with γ-phenoxypropyl bromide affords *diethyl-γ-phenoxypropylamine*, (I), b. p. 147—150°/20 mm., d_4^{20} 0·9425, n_D^{20} 1·4987 [*hydrochloride*, m. p. 98—102° (decomp.)], together with *diethyldi-γ-phenoxypropylammonium bromide*, m. p. 77·5—79°. When boiled with hydrobromic acid under such conditions that water and phenol are continuously boiled off, (I) yields *diethyl-γ-bromopropylamine hydrobromide*, hygroscopic, m. p. 91—94°. Treatment of the latter in ethereal solution with concentrated aqueous sodium hydroxide affords the corresponding *base*, (II), b. p. 60—64°/7mm., d_4^{25} 1·1524, n_D^{25} 1·4580, which isomerises rapidly when kept into a *quaternary ammonium bromide*, m. p. 180—185°, presumably an 8-membered ring compound (cf. Knorr and Roth, A., 1906, i, 457). Condensation of (II) with ethyl sodiomalonate in absolute alcohol affords *ethyl γ-diethylaminopropylmalonate*, b. p. 163—170°/23 mm., d_4^{25} 0·9686, n_D^{25} 1·4380. Treatment of δ-phenoxy-*n*-butylamine with ethyl bromide and aqueous sodium hydroxide yields *diethyl-δ-phenoxybutylamine*, b. p. 152—158°/21 mm., d_4^{25} 0·9424, n_D^{25} 1·4975, from which *diethyl-δ-bromobutylamine*, b. p. 68—70°/6 mm., d_4^{25} 1·0187, n_D^{25} 1·4415 (*hydrobromide*, hygroscopic, m. p. 62—68°), was obtained as above. When kept, the latter isomerises, presumably into *diethylpyrrolidinium bromide*, m. p. 170—175°. *Ethyl δ-diethylaminobutylmalonate* has b. p. 170—175°/24 mm., d_4^{25} 0·9621, n_D^{25} 1·4468. F. G. Willson.

Nuclear carboxylation of aromatic amines. A. P. Terentiev and A. M. Rubinstein (Ber., 1927, 60, [*B*], 1879—1882).—Magnesium powder, activated by iodine, reacts readily with *o*-anisidine in the absence of air, giving the compound $(OMe{\cdot}C_6H_4{\cdot}NH)_2Mg$, which is transformed by carbon dioxide at 150° into *magnesium* N-o-*anisylcarbamate*. If the latter compound is heated with an excess of *o*-anisidine at 250—270° it is converted into 3-*amino*-2-*methoxybenz*-o-*anisidide*, m. p. 178° (NN′-*di*-o-*anisylcarbamide* has m. p. 182°); the *formyl* derivative, m. p. 133°, is more stable than the anisidide itself. Hydrolysis of the anisidide gives *o*-anisidine and 3-*amino*-2-*methoxybenzoic acid*, m. p. 153°, identified by de-amination and subsequent oxidation to phthalic acid. H. Wren.

Nitrosation of phenols. IV. 3 : 5-Dichlorophenol. H. H. Hodgson and J. S. Wignall (J.C.S., 1927, 2216—2221; cf. Hodgson and Moore, *ibid.*, 1923, **123**, 2499).—During numerous unsuccessful attempts, both direct and indirect, to nitrosate 3 : 5-dichlorophenol, it was found that the supposed 3 : 5-dichloro-4-nitrosophenol obtained by Blanksma (Rec. trav. chim., 1908, 27, 25) as a by-product in the conversion of 3 : 5-dichloroaniline into the phenol, and by Willstätter and Schudel (A., 1918, i, 399) by the action of nitrous acid on sodium 3 : 5-dichlorophenoxide, is identical with 3 : 5-*dichloro*-4-*nitrophenol*, m. p. 150° (*acetate*, m. p. 99°), obtained together with 3 : 5-*dichloro*-2-*nitrophenol*, m. p. 51°, by direct nitration of 3 : 5-dichlorophenol. 3 : 5-Dichloro-2-nitrophenol does not form a hydrate (cf. 3-chloro-2-nitrophenol, Hodgson and Moore, A., 1926, 281). 3 : 5-*Dichloro*-2-*aminophenol*, m. p. 132°, and 3 : 5-*dichloro*-4-*aminophenol*, m. p. 154°, are prepared by reduction of the nitrophenols with sodium hyposulphite. 3 : 5-*Dichloro*-2-*nitroanisole*, m. p. 75°, and 3 : 5-*dichloro*-4-*nitroanisole*, m. p. 70°, were prepared by methylation of the appropriate nitrophenol. The latter by reduction with tin and hydrochloric acid gives 3 : 5-*dichloro*-p-*anisidine*, m. p. 71°, from which 3 : 5-*dichloro*-4-*nitrosoanisole*, m. p. 125°, was obtained by oxidation with Caro's acid. On hydrolysis with concentrated sulphuric acid, it gives colourless 3 : 5-*dichloro*-4-*nitrosophenol*, m. p. 165°, dissolving in alkali with a green colour. It resembles the nearly colourless 3-chlorobenzoquinone-4-oxime (Hodgson and Moore, *loc. cit.*) and is possibly better formulated as 3 : 5-dichlorobenzoquinone-4-oxime. No evidence of conversion or of geometrical isomerism was obtained.

3 : 5-Dichloro-*p*-anisidine may be prepared from 3-chloro-4-nitroanisole by simultaneous reduction and chlorination with tin and concentrated hydrochloric acid, whilst iron and acetic acid effect normal reduction to 3-chloro-*p*-anisidine (cf. Hodgson and Handley, A., 1926, 515). The latter on oxidation yields 3-*chloro*-4-*nitrosoanisole*, deep green, m. p. 59°. Since 3 : 5-dichloro-4-nitrosoanisole is colourless, whilst 3-chloro-4-nitrosoanisole is deep green, the suppression of colour may be ascribed to the chlorine atom in the 5-position. 3 : 5-Dichlorodimethylaniline is nitrated by nitrous acid in formic acid solution, yielding 3 : 5-*dichloro*-4-*nitrodimethylaniline*, m. p. 142°. The direct nitrosation of 3-chloro-5-iodophenol was attempted without success. W. J. Powell.

Complex metallic ammines. IX. Introduction of nitrophenol radicals into cobaltammine complexes. Distinctive behaviour of mononitrophenoxides. J. C. Duff and E. J. Bills (J.C.S., 1927, 2365—2375).—Unlike *o*- and *m*-nitrophenoxides, sodium *p*-nitrophenoxide reacts with aquopentamminocobaltic nitrate to give p-*nitrophenoxopentamminocobaltic* p-*nitrophenoxide* [I; X= $p{\cdot}C_6H_4(NO_2){\cdot}O{\cdot}$]. This compound is hydrolysed in

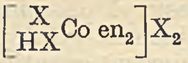
(I.) $[Co(NH_3)_5X]X_2$ $[Co(NH_3)_5,H_2O]X_3$ (II.)

(III.) $[Co(NH_3)_5X](OH)X$

presence of platinised electrodes to $[H_2O{\cdot}Co(NH_3)_5]X_3$. Sodium 2 : 4- and 2 : 6-dinitrophenoxides give simple aquopentammino-salts, *aquopentamminocobaltic* 2 : 4-*dinitrophenoxide* (+3H_2O), and *aquopentamminocobaltic* 2 : 6-*dinitrophenoxide* [II; $X=C_6H_3(NO_2)_2\cdot O\cdot$]. Sodium picrate gives *picratopentamminocobaltic picrate* (+3H_2O) [I; $X=C_6H_2(NO_2)_3\cdot O\cdot$] (cf. Morgan and King, J.C.S., 1922, 121, 1723). This compound is alternatively prepared by reaction of picric acid with carbonatopentamminocobaltic nitrate. If the latter be present in excess, however, a basic salt, *picratopentamminocobaltic hydroxypicrate* [III; $X=C_6H_3(NO_2)_3\cdot O\cdot]+2H_2O$, is produced.

Sodium *m*-nitrophenoxide reacts with bisaquobisethylenediamminocobaltic bromide, giving *bis*-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* +m-*nitrophenol* [IV; $X=m\text{-}C_6H_4(NO_2)\cdot O\cdot]+H_2O$.

(IV.) $[X_2\cdot Co\,en_2]X,HX$

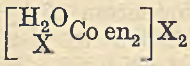


$$\left[\begin{matrix}X\\HX\end{matrix}Co\,en_2\right]X_2$$

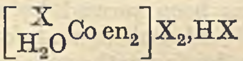
(V.)

The *o*-isomeride gives o-*nitrophenol*-o-*nitrophenoxobisethylenediamminocobaltic* o-*nitrophenoxide* [V; $X=o\text{-}C_6H_4(NO_2)\cdot O\cdot](+H_2O)$. Sodium *p*-nitrophenoxide yields, under varying conditions, four compounds: (A) p-*nitrophenol*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (V) (+3H_2O); (B) *aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (VI) (+2H_2O); (C) *aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide*+p-*nitrophenol* (VII) (+H_2O); and (D) *bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (IV) (+2H_2O). The compounds (B) and (C) are changed in dilute solution in presence of platinised electrodes into (D).

(VI.)



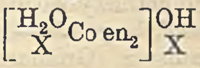
$$\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]X_2$$



$$\left[\begin{matrix}X\\H_2O\end{matrix}Co\,en_2\right]X_2,HX$$

(VII.)

(VIII.)



$$\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]\begin{matrix}OH\\X\end{matrix}$$

The colour reactions of the compound (A) and of the corresponding *o*-nitrophenol derivative are regarded as indicating a quinonoid structure for the nitrophenol molecule which is linked up with the cobalt in the complex through residual valency. Sodium *m*-nitrophenoxide, on the other hand, is not quinonoid in structure. Sodium 2 : 4- and 2 : 6-dinitrophenoxides react with bisaquobisethylenediamminocobaltic bromide to give *aquo*-2 : 4-*dinitrophenoxobisethylenediamminocobaltic* 2 : 4-*dinitrophenoxide* (VI) (+1H_2O) and *aquo*-2 : 6-*dinitrophenoxobisethylenediamminocobaltic hydroxy*-2 : 6 *dinitrophenoxide* (VIII). Sodium picrate gives *aquopicratobisethylenediamminocobaltic picrate* (VI) (+4H_2O). M. CLARK.

Detection and determination of thymol. F. W. KLINGSTEDT and E. SUNDSTROM (J. pr. Chem., 1927, [ii], 116, 307—313).—Whilst thymol ethyl and methyl ethers are unaffected either by alcoholic hydrogen chloride or by dilute aqueous alcoholic sodium nitrite, the two reagents together yield nitrosothymol. This has m. p. 169—170° (higher than that usually given), but is reduced to aminothymol of the accepted m. p. The best yields (93 and 90%, respectively) of the nitroso-compounds are obtained by the action of aqueous sodium nitrite on a solution of thymol or its methyl ether in alcohol–water–acetic acid. The ethers of carvacrol and *o*-cresol, and anisole yield no nitroso-derivatives and the reaction thus forms the basis for the approximate determination of thymol in carvacrol; it is shown that carvacrol obtained from sodium cymenesulphonate contains no thymol, the sulphonic acid group entering exclusively the position *ortho* to the methyl group. J. W. BAKER.

Direct introduction of substituents in aromatic mercaptans. T. VAN HOVE (Bull. Acad. roy. Belg., 1927, [v], 13, 206—224; cf. this vol., 555).—Attempts to brominate *p*-thiocresol in carbon tetrachloride solution were unsuccessful, the resulting product being di-*p*-tolyl disulphide, m. p. 45·2°, converted into *p*-nitrobenzoic acid by dilute nitric acid. Under similar conditions *p*-methylthioltoluene yields 3-*bromo*-4-*methylthioltoluene*, m. p. −16°, b. p. 275—275·5°, d_4^{15} 1·4696. Proof of the constitution of this compound is afforded by the preparation of the same substance from the corresponding mercaptan obtained from 3-bromo-*p*-toluidine by Leuckart's method (A., 1890, 603). Oxidation with acid permanganate gives 3-*bromo*-4-*methylsulphonyltoluene*, m. p. 99—100°, and 3-*bromo*-4-*methylsulphonylbenzoic acid*, m. p. 202—203°. Bromination of thioanisole in carbon disulphide solution results in the formation of the additive *compound*, $C_6H_4Br\cdot SMeBr_2$, m. p. 90—91°, which is readily hydrolysed to form *p*-bromophenylmethylsulphoxide, m. p. 83°, previously described (*loc. cit.*). Bromination of *p*-bromothioanisole in carbon tetrachloride solution at the b. p. gives a *dibromo*-derivative, m. p. 48°, oxidised by acid potassium permanganate to the corresponding *sulphone*, $C_6H_3Br_2\cdot SO_2Me$, m. p. 121—122°. 4-*Methylthiolphenetole*, m. p. 21·5°, b. p. 250—251°, is prepared by treating the corresponding mercaptan, obtained from *p*-phenetidine by Leuckart's process, with methyl sulphate. Bromination in carbon tetrachloride solution yields, among other products as yet unidentified, 2-*bromo*-4-*methylthiolphenetole*, m. p. 17·4°, b. p. 301—302°, d_4^{17} 1·4454. The constitution of this compound is established by its preparation from the corresponding mercaptan obtained from 2-bromo-*p*-phenetidine. J. S. CARTER.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. VI. Nitration of *m*- and *p*-chlorobenzyl ethers of guaiacol. A. E. OXFORD and R. ROBINSON (J.C.S., 1927, 2239—2244).—The directive powers of substituted benzyloxy-groups are studied by putting them separately in competition with methoxyl, and it has been shown that the directive powers of the *m*- and *p*-nitrobenzyloxy-groups are approximately equal (67; MeO=100; A., 1926, 397). By the nitration of *m*- and *p*-chlorobenzyl ethers of guaiacol, and analysis of the products, which behave thermally as binary mixtures, it is now found that the *m*-chlorobenzyloxy-group has the directive power 69, and *p*-chlorobenzyloxy- 82. The close approach of the directive power of *m*-chlorobenzyloxy- to that of *m*-nitrobenzyloxy- shows that the electron affinity of chlorine is almost as strong as that of the nitro-group, whilst the higher value for *p*-chlorobenzyloxy- is interpreted as being due to conjugation. The following were prepared: 2-m-*chlorobenzyloxyanisole*, m. p. 46—47°, b. p. 207—208°/15 mm.; 4-*nitro*-2-m-*chlorobenzyloxyanisole*, m. p. 129—130·5°; 5-*nitro*-2-m-*chlorobenzyloxyanisole*, m. p. 121°; 2-p-*chlorobenzyloxyanisole*, m. p. 70° (a crystallographic description is given); 4-*nitro*-2-p-*chlorobenzyloxyanisole*, m. p. 115—117°; 5-*nitro*-2-p-*chlorobenzyloxyanisole*, m. p. 120—120·5° (crystals described). The nitration product of 2-*m*-chlorobenzyloxyanisole contains 41% and that of 2-*p*-chlorobenzyloxyanisole 45% of the 5-nitro-isomeride. The m. p. of mixtures of the 4- and 5-nitro-isomerides in each case are given.

W. J. Powell.

Chlorination of creosol. W. Qvist [with G. Wük] (Ber., 1927, 60, [*B*], 1847—1850).—Creosol, dissolved in glacial acetic acid, is converted by chlorine in the dark or in diffused daylight at 20—25° into 2 : 5 : 6-*trichlorocreosol*, m. p. 130—131°, which, in alcoholic solution, can readily be titrated with alkali hydroxide in the presence of phenolphthalein. Further chlorination at 100° affords *pentachloro*-3 : 4-*diketotetrahydrotoluene* (anhydrous, monohydrate, and dihydrate, m. p. 86—88°).

H. Wren.

Fission of the methylenedioxy-group. E. Späth and H. Quietensky (Ber., 1927, 60, [*B*], 1882—1890).—With the object of elucidating the most promising conditions for the removal of the methylenedioxy-group from methylene ethers with the subsequent isolation of the dihydroxybenzene thereby produced, the behaviour of piperonylic acid, pyrocatechol methylene ether, and dihydrosafrole has been investigated. The action of concentrated acids on these compounds gives complex condensation products of the liberated formaldehyde and phenolic substance. It is therefore necessary to conduct operations in the presence of a compound which reacts more readily than the liberated *o*-dihydroxybenzene with formaldehyde. For this purpose phloroglucinol may be replaced by the cheaper resorcinol or phenol. Methylene ethers of phenolic bases may be hydrolysed by treatment with sulphuric acid (*d* 1·39) at 100° in the presence of phloroglucinol or resorcinol. If the methylene ether and the fundamental phenol are only slowly sulphonated at the ordinary temperature, the change can frequently be effected by concentrated sulphuric acid with addition of phloroglucinol, resorcinol, or phenol. If these methods give poor yields it is advisable to try the effect of fuming hydrochloric acid at 100—130° in a sealed tube in the presence of phenols which combine with formaldehyde. In the absence of other groups capable of reacting with magnesium methyl iodide, the methylenedioxy-compound may be transformed by the Grignard reagent into the monoethyl ether, which is subsequently hydrolysed by hydriodic acid.

H. Wren.

Photoactivity of cholesterol. J. Střítesky (Biochem. Z., 1927, 187, 388—397).—Ultra-violet rays have a much stronger effect on cholesterol than *X*-rays and the latter are a little stronger than sunlight. The photo-activity is due to the production from cholesterol in the presence of oxygen of a volatile substance and is probably dependent on the presence of the double linking, since, whereas cholesterol and its stearate and benzoate are photo-activated, cholesterol dibromide is not. The effect increases with rise in temperature, cholesterol at temperatures above its m. p. showing photo-activity without irradiation due to spontaneous oxidation.

P. W. Clutterbuck.

Phosphorus derivatives of sterols. H. von Euler and A. Bernton (Ber., 1927, 60, [*B*], 1720—1725).—Cholesterol is converted by successive treatments with phosphorus trichloride and water into cholesteryl phosphite, m. p. 158—159° (*aniline* salt, $C_{33}H_{52}NPO_3$, m. p. 170°), transformed by bromine into the *dibromo*-compound, m. p. 148°, also obtained by brominating cholesterol and treating the product with phosphorus trichloride. Acetic anhydride converts the ester into cholesteryl acetate, m. p. 114°. Cholesterol and phosphoryl chloride in benzene afford dicholesteryl phosphate, m. p. 195—199°, which is also obtained when phosphoryl chloride is added to an equivalent quantity of cholesterol in pyridine. If, however, a solution of cholesterol in pyridine is slowly added to the chloride in the same solvent and the product is treated with water, *monocholesteryl phosphate*, m. p. 195—196°, is produced. The latter ester is precipitated from alcoholic solution by cadmium chloride; its *sodium* salt is described.

H. Wren.

Action of phosphorus pentabromide on the isomeric β-methoxyphenylethyl alcohols. J. B. Shoesmith and R. J. Connor (J.C.S., 1927, 2230—2234).—With phosphorus pentabromide in benzene solution the isomeric β-methoxyphenylethyl alcohols give nuclear-brominated derivatives of the expected β-methoxyphenylethyl bromides, the orientation of which has been proved by elimination of hydrogen bromide and subsequent oxidation to the corresponding bromomethoxybenzoic acid. β-o-*Methoxyphenylethyl alcohol*, b. p. 130—131°/11 mm., prepared from *o*-bromoanisole (Grignard, A., 1905, i, 593; Shoesmith and Connor, this vol., 962) yields β-5-*bromo*-2-*methoxyphenylethyl bromide*, m. p. 55°, b. p. 160—165°/12 mm.: β-m-*methoxyphenylethyl alcohol*, b. p. 135—137°/12 mm., affords β-6-*bromo*-3-*methoxyphenylethyl bromide*, b. p. 163—165°/13 mm.; β-*p*-methoxyphenylethyl alcohol, b. p. 138—140°/11 mm., m. p. 24°, gives β-3-*bromo*-4-*methoxyphenylethyl bromide*, b. p. 187—188°/19 mm., with excess of phosphorus pentabromide, whilst with a limited quantity, β p-*methoxyphenylethyl bromide*, b.p. 130—131°/11 mm., is obtained. All these bromides are non-pungent and non-lachrimatory. β-Phenylethylamine with nitrous acid in hydrochloric acid solution gives considerable quantities of β-phenylethyl chloride, whilst with nitrous acid in sulphuric acid solution poor yields of the alcohol are obtained. *m*-Methoxybenzaldehyde with nitromethane and alkali yields m-*methoxy*-ω-*nitrostyrene*, light yellow, m. p. 93—94°, which on treatment with zinc dust and acetic acid affords m-*methoxyphenylacetaldoxime*, m. p. 92·5—93°. Reduction of the latter by means of sodium amalgam yields a small quantity of β-*m*-methoxyphenylethylamine, but this substance is more readily prepared by the method of Haworth, Perkin, and Rankine (A., 1924, i, 1098). A trustworthy method for the preparation of *o*-methoxybenzaldehyde from salicylaldehyde is described.

W. J. Powell.

Reactions of sodium compounds of aromatic ketones. I. Synthesis of triarylcarbinols and of triarylmethane dyes. E. H. Rodd and F. W. Linch (J.C.S., 1927, 2174—2178).—*pp*'-Tetramethyldiaminobenzophenone (Michler's ketone) reacts with sodium in an inert solvent to form a *sodio*-compound, which in turn reacts with aromatic chloro-compounds, if these are concurrently added, to give the sodium salt of a triarylcarbinol. The reaction constitutes a new synthesis of triarylcarbinols and of dyes from them. Michler's ketone in this way affords the following substances: from chlorobenzene, *pp*'-tetramethyldiaminotriphenylcarbinol; from *o*-chlorotoluene, pp'-*tetramethyldiaminodiphenyl*-o-*tolylcarbinol*, m. p. 132·5°, and in presence of toluene, pp'-*tetramethyldiaminodiphenylbenzylcarbinol* (see following abstract), m. p. 190° [basification of the oxalate of the former substance with ammonia yields pp'-*tetramethyldiaminodiphenyl*-o-*tolylmethylamine*, m. p. 163°, and reduction with zinc and 2*N*-hydrochloric acid yields *pp*'-tetramethyldiaminodiphenyl-*o*-tolylmethane, m. p. 102° (cf. Noelting and Saas, A., 1913, i, 522; Noelting and Gerlinger, A., 1906, i, 607)]; from 4-chloro-*m*-xylene, pp'-*tetramethyldiaminodiphenyl*-m-4-*xylylcarbinol*, m. p. 145°; from *p*-chloroanisole, pp'-*tetramethyldiaminodiphenyl*-p-*anisylcarbinol*, m. p. 153°; from β-chloronaphthalene, pp'-*tetramethyldiaminodiphenyl*-β-*naphthylcarbinol*, m. p. 181°; from α-chloronaphthalene, pp'-*tetramethyldiaminodiphenyl*-α-*naphthylcarbinol*, m. p. 167° (basification of the oxalate with ammonia gives pp'-*tetramethyldiaminodiphenyl*-α-*naphthylmethylamine*, m. p. 186°). The *sodio*-compound of *pp*'-tetraethyldiaminobenzophenone reacts with β-chloronaphthalene to afford pp'-*tetraethyldiamino*-β-*naphthylcarbinol*, m. p. 177°. The carbinols form green salts with acids which dye tannin-mordanted cotton bright green shades.

G. A. C. Gough.

Reactions of sodium compounds of aromatic ketones. II. Their reaction with methyl and methylene groups and their products of decomposition. E. H. Rodd and F. W. Linch (J.C.S., 1927, 2179—2188).—A toluene solution of Michler's ketone reacts with sodium to give *pp*'-tetramethyldiaminodiphenylbenzylcarbinol (preceding abstract) and Michler's hydrol together with small amounts of *p*-dimethylaminobenzoic acid, hexamethyltriaminotriphenylcarbinol, and dimethylaniline. This new type of reaction may be expressed:

$$2(NMe_2\cdot C_6H_4)_2CO+2Na+PhMe=$$
$$(NMe_2\cdot C_6H_4)_2CH\cdot ONa+(NMe_2\cdot C_6H_4)_2C(ONa)\cdot CH_2Ph.$$

Acids form blue salts with the benzylcarbinol and, on heating, convert it into ββ-pp'-*tetramethyldiaminodiphenylstyrene*, m. p. 135°. Oxidation with lead peroxide of the benzylcarbinol yields phenylacetic acid, and of the styrene, first a blue dye, then benzaldehyde. By extension of this reaction to substances containing a methylene group, the following are prepared: from *pp*'-tetramethyldiaminodiphenylmethane, *octamethyltetra-aminotetraphenylethanol*, m. p. 255°, oxidised to a violet dye by lead peroxide and converted by warm sulphuric acid into the corresponding ethylene, m. p. 314—316°; from *pp*'-tetraethyldiaminobenzophenone and *pp*'-tetramethyldiaminodiphenylmethane, αα-4 : 4'-*tetraethyldiaminodiphenyl*-ββ-4 : 4'-*tetramethyldiaminodiphenylethan*-α-*ol*, m. p. 228°; from *pp*'-tetramethyldiaminobenzophenone and *pp*'-tetraethyldiaminodiphenylmethane, αα-4 : 4'-*tetramethyldiaminodiphenyl*-ββ-4 : 4'-*tetraethyldiaminodiphenylethan*-α-*ol*, m. p. 229—230° (corresponding *ethylene*, m. p. 212°); from acenaphthene and Michler's ketone, 4 : 4'-*tetramethyldiaminodiphenylacenaphthenylcarbinol*, m. p. 232° (dehydrated by boiling aqueous hydrochloric acid to 4 : 4'-*tetramethyldiaminodiphenylmethyleneacenaphthene*, m. p. 209°); from fluorene, 4 : 4'-*tetramethyldiaminodiphenylmethylenefluorene*, m. p. 239—240°. The last compound is formed by dehydration of the carbinol at a stage in the preparation not determined.

Toluene is unattacked when less than 1 atomic proportion of sodium is taken for the reaction with Michler's ketone in toluene solution, the principal products being Michler's hydrol, *p*-dimethylaminobenzoic acid, and crystal-violet base.

G. A. C. Gough.

[Tetraphenylethane dyes.] F. Kehrmann (Ber., 1927, 60, [*B*], 1913—1914).—The tetraphenylethane dyes described by Wizinger (this vol., 764) can readily be formulated as quinonoid di-imonium or dioxonium salts; there is no evidence in favour of the carbonium structure.

H. Wren.

Colour and chemical constitution. XXI. Methyl derivatives of the phenolphthaleins. J. Moir (Trans. Roy. Soc. S. Africa, 1927, 14, 233—236).—Since the complete series of bromine derivatives of phenolphthalein could not be obtained (cf. A., 1921, ii, 365), the author has prepared and examined ten of the possible methyl derivatives, and, in addition, phenoltetrahydro-α-naphtholphthalein (λ 584) phenolthymolphthalein (λ 578), phenolcarvacrolphthalein (λ 580), thymolphthalein (λ 597), carvacrolphthalein (λ 601), *pp*'-phenol-α-naphtholphthalein (λ 601), *pp*'-α-naphtholphthalein (λ 650), phenol-8-hydroxyquinolinephthalein (λ 598), and phenol-6-iodo-*o*-cresolphthalein (λ 576). All the values found for these sixteen compounds agree within experimental error with the values obtained by adding to the number 554 the calculated additive value for each substituent (cf. A., 1921, ii, 6; 1923, ii, 108). Comparison of the value of λ calculated for 2 : 3-diethylphenolphthalein (577) with that observed for phenoltetrahydro-α-naphtholphthalein (584) indicates that the effect of ring closure of the two adjacent ethyl groups into the *cyclo*butane ring is only +7, a result in agreement with previous observations on the absorptions of dihydroxyxanthhydrol and succinylfluorescein. Phenol-*p*-cresolphthalein shows a band at λ 563, phenol-*as*-*m*-xylenolphthalein, 573, phenol-*as*-*o*-xylenolphthalein, 578, phenol-*p*-bromophenolphthalein, 559, phenolbromo-*o*-cresolphthalein, 570, phenolbromo-*p*-cresolphthalein, 569, phenol-*s*.-*m*-xylenolphthalein, 572, phenol-*ψ*-cumenolphthalein, 581, phenol-β-naphtholphthalein, 570, broad, phenol-2-α-naphtholphthalein, 612, whence the additive effects appear to be, 3- and 5-methyl-, 11; 3- and 5-bromo-, 7; 4-methyl, 13; 6-methyl-, 7.

R. Brightman.

Pinabietic acid. O. Aschan and P. Levy [with H. Brunotte] (Ber., 1927, 60, [*B*], 1923—1927).—Pinabietic acid yields tetrahydroxyabietic acid when oxidised by potassium permanganate and *iso*phthalic acid when treated with warm nitric acid. The production of the tetrahydroxy-acid establishes the presence of a common component in pinabietic acid and abietic acid from American colophony, whereas the production of *iso*phthalic and *trans*-hexahydrophthalic acids from the two parent acids is evidence against the presence of one and the same compound in each. H. WREN.

Manasse's ketonic acid, $C_{10}H_{16}O_3$, from camphorquinone. M. BREDT-SAVELSBERG, K. ZAUNBRECHER, and L. KNIEKE (Ber., 1927, 60, [*B*], 1801—1808; cf. A., 1903, i, 45).—The ketonic acid, $C_{10}H_{16}O_3$, obtained from camphorquinone by the method of Manasse and Samuel (*loc. cit.*) has m. p. 67—68° ($+H_2O$), b. p. 150°/3 mm. (anhydrous); the semicarbazone, decomp. 220° and methyl ester, m. p. 81—83° (cf. Gibson and Simonsen, A., 1925, i, 919), are described. The *ethyl* ester, b. p. 115—117°/3 mm., $d_4^{11\cdot3}$ 1·0382, $n_D^{11\cdot3}$ 1·46858, $[\alpha]_D^{18}$ +38·52°, yields two isomeric *semicarbazones*, needles and leaflets, decomp. 216·4°. The acid is proved to be 2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (cf. Gibson and Simonsen, *loc. cit.*) by the ability of its methyl and ethyl esters to yield *benzylidene* derivatives, b. p. 180°/1·75 mm. and 150—155°/0·3 mm., respectively, thus proving the presence of the ·CO·CH$_2$· group in the ring. Bromination of the anhydrous acid in chloroform solution without cooling gives the *dibromoketonic acid*, $C_{10}H_{14}O_3Br$, m. p. 158—159° (decomp.), whereas at 0° the *monobromolactone*, $C_{10}H_{13}O_3Br$, m. p. 116—117°, is obtained, converted by cold sodium carbonate solution into the *substance*, $C_{10}H_{12}O_3$, m. p. 211—212°. 2 : 2 : 3-Trimethyl*cyclo*hexan-4-ol-1-carboxylic acid, m. p. (anhydrous) 132—134°, prepared by reduction of the ketonic acid by sodium amalgam in the presence of carbon dioxide, is converted by acetic anhydride at 140—150° into a mixture of the corresponding *acetyl* derivative, $C_{12}H_{20}O_4,H_2O$, m. p. 85—87°, and the *anhydride*, $[C_9H_{16}(OAc)\cdot CO]_2O$, m. p. 115—116°. H. WREN.

Spectrophotometric comparison of natural and synthetic thyroxines. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1927, 169, 223—225).—The absorption curves of natural thyroxine and a commercial synthetic preparation (Hoffman–La Roche) prepared by the method of Harington and Barger (this vol., 358) appear to be identical. A. WORMALL.

Suggested mechanism of the splitting of the *cyclo*propane ring by bromine. B. H. NICOLET and H. SATTLER (J. Amer. Chem. Soc., 1927, 49, 2066—2071).—The action of bromine on ethyl *cyclo*propane-1 : 1-dicarboxylate affords *ethyl* 2-*bromo*cyclo*propane*-1 : 1-*dicarboxylate* (I), b. p. 135—140°/15 mm., and ethyl bromo-β-bromoethylmalonate (II), b. p. 146—151°/10 mm., neither of which could be obtained free from the other by repeated fractionation. The former preponderates when the reaction is carried out at a low temperature. Hydrolysis of (II) with boiling aqueous hydrobromic acid, with subsequent treatment of the product with silver oxide, affords αγ-dihydroxybutyric acid, which is also obtained in the same way from (I). It is therefore concluded that (I) is the primary product of the above bromination, (II) being subsequently produced from (I) by the action of the hydrobromic acid liberated. Bromination of *cyclo*propane-1 : 1-dicarboxylic acid in carbon tetrachloride in ultra-violet light affords bromo-β-bromoethylmalonic acid. In chloroform, the product is a viscous oil, which loses carbon dioxide on distillation, with formation of 2-*bromo*cyclo*propane*-1-*carboxylic acid*, b. p. 140°/20 mm. Bromination of ethyl 1-cyano*cyclo*propane-1-carboxylate affords *ethyl* 2-*bromo*-1-*cyano*cyclo*propane*-1-*carboxylate*, and *ethyl* αγ-*dibromo*-α-*cyanobutyrate*, b. p. 136—140°/11 mm. Bromine is without action, in ultra-violet light, on cyano*cyclo*propane and 1-cyano*cyclo*propane-1-carboxylic acid. Hypochlorous and hypobromous acids and iodine monochloride do not react with *cyclo*propane-1 : 1-dicarboxylic acid or 1-cyano*cyclo*propane-1-carboxylic acid. F. G. WILLSON.

Catalytic reduction of certain hydrophthalic anhydrides. F. P. MAZZA [with G. DI MASE, A. CALÒ, and A. CREMONA] (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], 32, 137—146).—See this vol., 664, 665.

Nature of the alternating effect in carbon chains. XXI. Directive influence of the groups $-CH_2\cdot CH(CO_2Me)_2$, $-CH{:}C(CO_2Me)_2$, $-C(CO_2Me){:}CH_2$, and $-CH{:}CH\cdot CH{:}C(CO_2Me)_2$ in aromatic substitution. J. W. BAKER and A. ECCLES (J.C.S., 1927, 2125—2133).—The following nitrations were effected by addition of the ester to nitric acid (*d* 1·49; 10 times the weight of ester) at −15° and the proportion of isomerides in the product determined by oxidation to the nitrobenzoic acids (this vol., 454). Methyl benzylmalonate gave 8% of *m*- and 68% of *p*-nitro-derivative; *methyl benzylidenemalonate*, b. p. 174—177°/15 mm., m. p. 41°, prepared by the condensation of benzaldehyde and methyl malonate, gave 3% of *m*- and 67% of *p*-nitro-derivative (65% of methyl *p*-nitrobenzylidenemalonate isolated); methyl atropate gave 5% *m*- and 55% p-*nitro*-derivative (m. p. 110°); methyl cinnamylidenemalonate gave less than 1% of *m*- and 40% of *p*-nitro-derivative. Partial decomposition of the nitration product takes place in the last case unless the nitration mixture is poured into alkaline ice-water, the precipitate removed and rapidly dried in a vacuum. These results are in agreement with the previous observations (*loc. cit.*) as to the propagation of the *m*-orienting effect of the fractional dipoles of the carboxyl groups through the side-chain. The following compounds were prepared for comparative purposes: *methyl* p-*nitrobenzylidenemalonate*, m. p. 136—137°, from *p*-nitrobenzaldehyde and methyl malonate; *methyl* m-*nitrobenzylidenemalonate*, m. p. 99—100°; *methyl* o-*nitrobenzylidenemalonate*, m. p. 65—66°; *methyl* o-*nitrobenzylmalonate*; m-*nitrobenzylmalonic acid*, m. p. 164° (decomp.; *amide*, m. p. 203°; *methyl* ester, oil), prepared from *m*-nitrobenzyl chloride, methyl malonate, and sodium methoxide in methyl alcohol; *methyl di*-m-*nitrobenzylmalonate*, m. p. 162—162·5° (by-product in the previous preparation); *methyl* p-*nitrobenzylmalonate*, m. p. 82·5—83·5°; *methyl cinnamylidenemalonate*, m. p. 67°, obtained by esterification of the acid; *methyl* m-*nitro*-

cinnamylidenemalonate, m. p. 125—126°, prepared by condensation of *m*-nitrocinnamaldehyde and methyl malonate; *methyl* o-*nitrocinnamylidenemalonate*, m. p. 114°; *methyl* p-*nitrocinnamylidenemalonate*, m. p. 146—147°. G. A. C. Gough.

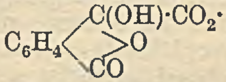
Diphenyl series. VII. Relative stability of optically active diphenic acids. F. Bell and P. H. Robinson (J.C.S., 1927, 2234—2239).—The "obstacle" theory advanced to account for the asymmetry of certain diphenyl derivatives (cf. this vol., 876) is supported by new experiments on optically active diphenic acids. As may be predicted, 6-nitrodiphenic acid, with only three groups in the central position, is optically less stable than 4 : 4′ : 6 : 6′-tetranitrodiphenic acid, which resists racemisation by boiling acetic anhydride to a much greater extent. *d*-6-Nitrodiphenic acid has $[\alpha]_{5461}$ +65·2° (c=3·01 in ethyl alcohol), $[\alpha]_{5461}$ −434° (c=4·73 in 0·426N-sodium hydroxide); *l*-6-nitrodiphenic acid has $[\alpha]_{5461}$ −66·4° (c=4·91 in ethyl alcohol), $[\alpha]_{5461}$ +433° (c=4·69 in 0·261N-sodium hydroxide); *l*+*dl*-tetranitrodiphenic acid, m. p. 224—226°, has $[\alpha]_{5461}$ −138·5° (c=1·7 in ethyl alcohol), whilst *d*-tetranitrodiphenic acid, m. p. 226—227°, has $[\alpha]_{5461}$ +142·3° (0·3696 g. in 20 c.c. of ethyl alcohol). By the action of thionyl chloride on *l*-6-nitrodiphenic acid, the *l*+*dl*-dichloride, m. p. 65—68°, $[\alpha]_{5461}$ −209·5°, is obtained. Attempts to resolve 5-nitrodiphenic acid (Schmidt and Lumpp, A., 1909, i, 34) and 2 : 2′-dinitrodiphenyl-4 : 4′-dicarboxylic acid were unsuccessful. 5-Nitrodiphenic acid readily forms an *anhydride*, m. p. 193—195°, and with sulphuric acid easily undergoes condensation forming 6(?)-*nitrofluorenone-4-carboxylic acid*, m. p. 282°, whilst 4 : 4′ : 6′-trinitrodiphenic acid is unaffected by sulphuric acid at 160°. 5-Nitrofluorenone-4-carboxylic acid (Moore and Huntress, this vol., 665) cannot be resolved by crystallisation of its morphine or quinidine salts, this result being interpreted as indicating that the 4 : 5-positions of fluorene are further apart than are the 6 : 6′-positions in a diphenic acid. 2 : 5 : 7(?)-*Trinitrofluorenone-4-carboxylic acid*, obtained by the action of nitric acid (d 1·5) at 100° on 5-nitrofluorenone-4-carboxylic acid, has m. p. 254—255°; the *quinine* salt of 4-nitrodiphenic acid has m. p. 180° (indef.), $[\alpha]_{5461}$ +106·4°, but the liberated 4-nitrodiphenic acid is inactive. W. J. Powell.

Constitution of acids formed by decomposition of cholic acid. W. Borsche (Z. physiol. Chem., 1927, 169, 306—307).—A reply to the criticism by Wieland (this vol., 767) of a previous paper (Borsche and Frank, this vol., 459). A. Wormall.

Constitution of the bile acids. XII. Cholamine, amides of cholic and deoxycholic acids. W. Borsche and A. Schwarz (Ber., 1927, 60, [*B*], 1843—1846).—Repetition of the work of Curtius (A., 1906, i, 400) and of Bondi and Müller (A., 1906, i, 633) has confirmed the transformation of ethyl cholate into cholylethylurethane, but the conversion of the latter substance into cholamine could not be effected and the identity of the latter compound appears insufficiently established. The following derivatives of cholic acid have been prepared by shaking freshly-prepared cholazide in aqueous suspension with the requisite amine; amide (+3H_2O), m. p. 136°, re-solidifying at 180° and again melting at 220°; *methylamide* (+H_2O), m. p. 186°; *dimethylamide*, m. p. 179°; *ethylamide*, m. p. 159°; *propylamide*, m. p. 146°; *allylamide*, m. p. 144°; *benzylamide*, m. p. 240°; *piperidide*, m. p. 246°. *Deoxycholamide*, m. p. 186° after softening at 162°, *deoxycholmethylamide*, m. p. 168°, and *deoxycholdimethylamide*, m. p. 203°, are described. H. Wren.

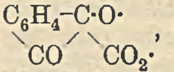
Tautomerism in the phthalonic and phthalidecarboxylic acid series. A. Cornillot (Ann. Chim., 1927, [x], 7, 275—313, and 8, 120—205; cf. this vol., 562).—The relations between phthalonic acid and its anhydride and their derivatives and compounds of the phthalidecarboxylic acid series afford little evidence of tautomerism or of the existence of desmotropic mixtures of isomerides. Throughout this series of compounds each grouping of substituents appears to involve a characteristic redistribution of the affinity capacities and in any reaction a new and independent distribution takes place. This behaviour is attributed to the unstable nature of the linkings of the carbon atom occupying the α-position with respect to the aromatic ring, this quaternary lactonic carbon being surrounded by saturated radicals, and also to the strong residual affinity of the ketonic oxygen. In consequence, compounds of this series cannot saturate their affinity capacities in either the ketonic or the lactonic structure. The complex affinities of the keto-lactonic system lead the authors to propose partial valency formulæ (cf. Skraup, A., 1919, i, 598), which are non-rigid and indicate the energy conditions of the linkings.

Oxidation of tetralin in aqueous suspension at 64—68° by addition of potassium permanganate affords only 56% (cf. von Braun and Braunsdorf, A., 1924, i, 48) of the theoretical yield of phthalonic acid, m. p. 148—149° (hydrate, +2H_2O, m. p. 37°). The acid is dibasic with thymol-blue, phenolphthalein, or litmus as indicators, but only monobasic with methyl-orange (cf. Tcherniac, A., 1898, i, 263; 1917, i, 33). Anomalies observed in the dissociation of phthalonic acid in aqueous solution are attributed to anomalies in the mobility of the ions

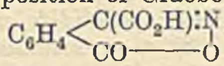


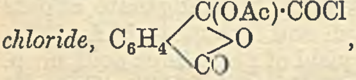
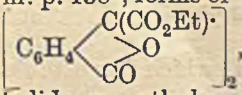
$C_6H_4<\{C(OH)\cdot CO_2\cdot,\ >O,\ CO\}$

and

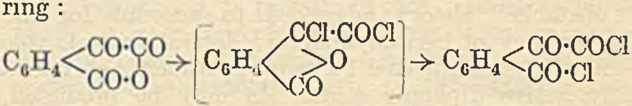


$C_6H_4-C\cdot O\cdot,\ CO,\ CO_2\cdot$

, the structure of the monobasic ion affording an explanation of the weakness of the acid (K=9×10^{-5}) as compared with benzoic acid. It is suggested that the increased conductivity observed by Böeseken (A., 1921, i, 844) on addition of boric acid is due to hydration and formation of boric acid complexes with the neutral molecule only of phthalonic acid, the proportion of neutral molecules decreasing as the dilution increases. In view of the readiness with which phthalonic acid undergoes hydration, no conclusions as to the structure of the anhydrous acid can be reached from the reactions of phthalonic acid in aqueous solution. With hydroxylamine in neutral aqueous solution phthalonic acid appears to afford first an oxime hydrate, $CO_2H\cdot C_6H_4\cdot C(OH)(NH\cdot OH)\cdot CO_2H$, which is unstable and affords phthalic acid derivatives by loss of carbon dioxide. The corresponding *oxime acetate*, $CO_2H\cdot C_6H_4\cdot C(OAc)(NH\cdot OH)\cdot CO_2H$, obtained in cold acetic acid, decomposes at 100° into phthalimide, water, acetic acid, and carbon dioxide, but no phthalimide was observed in the decomposition of Graebe and Trümpy's anhydro-oxime,  $C_6H_4<\begin{matrix}C(CO_2H){:}N\\ CO\text{——}O\end{matrix}$ (A., 1898, i, 318). In alkaline solution the latter oxime afforded phthalamic acid, for which a theoretical explanation is offered. With hydroxylamine hydrochloride and sodium acetate in acetic acid at 100°, phthalonic acid affords, in addition to the anhydro-oxime, a little of a neutral substance subliming at 250°, $C_{22}H_{14}O_7N_4$ or $C_{22}H_{16}O_7N_4$. Dehydration of the oxime hydrate with cold acetic anhydride yields *o*-cyanobenzoic acid; dehydration at 20° also affords the nitrile, and it is suggested that an unstable oxime, $CO_2H\cdot C_6H_4\cdot C(N\cdot OH)\cdot CO_2H$, forms an intermediate stage in all cases, the *anti*-form of which readily cyclises to the known anhydro-oxime, the *syn*-form of which affords the nitrile at 20°, or phthalamic acid at 0°. Formation of phthalamic acid from the anhydro-oxime at 100° is attributed to simple oxidation of the phthalonic acid by hydroxylamine.

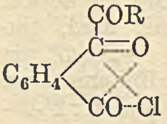
Phthalonic anhydride, m. p. 190—191° (decomp.), is best obtained by dehydration of the acid with acetyl chloride. Using acetic anhydride, the reaction product may contain, according to the duration of heating, up to 50% of *α-acetoxyphthalide-α-carboxylic acid*, decomp. 180°, also obtained by suspending phthalonic anhydride in glacial acetic acid; it is decomposed by water or alcohol into phthalonic acid and acetic acid or ethyl acetate. With aniline it forms a *salt*, m. p. 185°, but no anilide; from the *chloride*,  $C_6H_4<\begin{matrix}C(OAc)\cdot COCl\\ >O\\ CO\end{matrix}$, m. p. 112°, the *ethyl*, m. p. 110°, and *methyl*, m. p. 112°, esters are obtained. On prolonged contact with acetic anhydride, phthalonic anhydride affords *αα-diacetoxyhomophthalic anhydride*, m. p. 240° (decomp.), a reaction which is attributed to the residual affinity of the carbonyl oxygen in presence of electronegative groups. With phosphorus pentachloride in toluene, phthalonic anhydride affords *α-chlorophthalide-α-carboxyl chloride*, m. p. 70°, hydrolysed in moist air to *α-chlorophthalide-α-carboxylic acid*, m. p. 132—133°. The *methyl* ester has m. p. 92°, the *ethyl* ester, m. p. 48°, b. p. 164°/5 mm., and the *anilide*, m. p. 137·5°. With aluminium chloride in benzene, the ethyl ester affords *ethyl α-phenylphthalide-α-carboxylate*, m. p. 70°, together with a little benzhydrol-*o*-carboxylic acid, which on hydrolysis with alcoholic potassium hydroxide yields α-phenylphthalide. The methyl ester similarly affords methyl α-phenylphthalide-α-carboxylate, an oil, b. p. 275°/9 mm. (decomp.). These reactions support the lactone structure for the acid and its derivatives. Further support for this structure is afforded by the formation of the *racemic*, m. p. 188°, and *inactive*, m. p. 158°, forms of *ethyl bis-α-phthalide-α-carboxylate*,  $\left[C_6H_4<\begin{matrix}C(CO_2Et)\cdot\\ >O\\ CO\end{matrix}\right]_2$, by the action of zinc methyl iodide on ethyl α-chlorophthalide-α-carboxylate in toluene at 30°; the inactive form is also obtained with zinc ethyl iodide. On hydrolysis with alcoholic potassium hydroxide, both isomerides afford phthalonic acid and phthalide-α-carboxylic acid.

The foregoing facts indicate a lactone structure for phthalonic acid, but the formation of α-chlorophthalide-α-carboxylic acid (III) from phthalonic anhydride (I) involves the opening of the glutaric ring:

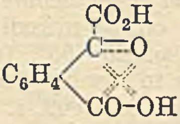


(I.) (II.) (III.)

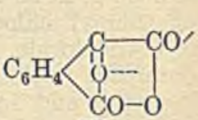
possibly an unstable intermediate chloride (II) is first formed (cf. Haller and Guyot, A., 1900, i, 170). The formation of α-chlorophthalide-α-carboxyl chloride from phthalonic acid is, however, more easily interpreted on the basis of a ketonic structure for phthalonic acid. The authors propose the term "mesomerism" for the structural relationships of this type, and structural formulæ involving partial valencies are proposed for the chlorophthalidecarboxylic derivatives (IV), phthalonic acid (V), and phthalonic anhydride (VI):



(IV.)

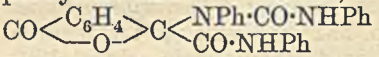


(V.)



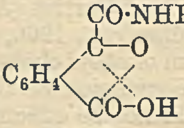
(VI.)

Phthalonic dianilide, m. p. 217—218°, affords with phenylcarbimide a *derivative*,

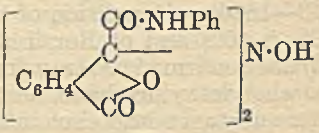


$CO<\begin{matrix}C_6H_4\\ O\end{matrix}>C<\begin{matrix}NPh\cdot CO\cdot NHPh\\ CO\cdot NHPh\end{matrix}$ (VII), m. p. 203·5°.

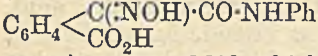
Phthalonanilic acid, m. p. 180°, is readily obtained by the action of phenylcarbimide on phthalonic acid in ether. With aniline in alcoholic solution it affords, in addition to the dianilide, a colloidal acidic *substance* (N, 8%), which is possibly a polymeric form of the anil of phthalonanilic acid, $[CO_2H\cdot C_6H_4\cdot C(NPh)\cdot CO\cdot NHPh]_n$, a reaction which would indicate that phthalonanilic acid can react in the ketonic form, the predominating reactivity being, however, lactonic. The dianilide is also obtained when phthalonanilic acid is warmed with 60% acetic acid containing a little hydrochloric acid. On alkaline hydrolysis α-chlorophthalide-α-carbanilide readily affords phthalonanilic acid; the reverse reaction takes place with thionyl chloride in benzene, a part of the phthalonanilic acid undergoing dehydration to *N*-phenylphthalonimide, m. p. 218·5°. This result indicates that the constitution of phthalonanilic acid is intermediate between the lactonic and the ketonic structures, and supports a valency formula (VIII). The analogous dynamic structure

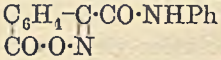


(VIII.)

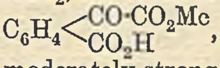


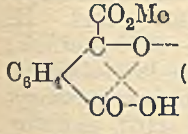
(IX.)

for α-chlorophthalide-α-carbanilide is further supported by the formation from this substance, under the influence of alcoholic pyridine, of *N*-phenylphthalonimide. With hydroxylamine in neutral alcoholic solution phthalonic acid affords only neutral products (the normal ketoxime,  $C_6H_4<^{C(:NOH)\cdot CO\cdot NHPh}_{CO_2H}$, being therefore absent), an *oxime*, m. p. 168°, which dissolves in dilute potassium hydroxide, and on hydrolysis with hydrochloric acid affords phthalic acid, aniline, and ammonia, together with a smaller amount of a *substance*, m. p. 168°, for which the structure (IX) is proposed. The oxime, m. p. 168°, is evidently α-hydroxylamino-phthalide-α-carboxyanilide. Both substances are also formed from hydroxylamine and phthalonanilic acid in aqueous solution, but not in alcoholic solution or with excess of hydroxylamine. With excess of phthalonanilic acid no oxime is formed, but the substance, m. p. 168°, accompanied by a little phthalanil; the latter substance is formed in about 50% yield in 60% acetic acid. Since the reaction medium is without dehydrating properties, the appearance of phthalanil suggests that the phthalonanilic acid has reacted in its ketonic form,

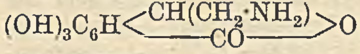


With semicarbazide in aqueous or alcoholic solution phthalonanilic acid affords no definite substance; in acetic acid *α-semicarbazidophthalide-α-carbonanilide*, decomp. at 180°, and an acidic *substance*, m. p. 250° (decomp.), possibly the semicarbazone, $CO_2H\cdot C_6H_4\cdot C(CO\cdot NHPh):N\cdot NH\cdot CO\cdot NH_2$, are formed.

Methyl hydrogen phthalonate,  $C_6H_4<^{CO\cdot CO_2Me}_{CO_2H}$, m. p. 94°, in aqueous solution is a moderately strong acid ($K=1\cdot36\times10^{-4}$), probably having the structure $CO_2H\cdot C_6H_4\cdot C(OH)_2\cdot CO_2Me$, analogous to the hydrate of phthalonic acid. With semicarbazide it affords a normal *semicarbazone*, m. p. 200° (decomp.), together with traces of *methylphthalazonecarboxylate*, m. p. 207°; the latter is obtained quantitatively by the action of hydrogen chloride in methyl alcohol on the semicarbazone and its formation establishes the ketonic structure of the semicarbazone. Acetic anhydride at 100°, however, converts the ester into methyl α-acetoxyphthalide-α-carboxylate, m. p. 112°, and thionyl chloride and phosphorus pentachloride give almost quantitative yields of the corresponding α-chlorophthalidecarboxylic ester, reactions indicating a lactonic structure for the hydrogen ester. The dynamic structure (X), involving a mobile hydroxyl group, is proposed. Methyl α-methoxyphthalide-α-carboxylate, m. p. 66°, obtained by the action of methyl iodide on silver phthalonate with phosphorus pentachloride in toluene, affords methyl α-chlorophthalide-α-carboxylate and, with semicarbazide, methyl phthalazonecarboxylate. Potassium methoxide in ethereal solution converts the lactonic ester into *methyl phthalonate*, $CO_2Me\cdot C_6H_4\cdot CO\cdot CO_2Me$, which does not crystallise at −15°, affords a normal *semicarbazone*, m. p. 250° (decomp.), and with phosphorus pentachloride in toluene is converted into methyl αα-dichlorohomophthalate. Esterification of phthalonic acid in presence of hydrogen chloride at 0° affords an uncrystallisable oil, which by the action of semicarbazide is shown to be a mixture of the neutral lactonic and ketonic esters. In alcoholic solution in presence of sulphuric acid methyl α-chlorophthalide-α-carboxylate affords only the neutral lactonic ester, and there is no evidence that the lactonic and ketonic esters are to be regarded as desmotropic forms. R. BRIGHTMAN.

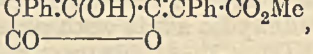
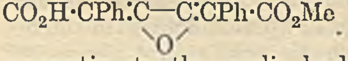
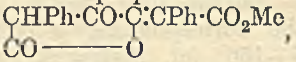


(X.)

Action of aminoacetals on phenols. II. O. HINSBERG and R. MEYER (Ber., 1927, 60, [*B*], 1914—1916).—The product of the action of aminoacetal on gallic acid, regarded previously as *r*-β-amino-α-hydroxy-α-carboxytrihydroxyphenylethane (A., 1923, i, 556), is shown to be the *anhydride* of 2-β-*amino-α-hydroxyethylgallic acid*,  $(OH)_3C_6H<^{CH(CH_2\cdot NH_2)}_{CO}>O$; the hydrochloride, m. p. 288°, and the *acetyl* derivative, $C_{17}H_{17}O_9N$, m. p. 173—174°, are described. Gallic acid and methylaminoacetal similarly afford the *anhydride* of 2-β-*methylamino-α-hydroxyethylgallic acid* (*hydrochloride*, m. p. 275—276°; *acetyl* derivative, $C_{18}H_{19}O_9N$, m. p. 172—173°). Pyrogallol is converted by successive treatments with concentrated sulphuric acid and aminoacetal into the *anhydride* of 3 : 4 : 5-*trihydroxy*-2-β-*amino*-α-*hydroxyethylbenzenesulphonic acid* (*hydrochloride*, $+1\cdot5H_2O$). H. WREN.

Structure of the condensation products of o-phthalaldehydic acids with phenols and phenol ethers. VIII. M. M. BRUBAKER and R. ADAMS (J. Amer. Chem. Soc., 1927, 49, 2279—2296; cf. this vol., 362).—Condensation of opianic acid with phenol in presence of 73% sulphuric acid at not above 30° affords 5 : 6-*dimethoxy*-2-o-*hydroxyphenylphthalide* (I), m. p. 177—178° (*methyl ether*, m. p. 103—104°), together with the corresponding *p*-hydroxy-derivative, m. p. 155—156° (cf. Bistrzycki, A., 1894, i, 600; 1899, i, 151). Opianic acid and anisole yield similarly 5 : 6-*dimethoxy*-2-p-*methoxyphenylphthalide*, m. p. 93—95°. Bromination of (I) in glacial acetic acid affords 5 : 6-dimethoxy-2-(5′-bromo-2′-hydroxyphenyl)phthalide (cf. Jacobson and Adams, A., 1925, i, 272). Condensation of opianic acid with *o*-bromophenol yields 5 : 6-*dimethoxy*-2-(3′-*bromo*-4′-*hydroxyphenyl*)*phthalide*, m. p. 207—208°, which is also obtained by brominating, in chloroform, the crude product from the condensation of opianic acid with phenol. Opianic acid and *o*-bromoanisole yield similarly 5 : 6-*dimethoxy*-2-(3′-*bromo*-4′-*methoxyphenyl*)-*phthalide*, m. p. 141° after softening, or melting and resolidifying, at 136·5—137°, whilst 3-bromo-*o*-cresol affords analogously 5 : 6-*dimethoxy*-2-(5′-*bromo*-4′-*hydroxy*-3′-*methylphenyl*)*phthalide*, m. p. 178—179° after melting and resolidifying at 163—164°. The latter is also obtained by brominating the condensation product from opianic acid and *o*-cresol (cf. Jacobson and Adams, A., 1925, i, 1076). Condensation of opianic acid with *m*-cresol yields (presumably) 5 : 6-*dimethoxy*-2-(4′-*hydroxy*-2′-*methylphenyl*)*phthalide*, m. p. 191·5—192·5°. Bromination of the crude product from the condensation of opianic acid with anisole, in chloroform, yields 5 : 6-*dimethoxy*-2-(5′-*bromo*-2′-*methoxyphenyl*)*phthalide*, m. p. 157—158°, which is also obtained by condensation of opianic acid with *p*-bromoanisole, or by bromination of the above methyl ether. 2-(5′-*Bromo*-2′-*methoxyphenyl*)-*phthalide*, m. p. 137·5—138·5°, and 5 : 6-*dimethoxy*-2-(4′-*hydroxy*-3′-*methylphenyl*)*phthalide*, m. p. 185—186°, are also described.

When phenols are condensed as above with excess of opianic acid, diphthalidyl derivatives are obtained, of which the following are described: 4 : 6-*di*-(5′ : 6′-*dimethoxyphthalidyl*)-*phenol*, m. p. 204·5—206°; -*anisole*, m. p. 210—211°; -2-*methylphenol*, m. p. 205—207°; -3-*methylphenol*, m. p. 227·5—229·5°; and -2-*bromophenol*, m. p. 215—216°; and 3 : 5-*di*-(4′-*bromo*-5′ : 6′-*dimethoxyphthalidyl*)-o-*cresol*, m. p. 266—268° (decomp.). Reduction of the above phthalides with zinc and sodium hydroxide affords the corresponding benzylbenzoic acids, of which the following are described: 5 : 6-*dimethoxy*-2-(p-*hydroxybenzyl*)*benzoic acid*, m. p. 173—174°; -(o-*hydroxy*-m-*methylbenzyl*)-, m. p. 138·5—139·5°; -(p-*hydroxy*-m-*methylbenzyl*)-, m. p. 140—142°; -(p-*methoxybenzyl*)-; and -(o-*methoxy*-p-*methylbenzyl*)-*benzoic acid*, m. p. 124·5—126·5°; and 2-(o-*methoxybenzyl*)*benzoic acid*, m. p. 115—116°. Some of the latter were also obtained by catalytic reduction. F. G. Willson.

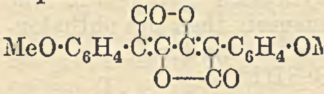
Constitution and physical properties of vulpinic acid. F. P. Mazza (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], 31, 182—193).—Spiegel (A., 1884, 841) ascribed to vulpinic acid (methyl pulvinate) the formula (I),  $\begin{array}{l}\mathrm{CPh{:}C(OH)\cdot C{:}CPh\cdot CO_2Me}\\ \mathrm{CO{-}{-}{-}{-}{-}{-}O}\end{array}$, and Volherd (A., 1895, i, 99) the formula (II),  $\begin{array}{l}\mathrm{CO_2H\cdot CPh{:}C{-}C{:}CPh\cdot CO_2Me}\\ \qquad\quad\mathrm{\diagdown O\diagup}\end{array}$. (I) ascribes the acidic properties to the enolic hydroxyl group; it should thus be possible to prepare derivatives of the ketonic form (III),  $\begin{array}{l}\mathrm{CHPh\cdot CO\cdot C{:}CPh\cdot CO_2Me}\\ \mathrm{CO{-}{-}{-}{-}{-}O}\end{array}$, which must also be considered. The mol. wt. in benzene solution shows no polymerisation, indicating that a hydroxy-compound is not present; the dissociation constant, $K_{25}=4{\cdot}94\times10^{-6}$, is that of an extremely feebly acidic substance, and is of the order of that of a phenol. The increase in molecular conductivity of a solution of the sodium salt on dilution is abnormally great.

In an alkaline medium, a *benzoyl* derivative, m. p. 171°, is obtained which is absolutely neutral; phenylcarbimide does not react in the cold, but at 165° a neutral *phenylurethane*, m. p. 237°, is formed. These reactions exclude the structure (II), and suggest that the normal form is (III), converted in the presence of alkali or on heating into (I); correspondingly, in neutral media a *semicarbazone*, m. p. 175°, is obtained.

Values of $[R_L]_\alpha$, $[R_L]_D$, and $[R_L]_\beta$ in various solvents are given; although exalted, they are all inferior to the values calculated for the enolic form; the differential method of Brühl gives, however, high values in an alcoholic solution of sodium ethoxide; in water R_L increases, in agreement with increased enolisation. The absorption spectrum in alcoholic sodium ethoxide solution shows three absorption bands; that in chloroform two only. In water the third band appears on dilution. The dielectric constant is 3·79; the solid compound gives no anomalous electrical absorption, and thus contains no free hydroxyl group; the supercooled liquid shows a slight absorption. E. W. Wignall.

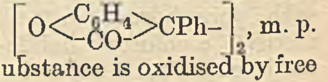
Hydroxyalkyl derivatives of vulpinic acid. A. Piutti and F. P. Mazza (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], 31, 148—155).—The lichen *Lepraria chlorina* contains 18% of its dry weight of vulpinic acid, with other substances containing a higher proportion of oxygen, suspected to be hydroxyalkyl derivatives. Some substances of the latter type are synthesised, but are not identical with any of the natural products.

The method of Volhard (A., 1895, i, 99) for synthesis of vulpinic acid by way of diphenylketipinodinitrile is extended. o-Methoxyphenylacetonitrile is condensed with ethyl oxalate and sodium ethoxide, and the product is acidified with acetic acid, giving *di*-o-*methoxyphenylketipinodinitrile*, m. p. 250° (decomp.) after turning brown at 190°. This is hydrolysed by sulphuric acid to the *dilactone*,


$\begin{array}{l}\qquad\quad\;\;\mathrm{CO{-}O}\\ \mathrm{MeO\cdot C_6H_4\cdot C{:}C\cdot C{:}C\cdot C_6H_4\cdot OMe}\\ \qquad\qquad\;\;\mathrm{O{-}{-}CO}\end{array}$, which on boiling with sodium carbonate solution yields *di*-o-*methoxypulvinic acid*, m. p. 195°, of which the *methyl* ester, *di*-o-*methoxyvulpinic acid*, m. p. 121° (*acetyl* derivative, m. p. 111°; *benzoyl* derivative, m. p. 151°), is obtained by dissolving in methyl-alcoholic potassium hydroxide solution and acidifying. An aqueous solution of this substance when heated with piperidine gives a *substance*, m. p. 98°.

Similarly are prepared: 3 : 4 : 3′ : 4′-*tetramethoxydiphenylketipinodinitrile*, m. p. 204° (decomp.); 3 : 4 : 3′ : 4′-*tetramethoxypulvinic acid*, m. p. 160°; *methyl* ester of the latter, *tetramethoxyvulpinic acid*, m. p. 97° (*acetyl* derivative, m. p. 103°; *benzoyl* derivative, m. p. 134°; *piperidine* salt, m. p. 93°).

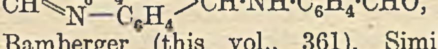
3 : 4-*Methylenedioxyphenylacetonitrile*, b. p. 180—190° in a cathode-ray vacuum, is prepared from homopiperonyl chloride; it yields *di*-3 : 4-*methylenedioxyphenylketipinodinitrile*, m. p. 225° (decomp.), *di*-3 : 4-*methylenedioxypulvinic acid*, m. p. 167°, and its *methyl* ester, *di*-3 : 4-*methylenedioxyvulpinic acid*, m. p. 103° (*acetyl* derivative, m. p. 122°; *benzoyl* derivative, m. p. 141°; *piperidine* salt, m. p. 101°). E. W. Wignall.

Radical dissociation of derivatives of arylated succinic acids. III. 2 : 2′-Dihydroxytetra-arylsuccinodilactones. A. Löwenbein and H. Schmidt (Ber., 1927, 60, [*B*], 1851—1861; cf. A., 1926, 168).—Bromo-2-hydroxydiphenylacetolactone is converted by boiling methyl alcohol into *methoxy*-2-*hydroxydiphenylacetolactone*, m. p. 116°, and by copper bronze in boiling benzene into 2 : 2′-*dihydroxytetraphenylsuccinodilactone*,  $\left[\mathrm{O{<}{}^{C_6H_4}_{-CO-}{>}CPh{-}}\right]_2$, m. p. 166° (indef.). The latter substance is oxidised by free oxygen in boiling benzene to 2-*keto*-3-*phenylcoumaranyl*-3-*peroxide*, m. p. 212°. 2-Hydroxy-4′-methoxy-5-methyldiphenylacetolactone is similarly converted successively into *bromo*-2-*hydroxy*-4′-*methoxy*-5-*methyldiphenylacetolactone*, m. p. 108°, 2 : 2′-*dihydroxy*-4″ : 4‴-*dimethoxy*-5 : 5′-*dimethyltetraphenylsuccinodilactone*, m. p. 215—220°, and 2-*keto*-3-p-*anisyl*-5-*methylcoumaranyl*-3-*peroxide*, m. p. 192°. α-Bromophenyl-2-hydroxy-1-naphthylacetolactone and copper bronze in boiling benzene afford *diphenyl*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylsuccinodilactone*, m. p. 148—150°, which is converted by bromine in warm benzene into α-bromophenyl-2-hydroxy-1-naphthylacetolactone, by phenylhydrazine into phenyl-2-hydroxy-1-naphthylacetolactone and by free oxygen into 2-*keto*-3-*phenylbenzocoumaranyl*-3-*peroxide*, m. p. 233°. α-*Bromo*-4′-*methoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 159°, yields analogously α-*methoxy*-αp-*dimethoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 125°, α-*ethoxy*-p-*methoxyphenyl*-2-*hydroxy*-1-*naphthylacetolactone*, m. p. 106°, and pp′-*dimethoxydiphenyl*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylsuccinodilactone*, m. p. 197—212°. A further method for the preparation of the dilactones is found in the action of sodium iodide on the bromolactones in acetone solution. All the succinodilactones dissociate into radicals when heated; the degree of dissociation has been determined for 2 : 2′-dihydroxytetraphenylsuccinodilactone, 2 : 2′-didihydroxy-4″ : 4‴-dimethoxy-5 : 5′-dimethyltetraphenylsuccinodilactone and diphenyl-2 : 2′-dihydroxy-1 : 1′-dinaphthylsuccinodilactone in boiling toluene and ethylene dibromide. Addition of concentrated aqueous hydrochloric acid to a boiling solution of the last-mentioned lactone in acetic anhydride causes the separation of intensely green crystals of the dilactone. The observation is explained by the hypothesis that, since crystallisation is induced at a temperature far above the association temperature, the product is a solid solution of the radical in the dilactone. When subjected to pressure the dilactones become more deeply coloured and the behaviour appears to extend to all ethanes capable of dissociation. The colour becomes less intense in course of time if the pressure is removed, but returns when the pressure is restored. Since in all cases the colour produced corresponds exactly with that of the free radical, it must be assumed that radical dissociation can be caused by high pressure on solid substances at the atmospheric temperature. It is probable that the aromatic nuclei become deformed by pressure or that the single ethane molecules are so modified in their structure by spatial proximity that liberation of radicals occurs locally and that solid solutions are thus produced which occupy a smaller volume than the original substance. H. Wren.

Oxidation products of aromatic aldehydehydrazones and their molecular transpositions. G. Minunni (Gazzetta, 1927, 57, 505—525).—A summary is given of previous work on the oxidation of the aromatic aldehydrazones and on the isomerisation and molecular transformations of the oxidation products. Oxidation of these phenylhydrazones yields various crystalline products, some of which, viz. the hydrotetrazones, dehydrohydrazones, and osazones of the α-diketones, arise by elimination of two atoms of hydrogen from two molecules of hydrazone. Other among these oxidation products result from the addition of one or two atoms of oxygen to a molecule of hydrazone. Under certain conditions benzaldehydephenylhydrazone gives compounds of analogous structure to the hydrotetrazones and dehydrohydrazones, but containing a benzoyl radical, these being formed by oxidation of the benzylidene group of one of the hydrazone molecules participating in the reaction. T. H. Pope.

Oxidation of hydrazine compounds. I. Behaviour of the *p*-tolylhydrazones of certain aromatic aldehydes with amyl nitrite. G. Minunni and S. D'Urso (Gazzetta, 1927, 57, 526—536; cf. preceding abstract).—When oxidised by treatment with amyl nitrite, *benzaldehyde*-p-*tolylhydrazone*, m. p. 114—115°, yields only *dibenzylidenedi*-p-*tolylhydrotetrazone*, $CHPh{:}N\cdot N(C_6H_4Me)\cdot N(C_6H_4Me)\cdot N{:}CHPh$, m. p. 174·5—175°, which cannot be transformed either into the dehydrohydrazone by heating or into benzil-*p*-tolylosazone by treatment with benzoyl chloride. Similarly, *piperonal*-p-*tolylhydrazone*, m. p. 116—117°, which turns red on prolonged exposure to light, yields only *dipiperonaldi*-p-*tolylhydrotetrazone*, $CH_2O_2{:}C_6H_3\cdot CH{:}N\cdot N(C_6H_4Me)\cdot N(C_6H_4Me)\cdot N{:}CH\cdot C_6H_3{:}CH_2O_2$, m. p. 155—156° (evolution of gas and browning); attempts to convert this into the dehydrotetrazone by heating proved unsuccessful, but treatment with benzoyl chloride gives *piperil*-β-p-*tolylosazone*, $CH_2O_2{:}C_6H_3\cdot C({:}N\cdot NH\cdot C_6H_4Me)\cdot C({:}N\cdot NH\cdot C_6H_4Me)\cdot C_6H_3\cdot CH_2O_2$, m. p. 214—215°. Salicylaldehyde-*p*-tolylhydrazone yields only *dehydro*-o-*hydroxybenzaldehyde*-p-*tolylhydrazone*, $OH\cdot C_6H_4\cdot CH{:}N\cdot N(C_6H_4Me)\cdot C(C_6H_4\cdot OH){:}N\cdot NH\cdot C_6H_4Me$, m. p. 194—196° (decomp.) or 197—199° (decomp.) according to the rapidity of the heating. m-*Nitrobenzaldehyde*-p-*tolylhydrazone*, m. p. 150°, gives, as principal products: (1) *di*-m-*nitrobenzylidenedi*-p-*tolylhydrotetrazone*, m. p. 167·5—169·5° (decomp.), which is converted into iso*dehydro*-m-*nitrobenzaldehyde*-p-*tolylhydrazone*, $C_{28}H_{24}O_4N_6$, m. p. 230° (decomp.), when heated and into m-*nitrobenzil*-β-p-*tolylosazone*, m. p. 251°, when treated with benzoyl chloride; (2) *dehydro*-m-*nitrobenzaldehyde*-p-*tolylhydrazone*, $NO_2\cdot C_6H_4\cdot CH{:}N\cdot N(C_6H_4Me)\cdot C(C_6H_4\cdot NO_2){:}N\cdot NH\cdot C_6H_4Me$, m. p. 193° (decomp.), which is converted into (1) by the action of nitrous acid. T. H. Pope.

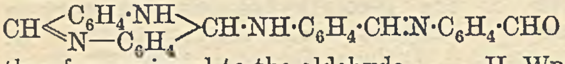
Anhydro-compounds of *o*-aminobenzaldehyde. F. Seidel and W. Dick (Ber., 1927, 60, [*B*], 2018—2023; cf. A., 1926, 1140).—Anhydrotris-*o*-aminobenzaldehyde, dissolved in acetone, is converted by the prolonged action of nitrous fumes into *dinitroso-anhydrotris*-o-*aminobenzaldehyde*, m. p. 155—158° (decomp.), and by less prolonged action into the *mononitroso*-compound, m. p. 171° (or $+C_6H_6$, m. p. 172—173°); the monoacetyl derivative yields a *mononitroso*-compound, m. p. 165—167°. These observations are incompatible with the constitution assigned by Seidel (*loc. cit.*) to anhydrotris-*o*-aminobenzaldehyde and confirm the structure,



$$CH{<}\begin{matrix}C_6H_4\cdot NH\\ N{-}C_6H_4\end{matrix}{>}CH\cdot NH\cdot C_6H_4\cdot CHO$$

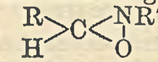
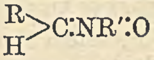
proposed by Bamberger (this vol., 361). Similarly, anhydrotetrakis-*o*-aminobenzaldehyde affords a *dinitroso*-

derivative, m. p. 176° (or $+CH_3\cdot CO\cdot CH_3$, m. p. 125—155°, and (?) $+0\cdot5C_6H_6$, m. p. 170—193°), and a *mononitroso*-compound, m. p. 222—223°. *Mononitrosomonoacetylanhydrotetrakis*-o-*aminobenzaldehyde*, m. p. 193° after darkening at 185°, is described. The constitution



$$CH\lessdot\begin{matrix}C_6H_4\cdot NH\\N{-}C_6H_4\end{matrix}\!>\!CH\cdot NH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CHO$$

is therefore assigned to the aldehyde. H. Wren.

***N*-Ethers of oximes.** H. Lindemann and K. T. Tschang (Ber., 1927, **60**, [*B*], 1725—1729).—In the hope of discriminating between the alternative constitutions  $\begin{matrix}R\\H\end{matrix}\!>\!C\!<\!\begin{matrix}NR'\\|\\O\end{matrix}$ and  $\begin{matrix}R\\H\end{matrix}\!>\!C{:}NR'{:}O$ for the *N*-ethers of aldoximes the authors have examined the possibility of resolving *p*-dimethylaminobenzaldoxime *N*-methyl ether into optical antipodes (cf. Kuhn and Albrecht, this vol., 749). Failure to accomplish this is conditional evidence in favour of the nitrone structure.

Anisaldoxime *N*-methyl ether is hydrolysed by tartaric acid with production of N-*methylhydroxylamine tartrate*, m. p. 235°. p-*Dimethylaminobenzaldoxime* N-*methyl ether* ($+H_2O$), m. p. 110° (*hydrochloride*, m. p. 86°), is prepared from *p*-dimethylaminobenzaldehyde and *N*-methylhydroxylamine hydrochloride; the d-*tartrate*, m. p. 163°, *l*-tartrate, m. p. 166°, and d-*bromocamphorsulphonate*, m. p. 164°, are described. Optical activity could not be detected in the base isolated from the salts containing optically active acids. Anisaldehyde is transformed by hydroxylamine hydrochloride in alcoholic solution into the α-oxime, whereas protracted boiling causes formation of the β-compound. α-Anisaldoxime *O*-methyl ether, from the α-oxime, methyl alcohol, methyl iodide, and silver oxide, has m. p. 43°, b. p. 129°/15 mm., $d_4^{64\cdot2}$ 1·0690, $n_\alpha^{64\cdot2}$ 1·53561, whereas the corresponding β-compound (prepared similarly at temperatures below 10°) has m. p. 36°, b. p. 129°/15 mm., $d_4^{64\cdot3}$ 1·0745, $n_\alpha^{64\cdot3}$ 1·53378. The β-compound is readily converted into the α-isomeride by hydrogen chloride. H. Wren.

Colour and chemical constitution. XXII. Dicyclic azomethines and their congeners. J. Moir (Trans. Roy. Soc. S. Africa, 1927, **14**, 301—303).—The absorption band at λ 330 of *p*-hydroxybenzaldehyde and the stilbenes $CHPh{:}CH\cdot C_6H_4\cdot ONa$ and $[ONa\cdot C_6H_4\cdot CH{:}]_2$ (λλ 330 and 370) in alkaline solution is attributed to association of the (*para*) auxochrome ONa with the double linking. Replacement of CH by N produces a band near λ 400 as in $O{:}N\cdot C_6H_4\cdot ONa$ (λ 400), benzylidene-*p*-aminophenol (λλ 367 and 393), *p*-hydroxybenzylidene-*p*-aminophenol (434 and 406), and *p*-hydroxyazobenzene (433 and 395). The absorption of *p*-dimethylaminobenzylidene-*p*-aminophenol (433 and 405) and the stilbene, $NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot ONa$ (λ 400), in alkaline solution, of the stilbenes, $OH\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot NMe_2$ (360 and 400), $CHPh{:}CH\cdot C_6H_4\cdot NMe_2$ (355), and $NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot NMe_2$ (430 and 461) and of *p*-dimethylamino-*p'*-hydroxyazobenzene (435 and 465), *p*-dimethylaminobenzylidene-*p'*-dimethylaminoaniline (496 and 464), *p*-hydroxybenzylidene-*p'*-dimethylaminoaniline (490 and 460), and *p*-dimethylaminobenzylideneaniline (430 and 460) in acetic acid indicate that substitution of the auxochrome NMe_2 for ONa shifts the band from 330 to 360. Since the colour of the stilbene derivatives is deeper than that of the hydroxy- and dimethylamino-benzaldehyde derivatives it is possible that the linking between C_6H_4 and CH and not the central double linking is concerned in these cases. The deep colour of *p*-dimethylaminoazobenzene (λλ 507 and 543), of bis-*pp'*-dimethylaminoazobenzene (λλ 505, 540, and 685), and of *p*-dimethylamino-*p'*-hydroxyazobenzene (λλ 507, 540, and 570) in acetic acid is attributed to a similar cause. In concentrated sulphuric acid *p*-dimethylamino-*p'*-hydroxyazobenzene shows a band (λ 692) similar to that of tetramethyldiaminoazobenzene in glacial acetic acid. *p*-Hydroxybenzylideneaniline has a band at λ 360, $NMe_2\cdot C_6H_4\cdot CHO$ (acetic acid) at λ 359, $NMe_2\cdot C_6H_4\cdot NO$ (acetic acid) at λ 458, *pp'*-dihydroxyazobenzene at λλ 487 and 455. Benzylidene-*p*-dimethylaminoaniline is exceptional in showing bands at λλ 482 and 514 in acetic acid. The twelve dihydroxybenzylideneanilines in alkaline solution show absorption bands as indicated: 2 : 2', λ 450; 2 : 3', 510; 2 : 4' and 2 : 5', 440; 2 : 6' and 4 : 2', 420; 3 : 2'; 430, 3 : 3' and 3 : 5', 470; 3 : 4' and 4 : 3', 410; 3 : 6'; 408 and 4 : 4', 434 and 406.

R. Brightman.

Abnormal reaction of certain aromatic aldehydes with Schiff's reagent. J. B. Shoesmith, C. E. Sosson, and A. C. Hetherington (J.C.S., 1927, 2221—2230).—On examination of a large number of aldehydes, it has been found that the abnormal reaction which consists in the production of yellow precipitates and colorations is dependent on the quantity of "free sulphur dioxide," *i.e.*, sulphur dioxide capable of reacting with iodine, present in the reagent. A large excess favours the aldehyde–hydrogen sulphite type of reaction, which is regarded by Wieland and Scheuing (A., 1922, i, 58) as being that which results in the production of colour. Certain of the aldehydes examined, notably *o*-hydroxyaromatic aldehydes, undergo an entirely different reaction resulting in the formation of precipitates having the properties of sulphites of hydrated Schiff's bases of the general formula $SO_3H\cdot C(C_6H_4\cdot NH\cdot CHR\cdot OH)_3$, in which R is an aromatic residue. The formation of these precipitates is retarded by a large excess of sulphurous acid, hence red precipitates (really yellow ones containing adsorbed red dye) result from reagents containing much free sulphur dioxide, and yellow ones from those deficient in free sulphur dioxide. Some of these aldehydes react abnormally with all types of reagent, others only under certain conditions. In order to ascertain the composition of the precipitates, that obtained from β-resorcylaldehyde was examined in detail. Since they cannot be separated as pure compounds owing to their insolubility in organic solvents or water and to their instability towards acids and alkalis, analytical results were only approximate, but a satisfactory clue to the constitution was obtained by comparison of the precipitates formed by interaction of the aldehyde with reagents made from other bases of the pararosaniline type.

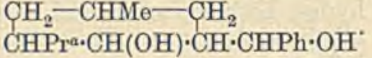
The red colour developed by Schiff's reagent on heating disappears on cooling, provided that much sulphur dioxide is not allowed to leave the solution. *pp'*-Diaminotriphenylcarbinol undergoes a similar reaction, the solution being violet when hot, colourless when cold. W. J. Powell.

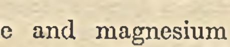
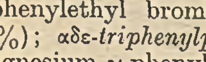
Preparation of nitrohydroxybenzaldehydes and colour relationships of their substituted phenylhydrazones. H. H. Hodgson and H. G. Beard (J.C.S., 1927, 2375—2384).—Nitration of 6-nitro-3-hydroxybenzaldehyde gives a mixture of 2 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 94° [*sodium* and *ammonium* salts; p-*nitrophenylhydrazone*, exploding 240—242°; p-*bromophenylhydrazone*, m. p. 166—167° (decomp.)], and 4 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 106° [*sodium* and *ammonium* salts; p-*nitrophenylhydrazone*, decomp. 282—283°; p-*bromophenylhydrazone*, m. p. 249—250° (decomp.)]. Nitration of 2- and 4-nitro-3-hydroxybenzaldehydes gives as single products the 2 : 6- and 4 : 6-dinitro-derivatives respectively. Further nitration of either compound yields 2 : 4 : 6-*trinitro*-3-*hydroxybenzaldehyde*, m. p. 161—162° (decomp.) [(*sodium* salt; p-*nitrophenylhydrazone*, exploding 228—230°; p-*bromophenylhydrazone*, exploding 218—220°; *azine*, exploding 150—160°)]. Nitration of 6-nitro-3-methoxybenzaldehyde yields in like manner a mixture of 2 : 6-dinitro-3-methoxybenzaldehyde, m. p. 157° [p-*nitrophenylhydrazone*, exploding 260°; p-*bromophenylhydrazone*, m. p. 196—197° (decomp.)], and 4 : 6-*dinitro*-3-*methoxybenzaldehyde*, m. p. 131° [p-*nitrophenylhydrazone*, m. p. above 300°; p-*bromophenylhydrazone*, m. p. 254—256° (decomp.)]. Tiemann and Ludwig's α-dinitro-*m*-methoxybenzaldehyde (cf. Ber., 1882, **15**, 2043) is thus the 2 : 6-dinitro-compound, whereas their β-isomeride is a mixture of the 2 : 6- and 4 : 6-dinitro-derivatives. Nitration of 3-nitro-4-hydroxybenzaldehyde with pure nitric acid gives 3 : 5-*dinitro*-4-*hydroxybenzaldehyde*, m. p. 102—103° [(*sodium* salt; p-*nitrophenylhydrazone*, decomp. 283—284°; p-*bromophenylhydrazone*, decomp. 242—244°; *phenylhydrazone*, m. p. 203°)], whereas if sulphuric acid is present only picric acid is formed. Nitration of 2 : 5-dichlorobenzaldehyde gives a mixture of 2 : 5-dichloro-6-nitrobenzaldehyde and, in lesser yield, 2 : 5-*dichloro*-3-*nitrobenzaldehyde* [*phenylhydrazone*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 290—292° (decomp.)]. 2 : 5-*Dichloro*-3-*nitrobenzoic acid* has m. p. 220°; 2 : 3 : 5-*trichlorobenzaldehyde* has m. p. 56°. The compounds described as 4-chloro-6-nitro-3-hydroxybenzaldehyde and 4-chloro-2-nitro-3-hydroxybenzaldehyde (A., 1926, 1040) are now shown to be 4-chloro-2-nitro-3-hydroxybenzaldehyde and 2-chloro-4-nitro-3-hydroxybenzaldehyde, respectively, the last-named compound being derived from 2-chloro-isomeride present as impurity in the 4-chloro-3-hydroxybenzaldehyde used in the preparation. The following are also described: p-*nitrophenylhydrazone*, m. p. 247—249° (decomp.), and p-*bromophenylhydrazone*, m. p. 192—193°, of 3-nitro-4-hydroxybenzaldehyde; 2 : 6-*dinitro*-3-*methoxybenzoic acid*, m. p. 199°.

The facility of decomposition of the *p*-nitrophenylhydrazones of the various nitrohydroxybenzaldehydes is shown to be dependent on the positions of the nitro-groups in the aldehyde residue. The colours of the nitro- and *p*-bromo-phenylhydrazones of these aldehydes, both as solids and in aqueous and alcoholic alkaline solution, are discussed in relation to positional influences. M. Clark.

Preparation of 2 : 5-dihydroxybenzaldehyde (gentisaldehyde). H. H. Hodgson and H. G. Beard (J.C.S., 1927, 2339—2340).—The method described gives an improved yield of a less crude product than that of Neubauer and Flatow (A., 1907, i, 771). *m*-Hydroxybenzaldehyde is treated at 30—35° with potassium persulphate in alkaline solution, and, after keeping, the mixture is rendered faintly acidic and the unchanged material extracted with ether. When the solution is strongly acidified, a dark brown, amorphous substance, which constitutes 40% of the yield, is precipitated. This substance chars above 330°, and contains an aldehyde group, since it yields a p-*nitrophenylhydrazone*, which gives the characteristic magenta colour with alkalis. 2 : 5-Dihydroxybenzaldehyde, m. p. 89—92°, is extracted from the filtrate with ether. The pure product has m. p. 98—99° (cf. Tiemann and Müller, A., 1882, 52). The p-*nitrophenylhydrazone*, brick-red, has m. p. 256—257° (decomp.); the *dibenzoate*, m. p. 106—107°, forms a p-*nitrophenylhydrazone*, orange, m. p. 272°; the dimethyl ether, m. p. 51° (cf. Tiemann and Müller, *loc. cit.*), forms a p-*nitrophenylhydrazone*, red, m. p. 216°; the monomethyl ether yields a p-*nitrophenylhydrazone*, orange, m. p. 206°.

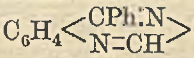
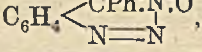
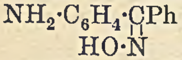
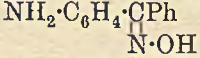
W. J. Powell.

Condensation of *cyclo*hexanones with aromatic aldehydes. Alkylation of *cyclo*hexanones. R. Cornubert and H. Le Bihan (Bull. Soc. chim., 1927, [iv], **41**, 1077—1087; cf. A., 1921, i, 422, 730).—Allylation of 2-methyl*cyclo*hexanone with sodamide and allyl chloride, bromide, and iodide gives a mixture of 2-allyl-2-methyl- and 2-allyl-6-methyl-*cyclo*hexanones (80 : 20 from chloride, 88 : 12 from bromide and iodide). Hydrogenation of these allyl compounds furnishes the corresponding *n*-propyl compounds, which condense with benzaldehyde in presence of hydrogen chloride, yielding *benzylidene*-2-*methyl*-6-n-*propyl*cyclo*hexanone*, m. p. 25°, and a "*tetrahydropyrone*," $C_{24}H_{28}O_2$, m. p. 136—137° (cf. A., 1926, 953), respectively. Allylation of 4-methyl*cyclo*hexanone with allyl chloride and bromide affords 2-allyl-4-methyl*cyclo*hexanone together with a mixture of 2 : 2-diallyl- and 2 : 6-diallyl-4-methyl*cyclo*hexanones (75 : 25 from chloride, 88 : 12 from bromide), all of which on hydrogenation yield the corresponding *n*-propyl compounds. 4-*Methyl*-2 : 6-*di*-n-*propyl*cyclo*hexanone* thus obtained using allyl bromide had b. p. 129—129·5°/20 mm., d_4^{16} 0·8925, n_D^{13} 1·4600, and yielded an *oxime*, m. p. 70°, b. p. 164—168°/26 mm., and a *semicarbazone*, m. p. 185·5—190°. The ketone on condensation with benzaldehyde in presence of hydrogen chloride yields a *benzylidene* derivative, b. p. 215—216°/16 mm., and the "*tetrahydropyrone*," $C_{27}H_{34}O_2$, m. p. 145°. Similar condensation of benzaldehyde with 4-methyl-2-*n*-propyl*cyclo*hexanone affords a *benzylidene* derivative, b. p. 194—196°/16 mm. (*semicarbazone*, m. p. 161°), whilst with sodium methoxide as the condensing agent there are obtained the benzylidene derivative and a *compound*, $C_{17}H_{26}O_2$, m. p. 150° (*diacetyl* derivative, m. p. 86°), which has probably the formula  $\begin{array}{l}CH_2—CHMe—CH_2\\ CHPr^{\alpha}\cdot CH(OH)\cdot CH\cdot CHPh\cdot OH\end{array}$. 2-Allyl-4-methyl*cyclo*hexanone and benzaldehyde in presence of sodium methoxide yield an impure *benzylidene* derivative, b. p. 202—203°/17 mm. (*semicarbazone*, m. p. 141°), together with a small amount of a *compound*, $C_{17}H_{24}O_2$, m. p. 135°, analogous to that obtained from the propyl derivative. Hydrogenation of 6-benzylidene-4-methyl-2-*n*-propyl*cyclo*hexanone yields impure 6-*benzyl*-4-*methyl*-2-n-*propyl*-cyclo*hexanone*, b. p. 189·5°/14 mm., which condenses with benzaldehyde in presence of hydrogen chloride to yield a small amount of a "*tetrahydropyrone*," $C_{31}H_{34}O_2$, m. p. 172°. H. Burton.

Semipinacolic and hydrobenzoinic transpositions in the alkylhydrobenzoin series. Alkylhydrobenzoins with branched chains. II. The *cyclo*hexane chain. A. Orékhov and M. Tiffeneau (Bull. Soc. chim., 1927, [iv], 41, 1174—1185).—α-*cyclo*Hexylhydrobenzoin, m. p. 159—160° (cf. Danilov, A., 1926, 519), undergoes a transposition of the semipinacolic type on dehydration with concentrated sulphuric acid forming *cyclo*hexyl benzhydryl ketone, m. p. 57—58°, its behaviour being therefore analogous to that of the corresponding benzyl and *iso*propyl derivatives of hydrobenzoin (cf. A., 1923, i, 333). Dehydration with hot dilute acid, however, leads to the formation of the three products theoretically possible, viz., *cyclo*hexyldiphenylacetaldehyde, m. p. 124°, by a semihydrobenzoinic change, *cyclo*hexyl benzhydryl ketone by a semipinacolic transposition, and *cyclo*hexyldeoxybenzoin, m. p. 120—121°, by dehydration followed by isomerisation without migration of the phenyl group. The last may be synthesised by the action of *cyclo*hexyl bromide on deoxybenzoin in presence of sodium ethoxide. The formation of a ketone rather than an aldehyde on dehydration is characteristic of hydrobenzoin derivatives in which the substituent is a radical of feeble affinity. Since the benzyl derivative with dilute acid undergoes exclusively the semipinacolic change, whilst the *iso*propyl like the *cyclo*hexyl derivative gives a mixture, the relative affinities are in the order $Bz < Pr^{\beta}$ and $C_6H_{11} < H$. *αγδ-Triphenylbutane-γδ-diol*, m. p. 147—148°, obtained from benzoin and magnesium β-phenylethyl bromide, yields, on oxidation with chromic acid, benzoic acid and phenyl β-phenylethyl ketone, m. p. 72—73°, and on dehydration with concentrated sulphuric acid affords an unsaturated *hydrocarbon*, $C_{22}H_{18}$, m. p. 85—86°, probably  $C_6H_4<\begin{array}{l}CH_2—CH\\ CHPh\cdot CPh\end{array}$ or  $C_6H_4<\begin{array}{l}CH_2\cdot CH_2\\ CPh:CPh\end{array}$. *ααδ-Triphenylbutan-β-ol*, prepared from diphenylacetaldehyde and magnesium β-phenylethyl bromide, has m. p. 61—62° (yield 48%); *αδε-triphenylpentane-δε-diol*, from benzoin and magnesium γ-phenylpropyl bromide, has m. p. 100—101°, and yields on oxidation with chromic acid in acetic acid, *phenyl γ-phenylpropyl ketone*, m. p. 57—58°. Benzoin is reduced by magnesium *tert.*-butyl chloride and by magnesium *sec.*-butyl bromide, the chief product being hydrobenzoin. W. J. Powell.

Pyrogenic decomposition of ketones under high pressures. V. N. Ipatiev and A. D. Petrov (Ber., 1927, 60, [*B*], 1956—1963).—Acetophenone, when heated under pressure at 270—300° in the presence of aluminium hydroxide, affords unchanged material, triphenylbenzene, 3 : 4-diphenylfuran, and a red resin; at 380—420° the reaction is complete and gives a mixture of benzene, toluene, ethylbenzene, and *o*-xylene (15% in all), the remainder being a resin which does not appear to contain diphenyl or *p*-diphenylbenzene and in which benzoic acid is present only in traces. The primary products of the change are therefore benzene and toluene, whereas ethylbenzene is formed by subsequent hydrogenation of acetophenone. Benzophenone remains unchanged at 430°, but suffers complete decomposition at 500—550°, yielding mainly carbon and gases; benzene and diphenylmethane, but not diphenyl or *p*-diphenylbenzene, are identified among the liquid products (12%). When heated with hydrogen in an iron tube at 400—430° in the presence of aluminium oxide, benzophenone affords diphenylmethane in very good yield; only about 20% of the ketone dissociates into benzene and resin. Acetone, under pressure in the presence of aluminium oxide at 350—400° yields mesityl oxide, *iso*phorone, xylitone, and mesitylene, reversible and irreversible reactions thus taking place. Increase of temperature to 500—550° favours the irreversible changes accompanied by maximal elimination of water whereby the unsaturated cyclic ketones (*iso*phorone and xylitone) are partly converted by loss of water into a mixture of aromatic compounds, mainly mesitylene, and partly by loss of methane into *s.*-*m*-xylenol. H. Wren.

Electrolytic reduction of ketoximes and aldoximes of the aromatic series. S. Kaplansky (Ber., 1927, 60, [*B*], 1842—1843; cf. Gulevitsch and others, A., 1924, i, 1285).—Aromatic ketoximes are considerably more smoothly reduced by Tafel's method than in the presence of colloidal palladium; the yields of primary amine vary from 50% to 70%. Tafel's process is applicable also to aldoximes. The electrolytic reduction of the oximes of benzophenone, acetophenone, dibenzyl ketone, benzaldehyde, and vanillin is described. H. Wren.

Oximes of *o*-amino-benzo- and -aceto-phenone. J. Meisenheimer, O. Senn, and P. Zimmermann (Ber., 1927, 60, [*B*], 1736—1748; cf. Meisenheimer and Meis, A., 1924, i, 433; von Auwers and Jordan, *ibid.*, 743).—The mixture of *n*- and *h*-oximes of *o*-aminobenzophenone is transformed by boiling formic acid into the *n*-oxime and 4 : 5-*benzo*-3-*phenyl*-*hept*-1 : 2 : 6-*oxdiazine*,  $C_6H_4<\begin{array}{l}CPh:N\\ N=CH\end{array}>O$, m. p. 173—174° (regarded by von Auwers and Jordan as the *N*-formyl derivative of the *n*-oxime). If the *n*-oxime dissolved in cold, dilute hydrochloric acid is treated with sodium nitrite, yellow 4 : 5-*benzo*-6-*phenyl*-1 : 2 : 3-*triazine*-1-*oxide*,  $C_6H_4<\begin{array}{l}CPh:N:O\\ N=N\end{array}$, m. p. 154° (decomp.), is immediately precipitated. If, however, diazotisation is accomplished in warm solution, phenylanthranil and benzenylphenyleneamidine, m. p. 285°, are produced. The *h*-oxime is almost quantitatively transformed by diazotisation into phenylindoxazene; if, however, the mixture is kept for some time before being heated and the small amount of resin is not immediately removed, 4 : 5-benzo-6-phenyl-1 : 2 : 3-triazine-1-oxide separates. The configurations  $\begin{array}{r}NH_2{\cdot}C_6H_4{\cdot}CPh\\ \|\;\;\\ HO{\cdot}N\end{array}$ and  $\begin{array}{r}NH_2{\cdot}C_6H_4{\cdot}CPh\\ \|\;\;\;\;\;\;\\ N{\cdot}OH\end{array}$ for the *h*- and *n*-oximes are therefore considered to be confirmed. The *N*-acyl derivatives of *o*-aminobenzophenone-oxime readily form seven-membered rings, the tendency being particularly marked in derivatives of the *h*-oxime. Evidence with regard to configuration cannot be deduced therefrom, since the precise mode of action is uncertain. Reopening of the ring occurs more uniformly and leads in all circumstances (in alkaline and hydrochloric acid solution and with superheated water) to the acyl-*N*-oxime whereby *trans* fission of the ring must be assumed.

Whereas aqueous sodium hydroxide causes transformation of benzophenone-*n*-oxime into the *h*-oxime, the homogeneous oximes are obtained by the action of concentrated alcoholic sodium hydroxide on the corresponding benzoyl derivatives. In dilute alcoholic solution the benzoyl-*h*-oxime is unchanged by sodium hydroxide, whereas the benzoyl-*n*-oxime is quantitatively transformed into the benzoyl-*h*-oxime.

o-Aminoacetophenoneoxime is converted by diazotisation and subsequent boiling of the solution into methylanthranil, 4 : 5-*benzo*-6-*methyl*-1 : 2 : 3-*triazine*-1-*oxide*, decomp. 185—188°, being formed intermediately. Attempts to reduce the oxide to the corresponding triazine resulted in the exclusive production of 3-methylindazole as defined product. Conversion of the triazine oxide into methylanthranil proceeds readily in cold, dilute sulphuric acid or boiling water, whereby *o*-azidoacetophenone is produced, identified as the *dinitrophenylhydrazone*, decomp. 182—183°; an additive *compound* of *o*-azidoacetophenone and mercuric chloride is described. The triazine oxide dissolves rapidly in aqueous or alcoholic alkali hydroxide and the dark red solution, if immediately acidified, affords o-*acetophenylazohydroxylamine* (or o-*acetanilinoazohydroxide*), decomp. 116—117° after softening, which with phenylcarbimide affords N-*phenyl*-N′-o-*acetophenylcarbamide*, m. p. 170° (decomp.) in a pre-heated bath. The carbamide derivative is also obtained from *o*-aminoacetophenone and phenylcarbimide. The conversion of *o*-aminobenzaldoxime into 4 : 5-*benzo*-1 : 2 : 3-*triazine*-1-*oxide* (Bamberger's "indiazoneoxime") occurs with very poor yield, but the corresponding change is easier with 3 : 5-dimethyl- and 3 : 6-dichloro-2-aminobenzaldoxime. The two latter oximes must certainly have the same configuration as *o*-aminoacetophenoneoxime, the hydrogen and hydroxyl groups being in the *cis*-position to one another. It appears probable that the more readily preparable and more stable forms of aromatic aldoximes have the aromatic nucleus and hydroxyl group in the *anti*-position (cf. Brady and Bishop, A., 1925, i, 930). H. Wren.

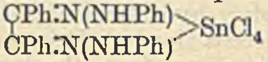
Indones. VIII. R. de Fazi (Gazzetta, 1927, 57, 545—550).—When heated for 2 hrs. with phosphoric anhydride in anhydrous benzene solution on a boiling water-bath, ethyl ββ-diphenyl-α-methyl-lactate is converted solely into ethyl β-phenyl-α-methylcinnamate, this being partly transformed into 3-phenyl-2-methylindone if the action is prolonged for about 8 hrs. Thus, although phosphoric anhydride readily removes the first molecule of water from the phenylmethyllactic ester, hydrolysis of this ester by phosphoric acid proceeds slowly. It is concluded that the formation of indones from the lactic esters proceeds by ring-closure of the cinnamic acid. 2 : 3-Diphenylindone, previously obtained in about 30% yield by the action of phosphoric anhydride on αβ-diphenyl-lactic acid (A., 1915, i, 542), may be prepared in almost theoretical yield by the action of concentrated sulphuric acid on αββ-triphenyl-lactic acid; the *phenylhydrazone* of this indone has m. p. 175—176° (cf. García Banús and Medrano, A., 1924, i, 180).

T. H. Pope.

Indones. IX. Truxones. R. de Fazi (Gazzetta, 1927, 57, 551—554).—With reference to Brass' statement that the author assumes the bimolecular constitution of the aryl- and alkyl-truxones (A., 1926, 838, 839) the author points out that he showed by mol. wt. determinations that the products of the action of concentrated sulphuric acid on ethyl ββ-diphenyl-lactate include two diphenyltruxones (A., 1915, i, 1063; 1916, i, 151; 1920, i, 316). Not all truxones are obtainable by a single method. Thus the action of concentrated sulphuric acid on β-phenylindone yields two diphenyltruxones, whereas this acid does not act under similar conditions on 3-phenyl-2-methylindone. The latter is converted into dimethyldiphenyltruxones by the radiations from a quartz mercury vapour lamp, and these also transform into two other isomerides the two diphenyltruxones formed by the action of sulphuric acid on β-phenylindone.

T. H. Pope.

Ring-closure in additive compounds. III. Determination of configuration of stereoisomeric hydrazones. W. Hieber and F. Sonnehalb (Annalen, 1927, 456, 86—110; cf. A., 1925, i, 1325).—The configurations of stereoisomeric compounds may be determined from a consideration of their cyclic co-ordinated additive compounds with metallic salts. Benzil-α-osazone in chloroform combines with 0·5 mol. of stannic chloride to form a yellow *compound*, decomp. above 145°, and with 1 mol. of stannic chloride to give a red *compound*, m. p. 120° (decomp.). The β-osazone, on the other hand, forms only a single (equimolecular) additive *compound*, m. p. 60°. No isomerisation takes place, for the corresponding osazones are regenerated by treatment with water. In similar manner stannic chloride combines with 2 mols. of benzaldehydephenylhydrazone, giving a yellowish-brown *compound*, m. p. 70—75° (decomp.); with 2 mols. of benzophenonephenylhydrazone (red *compound*, m. p. 190°); with 2 mols. of benzylideneaniline [yellow *compound*, m. p. 200° (decomp.)]; with 1 mol. of benzophenoneanil (yellow *compound*, m. p. 180°); with 1 mol. of benzildianil [yellow *compound*, m. p. 225° (decomp.); also a red *compound* containing more stannic chloride]; with 1 mol. and 1·5 mols. of benzilmonoanil (orange and red *compounds*, m. p. 175° and 90°, respectively);

with 1 mol. of benzilmonophenylhydrazone (brownish-red *compound*, m. p. 165°). The evolution of heat during the reaction with benzylideneaniline and benzophenoneanil and the great stability of these products indicate that in all the compounds the tin is attached to doubly-linked nitrogen atoms. This is confirmed by the colours of the compounds, and leads to the formula  $\begin{array}{l}\text{CPh:N(NHPh)}\\ \mid\\ \text{CPh:N(NHPh)}\end{array}\!>\text{SnCl}_4$ for the β-osazone product; *i.e.*, the β-osazone is the *anti*-compound, the α-osazone the *syn*-compound. The only known benzilmonophenylhydrazone has an *anti*-configuration.

2 : 3 : 5 : 6-Tetraphenylpyrazine gives with 1 mol. of stannic chloride a yellow *compound*, decomp. 135°; with 2 mols. a red *compound*, m. p. 100°. 5 : 6-Diphenyl-2 : 3-dihydropyrazine is more closely analogous with the osazones in constitution, and gives a yellow *compound*, sintering at 75°, with 0·5 mol. of stannic chloride, and an orange equimolecular *compound*, m. p. 115—120° (decomp.); this confirms the *syn*-configuration for the α-osazone. Mol. wt. determinations in benzene and in ethylene dibromide give values (allowing for dissociation) in accord with these views. C. Hollins.

Absorption spectra of derivatives of acetophenone. T. Tasaki (Acta Phytochim., 1927, 3, 259—315; cf. A., 1925, i, 1444, 1445; ii, 838).—The absorption spectra of acetophenone, deoxybenzoin, benzylacetophenone (hydrochalkone), benzoylacetone, propionylacetophenone, dibenzoylmethane, benzyl phenacyl ketone, and of 49 methyl, hydroxy-, alkoxy-, and acetoxy-derivatives of these were examined. Acetophenone and phenyl benzyl ketone in $M/1000$ alcoholic solution give indications of a band at 3600 Å., the latter compound being markedly hypochromic compared with phenyl styryl ketone. All the diketones show in $M/10,000$ alcoholic solution a single band, which lies at 3200 Å. for benzoylacetone, propionylacetophenone, and benzyl phenacyl ketone, but is displaced to 2900 Å. in dibenzoylmethane; as in the monoketones, replacement of methyl by benzyl has little effect. Introduction of hydroxyl or alkoxyl exerts both bathochromic and hyperchromic effects, the increased effect due to *o*- or *p*-position of the hydroxyl group being less marked in diketones than in monoketones, owing probably to the overwhelming influence of the two carbonyl groups. Acetylation of hydroxyl groups is without effect. Methyl groups have not the auxochromic effect here which they show in the benzophenone series.

The following new compounds are described: 2 : 4 : 5-*trimethylphenyl* β-*phenylethyl ketone*, m. p. 37—38°; *phenyl* β-p-*tolylethyl ketone*, m. p. 48—50°; o-, m-, and p-*hydroxyphenyl* β-*phenylethyl ketones*, m. p. 36—37°, 40—42°, and 62—64°, respectively; *phenyl* β-m-*hydroxyphenylethyl ketone*, m. p. 73—74°; *phenyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 54—55°; p-*anisyl* β-o-*hydroxyphenylethyl ketone*, m. p. 59—60°; p-*phenetyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 70—71°; 3 : 4-*dimethoxyphenyl* β-p-*anisylethyl ketone*, m. p. 65—66°; 2-*hydroxy*-4-*ethoxyphenyl* β-3-*methoxy*-4-*ethoxyphenylethyl ketone*, m. p. 77—79°; 2-*hydroxy*-4-*ethoxyphenyl* β-3 : 4-*methylenedioxyphenylethyl ketone*, m. p. 117° (this and all the preceding ketones are prepared by reduction of the corresponding chalkones); 3 : 4-*dimethoxybenzoylacetone*, m. p. 71—72°; 4-*methoxy*-2′-*ethoxydibenzoylmethane*, m. p. 90—91°; *dianisoylmethane*, m. p. 114°; α-*anisoyl*-γ-*phenylacetone*, m. p. 75—76° (the last four compounds are prepared by Claisen condensations).

The author's conclusion, from absorption spectra, that rutin is of the hydroxypyroneglucoside type (A., 1925, i, 1445) has since been confirmed chemically by Atree and Perkin (this vol., 231). Rutin compared with quercetin is appreciably hypso- and hypochromic. C. Hollins.

Synthesis of 4-hydroxy-3-methoxystyryl *n*-butyl ketone. H. Nomura and S. Tsurumi (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 563—564; cf. A., 1925, i, 1156).—Vanillin and methyl *n*-butyl ketone, when heated for 6 hrs. under a reflux condenser with alcohol and potassium hydroxide, condense to form 4-hydroxy-3-methoxystyryl *n*-butyl ketone, m. p. 39—40° ($1H_2O$, m. p. 66—100°). B. W. Anderson.

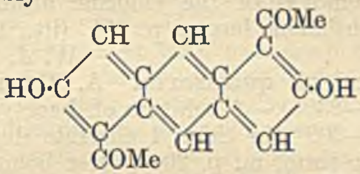
Homologues of zingerone. II. H. Nomura and S. Tsurumi (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 565—579).—Vanillin was condensed with methyl *n*-nonyl ketone to form 4-*hydroxy*-3-*methoxystyryl* n-*nonyl ketone*, m. p. 55·5—56·5° ($+1H_2O$, m. p. 68—100°), and this was reduced to 4-*hydroxy*-3-*methoxyphenylethyl* n-*nonyl ketone*, m. p. 42·5—43·5° (*benzoyl* derivative, m. p. 51—52°; *methyl ether*, m. p. 33·5—35°; *oxime* of the latter, m. p. 73·5—74·5°). The preparation of the *n*-hexyl, *n*-heptyl, and *n*-octyl homologues of the above is also described (cf. A., 1926, 1145). B. W. Anderson.

Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. II. Syntheses with anisole, *o*-bromoanisole, phenetole, *o*-, *m*-, and *p*-tolyl ethers, veratrole, and resorcinol ethers. J. Houben and W. Fischer (Ber., 1927, 60, [*B*], 1759—1778; cf. this vol., 143).—The extension of Gattermann's synthesis to mononuclear phenolic ethers and various nitriles is reported. α-Naphthol yields nuclear substituted products with acetonitrile, chloro- and trichloro-acetonitrile, benzonitrile, and phenylacetonitrile even in the absence of zinc chloride, whilst considerably enhanced yields are obtained in its presence. With benzene derivatives, the presence of halogen in the *ortho*-position to the alkoxyl group greatly diminishes the yield without entirely inhibiting the change. A methyl group in the *ortho*-position facilitates the reaction, whilst in the *meta*-position it diminishes the yield somewhat. The methoxy-group facilitates the reaction if in the *meta*-position. If the *para*-position to the alkoxy-group is replaced by methyl, condensation is still possible to a limited extent, but not if the alkoxy-group is here present. *o*-Nitro- and *o*-acetamido-groups inhibit reaction completely. *o*-Carboxy-groups introduce complications, since they react with the nitrile. Ether is the most suitable solvent. Methyl acetate may be used, but gives a less pure product, whilst small amounts of ketones are obtained when ethyl bromide is employed. Acetyl chloride, acetic anhydride, glacial acetic acid, and dioxan are quite unsuitable. It is frequently possible to improve the yield of ketone to a considerable extent by use of an excess of nitrile. The following substituted acetophenones are described; ωωω-*trichloro-4-ethoxy-*, m. p. 63—64° (*sulphonic acid*; *compound* of corresponding ketimine hydrochloride and zinc chloride); ωωω-*trichloro-4-methoxy-*, m. p. 33—34·5°; ωωω-*trichloro-4-ethoxy-3-methyl-*, m. p. 67—68°; ωωω-*trichloro-4-methoxy-2-methyl-*, b. p. 130°/0·8 mm.; ωωω-trichloro-2-methoxy-5-methyl-, b. p. 150—155°/12 mm. (accompanied by p-*tolyl trichloroacetate*, m. p. 67—68°); ωωω-*trichloro-3 : 4-dimethoxy-*, m. p. 101—102°; ωωω-*trichloro-2 : 4-dimethoxy-*, b. p. 153°/0·5—0·6 mm. (quinol monoethyl ether affords p-*ethoxyphenyl trichloroacetate*, m. p. 49—50°); ωωω-*trichloro-3-bromo-4-methoxy-* (N-*trichloroacet*-o-*methoxybenzamide*, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot CCl_3$, m. p. 184—185°, from *o*-methoxybenzoic acid); ωωω-*trichloro-4-phenoxy-*; ω-*chloro-4-ethoxy-*, m. p. 65—66·5°; ω-*bromo-4-ethoxy-*, m. p. 59—60° [accompanied by dibromodiacetamide, m. p. 195° (decomp.) after darkening at 190°]. α-Naphthyl ethyl ether is converted by trichloroacetonitrile, zinc chloride, and hydrogen chloride into ωωω-*trichloro-4-ethoxyacetonaphthone* [*4-ethoxy-α-naphthyl trichloromethyl ketone*], m. p. 74—74·5°, and by chloroacetonitrile into ω-*chloro-4-ethoxyacetonaphthone*, m. p. 132—132·5°. ω-*Bromo-4-ethoxyacetonaphthone*, m. p. 120—121°, and the corresponding *ketimine hydrochloride*, decomp. about 150°, are described. 4-Ethoxyacetonaphthone has m. p. 77—79°. α-Naphthol, hydrogen chloride, and trichloroacetonitrile in the absence of zinc chloride give an almost immediate precipitate of cinnabar-red *ketimine hydrochloride*, which becomes converted into a colourless substance, probably the imino-ether hydrochloride; in the presence of zinc chloride similar phenomena are observed and the semi-solid product affords ωωω-*trichloro-4-hydroxyacetonaphthone*, m. p. 100—101°, when decomposed by water. Benzonitrile and α-naphthol give the corresponding *ketimine hydrochloride* and 4-hydroxybenzonaphthone, m. p. 164—165°. *4-Hydroxynaphthyl benzyl ketone*, m. p. 185—187°, is derived from α-naphthol and phenylacetonitrile. β-Naphthol, trichloroacetonitrile, and hydrogen chloride give *trichloroacetimino-β-naphthyl ether hydrochloride*, $C_{10}H_7\cdot O\cdot C(CCl_3)\colon NH,HCl$, and β-*naphthyltrichloroacetate*, m. p. 86—87°. Phenyl 2-hydroxynaphthyl ketone, m. p. 141°, is derived from β-naphthol, benzonitrile, hydrogen chloride, and zinc chloride at 60°.

Unsuccessful attempts to induce isomerisation of trichloroacetiminophenyl ether hydrochloride by heat in the presence or absence of zinc chloride are recorded. H. WREN.

Quinonedisulphones. A. RÉCSEI (Ber., 1927, 60, [*B*], 1836—1840).—The term "quinonedisulphones" is applied to compounds, $O\colon Ar\colon(SO_2R)_2$, which contain two sulphonyl groups in place of a quinonoid oxygen. *p*-Benzoquinone dissolved in glacial acetic acid condenses with ethyl mercaptan in the presence of concentrated sulphuric acid and hydrogen chloride, giving a compound which is oxidised by permanganate to p-*benzoquinonedisulphone* [*1 : 1-diethanesulphonyl*-$\Delta^{2{\cdot}5}$-cyclo*hexadiene-4-one*], m. p. 84°, black-violet crystals, giving brownish-red solutions in organic solvents. The compound does not yield an oxime, semicarbazone, or phenylhydrazone; it is readily reduced to a colourless compound which becomes oxidised when exposed to air. It is converted by cold bromine into 2 : 3 : 5 : 6-*tetrabromo*-1 : 1-*diethanesulphonyl*-$\Delta^{2{\cdot}5}$-cyclo*hexadiene*-4-*one*, m. p. 286° (closed capillary), and by warm bromine into 2 : 2 : 3 : 3 : 5 : 5 : 6 : 6-*octabromo*-1 : 1-*diethanesulphonyl*cyclo*hexan-4-one*, m. p. 276° after softening at 230°. α-Naphthaquinone affords similarly 4 : 4-*diethanesulphonyl-α-naphthaquinone*, m. p. 86°, reduced by zinc dust to 1-*hydroxy*-4 : 4-*diethanesulphonyl*-1 : 4-*dihydronaphthalene*, m. p. 91°. 2-*Ethylthiol*-1 : 4-*naphthaquinone*, m. p. 142°, is obtained as by-product during the preparation of the naphthaquinonedisulphone. H. WREN.

Action of substances containing an active methylene group on quinones. M. V. IONESCU (Bull. Soc. chim., 1927, [iv], 41, 1094—1096).—Acetylacetone reacts with *p*-benzoquinone in pyridine solution forming a dark green *compound*, m. p. above 300°, probably



H. BURTON.

Formation of 1 : 2- and 2 : 3-dichloroanthraquinones from *o*-dichlorobenzene. H. E. FIERZ-DAVID (J. Amer. Chem. Soc., 1927, 49, 2334).—Treatment of *o*-3 : 4-dichlorobenzoylbenzoic acid with concentrated sulphuric acid at 150° yields, in addition to 2 : 3-dichloroanthraquinone (cf. Phillips, this vol., 362), a small proportion of the 1 : 2-dichloro-derivative, m. p. 196·5° (lit., 207°) (cf. Senn, Diss., Swiss Tech. High School, 1923). F. G. WILLSON.

Formation of 1 : 2- and 2 : 3-dichloroanthraquinones from *o*-dichlorobenzene. M. PHILLIPS (J. Amer. Chem. Soc., 1927, 49, 2335; cf. preceding abstract).—Acknowledgment of Fierz-David's correction. F. G. WILLSON.

Determination of the structure of α-hydroxyanthranols. A. GREEN (J.C.S., 1927, 2341—2345).—The reduction of an α-hydroxyanthraquinone to the anthranol may occur in two ways, viz., 1-hydroxyanthraquinone may yield either 1 : 9- or 1 : 10-dihydroxyanthracene or a mixture of the two. Structures may be assigned to these compounds by observing the differences in the resistance of the derived benzanthrones to methylation (Miller and Perkin, A., 1926, 174), but this method is tedious and the yields are low (cf., however, Cross and Perkin, this vol., 771). The reaction of the dihydroxyanthracene with thionyl chloride at the ordinary temperature may also be used for this purpose, since only those phenols possessing two hydroxy-groups in the *o*- or *peri*-position to each other yield thionyl derivatives (cf. this vol., 354, 457). 1 : 8-Dihydroxynaphthalene, when treated with thionyl chloride in carbon disulphide–pyridine solution, yields 1 : 8-*thionyldihydroxynaphthalene*, m. p. 97°, in quantitative yield, whereas, in the case of the 1 : 5-dihydroxy-compound, the product is a complex mixture which contains chlorine. The reduction product of 1-hydroxyanthraquinone yields a *thionyl* derivative, m. p. 115° (decomp.), and is therefore 1 : 9-dihydroxyanthracene, whilst that of 4-chloro-1-hydroxyanthraquinone is 4-*chloro*-1 : 9-*dihydroxyanthracene*, m. p. 170—171° (*diacetyl* derivative, m. p. 157°), since with thionyl chloride it yields 4-*chloro*-1 : 9-*thionyldihydroxyanthracene*, m. p. 123—124° (decomp.). Anthragallolanthranol yields with thionyl chloride only complex chlorine-containing mixtures, indicating that this anthranol is not 1 : 2 : 3 : 9-tetrahydroxyanthracene, since this would be expected to yield a thionyl derivative (cf. J.C.S., 1926, 2202) but 1 : 2 : 3 : 10-tetrahydroxyanthracene (cf. Cross and Perkin, *loc. cit.*). Liebermann and Mamlock's method (A., 1905, i, 521) for the preparation of anthranols from anthraquinones yields products which are more readily purified than that of Breare and Perkin (J.C.S., 1923, **123**, 2606), but the reduction of 4-chloro-1-hydroxyanthraquinone must be carefully controlled to avoid removal of the chlorine atom. 1 : 8-Diacetoxynaphthalene has m. p. 155° (lit., 147—148°).

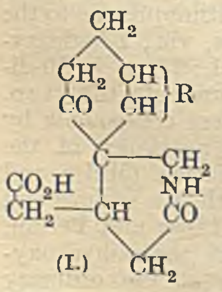
W. J. Powell.

Structure of quinizarin. A. Green (J.C.S., 1927, 2384—2385).—A solution of diacetylquinizarin, m. p. 207—208°, in thionyl chloride deposited the polymorphic form, m. p. 200°, after being boiled for 2 hrs. This lack of reactivity of a quinizarin derivative in which the hydroxyl hydrogens are replaced, renders improbable the second mechanism suggested (J.C.S., 1926, 1430) for the conversion of quinizarin into 10-chloro-1-hydroxy-4 : 9-anthraquinone by treatment with thionyl chloride. It is therefore probable that quinizarin assumes an *ortho*-quinonoid state (1 : 10-dihydroxy-4 : 9-anthraquinone) in this reaction (cf. Perkin, J.C.S., 1899, **75**, 433).

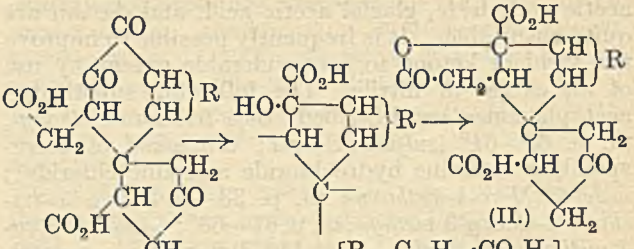
M. Clark.

Derivatives of the anthraquinone series. I. G. Farbenind. A.-G.—See B., 1927, 743.

Bile acids. XVII. M. Schenck and H. Kirchof (Z. physiol. Chem., 1927, **169**, 164—176; cf. this vol., 665).—Oxidation of the ketolactam-carboxylic acid, $C_{23}H_{35}O_4N$, m. p. 218—220° (this vol., 666), with potassium permanganate gives a *ketolactamdicarboxylic acid*, $C_{23}H_{35}O_6N$ (I), m. p. 277° (decomp.), a reaction similar to the preparation of the diketodicarboxylic acid from pyrodeoxybilianic acid (Wieland and Kulenkampff, A., 1921, i, 112).


(I.)

When bil*iso*idanic acid (Schenck, A., 1924, i, 179, 1318), is heated with sodium hydroxide solution it undergoes a benzilic acid rearrangement, and the product isolated is a *lactonic acid*, $C_{24}H_{32}O_9,2H_2O$ (II), which on heating shrinks at about 155°, becomes a frothy mass at 165°, assumes a white turbidity at 235—245°, and at 275—277° gives a clear brown-coloured melt.


$[R{=}C_{10}H_{19}{\cdot}CO_2H.]$

The lactonic acid is formed through the intermediate hydroxytetracarboxylic acid, which cannot be isolated, but its presence is proved definitely by titration values.

H. Burton.

New derivatives of caoutchouc. G. Bruni and E. Geiger (Atti R. Accad. Lincei, 1927, [vi], **5**, 823—828).—In benzene solution, nitrosobenzene (3 mols.) and caoutchouc ($1C_5H_8$) readily react (cf. Angeli, Alessandri, and Pegna, A., 1910, i, 552; Alessandri, A., 1915, i, 555), giving azoxybenzene, together with a 94—98% yield of a yellow iso*caoutchouc nitrone*, $\cdot CH{:}CMe{\cdot}C({:}NPh{:}O){\cdot}CH_2\cdot$ or $\cdot CH_2{\cdot}C({:}CH_2){\cdot}C({:}NPh{:}O){\cdot}CH_2\cdot$. The formation of this compound, which is obtained also when the latex of *Hevea brasiliensis* and nitrosobenzene react in pyridine solution, serves well for the determination of crude caoutchouc. It unites with bromine to form the *compound* $({:}C_5H_6Br_2{\cdot}NOPh)_x$.

Treatment of caoutchouc ($1C_5H_8$) with ethyl *o*-nitrosobenzoate gives azoxybenzene and a colloidal *acid*, $({:}C_5H_6{:}NO{\cdot}C_6H_4{\cdot}CO_2H)_x$, decomp. about 100°. Caoutchouc reacts also with the *p*-nitroso-derivatives of dimethylaniline, methylaniline, diphenylamine, and *o*-toluidine. Gutta percha reacts with nitroso-compounds in the same way as caoutchouc.

These nitrones do not react with hydroxylamine, but with phenylhydrazine the nitrone of *iso*caoutchouc yields the phenylhydrazone of a ketone which contains the carbonyl in the caoutchouc chain and is termed *cauccione*: $\cdot CH{:}CMe{\cdot}C({:}NPh{:}O){\cdot}CH_2\cdot + NH_2{\cdot}NHPh \longrightarrow \cdot CH{:}CMe{\cdot}C({:}NO{\cdot}NHPh){\cdot}CH_2\cdot + NHPh{\cdot}OH$.

T. H. Pope.

Formation and decomposition of ketonecyanohydrins. Some compounds recently classified as such. A. Lapworth, R. H. F. Manske, and E. B. Robinson (J.C.S., 1927, 2052—2056).—The formation of the cyanohydrin of menthone, as with other ketones, is a reversible reaction, and equilibrium is attained in a few min. or sec. in strongly alkaline solution. The extraordinary stability of the "menthonecyanohydrin" obtained from the nitroimine by Houben and Pfankuch (this vol., 364) is probably due to a Wagner transformation during the preparation. True menthonecyanohydrin has been prepared and shown to have a higher dissociation constant than *cyclo*hexanone cyanohydrin. The stability of the two supposed "camphorcyanohydrins" (*ibid.*) is similarly explained.

C. Hollins.

Menthone series. V. *d-neoiso*Menthylamine. J. Read and G. J. Robertson (J.C.S., 1927, 2168—2174).—Of the 12 menthylamines all but the 3-*neo*-

*iso*menthylamines have previously been described. d-neoiso*Menthylamine* is now isolated from the mixture of formylated bases obtained by heating *l*-menthone with ammonium formate. The free base has $[\alpha]_D$ +9° and gives the following derivatives: *hydrochloride*, not melted at 250°, $[\alpha]_D^{15}$ +20·9°; *formyl* derivative, $[\alpha]_D^{14}$ +3·9°; *acetyl* derivative, m. p. 99—100°, $[\alpha]_D^{15}$ −2·6°; *benzoyl* derivative, m. p. 151°, $[\alpha]_D^{15}$ −10·4°; β-*naphthalenesulphonyl* derivative, m. p. 120°, $[\alpha]_D^{15}$ −10·7°; *carbamide*, m. p. 115—116°, $[\alpha]_D^{15}$ −3·1°; *phenylcarbamide*, m. p. 149—150°, $[\alpha]_D^{15}$ −12·1°; *phenylthiocarbamide*, m. p. 99°, $[\alpha]_D^{15}$ −6·7°; *benzylidene* derivative, m. p. 68—69°, $[\alpha]_D^{15}$ −34·2°; *salicylidene* derivative, m. p. 98—100°, $[\alpha]_D^{15}$ −17·9°. The hydrochloride is converted by nitrous acid mainly into partly racemised *d*-Δ^3-menthene, and a little *d*-*iso*menthol. The salicylidene derivatives of *neo*- and *d*-*neoiso*menthylamines are non-phototropic, whilst those of menthylamines and *iso*menthylamines are distinctly so. The molecular configuration of *neoiso*menthylamine is discussed and numerical powers of derivatives of the four stereoisomeric types of menthylamines are pointed out. C. Hollins.

Mononitriles of camphoric acid. F. Salmon-Legagneur (Ann. Chim., 1927, [x], 7, 385—407; 8, 5—70).—The action of Grignard reagents on the esters of camphoric semi-nitrile (*i.e.*, of α-camphornitrilic acid) is in general more complex than in the case of cyanocampholic esters, and may take either course (A) or, in addition, course (B), according to the nature and proportion of Grignard reagent and solvent used. It is, however, only slightly affected by variation of the ester group:

$$\cdot CMe(CO_2R)\cdot CMe_2\cdot CH(CN)\cdot \xrightarrow{(A)} \cdot CMe(CR_2OH)\cdot CMe_2\cdot CH(CN)\cdot \xrightarrow{(B)} \cdot CMe(CR_2OH)\cdot CMe_2\cdot CH(CO\cdot R)\cdot.$$

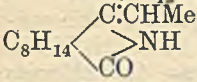
Thus with 5 mols. of magnesium methyl iodide in ether course (A) is followed, the yield of product varying from 43% with the methyl to 32% with the *o*-tolyl ester; in the latter case rather more of a compound, m. p. 164° (below), is produced. In boiling benzene or toluene solution course (B) is also followed. With magnesium phenyl bromide course (B) is followed even in ethereal solution, the intermediately-formed ketimine being isolable, together with an amide. Course (A) is followed when magnesium ethyl bromide is used, but other products are also formed (below).

When either the *syn*- or the *anti*-form of *iso*nitrosocamphor is treated in benzene solution with thionyl chloride and the product formed is treated with an alcohol or a phenoxide, the corresponding α-camphornitrilic ester is formed in the yield indicated: methyl, m. p. 40° (85%); ethyl, m. p. 25—28°, b. p. 162°/18 mm., *phenyl*, m. p. 76—77°, b. p. 215—225°/18 mm., $[\alpha]_D^{22}$ +30° 27′; o-*tolyl* (70%), m. p. 99—100°, b. p. 228—233°/18 mm., $[\alpha]_D^{23}$ +25° 7′; p-*tolyl*, m. p. 96—97°, b. p. 228—233°/18 mm., $[\alpha]_D^{23}$ +28° 52′; *benzyl* (86%; a little camphorimide is also formed), b. p. 223—224°/17 mm., $[\alpha]_D^{20}$ +59° 24′ (in alcohol), $[\alpha]_D^{22}$ +56° 3′ (in benzene). The chloride of α-camphornitrilic acid obtained in 86% yield by the action of thionyl chloride on the pure acid (Borsche and Sander, A., 1915, i, 148) has m. p. 93—95°, b. p. 152—154°/15 mm. Attempts to alkylate the tolyl ester with sodamide in ether or in benzene were unsuccessful, and even in toluene and xylene only 25% and 50%, respectively, of the theoretical amount of ammonia was liberated, and no substitution product was obtained with butyl iodide. Similarly the methyl ester could not be benzylated. Possibly the ester group is attacked affording an amide, converted by the alkyl halide into a substituted amide (cf. Ramart and Haller, A., 1924, i, 732). β-Camphornitrilic acid, m. p. 108—109°, obtained in 67% yield from camphorimide (Rupe and Splittgerber, A., 1907, i, 1016), is converted by thionyl chloride into the *chloride* (yield 80%), b. p. 148—149°/17 mm., from which the o-*tolyl* ester, m. p. 68—69°, b. p. 219—221°/15 mm., $[\alpha]_D^{14}$ −105° 39′, is obtained in the usual way.

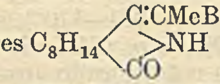
o-Tolyl α-camphornitrilate and 5 mols. of magnesium methyl iodide in ethereal solution afford 3-*cyano*-1-α-*hydroxy*iso*propyl*-1 : 2 : 2-*trimethyl*cyclo*pentane* (2 : 2 : 3-*trimethyl*-3-α-*hydroxy*iso*propyl*cyclo*pentane*-1-*carboxylonitrile*), m. p. 93—94°, $[\alpha]_D^{23}$ +78° 15′ (*phenylurethane*, m. p. 169—170°), together with a *compound*, $C_{11}H_{17}ON$, m. p. 164°, which gives iodoform when treated with potassium hydroxide and alcoholic iodine and forms no oxime or semicarbazone. With bromine in chloroform it gives a *monobromo*-compound, m. p. 161—162°, does not react with phenylcarbimide, whilst with potassium permanganate it yields only the above compound, $C_{11}H_{17}ON$. Substitution of ether by toluene is accompanied by the formation of 3-*acetyl*-1-α-*hydroxy*iso*propyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 95—96° (*semicarbazone*, m. p. 221—222°), giving, when distilled at 144—145°/15 mm., 3-*acetyl*-1-α-*methylethenyl*-1 : 2 : 2-*trimethyl*-cyclo*pentane* (yield 47%), m. p. 164°, $[\alpha]_D^{21}$ +40° 44′ (*oxime*, m. p. 103—104°; *semicarbazone*, m. p. 229—230°), which yields indefinite products with bromine in chloroform, and is oxidised by potassium permanganate to 1 : 3-*diacetyl*–1 : 2 : 2-*trimethyl*cyclo*pentane*, b. p. 154—156°/19 mm. [*disemicarbazone*, m. p. 305—307° (decomp.)].

When the product of interaction, in ether, of magnesium phenyl bromide (4 mols.) and the methyl ester of α-camphornitrilic acid is acidified with hydrobromic acid there is formed the *ketimine hydrobromide*, $COPh\cdot C_8H_{14}\cdot CPh{:}NH,HBr$, m. p. 211—213°, $[\alpha]_D^{14}$ −53° 16′, converted by boiling alcoholic, hydrochloric, or hydrobromic acid into 1 : 3-*dibenzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 118°, $[\alpha]_D^{20}$ −60° 10′ (α-*monoxime*, m. p. 199—200°), together with the *amide*, m. p. 172—175°, $[\alpha]_D^{16}$ +44° 51′ (*oxime*, 194—196°), of 3-*benzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 169—170° (*silver* salt). The structure of the amide follows from its formation by hydrolysing 3-*benzoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*-1-*carboxylonitrile*, m. p. 58—59° (*oxime*, 152—153°), formed from the chloride of β-camphornitrilic acid, benzene, and aluminium chloride. The chloride of α-camphornitrilic acid, however, under similar conditions, affords in 75% yield a *nitrile*, $C_{15}H_{19}N$, b. p. 153—155°/3·5 mm., $[\alpha]_D^{14}$ +21° 12′, slowly hydrolysed at 125—130° by acetic–hydrochloric acid to an *acid*, $C_{15}H_{20}O_2$, m. p. 140°, identical with that obtained from benzene and camphoric anhydride by Bürcker

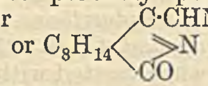
(A., 1896, i, 179) and Blanc (A., 1899, i, 925) ("phenyldihydro*iso*lauronolic" acid). Ethereal magnesium *p*-tolyl bromide similarly affords 1 : 3-*di*-p-*toluoyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 143—144°. Ethereal magnesium ethyl bromide and the methyl ester of α-camphornitrilic acid afford camphorimide, 3-*cyano*-1-α-*hydroxy*isopropyl-1 : 2 : 2-*trimethyl*cyclo*pentane*, m. p. 79—80°, b. p. 185—187°/18 mm., $[\alpha]_D^{18}$ +63° 54′ (o-*nitrobenzoate*, m. p. 112—113°), together with an oil, $[\alpha]_D^{21.5}$ +40° 48′, which is probably a mixture of *isomerides*, $C_{12}H_{21}ON$, and *α-ethylidene campholidene*,


$C_8H_{14}<\begin{matrix}C{:}CHMe\\ \\ CO\end{matrix}>NH$

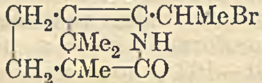
, m. p. 206°, b. p. 200°/18 mm., $[\alpha]_D^{16}$ +11° 16′ (yield 30%) [*hydrochloride*, $C_{12}H_{20}ONCl$, m. p. 230—235°, *hydrobromide*, $(C_{12}H_{19}ON)_2,HBr$(?), m. p. 245—248°], which is very stable both to acids and alkali but which affords a *dibromide*, softening at 140—145° (decomp.). Decomposed with cold water the latter affords a *substance*, $C_{12}H_{18}ONBr$, m. p. 126—127°, boiling water giving an *isomeride*, m. p. 67—68°. These isomerides probably possess the structures


$C_8H_{14}<\begin{matrix}C{:}CMeBr\\ \\ CO\end{matrix}>NH$

or


$C_8H_{14}<\begin{matrix}C\cdot CHMeBr\\ \\ CO\end{matrix}\gg N$

, the structure


$\begin{matrix}CH_2\cdot C=\!=\!=C\cdot CHMeBr\\ |\quad CMe_2\ NH\\ CH_2\cdot CMe-CO\end{matrix}$

being less probable.

Oxidation of α-ethylidenecampholidone with chromic–sulphuric acid yields camphoric and acetic acids, whilst sodamide and benzyl chloride in toluene convert it into *α-ethylidene*-N-*benzylcampholidone*, m. p. 140—141°, $[\alpha]_D^{18}$ +43° 46′, oxidised by chromic–sulphuric acid to camphoric acid, a little camphoric anhydride, acetic acid, and benzylamine; this reaction establishes the structure of α-ethylidenecampholidone. *α-Ethylidene*-N-*allylcampholidone*, m. p. 125—126°, $[\alpha]_D^{21}$ +67° 34′, is prepared similarly. Reduction of the benzyl or *p*-tolyl ester of α-camphornitrilic acid with sodium and absolute alcohol at 150—160° affords α-campholidone, α-aminocampholic acid, and *α-aminocampholic alcohol* (yield 36%), b. p. 163—165°/9 mm., $[\alpha]_D^{24}$ −14° 39′ (*hydrochloride*, m. p. 190—200°; *chloroplatinate*; *phenylcarbamide-urethane*, $NHPh\cdot CO\cdot CH_2\cdot C_8H_{14}\cdot CH_2\cdot O\cdot CO\cdot NHPh$).

R. BRIGHTMAN.

[Camphorchloroanilic] acids and camphorochlorophenylimides. M. SINGH and R. SINGH (J.C.S., 1927, 1994—1997; cf. Wootton, *ibid.*, 1910, **97**, 405).—Camphoric anhydride is condensed with the three chloroanilines to give mixtures of the chloroanilic acids and the chloroanils, separable by means of sodium carbonate. The chloroanilic acids have increasing mol. rotatory power in the order *o*-, *m*-, *p*-, and melt at 165° (*o*-), 216—217° (*m*-), and 197° (*p*-). The chlorophenylimides have m. p. 128° (*o*-), 176° (*m*-), and 165° (*p*-). Rotatory powers of the six compounds in various solvents are given.

C. HOLLINS.

Hydration of nopinene. III. Comparison of the hydration of pinene and nopinene. G. AUSTERWEIL (Bull. Soc. chim., 1927, [iv], **41**, 1088—1094; cf. this vol., 60, 156).—The reaction between pinene and organic acids forming bornyl esters is bimolecular as for nopinene, and it is accompanied by a unimolecular reaction affording limonene. The reaction velocities are smaller than those for nopinene. In the production of limonene from nopinene it appears improbable that pinene is the intermediate product, and alternative mechanisms for the formation of limonene from pinene and nopinene, through the intermediate *iso*pinene, are formulated.

H. BURTON.

δ-*d*-Bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide. J. A. GOODSON (J.C.S., 1927, 1997—2000).—Acetonesemicarbazone, when heated with anhydrous *d*-bornylamine at 175° gives *acetone*-δ-d-*bornylsemicarbazone*, m. p. 141—148°, $[\alpha]_D^{20}$ +25·5°, which is hydrolysed with 10% hydrochloric acid to δ-d-*bornylsemicarbazide*, m. p. 75°, $[\alpha]_D^{20}$ +17° (*hydrochloride*, m. p. 190—198°, $[\alpha]_D^{20}$ +2·6°). δ-d-*Bornylsemicarbazones* of the following ketones are described: *iso*pulegone, m. p. 224—226°, $[\alpha]_D^{20}$ +9·2°; 4-methyl*cyclo*hexanone, m. p. 154°, $[\alpha]_D^{20}$ +27·2°; 3-methyl*cyclo*hexanone, m. p. 172—177°, $[\alpha]_D^{20}$ +27·4°; *d*-3-methyl*cyclo*hexanone, m. p. 173—179°, $[\alpha]_D^{20}$ +7·4°.

Acetone-δ-d-neo*bornylsemicarbazone*, m. p. 175—179°, $[\alpha]_D^{20}$ −92·1°, similarly prepared, gives on hydrolysis δ-d-neo*bornylsemicarbazide hydrochloride*, m. p. 198—202°, $[\alpha]_D^{20}$ −50·8°. 4-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone*, m. p. 151—155°, $[\alpha]_D^{20}$ −91·3°, and the 3-*methyl isomeride*, m. p. 157—161°, $[\alpha]_D^{20}$ −91·2°, are described. All m. p. are corrected.

No resolution into optical enantiomorphs could be achieved by means of the active semicarbazides.

C. HOLLINS.

Action of bromine on dimethylpyrone. J. N. COLLIE and L. KLEIN (J.C.S., 1927, 2162—2164).—Bromination of dimethylpyrone in chloroform with 1 mol. of bromine yields dimethylpyrone hydrobromide perbromide, $C_{14}H_{17}O_4Br_3$, m. p. 136° (Hantzsch and Denstorff, A., 1906, i, 745). Excess of bromine gives Feist and Baum's dibromodimethylpyrone, m. p. 163° (A., 1905, i, 914), and in the absence of a solvent *tetrabromodimethylpyrone*, m. p. 229°. When bromine is added to an aqueous suspension of the barium salt of dimethylpyrone there is formed a *compound*, $C_7H_7O_3Br$, m. p. 106°, b. p. about 310° [decomp.; *monobenzoyl* derivative, m. p. 112°; *phenylhydrazine* compound, m. p. 142° (decomp.)], similar in all respects to the iodine compound obtained by Collie (J.C.S., 1921, **119**, 1550).

C. HOLLINS.

Coumarin series. I. Action of the Grignard reagent on substituted coumarins. I. M. HEILBRON and D. W. HILL (J.C.S., 1927, 2005—2013).—Magnesium phenyl bromide reacts with 4-hydroxycoumarin and its methyl ether to give 4-*hydroxy*-2 : 2-*diphenyl*-Δ³-*chromen*, m. p. 230—231°, and the 4-*methoxy*-compound, m. p. 135°, respectively. The constitution of the latter follows from its conversion by boiling concentrated alkali, into benzophenone. 4-*Methoxy*-2 : 2-*di*-p-*anisyl*-Δ³-*chromen* melts at 155°. 2 : 2-*Diphenyl*-4-*methyl*-Δ³-*chromen*, m. p. 89°, prepared from 4-methylcoumarin and magnesium phenyl bromide, gives on hydrolysis phenyl benzhydryl ether, $CHPh_2\cdot OPh$, m. p. 56°. 2 : 2-*Diphenyl*-4 : 6-*dimethyl*-Δ³-*chromen*, m. p. 126°, similarly prepared, is hydrolysed to p-*tolyl benzhydryl ether*, m. p. 96°. By the action of magnesium phenyl bromide on

4 : 7-dimethylcoumarin the ring is opened, with formation of *diphenyl-*o*-hydroxy-*β-p*-dimethylstyrylcarbinol*, m. p. 146°; the main product is 2 : 2-*diphenyl*-4 : 7-*dimethyl*-Δ^3-*chromen*, m. p. 87° (also obtainable by heating the carbinol in acetic acid), which is hydrolysed to m-*tolyl benzhydryl ether*, m. p. 125°, and lactaldehyde, m. p. 103—105°.

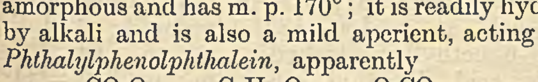
On the other hand when 3-methylcoumarin is treated with magnesium phenyl bromide the product is 2 : 4-*diphenyl*-3-*methylchroman*-4-*ol*, m. p. 149°, which is converted into 2 : 2-*diphenyl*-3-*methyl*-Δ^2-*chromen*, m. p. 91°, by boiling with acetic acid. 3-Phenylcoumarin behaves similarly (Löwenbein, A., 1924, i, 1221; Löwenbein and Rosenbaum, A., 1926, 955).

These reactions are explained on the assumption that the initial reaction with either 3- or 4-substituted coumarins is ring scission with formation of β-unsaturated ketones, the subsequent reactions of which follow the Kohler rule (A., 1907, i, 535). C. HOLLINS.

Constitution of gentisin. J. SHINODA (J.C.S., 1927, 1983—1985).—Since 1 : 3-*dihydroxy*-7-*methoxyanthrone* ("*iso*gentisin"), m. p. 241° (*acetyl* derivative, m. p. 211—212°), synthesised by condensing 2-*hydroxy*-5-*methoxybenzonitrile*, m. p. 136°, with phloroglucinol in ether in presence of zinc chloride and hydrogen chloride and hydrolysis of the resulting *ketimine hydrochloride*, differs from gentisin, the latter must have the structure of 1 : 7-dihydroxy-3-methoxyxanthone as indicated by Perkin (J.C.S., 1898, **73**, 1028). The nitrile is prepared by dehydration of 2-*hydroxy*-6-*methoxybenzaldoxime*, m. p. 118°. *iso*-Gentisin gives on demethylation gentisein, m. p. 318°.

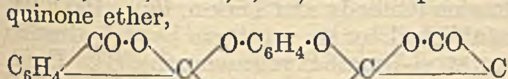
C. HOLLINS.

Synthetic medicinals. II. Theory of laxatives. H. P. KAUFMANN [with H. HAAS] (Z. angew. Chem., 1927, 40, 831—836, 858—863).—Laxatives can be differentiated from, and stand between, drastic purgatives and mild aperients, although the classification is not precise. The copious literature of this subject is reviewed, and attention is drawn to the anomalous position of phenolphthalein and its analogues, which are usually classed with the anthraquinone derivatives and other substances the action of which is chiefly on the lower bowel. *Succinylphenolphthalein*, prepared by heating together phenolphthalein and succinyl chloride at 120° for 5 hrs., is amorphous and has m. p. 170°; it is readily hydrolysed by alkali and is also a mild aperient, acting slowly. *Phthalylphenolphthalein*, apparently



$$C_6H_4{<}\overset{CO\cdot O}{\rule{2em}{0.4pt}}{>}C{<}\begin{matrix}C_6H_4\cdot O\\C_6H_4\cdot O\end{matrix}{>}C{<}\overset{O\cdot CO}{\rule{2em}{0.4pt}}{>}C_6H_4$$

amorphous, m. p. 250° (decomp.), on the other hand, resists hydrolysis and is inactive as a purgative. It is prepared by heating phenolphthalein and phthalyl chloride at 120—130°; the preparation of the latter is described and its b. p. at various pressures are recorded, thus, 147°/13 mm., 150·5°/15 mm., 153—154°/21 mm. In passing it is noted that Pawlewsky's compound (A., 1895, i, 219; 1896, i, 50) is a bisphthalidenehydroquinone ether,



$$C_6H_4{<}\overset{CO\cdot O}{\rule{2em}{0.4pt}}{>}C{<}\begin{matrix}O\cdot C_6H_4\cdot O\\O\cdot C_6H_4\cdot O\end{matrix}{>}C{<}\overset{O\cdot CO}{\rule{2em}{0.4pt}}{>}C_6H_4$$

as the mol. wt. in molten phenol agrees with this formula.

The above results, taken in conjunction with other data, suggest that purgative properties depend on the presence, or formation by hydrolysis, of free hydroxy-groups. That the two phenyl groups must also be free in other respects is shown by the fact that fluorescein, thiofluorescein, and similar compounds, have no purgative action. *Phenolhomophthalein*, however, is a powerful purgative. This compound, m. p. 227°, is obtained by heating together, at 125°, homophthalic anhydride, phenol, and zinc chloride. It dissolves readily in alkalis, but the solutions exhibit only a yellow colour, like that of 4-hydroxycoumarin; this indicates that a quinonoid modification is not formed, and if this is so, the hypothesis that purgative properties are associated with a quinonoid arrangement is disproved.

The (di?)-*acetyl* derivative, m. p. 161°, is weakly purgative; the *tribenzoyl* derivative, m. p. 185°, is inactive. Homophthalic acid does not yield its chloride when it is heated with phosphorus pentachloride; the product is 4-*chloroisocoumarin*, m. p. 96—97°. Bis-(4-hydroxyphenyl)isatin (Baeyer and Lazarus, A., 1886, 154) is also an active purgative, but its acetyl derivative is weak and its *phthalyl* derivative, m. p. about 280°, is inactive. Phenolnaphthalein is more active than phenolphthalein; its *diacetyl* derivative, m. p. 198°, acts mildly, whilst its *phthalyl* derivative, m. p. 175° (decomp.), which is not readily hydrolysed, is inactive. These results demonstrate that the important grouping in respect to purgative properties is the 4 : 4′-dihydroxydiphenylmethylene radical. In accordance with this conclusion it is found that 4 : 4′-dihydroxybenzophenone is an active purgative; its acetyl derivative is mildly active, its *phthalyl* derivative, m. p. 125° (decomp.), is more stable and inactive; and 4 : 4′-dihydroxydiphenyldimethylmethane and 4 : 4′-dihydroxytetraphenylmethane both also possess laxative properties.

W. A. SILVESTER.

Synthesis of pyrylium salts of anthocyanidin type. XII. D. D. PRATT, A. ROBERTSON, and R. ROBINSON (J.C.S., 1927, 1975—1983; cf. this vol., 974).—Benzoylacetaldehyde condenses with phloroglucinol in formic acid to give *trianhydrobisbenzoylacetaldehydephloroglucinol*, $C_{30}H_{22}O_7$, which chars without melting above 280°, and is converted by boiling hydrochloric-acetic acid into chrysinidin chloride (5 : 7-dihydroxyflavylium chloride), obtained also by condensing the components in ether or glacial acetic acid in presence of hydrogen chloride. *O*-Benzoylphloroglucinaldehyde and acetophenone in ethyl acetate saturated with hydrogen chloride yield *O*-benzoylchrysinidin chloride, from which chrysinidin chloride is obtained by treatment with methyl-alcoholic ammonia and addition of hydrochloric acid. Chrysinidin perchlorate melts at 244° (decomp.). From *p*-methoxyacetophenone O-*benzoylacacetinidin chloride* and acacetinidin chloride [dimorphic perchlorate, m. p. 278—280° (decomp.); picrate, m. p. 231—233° (decomp.)]. Demethylation of acacetinidin chloride with hydriodic acid and phenol gives a purer apigenidin iodide (chloride, *mercurichloride*, *perchlorate*, and *periodide* prepared) than previously obtained.

Hydroxymethyleneacetoveratrone (*copper* compound, decomp. 188°) condenses with phloroglucinol in ether in presence of hydrogen chloride to form 5 : 7-*dihydroxy*-3′ : 4′-*dimethoxyflavylium chloride*, decomp. 272°, which gives on demethylation a luteolinidin chloride monomethyl ether (probably 5 : 7 : 4′-*dihydroxy*-3′-*methoxyflavylium chloride*), decomp. 282°, and eventually luteolinidin chloride. 7-*Hydroxy*-3 : 2′ : 4-*trimethoxyflavylium chloride*, decomp. 185°, from ω : 2 : 4-trimethoxyacetophenone and β-resorcylaldehyde, and its demethylation product, *resomorindin chloride*, decomp. 216°, are described. The *copper* compound of hydroxymethylene-2 : 4-dimethoxyacetophenone has m. p. 190°. Phloroacetophenone trimethyl ether condenses with ethyl oxalate to give *ethyl* 2 : 4 : 6-*trimethoxybenzoylpyruvate*, m. p. 84°.

C. Hollins.

Synthesis of pyrylium salts of anthocyanidin type. XIII. Some monohydroxyflavylium salts. F. M. Irvine and R. Robinson (J.C.S., 1927, 2086—2094).—Attempts to demethylate 8-methoxyflavylium chloride, m. p. 190° (decomp.), prepared from *o*-vanillin and acetophenone, or *iodide*, m. p. 134°, were unsuccessful. Condensation of 5-methoxysalicylaldehyde with acetophenone in aqueous-alcoholic potassium hydroxide gives 40% of 5-*methoxysalicylidenediacetophenone* [αγ-dibenzoyl-β-2-hydroxy-5-methoxyphenylpropane], m. p. 125°, and 50% of *phenyl*-2-*hydroxy*-5-*methoxystyryl ketone*, m. p. 104°, which is converted by hydrochloric–acetic acid into 6-*methoxyflavylium chloride*, m. p. 97° [$+2H_2O$; *ferrichloride*, m. p. 203°; *iodide*, m. p. 143°; *periodide*, m. p. 86—87°; *perchlorate*, m. p. about 200° (decomp.)]. Careful demethylation with phenol and hydriodic acid gives 6-*hydroxyflavylium chloride* (*ferrichloride*, m. p. 198°; *chloroaurate*). 4′-*Hydroxyflavylium iodide* yields on demethylation 4′-*hydroxyflavylium periodide*, m. p. 208—209° [*chloride*, m. p. 142° ($+2H_2O$); *chloroaurate*, m. p. 177°]. The corresponding 4′-*hydroxyflavanhydrone*, m. p. 200°, gives no methiodide.

p-Hydroxyacetophenone, m. p. 110° (*acetate*, m. p. 54°), obtained in 33% yield by a modification of Nencki and Stoeber's method (A., 1897, i, 521), condenses with *o*-vanillin in formic acid to form 4′-*hydroxy*-8-*methoxyflavylium chloride*, m. p. 190° [decomp.; *ferrichloride*, m. p. 217°; *periodide*, m. p. 170—173° (decomp.)]; 4′-*hydroxy*-8-*methoxyflavanhydrone* decomposes at 206°.

o-Hydroxyacetophenone gives with salicylaldehyde a scarlet *solid*, which is not a flavylium salt. 2′-*Hydroxyflavylium ferrichloride*, m. p. 125°, is obtained by using *o*-acetoxyacetophenone. For the condensation with *o*-vanillin, *o*-hydroxyacetophenone is more suitable than the acetate, and yields 2′-*hydroxy*-8-*methoxyflavylium chloride*, m. p. 188° (decomp.).

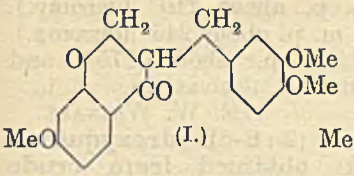
6-*Methoxy*-4-*phenacylideneflavene*, m. p. 146°, obtained with acetophenone and *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* (*semicarbazone*, m. p. 184°; p-*nitrophenylhydrazone*, m. p. 163—165°), from 5-methoxysalicylidenediacetophenone, resembles the pyrones in that the ketone group is unattacked by magnesium phenyl bromide, and the flavene yields a *ferrichloride*, m. p. 170° (decomp.), readily hydrolysed by water. In this flavene the pyrone system ·O·C:C·C:O is extended to ·O·C:C·C:C·C:O.

C. Hollins.

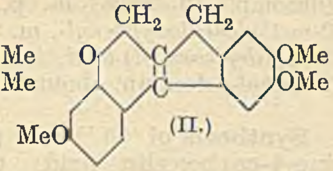
Pyrylium salts of anthocyanidin type. XIV. A. Robertson and R. Robinson (J.C.S., 1927, 2196—2206).—Flavylium salts containing free hydroxyl groups in positions 3, 5, 3′, and 4′ have been prepared. Their colour reactions with alkalis are described and compared with those of cyanin and mecocyanin. 2 : 6-*Dimethoxy*-4-*methylbenzoyl chloride*, m. p. 84—85°, obtained by the action of phosphorus pentachloride on *p*-orsellinic acid dimethyl ether, yields a corresponding p-*toluidide*, m. p. 168—169°, *iminochloride*, *amide*, m. p. 199°, and *nitrile*, m. p. 138—139°. Reduction of the last-named compound by Stephen's method (A., 1925, i, 1131) gives 2 : 6-*dimethoxy*-4-*methylbenzaldehyde*, m. p. 90—91° (p-*nitrophenylhydrazone*), which could not be condensed with ω-methoxyacetoveratrone. Application of the Gattermann synthesis to *m*-xylorcin .yields m-*xylorcylaldehyde*, a bright yellow substance, m. p. 155—156°, which condenses with ω-4-dimethoxyacetophenone in formic acid solution under the influence of hydrogen chloride giving 5-*hydroxy*-3 : 4′-*dimethoxy*-6 : 8-*dimethylflavylium chloride* (*ferrichloride*, m. p. 211—212°). Demethylation yields 3 : 5 : 4′-*trihydroxy*-6 : 8-*dimethylflavylium chloride* (*iodide*). Similar condensation of *m*-xylorcylaldehyde with ω-methoxyacetoveratrone yields 5-*hydroxy*-3 : 3′ : 4′-*trimethoxy*-6 : 8-*dimethylflavylium chloride* (*ferrichloride*, m. p. 200—203°). Demethylation gives 3 : 5 : 3′ : 4′-*tetrahydroxy*-6 : 8-*dimethylflavylium chloride* (*iodide*). Rhamnetin was acetylated and reduced by zinc dust in boiling acetic anhydride solution. The product was hydrolysed with aqueous-alcoholic hydrogen chloride, giving *rhamnetidin chloride* and insoluble by-products. Salicylaldehyde condenses with ω-4-dimethoxyacetophenone in presence of hydrogen chloride giving 3 : 4′-*dimethoxyflavylium chloride* (ferrichloride, m. p. 151—152° dimorphic [?]; lit. 135°). Demethylation yields 3 : 4′-*dihydroxyflavylium chloride* (*iodide*). Comparison of the colour of alkaline solutions of this salt with those of 7 : 3′ : 4′-trihydroxyflavylium chloride and the representative of the 5 : 3′ : 4′-hydroxylated series described above, demonstrates the relatively feeble hypsochromic character of the hydroxyl groups in positions 7 and 5. An improved method for the preparation of *p*-orsellinic acid is described. The following are mentioned: methyl *p*-orsellinate, m. p. 93—94°; 3 : 5-dimethoxy-*p*-toluic acid, m. p. 180—182° (decomp.); 2 : 4-dimethoxy-6-methylbenzaldehyde, m. p. 64—65°; orsellinic acid dimethyl ether, m. p. 143—144° (decomp.) [lit. gives 98—99°, 178°, 62°, and 140°, respectively].

M. Clark.

Synthesis of brazilin and hæmatoxylin and their derivatives. II. Synthesis of deoxytrimethylbrazilone and of *iso*brazilein ferrichloride trimethyl ether. W. H. Perkin, jun., J. N. Rây, and R. Robinson (J.C.S., 1927, 2094—2100).—The constitution of deoxytrimethylbrazilone (II), originally obtained by reduction of trimethylbrazilone with phenylhydrazine (Gilbody and Perkin, *ibid.*, 1902, 81, 1046), is established by its synthesis by dehydration of 3-homoveratryl-7-methoxychromanone (I). Oxidation with ferric chloride yields *iso*brazilein ferrichloride trimethyl ether, which therefore has the structure (III). Trimethylbrazilone is probably best represented by V in equilibrium with (IV) and (VI).



(I.)



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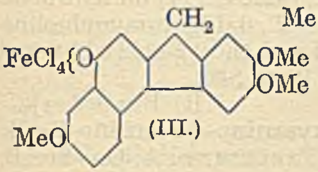

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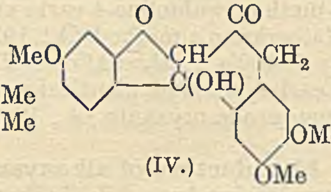

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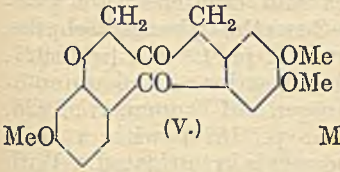

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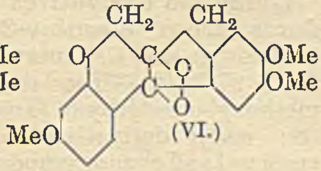


(VI.)

7-Methoxychromanone is best prepared by heating β-*m*-methoxyphenoxypropionic acid (*ethyl* ester, m. p. 45°) in 80% sulphuric acid at 60—90°; its veratrylidene derivative, m. p. 141°, forms a *dibromide*, m. p. 137—138°, and an *oxamino-oxime*. The 3-mp-*dihydroxybenzylidene* derivative, m. p. 212°, is reduced smoothly by hydrogen and palladium to 3-mp-*dihydroxybenzyl-7-methoxychromanone*, m. p. 138°, and a *substance*, m. p. 139°. The benzyl compound is methylated with methyl sulphate to give 3-*homoveratryl-7-methoxychromanone* (I), m. p. 92°, obtainable, although in poor yield, by reduction of 3-veratrylidene-7-methoxychromanone. The dehydration of 3-homoveratryl-7-methoxychromanone to deoxytrimethylbrazilone, m. p. 166—171°, is accomplished by boiling in benzene with phosphorus pentoxide.

C. Hollins.

Manufacture of vat dyes containing sulphur [*peri*naphthathioindoxyls]. I. G. Farbenind. A.-G.—See B., 1927, 809.

[Transformations of ethyl isatin-*N*-carboxylate.] N. Putochin (Ber., 1927, 60, [*B*], 2033; cf. this vol., 885).—The course of the reaction between sodioisatin and ethyl chloroformate has been elucidated previously by Heller and Lauth (A., 1926, 957; cf. also Heller, A., 1918, i, 309).

H. Wren.

5 : 6-Dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and its derivatives. R. D. Haworth (J.C.S., 1927, 2281—2284).—Treatment of the *amide*, m. p. 99—100°, of β-2 : 3-dimethoxyphenylpropionic acid with sodium hypochlorite yields β-2 : 3-*dimethoxyphenylethylamine*, b. p. 190°/70 mm. (*hydrochloride*; *picrate*, m. p. 174—176°). The N-*formyl* derivative of the amine reacts with phosphorus oxychloride to give 5 : 6-*dimethoxy*-3 : 4-*dihydro*isoquinoline. Reduction of the *methiodide*, m. p. 174—175°, of this base with zinc and dilute sulphuric acid gives 5 : 6-*dimethoxy-2-methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline [*hydrochloride*; *hydriodide*, m. p. 201°; *picrate*, m. p. 164° (decomp.)]. Nitration of the tetrahydro-base in glacial acetic acid gives 8-*nitro*-5 : 6-*dimethoxy-2-methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m. p. 104—105°, which fails to condense with piperonal or veratraldehyde in presence of either piperidine or methyl-alcoholic potassium hydroxide. It is inferred that the effect of the nitro-group on the 1-methylene group is neutralised by the methylimino-grouping. Reaction of β-2 : 3-dimethoxyphenylethylamine with 6-bromohomopiperonylic acid at 180° yields 6′-*bromo*-3′ : 4′-*methylenedioxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide*, m. p. 131°, which is converted by treatment with phosphorus oxychloride into 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline, m. p. 134—135°. The last-named compound is oxidised by the air to 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline, m. p. 168°.

M. Clark.

Resolution of racemic *N*-ethyltetrahydroquinoline oxide. J. Dodonow (J. pr. Chem., 1927, [ii], 117, 154—160).—Oxidation of *N*-ethyltetrahydroquinoline for 74 hrs. with 3% hydrogen peroxide at 60—70° yields N-*ethyltetrahydroquinoline oxide*, an unstable syrup (dl-*picrate*, m. p. 124·5°; dl-*hydrochloride*, m. p. 125—126°). Treatment of an aqueous solution of the *dl*-hydrochloride with silver *d*-bromocamphorsulphonate and concentration of the solution in a vacuum yields d-N-*ethyltetrahydroquinoline oxide* d-α-*bromocamphor*-π-*sulphonate*, m. p. 165—166°, $[\alpha]_D$ +69·4°, in practically quantitative yield; whilst further evaporation of the mother-liquor yields l-N-*ethyltetrahydroquinoline oxide bromocamphorsulphonate* (+H_2O), m. p. 85—87°; anhydrous, m. p. 137—138°, $[\alpha]_D$ +45°, mixed with a little of the *dl*-salt. From these salts in the usual manner are obtained the d-*picrate*, m. p. 97—98°; l-*picrate*, m. p. 98—104°; d-*hydrochloride*, m. p. 139—140°, $[\alpha]_D$ +30·6°; and l-*hydrochloride*, m. p. 138—139°, $[\alpha]_D$ −29·4°. Although the active bases themselves could not be isolated the optical rotations of the *d*- and *l*-forms were found to be $[\alpha]_D$ +41° and $[\alpha]_D$ −40° respectively by exact neutralisation of solutions of the active chlorides with barium hydroxide.

J. W. Baker.

Dimeride of 4 : 6-dichloro-5-cyano-2-styrylpyridine. G. Koller (Ber., 1927, 60, [*B*], 1920—1922; cf. Späth and Koller, A., 1925, i, 1446).—The dimeric substance formed by the action of light on 4 : 6-dichloro-5-cyano-2-styrylpyridine probably owes its production to the disappearance of the ethylenic linking and consequent transformation into a *cyclo*butane derivative. In favour of this view it is noted that the dimeride is colourless, whereas the monomeride is yellow and that the former is stable to potassium permanganate in the presence of acetone whereas the latter is not. Under certain conditions, depolymerisation of the dimeride to monomeride can be effected by distillation. Photopolymerisation is not a general property of stilbazoles. 4-*Chloro*-2-*hydroxy*-6-*styrylpyridine*, m. p. 234—235° after softening at 233°, 4 : 6-*dichloro*-5-*cyano*-2-m-*nitrostyrylpyridine*, m. p. 263—264°, and 4 : 6-*dichloro*-5-*cyano*-2-m-*chlorostyrylpyridine*, m. p. 182—183°, are incidentally described.

H. Wren.

Action of sulphuryl azide on *p*-cymene. A. Bertho, T. Curtius, and F. Schmidt (Ber., 1927, 60,

[*B*], 1717—1720).—*p*-Cymene is converted by sulphurylazide at 180° into nitrogen, sulphur dioxide, and a non-acetylable base, $C_9N_{13}N$, isolated as the *picrate*, m. p. 146°, and *chloroplatinate*, m. p. 163—164° (decomp.). Since the base does not lose ammonia when repeatedly evaporated with hydrochloric acid, the presence in it of a seven-membered ring appears excluded. It and the isomeric base derived from *p*-xylene and carbonyl azide (A., 1926, 509) are therefore considered to be the two possible methyl*iso*propylpyridines containing the alkyl groups in the 2 : 5-position. In addition, a neutral *substance*, (?) $C_{10}H_{10}NCl$, m. p. 79°, is obtained in small amount owing to the presence of chloride in the azide solution, whilst the mother-liquors from the picrate, m. p. 146°, yield a second *picrate*, m. p. 149°. H. WREN.

Manufacture of quinoline derivatives [zincichlorides]. BRITISH DYESTUFFS CORP., LTD., etc. —See B., 1927, 809.

Condensation of acetaldehyde and paracetaldehyde with aniline in the presence of aluminium oxide as contact substance. A. E. TSCHITSCHIBABIN and M. P. OPARINA (Ber., 1927, 60, [*B*], 1873—1876; cf. A., 1924, i, 709, 766).—Condensation is effected between aldehydes and aniline in much the same manner as between aldehydes and ammonia (*loc. cit.*), but the use of considerably higher temperatures is advantageous for the production of quinoline bases in general and of 4-methylquinoline in particular. The production of 2- and 4-methylquinolines from acetaldehyde and aniline is precisely analogous to that of 2- and 4-methylpyridines from acetaldehyde and ammonia. Probably crotonaldehyde is intermediately formed. Skraup's reaction appears therefore as a special case of the reactions of Döbner and von Miller (production of 2-substituted quinoline homologues) and Tschitschibabin (production of 4-substituted quinoline homologues). H. WREN.

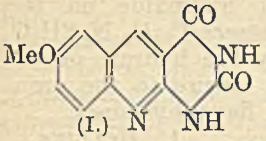
Condensation of crotonaldehyde with ammonia in the presence of aluminium oxide. A. E. TSCHITSCHIBABIN and M. P. OPARINA (Ber., 1927, 60, [*B*], 1877—1879).—Substitution of crotonaldehyde for acetaldehyde in the synthesis of pyridine bases from aldehydes and ammonia in the presence of aluminium oxide causes a very marked reduction in the amount of the picoline fraction (the formation of these is due to the partial depolymerisation of crotonaldehyde to acetaldehyde) and a great increase in the proportion of collidines of which the main component is β-collidine. The yield of the latter substance amounts to 20% of the crude bases. The isolation of a *collidine picrate*, m. p. 163—164°, is recorded. H. WREN.

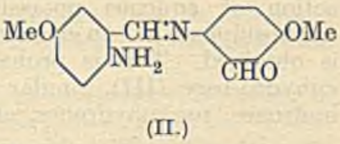
Synthesis of quinoline-4-carboxylic acids. S. BERLINGOZZI and A. TURCO (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 50—52).—Substituted derivatives of 2-phenylcinchoninic acid (" atophan "), shown by Nicolajer and Dorn (Det. Arch. klin. Med., 1908, 93, 331) to increase excretion of uric acid in the urine, are prepared by condensing pyruvic acid and acetylbenzidine with various aldehydes by the method of Knorr (A., 1884, 1198). The following are described: 6-p-*acetamidophenyl-2-phenylquinoline-4-carboxylic acid*, decomp. about 250°, and the corresponding 2-(?)*methoxyphenyl-*, m. p. about 199° (decomp.), 2-*styryl-*, m. p. about 210° (decomp.), 2-*methylenedioxyphenyl-*, m. p. about 245° (decomp.), 2-(?)*dihydroxy-*(?)-*tolyl*, m. p. about 175°, and 2-*methyl-*, decomp. about 260°, derivatives. E. W. WIGNALL.

Synthesis of "β" acid (2 : 6-dihydroxyquinoline-4-carboxylic acid) obtained from crude "cryzanin" by hydrolysis. Y. SAHASHI (Proc. Imp. Acad. Tokyo, 1927, 3, 437—438).—2-Hydroxy-6-methoxyquinoline-4-carboxylic acid, synthesised by Halberkann's method (A., 1922, i, 174) on hydrolysis by Zeisel's method affords 2 : 6-dihydroxyquinoline-4-carboxylic acid, identical with the "β-acid" obtained from crude oryzanin (A., 1926, 846). R. BRIGHTMAN.

Manufacture of alkoxyamino- [8-amino-6-alkoxy-]quinolines. I. G. FARBENIND. A.-G.—See B., 1927, 797.

Quinoline derivatives and condensation products from 6-amino-3-methoxybenzaldehyde. J. TRÖGER and C. COHAUS (J. pr. Chem., [ii], 1927, 117, 97—116).—The condensation of 6-amino-3-methoxybenzaldehyde (Tröger and Fromm, A., 1926, 68; *acetyl* derivative, m. p. 187°) with various carbonyl and cyano-compounds is investigated. With ethyl acetoacetate and ethyl benzoylacetate in hot alcoholic solution in presence of a few drops of sodium hydroxide it yields respectively *ethyl 6-methoxy-2-methylquinoline-3-carboxylate*, an oil (*chloroplatinate*), and *ethyl 6-methoxy-2-phenylquinoline-3-carboxylate*, m. p. 115° (*acid*, m. p. 232°; *chloroplatinate* and *silver* salt of the acid), whilst when heated together in a sealed tube at 160° for 4 hrs. without solvent or catalyst the products are respectively 2-*hydroxy-6-methoxy-3-acetylquinoline*, m. p. 297° (*phenylhydrazone*, m. p. 252°), and 2-*hydroxy-6-methoxy-3-benzoylquinoline*, m. p. 293° (*phenylhydrazone*, m. p. 229°). Condensation with compounds of the type $R\cdot CH_2\cdot CN$ in alcoholic solution with sodium hydroxide as a catalyst yields 2-aminoquinoline derivatives: thus *p*-bromobenzenesulphonacetonitrile, phenylacetonitrile, and malononitrile yield, respectively, 2-*amino-6-methoxy-3-*p*-bromobenzenesulphonyl-*, m. p. 89—90°; -3-*phenyl-*, m. p. 143° (*hydrochloride*; yields 2-*hydroxy-6-methoxy-3-phenylquinoline*, m. p. 109°, on treatment with nitrous acid), and -3-*cyano-quinoline*, m. p. 243—244° [which, on treatment with nitrous acid, yields 2-*hydroxy-6-methoxy-3-cyanoquinoline*, m. p. 263°, and, on hydrolysis, 2-*amino-6-methoxyquinoline-3-carboxylic acid*, m. p. above 300° (*silver* salt; *chloroplatinate*) whilst subsequent treatment with nitrous acid yields 2-*hydroxy-6-methoxyquinoline-3-carboxylic acid*, m. p. 283° (*disilver* salt)]. In all three cases the 2-amino-group is eliminated as ammonia on reduction with tin and hydrochloric acid. Condensation with ethyl cyanoacetate yields 2-hydroxy-6-methoxy-3-cyanoquinoline (above) whilst the corresponding -3-carboxylic acid is also obtained by condensation with malonic acid. Condensation with phenacyl cyanide yields 6-*methoxy-3-cyano-2-phenylquinoline*, m. p. 170° (*chloroplatinate*), irrespective of the method of condensation employed. Condensation with barbituric acid in the presence of alkali yields 2 : 4-*diketo-*1 : 2 : 3 : 4-*tetrahydro-*9-*methoxyquinoline-*1 : 3-*diazine*





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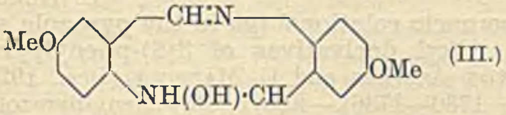


(I), m. p. 273° (*sodium* and *silver* salts). 6-Amino-3-methoxybenzaldehyde itself is unstable and readily condenses to a yellow solid *substance*, possibly (II) or (III). J. W. Baker.

β-Substituted derivatives of "atophan" [2-phenylquinoline-4-carboxylic acid]. S. Berlingozzi and A. Turco (Rend. Accad. Sci. fis. mat. Napoli, 1925, [iii], 31, 191—193).—On condensing a solution of isatin in potassium hydroxide solution with ω-phenoxyacetophenone in alcohol, there is obtained, on acidification, 3-*phenoxy-*2-*phenylquinoline-*4-*carboxylic acid*, m. p. 232° (heavy metal salts insoluble, but *barium* salt soluble in water), which when heated yields 3-*phenoxy-*2-*phenylquinoline*, m. p. 130—131°. E. W. Wignall.

3-Substituted quinolines. S. Berlingozzi and W. E. Burg (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **33**, 39—40).—By condensing *N*-*p*-hydroxyphenacylphthalimide (obtained from *p*-chloroacetylanisole and potassium phthalimide) with *o*-aminobenzaldehyde, and hydrolysing, 3-*amino-*2-p-*methoxyphenylquinoline*, m. p. 138° (*acetyl* derivative, m. p. 165°), is obtained, which on diazotisation yields 3-hydroxy-2-*p*-methoxyphenylquinoline.

Using isatoic acid, 3-*amino-*2-p-*methoxyphenylquinoline-*4-*carboxylic acid*, decomp. about 150° (*acetyl* derivative, m. p. 212°), is obtained, which on diazotisation yields the corresponding 3-hydroxy-compound (Berlingozzi and Capuano, A., 1924, i, 1345). E. W. Wignall.

[Nitro- and amino-acridines.] H. Jensen (Ber., 1927, **60**, [*B*], 2033).—The constitution of the nitroacridines established by Lehmstedt by oxidation to the known nitroacridones (this vol., 776) has been confirmed by synthesis by Jenson and Friedrich (this vol., 575). 4-Aminoacridine has been described previously by Clemo, Perkin, and Robinson (A., 1924, i, 1339). H. Wren.

4-Amino-1-phenyl-5-pyrazolone-3-carboxylic acid. F. D. Chattaway and W. G. Humphrey (J.C.S., 1927, 2133—2139).—4-*Amino-*1-*phenyl-*5-*pyrazolone-*3-*carboxylic acid*, m. p. 225° [decomp.; *hydrochloride*, decomp. 160°; *acetyl* derivative, m. p. 216°; ON-*dibenzoyl* derivative, m. p. 205°], is obtained by reduction with sodium amalgam of 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone, or of the 4-*oxime*, m. p. 209° (decomp.), prepared by nitrosation of 1-phenyl-5-pyrazolone-3-carboxylic acid. Anhydrodiketosuccinic acid phenylosazone is reduced with sodium amalgam first to sodium amino-oxalacetate phenylhydrazone, which on acidification gives 4-amino-1-phenyl-5-pyrazolone-3-carboxylic acid, and finally to the two stereoisomeric diaminosuccinic acids.

When 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone is brominated in glacial acetic acid the product is the 4-p-*bromophenylhydrazone*, m. p. 258° (decomp.), which is synthesised from 1-phenyl-5-pyrazolone-3-carboxylic acid and *p*-bromodiazobenzene.

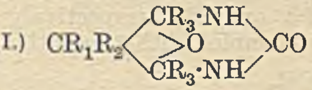
The following esters of 1-phenyl-4 : 5-diketopyrazolone-3-carboxylic acid 4-phenylhydrazone are prepared by action of alcohols and hydrogen chloride on anhydrodiketosuccinic acid phenylosazone: *methyl*, m. p. 138°; ethyl, m. p. 153°; n-*propyl*, m. p. 116·5°; n-*butyl*, m. p. 117°. C. Hollins.

Condensation of dimethylbarbituric acid with aldehydes. Colour reaction of furfuraldehydes. S. Akabori (Proc. Imp. Acad. Tokyo, 1927, 3, 342—344).—Dimethylbarbituric acid condenses readily in aqueous or alcoholic solution with benzaldehyde, vanillin, furfuraldehyde, methylfurfuraldehyde, hydroxymethylfurfuraldehyde, β-indolealdehyde, cinnamaldehyde, and citral, forming crystalline *products*, m. p. 159—159·5°, 222·5—223·5°, 194·5—195°, 172—172·5°, 181—182°, 291—292° (decomp.), 195·5—196°, and 101—101·5°, respectively. Barbituric and dimethylbarbituric acid derivatives of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde give intense colorations with aniline and aniline acetate, recognisable up to dilutions of 1 in 10^6. B. W. Anderson.

Barbituric acid derivative. E. H. Volwiler.—See B., 1927, 797.

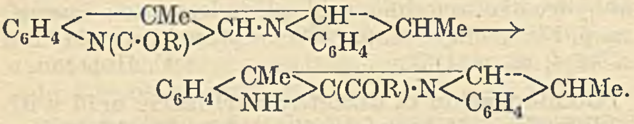
Action of the Grignard reagent on alkylbarbituric acids. A. W. Dox (J. Amer. Chem. Soc., 1927, 49, 2275—2279).—Treatment of 5 : 5′-dialkylbarbituric acids with Grignard reagents results in reaction of two carbonyl groups, with subsequent elimination of 1 mol. of water. The products are highly resistant to hydrolytic agents, and are therefore regarded as *endo-ethers* of 4 : 6-*dihydroxy-*2-*keto-*4 : 5 : 5 : 6-*tetra-alkylhexahydropyrimidines* (I). Derivatives of this type were prepared from magnesium ethyl bromide and 5 : 5′-diethyl-, 5-ethyl-5′-phenyl-, 5-ethyl-5′-*iso*amyl-, and 5 : 5′-diallyl-barbituric acids; from magnesium phenyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium propyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium propyl bromide and 5 : 5′-diethylbarbituric acid; from magnesium *n*-butyl bromide and 5 : 5′-diethylbarbituric acid, and from magnesium *iso*amyl bromide and 5 : 5′-diallylbarbituric acid. They all have m. p. not below 250°, whilst some can be sublimed. 1 : 3-*Diphenyl-*5 : 5′-*dipropylbarbituric acid*, m. p. 104—105°, obtained by condensing dipropylmalonic acid with carbanilide in chloroform in presence of phosphoryl chloride, yields, when treated with magnesium ethyl bromide, the *endo-ether* of 2 : 4 : 6-*trihydroxy-*1 : 3-*diphenyl-*2 : 4 : 6-*triethyl-*5 : 5′-*dipropylhexahydropyrimidine*, m. p. 102° (cf. Béis, A., 1904, i, 503, 671; Sachs and Ludwig, A., 1904, i, 266). F. G. Willson.

(I.)



$$CR_1R_2<\begin{matrix}CR_3\cdot NH\\ >O\\ CR_3\cdot NH\end{matrix}>CO$$

Transpositions in discatole. B. Oddo and Q. Mingoia (Gazzetta, 1927, 57, 480—485).—*Acetyldiscatole*, $C_{20}H_{20}ON_2$, m. p. 180°, and *benzoyldiscatole*, m. p. 207°, are resistant to hot aqueous alkali, and form silver compounds with the silver atom attached to the imino-nitrogen atom. These derivatives are hence carbon-substituted compounds, and it must be assumed that the mobility of the imino-hydrogen atom of the tetrolic nucleus remains unaltered in the discatole molecule and that transposition of the substituent group to the only available carbon atom, that in the α-position of the tetrolic nucleus, takes place :



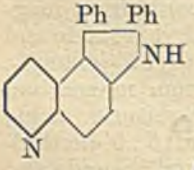
$$C_6H_4<\begin{matrix}CMe\\N(C\cdot OR)\end{matrix}>CH\cdot N<\begin{matrix}CH\\C_6H_4\end{matrix}>CHMe\longrightarrow C_6H_4<\begin{matrix}CMe\\NH\end{matrix}>C(COR)\cdot N<\begin{matrix}CH\\C_6H_4\end{matrix}>CHMe.$$

Formyldiscatole (*α-discatolealdehyde*), m. p. 187°, and *ethyldiscatole*, m. p. 157°, have similar structures. Scatole picrate, m. p. 170—171°, undergoes transformation into a *compound*, m. p. 216—217°, when exposed to the air (cf. A., 1924, i, 427).

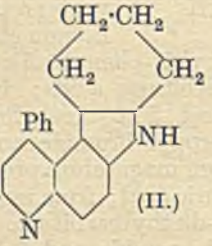
T. H. Pope.

Polynuclear heterocyclic aromatic types. III. Pyrroloquinoline derivatives. R. C. Fawcett and R. Robinson (J.C.S., 1927, 2254—2261).—Condensation of 6-aminoquinoline with benzoin gives 5 : 6-(2′ : 3′-*diphenyl*-4′ : 5′-*pyrrolo*)*quinoline* (I), m. p. 167—168° [+H_2O; *hydrogen sulphate, hydrochloride*, and *picrate*, m. p. 218° (decomp.), described; crystallographic data for the base by H. E. Buckley]. The yellow *methosulphate*, m. p. 218—219°, does not give an anhydro-base (cf. Armit and Robinson, A., 1925, i, 1170), but is converted by alkaline ferricyanide into 2-*keto*-1-*methyl*-5 : 6-(2′ : 3′-*diphenyl*-4′ : 5′-*pyrrolo*)-1 : 2-*dihydroquinoline*, m. p. 195·5°.

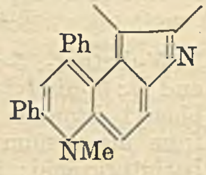
Dibenzoylmethane gives with *p*-aminoacetanilide an anil, which is converted by sulphuric acid into a *substance*, m. p. 237·5—238·5°, probably the sodium salt of a sulphonic acid of the desired quinoline. From dibenzoylmethane and *m*-phenylenediamine, heated at 140° and then cyclised with zinc chloride at 175—180°, are obtained 5-*amino*- and 7-*amino*-2 : 4 *diphenylquinolines*, m. p. 168·5° and 187°, respectively : these may be diazotised and coupled with β-naphthol.



(I.)



(II.)



(III.)

6-Nitro-1 : 2 : 3 : 4-tetrahydrocarbazole (Borsche, Witte, and Bothe, A., 1908, i, 365) is best reduced with iron powder and alcoholic hydrochloric acid. The 6-amino-compound condenses with dibenzoylmethane to form *phenyl* 1 : 2 : 3 : 4-*tetrahydro*-6-*carbazyl*-*α*-*aminostyryl ketone*, m. p. 229·5—230°, which is converted by phosphoryl chloride into 2 : 4-*diphenyl*-5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydro*-2′ : 3′-*indoloquinoline* (II) m. p. 235° [*picrate*, m. p. 241° (decomp. 243°); *methosulphate*; *methopicrate*, m. p. 252—254° (decomp.)]. The base is yellow, gives red salts, and absorbs oxygen from the air, forming a *dioxy*-derivative, $C_{27}H_{22}O_2N_2$, decomposing at 168° with incandescence. By the action of aqueous potassium hydroxide on the methosulphate a deep green *substance*, $C_{28}H_{24}N_2,2H_2O$, is obtained. This is probably the hydrate of the anhydro-base (III), similar in nature to the quinhydrones, pyranhydrones, and flavanhydrones.

C. Hollins.

Isomeric relationships in the pyrazole series. XI. Alkyl derivatives of 3(5)-phenylpyrazole. K. von Auwers and C. Mausolf (Ber., 1927, 60, [*B*], 1730—1736).—Ethyl 5(3)-phenylpyrazole-3(5)-carboxylate, m. p. 140°, prepared from ethyl benzoylpyruvate and hydrazine hydrate, is hydrolysed to 5(3)-*phenylpyrazole*-3(5)-*carboxylic acid*, m. p. 234° after softening (*methyl* ester, m. p. 182°). Treatment of the esters with methyl iodide and methyl-alcoholic sodium methoxide followed by hydrolysis of the product affords a mixture of 5-*phenyl*-1-*methylpyrazole*-3-*carboxylic acid*, m. p. 143—144°, and the isomeric 3-*phenyl*-1-*methylpyrazole*-5-*carboxylic acid*, m. p. 183—184°. Bromination of the acid of m. p. 143—144° in glacial acetic acid affords the *bromo*-derivative, $C_{11}H_9O_2N_2Br$, m. p. 205°, which is converted by methyl-alcoholic hydrogen chloride into the *methyl* ester, $C_{12}H_{11}O_2N_2Br$, m. p. 114—115°, whereas the *bromo*-derivative, m. p. 208°, of the acid, m. p. 183—184°, cannot be esterified in this manner. The position of the substituents is thus established (cf. von Auwers and Hollmann, A., 1926, 623, 847). The acid of m. p. 143—144° when decarboxylated affords 5-phenyl-1-methylpyrazole, b. p. 118°/12 mm. (picrate, m. p. 143°), whereas similar treatment of the acid of m. p. 183—184° yields 3-phenyl-1-methylpyrazole, m. p. 56° (picrate, m. p. 132°), thus confirming the constitution of the phenylmethylpyrazoles obtained by von Auwers and Schmidt (A., 1925, i, 585). The bromo-acid, m. p. 205°, gives a bromo-*base*, m. p. 53—54°. Ethylation of ethyl 5(3)-phenylpyrazole-3(5)-carboxylate gives a mixture of esters which can be roughly separated by fractional distillation. Hydrolysis of the separate fractions leads to the isolation of 3-*phenyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 162—163°, and 5-*phenyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 137—138°, which afford respectively 4-*bromo*-3-*phenyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 154—155°, and 4-*bromo*-5-*phenyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 179—180° after softening (converted by methyl-alcoholic hydrogen chloride into the *methyl* ester, m. p. 111°). Decarboxylation of the corresponding acids yields 3-phenyl-1-ethylpyrazole. b. p. 146°/12 mm., m. p. 34—36° (picrate, m. p. 104—106°) (cf. A., 1925, i, 586), and 5-*phenyl*-1-*ethylpyrazole*, b. p. 129°/12 mm., $d_4^{17\cdot4}$ 1·0595, n_{He} 1·57077 (*picrate*, m. p. 106·5—107°). During the direct ethylation of 3(5)-phenylpyrazole with ethyl bromide 5-phenyl-1-ethylpyrazole is produced in relatively very small amount (cf. A., 1925, i, 585).

H. Wren.

Porphyrin syntheses. X. Synthesis of *iso*-uroporphyrin and carboxyhæmatic acid. H. Fischer and P. Heisel (Annalen, 1927, 457, 83—102; cf. this vol., 469).—In uroporphyrin, the octa-carboxylic acid corresponding with coproporphyrin, the four additional carboxyl groups are most probably attached to the same carbon atoms as the remaining four; *i.e.*, uroporphyrin contains four malonic acid groupings. This view is confirmed by the synthesis of *iso*uroporphyrin.

Bromination of ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-1-carboxylate (Fischer and Andersag, unpublished work) in ether gives the 4-*bromomethyl* compound, m. p. 90° (4-*anilinomethyl* compound, m. p. 100°), which is converted by boiling with water or methyl alcohol, with loss of formaldehyde and hydrogen bromide, into *bis*(1-*carbethoxy*-2-*methyl*-3-ββ-*dicarbethoxyethyl*-4-*pyrryl*)*methane*, m. p. 126°; when methyl alcohol is used there is also formed, by exchange of alkyl groups, *bis*(1-*carbethoxy*-2-*methyl*-3-ββ-*dicarbomethoxyethyl*-4-*pyrryl*)*methane*, m. p. 168°. The *hexasodium* salt (free *acid*, m. p. 176°), obtained by alkaline hydrolysis, is converted, when heated in formic or acetic acid, into a mixture of copro- and *iso*copro-porphyrins, separable by means of their tetramethyl esters. This loss of four "malonic" carboxyl groups is prevented, however, by aërating a solution of the hexasodium salt in 95% formic acid maintained at 40°. Under these conditions iso*uroporphyrin* separates after 24—48 hrs. The octa*methyl* ester, m. p. 263° (cf. uroporphyrin octamethyl ester, m. p. 292°), gives complex *iron* and *copper* salts. *iso*Uroporphyrin loses $4CO_2$ at 150—170°, forming *iso*coproporphyrin, and is reduced by sodium amalgam to a *leuco*-compound, readily re-oxidised to the porphyrin. Oxidation of *iso*uroporphyrin with chromic acid gives a carboxyhæmatic acid, α-methyl-β(ββ-dicarboxyethyl)maleinimide, m. p. 178°, which sublimes in a vacuum at 115—120° and is identical with the oxidation product from natural uroporphyrin [crystallographic data by STEINMETZ]. *iso*Uroporphyrin strikingly resembles uroporphyrin in physiological action, but is more poisonous.

Reduction of ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-1-carboxylate with hydriodic acid gives cryptopyrrolecarboxylic acid, m. p. 138° (picrate, m. p. 153°). Fischer and Nenitzescu's bis-(2 : 4-dimethyl-3-ββ-dicarbomethoxyethyl-5-pyrryl)-methene (A., 1926, 178) forms a complex *copper* salt, $C_{50}H_{62}O_{16}N_4Cu$. C. HOLLINS.

Action of diacetyl on magnesylpyrrole. N. A. NARYSCHKIN (Ber., 1927, **60**, [*B*], 1928—1930; cf. A., 1926, 183; this vol., 162).—Diacetyl is converted by magnesium pyrryl iodide into a *compound*, $C_{12}H_{16}O_2N_2$, converted by hydrochloric acid into an unstable, coloured *hydrochloride*. H. WREN.

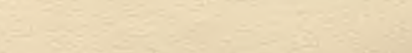
1 : 8-Naphthyridine. G. KOLLER (Ber., 1927, **60**, [*B*], 1918—1920; cf. this vol., 367, 886).—1 : 8-*Naphthyridine*, m. p. 98—99° after softening at 95° (in an evacuated tube), is isolated from the products of the catalytic reduction of 2 : 4-dichloro-1 : 8-naphthyridine by cautious fractional distillation in a vacuum. Its sensitiveness towards hydrogenation and oxidation is remarkable. The *picrate*, m. p. 207—208° after softening at 200°, and *methiodide*, $C_9H_9N_2I$, m. p. 180—181°, are described; the latter substance regenerates 1 : 8-naphthyridine when heated. H. WREN.

Derivatives of 2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine. R. D. HAWORTH and H. S. PINK (J.C.S., 1927, 2345—2349).—Homophthalimide condenses with *o*-nitrobenzaldehyde in pyridine solution in presence of a trace of piperidine, giving o-*nitrobenzylidenehomophthalimide*, m. p. 236°, which is reduced with stannous chloride in alcoholic solution to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (I), m. p. 246—247° (*potassium* salt; *sodium* salt). Further reduction with zinc dust in glacial acetic acid saturated with hydrogen chloride gives 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (II), m. p. 250° (*monohydrochloride*, decomp. 270°; *nitrosoamine*; *picrate*, m. p. 270°). The corresponding derivatives from *N*-β-phenylethyl- and *N*-β-piperonylethylhomophthalimide were also prepared: o-*nitrobenzylidene*-N-β-*phenylethylhomophthalimide*, m. p. 146°; 7-*keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine*, m. p. 220°; 7-*keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, m. p. 217°; o-*nitrobenzylidene*-N-β-*piperonylethylhomophthalimide*, m. p. 176°; 7-*keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine*, m. p. 217°; 7-*keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, m. p. 211°. When (I) is heated with phosphorus oxychloride and phosphorus pentachloride at 180° and the resulting unstable chloro-compound is reduced with phosphorus and hydriodic acid at 160—170°, a *base*, 2 : 3 : 5 : 6-*dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (?), m. p. 232° (*monohydrochloride*; *hydriodide*), is obtained, in addition to (II). M. CLARK.

Cyanine dyestuffs. I. Synthesis of pinacyanol. II. Synthesis of pinacyanol using trioxymethylene. T. OGATA (Proc. Imp. Acad. Tokyo, 1927, **3**, 334—338).—2-Methylquinoline ethiodide reacts with 2-β-*hydroxyethylenequinoline ethiodide*, decomp. 214—218° (obtained from 2-β-hydroxyethylenequinoline), in presence of sodium ethoxide to form pinacyanol iodide. 6-Ethoxy-2-methylquinoline when heated with formaldehyde and alcohol, yields 6-*ethoxy*-2-β-*hydroxyethenylquinoline*, m. p. 85—86° (*platinum* derivative, m. p. 135—140° [decomp.]), the *ethiodide*, decomp. 193—195°, of which combines with 6-ethoxy-2-methylquinoline ethiodide, yielding 6 : 6′-*diethoxy*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide* (*diethoxypinacyanol iodide*), m. p. 290—291°. Similarly 6-ethoxy-2-methylquinoline ethiodide combines with 2-β-hydroxyethenylquinoline ethiodide to form 6-*ethoxy*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide*, m. p. 278—279° (decomp.).

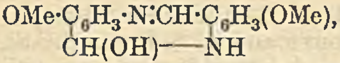
2-Methylquinoline ethiodide (2 mols.) reacts with trioxymethylene (1/3 mol.) in presence of sodium (2 mols.) to give a 75% yield of pinacyanol iodide. B. W. ANDERSON.

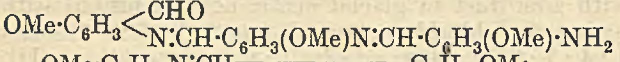
Condensation of 2-amino-3-methoxybenzaldehyde, its acyl derivatives and quinazolines derived from them. J. TRÖGER and V. SABEWA (J. pr. Chem., 1927, [ii], **117**, 117—141).—2-Amino-3-methoxybenzaldehyde readily condenses with itself, the best yield of crystalline *anhydrobis-2-amino-3-methoxybenzaldehyde*, m. p. 265°, possibly



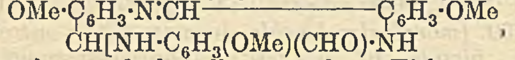
$$OMe{\cdot}C_6H_3{<}\begin{matrix}CHO\\ N{:}CH{\cdot}C_6H_3(OMe){\cdot}NH_2\end{matrix}$$

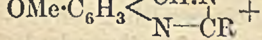
or


$OMe\cdot C_6H_3\cdot N{:}CH\cdot C_6H_3(OMe),\ \overline{CH(OH)\text{——}NH}$ being obtained by keeping its solution in acetic acid for 12—15 hrs. The same product is obtained in an amorphous form in the preparation of various of the acyl derivatives described below. When the aldehyde is heated for a long time in benzene solution with ethyl chloroformate, *anhydrotris-2-amino-3-methoxybenzaldehyde*, m. p. 259°, possibly


$OMe\cdot C_6H_3{<}{\begin{matrix}CHO\\ N{:}CH\cdot C_6H_3(OMe)N{:}CH\cdot C_6H_3(OMe)\cdot NH_2\end{matrix}}$

or


$\begin{matrix}OMe\cdot C_6H_3\cdot N{:}CH\text{————}C_6H_3\cdot OMe\\ CH[NH\cdot C_6H_3(OMe)(CHO)\cdot NH\end{matrix}$, is obtained as a dark yellow powder. Either product is reconverted into the original aldehyde (isolated as its chloroplatinate) by hot concentrated hydrochloric acid, but subsequent treatment with phenylhydrazine yields a *phenylhydrazone*, m. p. 190°, of the bis- or tris-compound. A series of acyl derivatives of 2-amino-3-methoxybenzaldehyde has been prepared, the method varying somewhat from case to case. By the action of acetic anhydride in ether is obtained 2-*acetamido*-, m. p. 156° (*phenylhydrazone*, m. p. 214°); the action of butyric anhydride for 2 hrs. at 100° yields 2-*butyramido*-, m. p. 100° (*phenylhydrazone*, m. p. 165°); 2-*benzamido*-, m. p. 115° (*phenylhydrazone*, m. p. 166°), is obtained by the action of benzoyl chloride on a suspension of the aldehyde in potassium hydrogen carbonate solution, whilst by the Schotten–Baumann method using the appropriate acid chloride are obtained 2-*phenylacetamido*-, m. p. 98° (*phenylhydrazone*, m. p. 194°) [which on treatment with alcoholic potassium hydroxide solution yields 2-hydroxy-8-methoxy-3-phenylquinoline (Tröger and Gerö, A., 1926, 1045)]; 2-*toluoylamido*-, m. p. 150° (*phenylhydrazone*, m. p. 180°); 2-o-*chlorobenzamido*-, m. p. 140° (*phenylhydrazone*, m. p. 212°); 2-(2 : 4)-*dichlorobenzamido*-, m. p. 161° (*phenylhydrazone*, m. p. 225°); and 2-p-*bromobenzamido*-, m. p. 134° (*phenylhydrazone*, m. p. 192°) -3-*methoxybenzaldehyde*. It was not found possible to prepare the 2-*p*-nitrobenzamido-compound, the only product obtained by the action of *p*-nitrobenzoyl chloride being the condensation product of the aldehyde, m. p. 265°. These acyl derivatives, on treatment with alcoholic ammonia, yield 8-methoxyquinazoline derivatives in accordance with the scheme $OMe\cdot C_6H_3(CHO)\cdot NH\cdot COR+NH_3=$


$OMe\cdot C_6H_3{<}{\begin{matrix}CH{:}N\\ N\text{—}CR\end{matrix}}+2H_2O$, and thus from the appropriate acyl derivative are obtained 2-*methyl*-, m. p. 128° (*chloroplatinate*; *chloromercurate*, m. p. 140°; picrate, m. p. 118°); 2-n-*propyl*-, m. p. 60° (*chloroaurate*, m. p. 116°; *picrate* $+2H_2O$, m. p. 140°); 2-*phenyl*-, m. p. 99° (*chloroplatinate* $+1{\cdot}5H_2O$; *picrate*, m. p. 178°; *perchlorate*); 2-*benzyl*-, m. p. 88°; 2-p-*tolyl*-, m. p. 70° (*chloroplatinate* $+4H_2O$; *picrate*, m. p. 169°); 2-o-*chlorophenyl*-, m. p. 118° (*chloroplatinate*; *chloromercurate*); 2-(2 : 4-)-*dichlorophenyl*-, m. p. 132° (*picrate*, m. p. 105°); 2-p-*bromophenyl*-, m. p. 127° (*picrate*, m. p. 129°; *chloromercurate*) -8-*methoxyquinazolines*.

J. W. Baker.

Triazoles. VII. Substituted 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazoles. F. Hernler (Monatsh., 1927, **48**, 391—403).—1-*p*-Bromophenyl-3 : 5-dimethyl-1 : 2 : 4-triazole, m. p. 93—94° (picrate, m. p. 166—167°) (cf. Hernler and Matthes, this vol., 468), is prepared in good yield from 3 mols. of diacetamide and 1 mol. of *p*-bromophenylhydrazine. It is also obtained by the usual method from the corresponding amino-compound, which in turn is prepared from the bromo-derivative by the action of ammonia in presence of copper bronze. 1-p-*Cyanophenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, m. p. 68—70° (*picrate*, m. p. 143·5—144°), is hydrolysed by alcoholic potassium hydroxide to 1-*phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*-4′-*carboxylic acid*, m. p. 293—294°. This acid is also obtained from the bromo-compound by the action of cuprous potassium cyanides (cf. Rosenmund and Struck, A., 1920, i, 44), but not by the action of magnesium and carbon dioxide.

H. Burton.

7 : 9-Dimethyl-[$\Delta^{3:4}$-]*iso*uric acid. H. Biltz and H. Bülow (Annalen, 1927, **457**, 103—131).—8-Thio-7 : 9-dimethyl-ψ-uric acid (Biltz and Bülow, A., 1922, i, 381) dissolves in sodium hydrogen carbonate solution with evolution of carbon dioxide; after cooling with ice, iodine is added, whereupon carbon dioxide is again evolved, and 7 : 9-*dimethyl*-$\Delta^{3:4}$-iso*uric acid*, decomp. 262—263°, separates. This gives a strong murexide reaction. The *dihydrate*, *monohydrate*, *anhydride* (all of the above decomp. temperature), *hydrochloride* (darkens from 270°, decomp. 350—360°, easily hydrolysed by water), *nitrate* (decomp. 130°), *perchlorate* (probably $C_7H_8O_3N_4,HClO_4,2H_2O$), and *hydrogen sulphate* (sinters at about 190°), *potassium* salt ($C_7H_7O_3N_4K,H_2O$), *sodium*, *ammonium*, and *lead* salts are described.

Attempts to determine the position of the replaceable hydrogen atom by the action of methyl sulphate or of methyl iodide on the salts give no crystallisable product, whilst diazomethane has no action on the free dimethyl*iso*uric acid. Oxidation by chromic acid yields dimethylparabanic acid: the methylated glyoxaline ring is more resistant than the unsaturated pyrimidine ring. 7 : 9-Dimethyluric acid yields the same product.

Dimethyl*iso*uric acid is not reduced by ordinary reducing agents even at high temperatures. Zinc and hydrochloric acid give oily products. Chlorine and water cause oxidation to 7 : 9-dimethyluric acid glycol, or, in presence of alcohol, to the dimethyl ether of the glycol.

A boiling solution of sodium 7 : 9-dimethyl*iso*urate with hydrochloric acid yields 7 : 9-dimethyluric acid; this transformation does not occur when acetic acid is used, nor when the solution is well cooled during acidification. Treatment of the acid with hydrochloric acid in a sealed tube has the same action; on boiling with water, however, only one fifth of the theoretical yield of dimethyluric acid is obtained, the rest decomposing.

The action of organic acids on 7 : 9-dimethyl*iso*uric acid causes a new condensation. The hydrocarbon radical of the acid becomes attached to the 4-carbon atom, and hydrogen to the 3-nitrogen atom, carbon dioxide being evolved. It is suggested that the first product is a 4-hydroxy-3-acyl derivative, which then inverts thus: $\cdot N{:}C{<}\longrightarrow\cdot N(COR)\cdot C(OH){<}\longrightarrow\cdot NH\cdot CR{<}+CO_2$. This is thought to be more probable than the intermediate formation of $\cdot\mathrm{NH(CO_2R){:}C}\cdot$ (cf. the formation of 8-alkylxanthines by the action of acid anhydrides on uric acid; Biltz and Schmidt, A., 1923, i, 489).

When formic acid is used, the group R becomes hydrogen and the acid is reduced. Thus on boiling the dihydrate with 80% formic acid, 7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, sintering from 250°, decomp. 268°, is obtained. A *sodium* salt is prepared; although the substance is soluble in hydrochloric acid, no hydrochloride can be isolated, in agreement with the absence of an unsaturated tertiary nitrogen atom. Oxidation by chromic acid yields a substance which may be *formylmethylbiuret*, CHO·NH·CO·NH·CO·NHMe, m. p. 250° (decomp.), and dimethylparabanic acid; by chlorine water, amorphous products are obtained.

Dimethyl*iso*uric acid dihydrate in hot acetic acid gives, with evolution of carbon dioxide, 4 : 7 : 9-*trimethyl*-4 : 5-*dihydro*isouric *acid*, decomp. 250°, soluble in alkali without change on acidification, soluble in hydrochloric acid. As the murexide reaction is not given, a methyl group is considered to be present in the 4-position; chromic acid oxidation yields the same products as 7 : 9-dimethyl-4 : 5-dihydro*iso*uric acid.

Dimethyl*iso*uric acid when heated with benzoic acid at 150—160° gives, with another substance, m. p. 241—244°, 4-*phenyl*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, m. p. 244° (decomp.), which is only slightly soluble in sodium hydroxide solution, gives no murexide reaction, and is not reduced by hydriodic acid. In accordance with the formulation, dimethylparabanic acid cannot be obtained by oxidation.

The above dimethyldihydrouric acids on heating with sodium hydroxide solution evolve ammonia, and by fission of the pyrimidine ring are converted into glyoxalonecarboxylic acids. Thus 7 : 9-dimethyl-4 : 5-dihydrouric acid gives 1 : 3-*dimethylglyoxalone*-5-*carboxylic acid*, sintering from 205°, decomp. 220° (*silver* salt, from which the *methyl* ester, m. p. 127°, is obtained, although unobtainable from the acid by the action of methyl alcohol and hydrogen chloride). This is oxidised by chromic acid to dimethylparabanic acid, and on distillation gives 1 : 3-*dimethylglyoxalone*, m. p. about 100°, which becomes oily in contact with water, and forms a hygroscopic hydrochloride. Heating the 5-carboxylic acid with hydrochloric acid gives, however, other decomposition products.

1 : 3-Dimethylglyoxalone in water, alcohol, or acetic acid gives with bromine a dark violet coloration, turning red and then yellow on further addition of bromine. Chromic acid oxidation yields dimethylparabanic acid. Attempted catalytic hydrogenation was unsuccessful, as was an attempt to isolate *s*-diformyldimethylcarbamide from the products of nitric acid oxidation.

4 : 7 : 9-Trimethyl-4 : 5-dihydrouric acid yields 1 : 3 : 4-*trimethylglyoxalone*-5-*carboxylic acid*, decomp. 179° (*silver* salt, decomp. 182°, yielding a *methyl* ester, m. p. 88—89°, unobtainable from the acid). The acid easily loses carbon dioxide in water at 100° to give 1 : 3 : 4-*trimethylglyoxalone*, b. p. about 210°. Attempted catalytic hydrogenation failed, as did oxidation by nitric acid, which gave syrupy products.

4-Phenyl-7 : 9-dimethyl-4 : 5-dihydrouric acid yields with sodium hydroxide 4-*phenyl*-1 : 3-*dimethylglyoxalone*-5-*carboxylic acid*, decomp. 217—218° (*silver* salt, decomp. 195°, giving a *methyl* ester, m. p. 124°), which when heated with aqueous or alcoholic hydrochloric acid gives 4-*phenyl*-1 : 3-*dimethylglyoxalone*, m. p. 92° (*hydrochloride*, m. p. 93—94°). This is oxidised by nitric acid in acetic acid to N-*formyl*-N′-*benzoyl*-NN′-*dimethylcarbamide*, m. p. 115° (decomp.), and is converted by chromic acid into 5-*hydroxy*-5-*phenyl*-1 : 3-*dimethylhydantoin*, m. p. 115—118°. The latter is reduced by hydriodic acid to 5-phenyl-1 : 3-dimethylhydantoin, m. p. 105—106° (cf. Gabriel, A., 1907, i, 91).

E. W. Wignall.

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid, its chlorination products and degradation. H. Biltz and H. Krzikalla [in part with K. Slotta] (Annalen, 1927, 457, 131—139).—Experiments on the chlorination of 3 : 9-dimethyluric acid (Biltz and Krzikalla, A., 1921, i, 614) gave under very similar conditions varied products. Continuing this work, a 3 : 9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid* has been prepared by reduction of the chloro-derivatives, the structure of which has been established. By degradation, hydantoins are obtained, including one with a new fused ring system, a hydantoinohydantoin.

The preparation of 3 : 9-dimethyluric acid by methylation of dipotassium urate is improved at all stages. For the methylation, methyl toluene-*p*-sulphonate is now employed, at atmospheric pressure in *o*-dichlorobenzene at 145—155°, and much of the decomposition caused by methyl sulphate is thus avoided, improved yields being obtained.

There are three main products of chlorination, according to the conditions.

(1) Chlorination in acetic acid, followed by removal of chlorine in a current of air and precipitation by ether, gives 4-*chloro*-3 : 9-*dimethyl*-$\Delta^{5:7}$-isouric *acid*, (I), which (+0·5AcOH) sinters from 70° to 80°, and then decomposes, and gives a strong murexide reaction. This on treatment with water yields 3 : 9-dimethyluric acid glycol, and in methyl and ethyl alcohols the corresponding dialkyl ethers (*loc. cit.*). By reduction with hydriodic acid, the original 3 : 9-dimethyluric acid is obtained. Other reducing agents yield a different product (see below). By the action of hydrogen chloride in acetic acid, 1 : 7-dimethyl*spiro*-dihydantoin (*loc. cit.*) is formed.

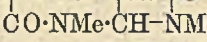
Similarly 1-acetyl-3 : 9-dimethyluric acid (*loc. cit.* : the method of preparation has been improved) chlorinates to the 4-*chloro*-derivative, decomp. 205°. This, which is remarkably stable to water and to alcohol, liberates iodine from potassium iodide solution, and gives on reduction 3 : 9-dimethyluric acid. The formulation is confirmed by the production of methylamine on heating with sodium hydroxide solution, and of 4-*hydroxy*-3 : 9-*dimethyl*-$\Delta^{5:7}$-isouric *acid*, m. p. 265—267°, by hydrolysis with 30% acetic acid. The hydroxy-compound is converted by diazomethane into tetramethyl*spiro*dihydantoin, with the probable intermediate formation of the 5 : 7-glycol.

That the acetyl group in acetyldimethyluric acid is in the 1-position is confirmed by implication in the above reaction, for the shifting of the double linking from the 4 : 5- to the 5 : 7-position is probably due to addition of chlorine at the 5- as well as at the 4-position (see also II, below), followed by loss of hydrogen chloride by removal of the 7-hydrogen atom, which would not be possible if acetyl were present at the 7- instead of at the 1-position. A definite proof is, however, given by methylation : by the action of methyl sulphate and sodium hydroxide solution, followed by removal of the acetyl group by heating in absence of methyl sulphate, 3 : 7 : 9-trimethyluric acid is obtained.

(2) Chlorination of 3 : 9-dimethyl-$\Delta^{5:7}$-*iso*uric acid in a similar manner, using carefully dried materials, gives on slow crystallisation, instead of precipitation by ether, 4 : 5-*dichloro*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid* (II), decomp. (+0·5AcOH) from 210° to 230°, with some 1 : 7-dimethyl*spiro*dihydantoin. The dichloro-compound does not react with cooled methyl alcohol, and gives no murexide reaction. It is reduced by zinc and acetic acid to 3 : 9-dimethyluric acid; attempted removal of hydrogen chloride to give an *iso*uric acid gave no crystalline product. The substance was at first thought to be 4 : 7-dichloro-3 : 9-dimethyl-4 : 5-dihydrouric acid, which formulation would make the formation of a hydantoin derivative (see later) more easily understood; this formula was, however, discarded.

(3) Chlorination in acetic anhydride, or in an equal mixture of the anhydride and the acid, gives 4-*chloro*-5-*acetoxy*-4 : 9-*dimethyl*-4 : 5-*dihydrouric acid* (III) (sintering from 190° to 200°, followed by decomposition), also obtainable by the action of acetic anhydride on I. The new substance reacts with alcohol, but no product has been isolated; it gives no murexide reaction. Reduction by zinc and acetic acid yields 3 : 9-dimethyluric acid.

Similarly 1-acetyl-3 : 9-dimethyluric acid yields its 4-*chloro*-5-*acetoxy*-derivative, decomp. 168—170°, also obtainable from the 4-chloro-derivative.

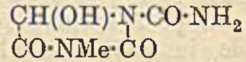
All chlorination products in the above three groups (the usual starting material being the dichloride) are reduced by potassium iodide and sodium thiosulphate to 3:9-*dimethyl*-$\Delta^{5:7}$-iso*uric acid*,  $\begin{array}{l}\mathrm{NH{\cdot}CO{-}C{:}N{\cdot}CO} \\ \mathrm{CO{\cdot}NMe{\cdot}CH{-}NMe}\end{array}$ (IV), decomp. 418—420°, the same temperature as that of 3 : 9-dimethyluric acid, into which it inverts. The new acid is distinguished from the latter by giving no murexide reaction, whether treated with nitric acid or with chlorine water. By hydrolysis with barium hydroxide solution, or with dilute mineral acids (in which its solubility is a characteristic), methylamine is produced, and a substance described below. Diazomethane causes no methylation, although nitrogen is evolved (cf. acetylcarbamide, which behaves similarly). Unlike 3 : 9-dimethyluric acid, the *iso*-acid crystallises without water; it reduces ammoniacal silver nitrate solution. The solid has d_4^{23} 1·591 (L. Klemm); the mol. vol. is thus 123·2 c.c., 1·6 c.c. greater than that of the stable 3 : 9-dimethyluric acid (Klemm and Klemm, this vol., 498).

Reduction of 4-chloro-5-acetoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid gives an acetoxycarbamylmethylhydantoin (see below).

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid forms a loosely combined *hydrochloride*, a *hydrotri-iodide*, $C_7H_8O_3N_4,HI_3$, decomp. 107°, and a *perchlorate*, in agreement with its possession of the $-\overset{|}{C}{:}N{\cdot}\overset{||}{C}-$ grouping.

3 : 9-Dimethyl-$\Delta^{5:7}$-*iso*uric acid is oxidised by hydrogen peroxide on the water-bath to ammonium methyloxalurate (Slotta, A., 1925, i, 1189). At the ordinary temperature, an intermediate substance, regarded as 4 : 5-*dihydroxy*-4-α-*methylcarbamido*-3-*methyl*-2-*glyoxalidone*, decomp. 175—180°, is formed; this on heating with acetic anhydride yields an *isomeride* (?), m. p. 226°.

The inversion of the *iso*-acid to 3 : 9-dimethyluric acid, which occurs on melting, is produced on heating at 310—320°, or on heating with acetic or formic acid. The inversion in presence of acetic acid explains the formation of dimethyluric acid when the above chloro-derivatives are reduced by zinc and acetic acid. The action of chlorine upon the *iso*-acid in methyl alcohol yields 4 : 5-dichloro-3 : 9-dimethyldihydrouric acid, free from acetic acid, darkening from 200°, decomp. about 310°.

Degradation of the above chloro-derivatives yields a substance $C_5H_7O_4N_3$, possibly as the result of inversion with rupture of the pyrimidine ring, to give a carbamylhydantoin (cf. following abstract for synthesis). Thus 4 : 5-dichloro-3 : 9-dimethyldihydrouric acid dissolves slowly in boiling water, with the evolution of carbon dioxide and separation of methylamine hydrochloride to form 5-*hydroxy*-1-*carbamyl*-3-*methylhydantoin*,  $\begin{array}{l}\mathrm{CH(OH){\cdot}N{\cdot}CO{\cdot}NH_2} \\ \mathrm{CO{\cdot}NMe{\cdot}CO}\end{array}$ (V), decomp. 216—217°, resolidifying at 230°, decomp. 235°, b. p. about 200°/20 mm. (?), which crystallises out on cooling. The same substance is obtained from 4-chloro-3 : 9-dimethyl*iso*uric acid, or from 3 : 9-dimethyl*iso*uric acid itself by passing chlorine into a suspension in water. This substance gives no murexide reaction; it is unaltered by boiling water, by hydrochloric acid, by concentrated sulphuric acid, by boiling aniline or nitrobenzene, by gentle heating with hydriodic acid or hydrochlorostannic acid, by diazomethane or by nitrous acid; it is oxidised, however, by ammoniacal silver nitrate solution. Attempts to prepare a derivative by action of benzoic anhydride or benzoyl chloride were unsuccessful, as were those to induce reaction with phenyl- or methyl-carbimide.

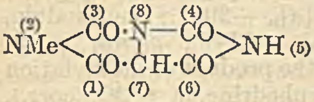
The hydantoin (V) on heating in a flame gives the acrid odour of cyanic acid; it is oxidised by chromic acid to methylparabanic acid, and reduced by fuming hydriodic acid in presence of phosphonium iodide at 100° to 1-carbamyl-3-methylhydantoin (see below), and 3-methylhydantoin.

5-*Acetoxy*-1-*carbamyl*-3-*methylhydantoin*, m. p. 212—215° (slight decomp.), is obtained by acetylation of the hydroxy-compound in boiling acetic anhydride, or by treating 4-chloro-5-acetoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid (in the reduction of which, above, it is formed as a by-product) with boiling water, or, better, with 50% acetic acid. The acetoxy-compound is hydrolysed by concentrated sulphuric acid, is oxidised to methylparabanic acid, and reduced to 1-carbamyl-3-methylhydantoin.

The compound (V) is nitrated by fuming nitric acid to 5-*hydroxy*-1-*nitrocarbamyl*-3-*methylhydantoin*, m. p.

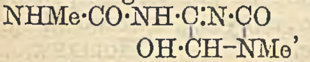
180°, reduced to 3-methylhydantoin more easily than the parent substance.

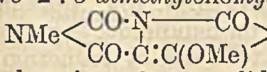
Degradation of (V) by treatment with barium hydroxide solution gives a *barium* salt, which on dissolving in hydrochloric acid and precipitating the barium as sulphate, yields oxalic acid; whilst treatment with sodium hydroxide solution, followed by acidification and addition of phenylhydrazine, gives glyoxylic acid phenylhydrazone. The filtrate from the above barium salt yields ω-methylbiuret (cf. Biltz and Jeltsch, A., 1923, i, 1074). The hydantoin ring has thus been broken between the 3- and the 4-, and between the 5- and the 1-positions.

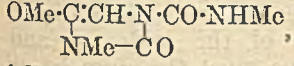


$\overset{(2)}{\mathrm{NMe}}<\begin{array}{l}\overset{(3)}{\mathrm{CO}}\cdot\overset{(8)}{\mathrm{N}}—\overset{(4)}{\mathrm{CO}}\\ \underset{(1)}{\mathrm{CO}}\cdot\underset{(7)}{\mathrm{CH}}\cdot\underset{(6)}{\mathrm{CO}}\end{array}>\mathrm{NH}\ (5)$

(VI.)

Degradation of 3 : 9-dimethyl-$\Delta^{5:7}$-*iso*uric acid by dilute acids yields, as mentioned above, methylamine hydrochloride, and a compound $C_6H_5O_4N_3$. This, to which is ascribed formula (VI), and the name 2-*methylhydantoinohydantoin*, decomp. 262°, is considered to be formed by rupture of the linking between the 3- and 4-positions, to give  $\begin{array}{l}\mathrm{NHMe\cdot CO\cdot NH\cdot C{:}N\cdot CO}\\ \qquad\qquad\mathrm{OH\cdot CH—NMe}\end{array}$, which then loses methylamine, hydrogen being lost from the 4-position in the hydantoin ring, the 2-carbonyl group of the original *iso*uric acid becoming attached to the 1-nitrogen of the hydantoin ring. The product thus consists of two hydantoin rings fused in the 1 : 5-positions. The substance in aqueous solution is neutral to indicators; when, however, it is treated with sodium hydroxide solution, and the excess is titrated, it behaves as a dibasic acid. This is attributed to the opening of the rings to give N-*carbamyl*-N-*methylcarbamylaminomalonic acid*, $NHMe\cdot CO\cdot N(CO\cdot NH_2)\cdot CH(CO_2H)_2$.

The methylhydantoinohydantoin is oxidised by hydrogen peroxide to 5-hydroxy-1-carbamyl-3-methylhydantoin. The action of diazomethane causes the introduction of one methyl group, followed by a second when the methylation is continued for 10 days, to give 2 : 5-*dimethyl*enol*hydantoinohydantoin methyl ether*, NMe $\mathrm{NMe}<\begin{array}{l}\mathrm{CO\cdot N——CO}\\ \mathrm{CO\cdot C{:}C(OMe)}\end{array}>\mathrm{NMe}$ (VII), m. p. 198—200°, changing after resolidification to a substance, $C_7H_{11}O_3N_3$ (?), m. p. 232—234°.

Demethylation of (VII) by hydriodic acid not giving isolable products, hydrochloric acid was employed. This gives, in very small yield, a substance which is probably the *methyl ether* of the *enol* form of 1-methylcarbamyl-3-methylhydantoin,  $\begin{array}{l}\mathrm{OMe\cdot C{:}CH\cdot N\cdot CO\cdot NHMe}\\ \quad\mathrm{NMe—CO}\end{array}$, m. p. 128—138° (see following abstract); or, in two experiments, the desired 2 : 5-*dimethylhydantoinohydantoin*, m. p. 272°. This is also obtained, very slowly, by hydrolysis by boiling water: the rate of evolution of carbon dioxide and of methylamine in this case is shown graphically, and in one experiment is stopped at the stage of 1-methylcarbamyl-3-methylhydantoin.

Similar hydrolysis of 2-methylhydantoinohydantoin by boiling water yields 1-*carbamyl*-3-*methylhydantoin*, m. p. 250°, or after purification by heating with hydriodic acid, 258—260°. This substance is also obtained directly by the action of boiling 2*N*-hydrochloric acid on 3 : 9-dimethyl*iso*uric acid, or by the action of fuming hydriodic acid to which a small quantity of water and some phosphonium iodide are added, or from 5-hydroxy-1-carbamyl-3-methylhydantoin, in which case some 3-methylhydantoin is formed as a by-product. Chromic acid prepared from potassium dichromate and sulphuric acid has no action, but when chromium trioxide dissolved in acetic acid is used, methylparabanic acid is obtained. Reduction by fuming hydriodic acid yields 3-methylhydantoin.

The product of the nitration of 1-carbamyl-3-methylhydantoin by fuming nitric acid is the 1-*nitrocarbamyl* derivative, m. p. 170°, reduced more readily to 3-methylhydantoin by hydriodic acid than is the parent substance.

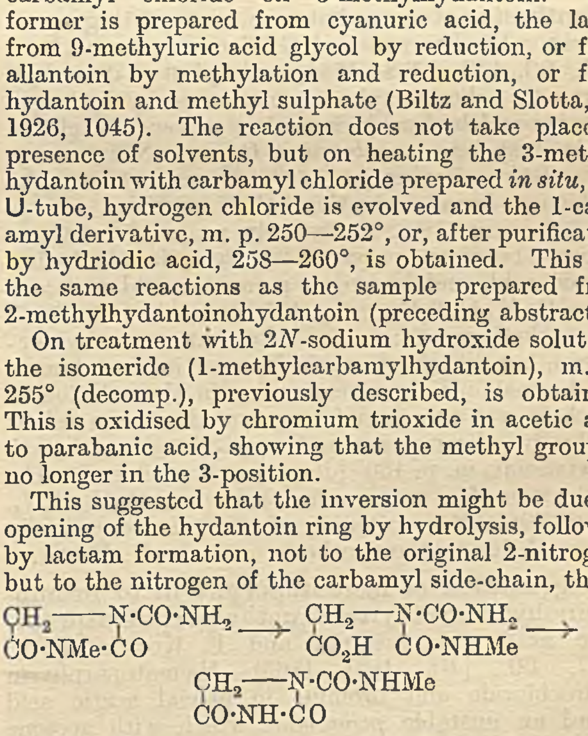
The action of barium hydroxide solution gives a *barium* salt; that of 2*N*-sodium hydroxide solution gives, however, the *sodium* salt of an isomeride, $C_5H_6O_3N_3Na,2H_2O$, decomp. 278—280°, converted by hydrochloric acid into a substance, $C_5H_7O_3N_3$ (1-*methylcarbamylhydantoin*, cf. following abstract), m. p. 255° (decomp.), giving with barium hydroxide solution a *barium* salt. The isomeride cannot be reconverted into 1-carbamyl-3-methylhydantoin by acids.

E. W. Wignall.

Carbamyl derivatives of hydantoins and their inversion. H. Biltz and (Frl.) D. Heidrich (Annalen, 1927, 457, 190—208).—The 1-carbamyl-3-methylhydantoin described by Biltz and Krzikalla (preceding abstract) is synthesised by the action of carbamyl chloride on 3-methylhydantoin. The former is prepared from cyanuric acid, the latter from 9-methyluric acid glycol by reduction, or from allantoin by methylation and reduction, or from hydantoin and methyl sulphate (Biltz and Slotta, A., 1926, 1045). The reaction does not take place in presence of solvents, but on heating the 3-methylhydantoin with carbamyl chloride prepared *in situ*, in a U-tube, hydrogen chloride is evolved and the 1-carbamyl derivative, m. p. 250—252°, or, after purification by hydriodic acid, 258—260°, is obtained. This has the same reactions as the sample prepared from 2-methylhydantoinohydantoin (preceding abstract).

On treatment with 2*N*-sodium hydroxide solution, the isomeride (1-methylcarbamylhydantoin), m. p. 255° (decomp.), previously described, is obtained. This is oxidised by chromium trioxide in acetic acid to parabanic acid, showing that the methyl group is no longer in the 3-position.

This suggested that the inversion might be due to opening of the hydantoin ring by hydrolysis, followed by lactam formation, not to the original 2-nitrogen, but to the nitrogen of the carbamyl side-chain, thus:



$$\begin{array}{l}\mathrm{CH_2——N\cdot CO\cdot NH_2}\\ \mathrm{CO\cdot NMe\cdot CO}\end{array}\longrightarrow\begin{array}{ll}\mathrm{CH_2——N\cdot CO\cdot NH_2}\\ \mathrm{CO_2H\quad CO\cdot NHMe}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_2——N\cdot CO\cdot NHMe}\\ \mathrm{CO\cdot NH\cdot CO}\end{array}$$

(cf. the inversion of 2-imino-1 : 3-diphenylparabanic acid under the action of sodium alkoxide to give 2-anilo-1-phenylparabanic acid, Dieckmann and Kämmerer, A., 1907, i, 979).

Reduction was not brought about by hydriodic acid, whilst the fuming acid gave no isolable product.

In the hope that a nitro-derivative would, as before, be more easily reduced, nitration was attempted, but without success. Methylation of the sodium salt by methyl sulphate yields 1-*methylcarbamyl*-3-*methylhydantoin*, m. p. 128—130°, also, and better, obtainable by the action of an ethereal diazomethane solution; the product is oxidised by chromium trioxide in acetic acid to methylparabanic acid, showing that the 3-position is again substituted by methyl. Attempted synthesis by heating 3-methylhydantoin with methylcarbimide was unsuccessful. When, however, hydantoin itself is heated in a sealed tube with methylcarbimide, 1-methylcarbamylhydantoin is obtained.

1-*Carbamyl*-3-*ethylhydantoin*, m. p. 205—208°, is obtained by the action of carbamyl chloride on 3-ethylhydantoin, prepared from 9-ethyluric acid glycol. The product gives with fuming nitric acid 1-*nitrocarbamyl*-3-*ethylhydantoin*, m. p. 99°. On treatment with 2*N*-sodium hydroxide solution, the *sodium* salt, m. p. 125°, of 1-*ethylcarbamylhydantoin*, m. p. 185—187°, is obtained; this is oxidised to parabanic acid, is synthesised by the action of ethylcarbamyl chloride (prepared from *s*-diethylcarbamide) on hydantoin, and is methylated by diazomethane to 1-*ethylcarbamyl*-3-*methylhydantoin*, m. p. 93—94°. The isomeric 1-*methylcarbamyl*-3-*ethylhydantoin*, m. p. 91—92°, is obtained by heating 3-ethylhydantoin with methylcarbimide, and gives a *sodium* salt, decomp. from 40°; by the action of fuming nitric acid, a *nitro*-derivative, $C_7H_{10}O_5N_4$ (?), m. p. 91—92°, is obtained. E. W. Wignall.

Synthesis of a substance resembling porphyrin. W. Küster and G. Koppenhöfer (Ber., 1927, 60, [*B*], 1778—1781).—Ethyl 3 : 5-dimethylpyrrole-2 : 4-dicarboxylate is converted by hydrogen peroxide and hydrochloric acid in presence of glacial acetic acid into a *substance*, $C_{12}H_{13}O_4NCl_4$, m. p. 166° after softening at 150°, decomp. 170°; the analogous *bromo*-derivative, $C_{12}H_{15}O_4NBr_2$, m. p. 131°, decomp. 180°, is similarly prepared. 4-Carbethoxy-3 : 5-dimethylpyrrole-2-carboxylic acid, hydrobromic acid, and hydrogen peroxide yield the *compound* $C_{36}H_{34}O_8N_4Br_4$, m. p. 137° (possibly 1 : 3 : 5 : 7-tetracarbethoxy-2 : 4 : 6 : 8-tetrabromomethylporphyrin, but differing in optical properties from known porphyrins). If the dye remains in the solution in which it was prepared for several days, the colour gradually disappears and *carbethoxybromomethylmaleinimide*, m. p. 130° (decomp.), is produced. The production of a bromine-free *substance*, $C_{36}H_{38}O_8N_4$, m. p. 208° after softening at 190°, is occasionally observed during the synthesis. H. Wren.

Degradation of hæmatoporphyrin to bromobromohydroxyethyltetramethylporphindipropionic acid. H. Fischer and F. Kotter (Ber., 1927, 60, [*B*], 1861—1865).—Hæmatoporphyrin hydrochloride and bromine in glacial acetic acid afford an unstable *perbromide* which with acetone yields bromoacetone and *bromobromohydroxyethyltetramethylporphindipropionic acid* (*bromoporphyrin* I), $C_{32}H_{30}O_5N_4Br_2$ or $C_{32}H_{32}O_5N_4Br_2$; the *iron*, *cobalt*, *copper*, *nickel*, and *zinc* complex salts are described. It is converted by methyl-alcoholic hydrogen chloride into the *dimethyl* ester, $C_{34}H_{34}O_5N_4Br_2$, m. p. 273°, and oxidised by chromic acid to bromocitraconimide, m. p. 174°. H. Wren.

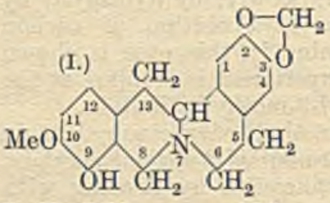
Manufacture of vat dyes of the 1-thionaphthen-2′-indoleindigo series. I. G. Farbenind. A.-G.—See B., 1927, 743.

Preparation of arecoline. F. Chemnitius (J. pr. Chem., 1927, [ii], **117**, 147—150).—Details are given for the extraction of arecoline from betel nuts in 500 kg. quantities. The yield of pure hydrobromide is 0·35—0·4%. J. W. Baker.

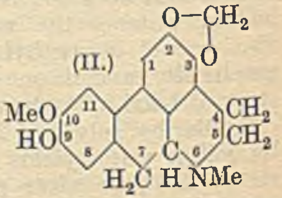
***l*-Methylephedrine, an alkaloid from *Ephedra* species.** S. Smith (J.C.S., 1927, 2056—2059).—The Chinese drug Ma Huang contains, in addition to *d*-ψ- and *l*-ephedrines, a third alkaloid, *l*-methylephedrine, m. p. 87—88° (corr.), $[\alpha]_D$ −29·2° [hydrochloride, m. p. 188—189°, $[\alpha]_D$ −29·8°; methiodide, m. p. 212—213° (corr.), $[\alpha]_D$ −21·8°; *picrate*, m. p. 144° (corr.)], identical with the product of methylation of *l*-ephedrine. *d*-ψ-Methylephedrine, m. p. 30° (corr.), $[\alpha]_D$ +48·1° [*methiodide*, m. p. 216—217° (corr.); *picrate*, m. p. 152—153° (corr.); *hydrogen tartrate*, m. p. 84° (corr., +2H_2O), or 152° (corr., anhyd.)], is obtained by methylation of *d*-ψ-ephedrine. C. Hollins.

***iso*Quinoline alkaloids. I. Constitution of nandinine. II. Constitution of domesticine; *iso*domesticine. III. Constitution of coptisine. IV. Worenine. V. Synthesis of some new *iso*quinoline alkaloids. VI. Spectrographic researches.** Z. Kitasato (Acta Phytochim., 1927, 3, 175—258).—By an improved method of extraction, nandinine, $C_{19}H_{19}O_4N$, (I), the amorphous alkaloid isolated from *Nandani domestica*, Thunb., by Eijkmann (A., 1885, 565), is obtained crystalline, m. p. 145—146°, $[\alpha]_D$ +63·2° in alcohol. It contains one phenolic hydroxyl and one methoxyl group, and gives with diazomethane a racemised methyl ether, m. p. 166°, identical with *dl*-tetrahydroberberine. Under special conditions, *d*-nandinine methyl ether, m. p. 139°, $[\alpha]_D$ +246·73°, identical with *d*-canadine, is obtained. The d-*ethyl ether*, m. p. 109°, obtained by the action of diazoethane on nandinine, is converted, by oxidation with iodine followed by reduction, into the dl-*ethyl ether*, m. p. 128°. Reduction of berberrubine (Frerichs, A., 1910, i, 500) with zinc and sulphuric acid gives *dl*-tetrahydroberberrubine, m. p. 168°, which is resolved by means of its *d*-bromocamphorsulphonate into *d*-tetrahydroberberrubine, m. p. 144°, $[\alpha]_D$ +62·9°, identical with nandinine, and a little impure *l*-isomeride; *dl*-tetrahydroberberrubine ethyl ether, m. p. 128°, is identical with *dl*-nandinine ethyl ether. The positions of the hydroxyl and methoxyl groups in nandinine must therefore be as in (I). From the residues after extraction of nandinine a second crystalline alkaloid, *domesticine*,

(I.)



(II.)



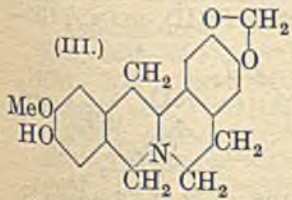
$C_{19}H_{19}O_4N$, m. p. 115—117°, $[\alpha]_D$ +60·51° (*hydrochloride* and *chloroplatinate* described), is isolated, which also contains a phenolic hydroxyl, a methoxyl, and a methylenedioxy-group, but has the absorption spectrum of a phenanthraquinoline alkaloid (see below). The *methyl ether*, m. p. 139°, $[\alpha]_D$ +101·7° in chloroform, differs from bulbocapnine methyl ether, dicentrine, and synthetic *d-epi*dicentrine, and has probably the *iso*dicentrine structure (II). For the synthesis of dl-epi*dicentrine*, m. p. 119° (*hydrochloride*, m. p. about 147°), *homopiperonylhomoveratrylamine*, m. p. 130—131°, obtained from homopiperonyl chloride and homoveratrylamine, is converted by phosphoryl chloride in toluene into 6 : 7-*dimethoxy*-1-(3′ : 4′-*methylenedioxybenzyl*)-3 : 4-*dihydro*-iso*quinoline* (*methiodide*, m. p. 135—138°), and thence, by reduction of the methochloride, into 6 : 7-*dimethoxy*-1-(3′ : 4′-*methylenedioxybenzyl*)-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 116° (*sulphate*, m. p. 110°). This is nitrated, giving the 6′-*nitro*-compound, m. p. 151°, and a *substance*, m. p. 198°; the 6′-*amino*-compound, m. p. 110°, by diazotisation and treatment with copper, yields *dl-epi*dicentrine, which is resolved by means of *d*-tartaric acid to give the *d*-compound, m. p. about 110°. Oxidation of domesticine with alkaline permanganate yields 4 : 5-*methylenedioxybenzene*-1 : 2 : 3-*tricarboxylic acid*, m. p. about 170°, thus confirming the structure (II).

The acid mother-liquor, after removal of nandinine and domesticine, contains a third alkaloid, iso-*domesticine*, m. p. 85°, which gives the same methyl ether as domesticine, but a different *ethyl ether*, m. p. 82°. The m. p. of the alkaloids indicate that domesticine is the 9-hydroxy-10-methoxy-compound, *iso*-domesticine the 10-hydroxy-9-methoxy-compound (see II).

Coptis japonica, Mak., contains, in addition to berberine and the yellow alkaloid coptisine already reported (A., 1926, 1160), a new, crystalline alkaloid *worenine*, $C_{20}H_{17}O_5N$ (*hydrochloride*, m. p. 295°), isolated as *tetrahydro*-derivative, m. p. 212—213°, from which it is regenerated by the action of iodine. *Coptisine iodide* decomposes above 280° : the *chloride* is not melted at 300°. Tetrahydrocoptisine, m. p. 217—218° (previously given as 215°), is different from tetrahydro-ψ-coptisine (2 : 3 : 10 : 11-bismethylenedioxytetrahydroprotoberberine; Buck, Perkin, and Stevens, A., 1925, i, 958), m. p. 214°, which is synthesised independently by the method of these authors. Tetrahydroworenine yields a N-*methyl* derivative (*hydrochloride*, m. p. 281°; *hydriodide*, m. p. 263°). Since 8-*methyltetrahydrocoptisine*, m. p. 215°, obtained by the action of magnesium methyl iodide on coptisine chloride, followed by reduction, differs from tetrahydroworenine, worenine is most probably 13-methylcoptisine.

For the synthesis of *tetrahydro-ψ-berberrubine* (III), m. p. 181° (*ethyl ether*, m. p. 131°), vanillin is converted by way of the azlactone, m. p. 191° (which on hydrolysis yields α-benzamido-4-hydroxy-3-methoxycinnamic acid, m. p. 210°; cf. Sugii, A., 1921, i, 346), into 4-hydroxy-3-methoxyphenylpyruvic acid, which by condensation with ethyl chloroformate and oxidation with hydrogen peroxide gives *ethylcarbonatohomovanillic acid*, m. p. 138—139°, also prepared by the action of ethyl chloroformate on homovanillic acid, m. p. 140—141°, obtained by oxidation of eugenyl acetate, m. p. 30°, with permanganate in acetone. The acid at 200°, or the corresponding *acid chloride* in benzene, is condensed with homopiperonylamine, and the resulting *homopiperonylamide* is cyclised by means of phosphoryl chloride in toluene to a *dihydro*iso*quinoline* derivative, which is reduced and hydrolysed to the oily 6 : 7-*methylenedioxy*-1-p-*hydroxy*-m-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (*ethyl ether*, m. p. 99°). Condensation of this compound with formaldehyde gives tetrahydro-ψ-berberrubine, which on methylation with diazomethane yields tetrahydro-ψ-berberine, m. p. 177° (Haworth, Perkin, and Rankine, A., 1924, i, 1098).

(III.)



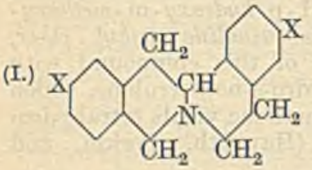
Tetrahydroprotoberberine, m. p. 254—260°, is synthesised by condensing formaldehyde with *tetrahydroprotopapaverine* (*sulphate*, m. p. 174—175°) obtained from dihydroprotopapaverine (Pictet and Gams, A., 1909, i, 671; cf. Rügheimer, A., 1900, i, 522). For the synthesis of its 2 : 3-*methylenedioxy*-derivative, m. p. 169°, phenylacethomopiperonylamide, m. p. 97—98°, is converted into the *dihydro*iso*quinoline*, reduced to 6 : 7-*methylenedioxytetrahydroprotopapaverine*, m. p. 57°, and condensed with formaldehyde.

Homoveratroyl-β-*phenylethylamine*, m. p. 105—106°, is described.

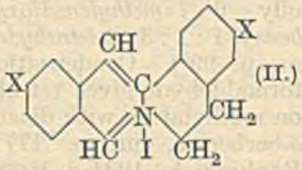
The absorption spectra of 42 alkaloids are examined. Alkaloids of the tetrahydro*iso*quinoline series containing methylenedioxy- or methoxyl groups show a single band at about 3500 Å. Those of the *apo*morphine type in the phenanthraquinoline series show two bands at 3200 and 3650 Å., the former being due to methylenedioxy- or two methoxyl groups in positions 1 : 2, the latter in positions 10 : 11; absence of 1 : 2-substituents results in a flat curve at 3200 Å., whilst 9 : 10-substitution in place of 10 : 11 has a bathochromic effect on the second band. The methylenedioxy-group is rather more bathochromic than two *o*-methoxyl groups. Change from tervalent to quinquevalent nitrogen, especially from carbinol form to ammonium form, exerts a hyper- and bathochromic effect. Absorption spectra curves are given for the following substances: Class I (structure analogous with I): (*a*) Hydrohydrastinine, 6 : 7-methylenedioxytetrahydro-protopapaverine and -protoberberine; (*b*) tetrahydro-berberine, -coptisine, -palmatine, -ψ-berberine, -ψ-coptisine, -berberrubine, -worenine, -papaverine, 8-methyltetrahydroberberine, *dl*-laudanosine, 6 : 7-dimethoxy-1-*m* : *p*-dimethoxybenzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline; (*c*) cryptopine, protopine, hydrastinone (6 : 7-dimethoxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline); (*d*) hydrastine, narcotine, narceine; (*e*) papaverine and its methochloride; (*f*) hydrastinine, cotarnine, berberine, coptisine, worenine; Class II (structure analogous with II): (*a*) *apo*morphine, bulbocapnine, dicentrine, *iso*dicentrine (domesticine methyl ether); (*b*) thebaine; (*c*) morphine, codeine, sinomenine, dihydrosinomenine, dehydrosinomenine. The groups (*a*, *b*, *c*, etc.) within the two main classes indicate closely similar spectra.

C. Hollins.

Synthetical experiments in the *iso*quinoline group. VII. Synthesis of 3 : 11-dimethoxyprotoberberinium salts. VIII. Synthesis of protoberberinium salts. S. N. Chakravarti, R. D. Haworth, and W. H. Perkin, jun. (J.C.S., 1927, 2265—2274, 2275—2281).—VII. The influence of methoxyl groups on the ease of synthesis of alkaloids of the berberine type has been investigated by the preparation of 3 : 11-dimethoxytetrahydroprotoberberine (I, X=OMe). m-*Methoxyphenyl*-β-m-*methoxyphenylethylamide*, an oil, obtained by condensation of β-*m*-methoxyphenylethylamine and *m*-methoxyphenylacetic acid (or the corresponding chloride) yields, when heated with phosphorus oxychloride, 6-*methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydro*-iso*quinoline*, an oil (*picrate*, m. p. 155°). The *sulphate* of this base is reduced by zinc and sulphuric acid to 6-*methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*-iso*quinoline*, an oil (*hydrochloride*, m. p. 192°; *sulphate*; *picrate*, m. p. 148°). Condensation of the tetrahydro-base with formic acid affords the N-*formyl* derivative and when heated with phosphorus oxychloride, this undergoes ring closure in what is presumed to be the *para*-position to give 3 : 11-*dimethoxydihydroprotoberberine*, m. p. 130° (*hydrochloride*, $+4H_2O$; *hydriodide*; *picrate*, m. p. 232°). Reduction of this base with zinc dust and sulphuric acid yields 3 : 11-*dimethoxytetrahydroprotoberberine* (I), m. p. 111° [*hydrochloride*; *hydriodide*, m. p. 205°; *picrate*, m. p. 139—140° (decomp.)]. Addition of iodine to a boiling alcoholic solution of (I) in the presence of sodium acetate gives a *periodide* from which is obtained 3 : 11-*dimethoxyprotoberberinium iodide* (II), m. p. 242° (*chloride*, m. p. 200° and $+3H_2O$; *picrate*, m. p. 238°). Treatment of the chloride with hot potassium hydroxide solution yields a mixture of 3 : 11-*dimethoxyoxyprotoberberine*, m. p. 143°, and 3 : 11-dimethoxydihydroprotoberberine, separated by extraction of the latter compound with dilute hydrochloric acid. When (I) is heated with methyl iodide it gives a mixture of α-3 : 11-*dimethoxytetrahydroprotoberberinium methiodide*, m. p. 224° (α-*methochloride*), with the β-*methiodide*, m. p. 245° (decomp.) [β-*methochloride*, m. p. 245° (decomp.)]. Treatment of the mixed methochlorides with alcoholic potassium hydroxide yields *anhydro*-3 : 11-*dimethoxytetrahydroberberine* (III) (*hydrochloride*, m. p. 236°), an oil which is unchanged by boiling with chloroform or aqueous alcohol but decolorises bromine in chloroform solution or acid permanganate. Base (III), together with some 3 : 11-*dimethoxytetrahydroprotoberberiniummethocarbonate*, m. p. 216°, is the only base obtained by the action of silver hydroxide on the mixed αβ-protoberberinium salts.



(I.)



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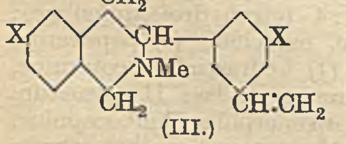


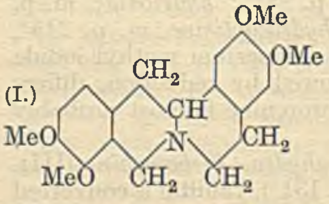
(III.)

VIII. The synthesis of tetrahydroprotoberberine (I) (X=H), the parent substance of the alkaloids in the palmatine–berberine series, has been effected by a group of reactions similar to those described above. The very poor yields obtained in the two stages where ring closure is involved are ascribed to the absence of the methoxyl groupings. 1-Benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (cf. Forsyth, Kelly, and Pyman, A., 1925, i, 1167) [*sulphate*, $+5H_2O$, $+H_2O$, m. p. 191° (decomp.)] from 1-benzyl-3 : 4-dihydro*iso*quinoline (*sulphate*, m. p. 216°) reacts with anhydrous formic acid to give the N-*formyl* derivative. This compound when treated with phosphorus oxychloride under strictly defined conditions yields dihydroprotoberberine (not isolated), which is reduced with zinc dust and hydrochloric acid to *tetrahydroprotoberberine* (I), m. p. 85° (*hydrochloride*, m. p. 232°; *hydriodide*; *picrate*, m. p. 151°). Compound (I) is oxidised by alcoholic iodine in the presence of sodium acetate to a *periodide*, from which *protoberberinium iodide* (II) (X=H), m. p. 232°, is obtained (*chloride*, $+4H_2O$, $+0{\cdot}5H_2O$; *picrate*, m. p. 192—193°). Treatment of protoberberinium chloride with hot aqueous potassium hydroxide yields *oxyprotoberberine*, m. p. 102°, and dihydroprotoberberine (not isolated). With methyl iodide, tetrahydroprotoberberine gives the α- and β-*methiodides*, m. p. 210° and 230—232°, respectively (*methochloride*). The methiodide with methyl-alcoholic potassium hydroxide gives *anhydromethyltetrahydroprotoberberine* (III) (X=H), an oil (*hydrochloride*, hydrated, m. p. 234—235°), also produced by the action of silver hydroxide on the quaternary salt. This anhydro-compound is unchanged when boiled with methyl alcohol or chloroform or when heated with dilute hydrochloric acid.

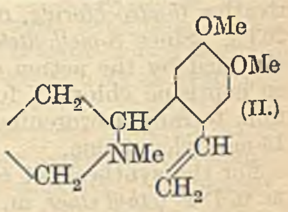
M. Clark.

Manufacture of derivatives of cinchona alkaloids. C. F. Boehringer and Soehne, etc.—See B., 1927, 828.

Conversion of palmatine into its cryptopine analogue (cryptopalmatine). R. D. Haworth, J. B. Koepfli, and W. H. Perkin, jun. (J.C.S., 1927, 2261—2265).—Tetrahydropalmatine (I) forms an α-*methiodide*, m. p. 230°, and a less soluble β-*methiodide*, m. p. 266° (decomp.), which are converted into methiodides [α, syrupy; β, m. p. 250° (decomp.)]. The methochlorides or methiodides when treated with methyl-alcoholic potassium hydroxide give *anhydromethyltetrahydropalmatine B* (II), m. p. 115—116° [*hydrochloride*, m. p. 210° ($+H_2O$, decomp.)]. The methohydroxide, obtained by the action of



(I.)



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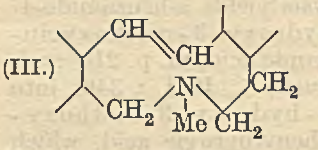

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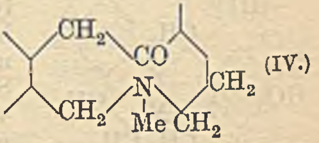
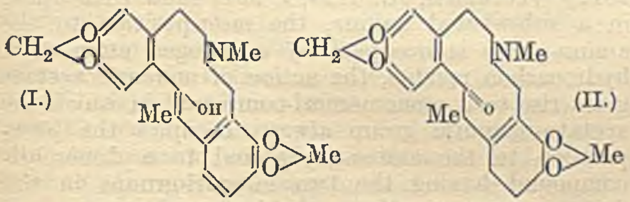


(IV.)

silver hydroxide on the methiodide, when evaporated in a vacuum yields a mixture of this compound with *anhydromethyltetrahydropalmatine A* (III), m. p. 131—132°. The latter, oxidised with perbenzoic acid in chloroform, is converted into the *amine oxide* [*hydrochloride*, m. p. 198—200° (decomp.)], from which *cryptopalmatine* (IV), m. p. 148—150°, is obtained by warming with hydrochloric–acetic acid.

C. Hollins.

Alkaloids of *Corydalis cava*. IX. Constitution of corycavine and corycavamine. E. Späth and H. Holter (Ber., 1927, 60, [*B*], 1891—1898; cf. von Bruchhausen and Stippler, this vol., 683).—Corycavine is reduced to dihydrocorycavine and the latter substance is converted into the quaternary *iodide*, $C_{21}H_{22}O_4NI$, m. p. 296—297° (corr.), which, when heated at 260°/0·01 mm., gives a mixture of bases in 50% yield separable by means of their hydrochlorides into two stereoisomeric *substances*, $C_{20}H_{19}O_4N$, m. p. 140° and 203°, respectively. Removal of the methylenedioxy-groups from the base of m. p. 140°, followed by exhaustive methylation of the tetrahydroxy-base thus produced with diazomethane, affords *dl-meso*-corydaline, m. p. 162—163°, whilst similar treatment of the base of m. p. 203° gives *dl*-corydaline, m. p. 135—136°. The results show that corycavine has the structure of corydaline if its protopine-like constitution is taken into account and confirm in its essentials the formula (I) proposed by Gadamer and von Bruchhausen. The authors, however, prefer the ketonic form (II) in analogy with other protopine alkaloids and also because corycavine does not evolve methane when heated with magnesium methyl iodide. The conversion of corycavamine above its m. p. into corycavine, regarded by Gadamer and von Bruchhausen as a transformation of the ketonic into the enolic form, is considered by the authors as a case of simple racemisation and corycavamine as the optically active form of corycavine. Oxidation of corycavine in dilute aqueous solution at the atmospheric temperature with potassium permanganate gives a mixture of crystalline acids from which hydrastethylimide, m. p. 167°, and 3 : 4-*methylenedioxybenz*-1 : 2-*dicarbonethylimide*, m. p. 125°. Synthesis of the latter compound is effected by the oxidation of 3 : 4-methylenedioxyphthalide dissolved in potassium hydroxide by permanganate and conversion of the dicarboxylic acid into the ethylimide.



(I.)

(II.)

H. Wren.

Yohimbine. A. Schomer (Arch. Pharm., 1927, 265, 500—524).—Analyses of the free base, m. p. 231—232°, agree with the formula $C_{22}H_{28}O_3N_2$ (cf. Barger and Field, A., 1915, i, 835), but the *hydrochloride*, *hydrobromide*, *hydriodide*, and *nitrate*, m. p. 269—270°, agree with the formula $C_{21}H_{26}O_3N_2$, as do analyses of yohimboaic acid, m. p. 258—259°, and its hydrochloride. Yohimbine is converted by acetic anhydride and sodium acetate into *diacetylyohimbine* m. p. 183° (*hydrochloride*, $3H_2O$, $[\alpha]_D^{20}$ −7·5°), and an amorphous *monoacetylyohimbine*, m. p. about 150° (*chloroaurate*, blood-red, m. p. 170°), indicating the presence of a secondary nitrogen atom. Oxidation with mercuric acetate produces a mercury *derivative*, but neither this nor the demercurated oxidation product was obtained crystalline. The latter on reduction gives the original dextrorotatory yohimbine, together with a sparingly soluble isomeride, l-*yohimbine*, m. p. 253—254° (*hydrochloride*, $[\alpha]_D^{20}$ −27·22°). The alkaloid reacts with bromine water to give mono- and di-bromoyohimbines, described by Barger and Field, the analyses agreeing with $C_{21}H_{25}O_3N_2Br,HBr$ and $C_{21}H_{24}O_2N_2Br_2,HBr$, respectively. Ring scission of yohimbine cannot be effected by treating the methiodide, m. p. 249—250°, or the methochloride with sodium hydroxide or amalgam and alcohol. Yohimbine is reduced by sodium and alcohol to *yohimbyl alcohol*, m. p. 202°, or $+2H_2O$, m. p. 148—149° (*hydrochloride*, $[\alpha]_D^{20}$ +37·5°). The ring in yohimbyl alcohol is extremely stable, since the *methiodide*, m. p. 215°, is unaffected by alkalis, the *methochloride* by sodium amalgam and alcohol, and the methiodide on distillation gives methyl and yohimbyl alcohols. Cyanogen bromide reacts with yohimbine, giving 70% of yohimbine hydrobromide, $[\alpha]_D^{20}$ +52·22°, and an amorphous *substance*, m. p. 70—80°, $[\alpha]_D^{20}$ −26·61°. It is concluded, therefore, that yohimbine contains a tetrahydroquinoline ring (cf. von Braun, A., 1907, i, 899; 1917, i, 169; 1918, i, 185).

S. Coffey.

Preparation of homatropine. F. Chemnitius (J. pr. Chem., 1927, [ii], **117**, 142—146).—Full experimental details are given for isolating tropic acid and tropine from the mother-liquors in the preparation of atropine (Chemnitius, B., 1927, 669) in kilogram quantities, by hydrolysis with barium hydroxide. The isolated tropine is then converted, by treatment with mandelic acid in aqueous hydrochloric acid solution, into homotropine, which is purified by conversion into its hydrobromide, etc. The preparation of homotropine hydrochloride, sulphate, and salicylate is also described. J. W. Baker.

Alkaloids of *Aconitum Stoerckianum*, Reichenbach. H. Schulze and G. Berger (Arch. Pharm., 1927, **256**, 524—541).—The alkaloids are similar to those of *Aconitum napellus*, L., the chief constituent being identical or isomeric with aconitine and the minor constituent neopelline (A., 1925, i, 282). The crude alkaloid mixture was separated into ether-insoluble, ether-soluble, and chloroform-soluble fractions. The main constituent from the ether-insoluble fraction had m. p. 191·5° (mixed m. p. with aconitine, m. p. 198°, 194·5°) [*hydrochloride*, $+3\frac{1}{2}H_2O$, m. p. 158° (decomp.) after sintering at 155°; *hydrobromide*, m. p. 203° after sintering at 198°; *hydriodide*, m. p. 221°, decomp. 224°; *perchlorate*, blackening at 220—226°, decomp. 229° (a mixed m. p. with aconitine perchlorate showed no change), $[\alpha]_D^{17}$ −47·73°]. From a comparison with aconitine (see A., 1906, i, 599) it is difficult to say whether the two alkaloids are identical or isomeric.

Neither the ether-soluble alkaloid nor its salts could be obtained crystalline. Treatment with alcoholic potassium hydroxide furnished neoline (hydrobromide darkening at 198°, sintering at 200°, m. p. 205°) together with benzoic and acetic acids.

S. Coffey.

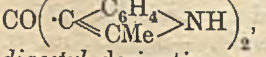
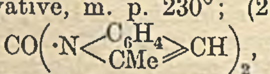
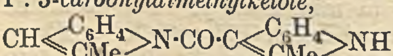
Alkaloid trichloroacetates. Use of trichloroacetic acid in toxicology. G. Florence (Bull. Soc. chim., 1927, [iv], **41**, 1097—1100).—*Trichloroacetates* of the following have been prepared: aniline ($+H_2O$), *o*-toluidine ($+H_2O$), *p*-toluidine ($+H_2O$), strychnine ($+3H_2O$), brucine ($+3H_2O$), morphine ($+3H_2O$), codeine ($+2H_2O$), quinine ($+4H_2O$), quinidine ($+4H_2O$). They are well-defined, crystalline salts decomposing in boiling aqueous solution to the alkaloid, chloroform, and carbon dioxide. The solubilities of the salts in water are given, and are such as enable their easy separation from coagulated albumins. Crystalline salts could not be obtained from cocaine, nicotine, atropine, and cinchonine.

H. Burton.

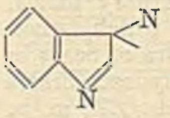
Alkaloids of the animal kingdom. M. Schenck (Z. angew. Chem., 1927, **40**, 1081—1086).—A summary of recent work.

Derivatives of *o*-aminophenylarsinic acid. H. Burton and C. S. Gibson (J.C.S., 1927, 2387—2388).—When either o-*ethylaminophenylarsinic acid*, m. p. 128—129° [*nitroso*-derivative, m. p. 160° (decomp.)], or its *acetyl* derivative, m. p. 187—188° (*silver* salt), is reduced by sulphur dioxide in alcohol–hydrochloric acid–iodine solution, arsenic is eliminated from the molecule. 4-*Nitro*-2-*aminodiethylaniline* (*hydrochloride*, m. p. 205—206°; *benzylidene* derivative, m. p. 97—98°), prepared by reduction of 2 : 4-dinitrodiethylaniline with ammonium sulphide, is converted by the Bart reaction into 3-*nitro*-6-*diethylaminophenylarsinic acid*, m. p. 195—196° (decomp.), which is convertible normally into 3-*nitro*-6-*diethylaminophenylarsenious chloride* [3-*nitro*-6-*diethylaminophenyldichloroarsine*], m. p. 143—144°. M. Clark.

9-Methylcarbazole-3-arsinic acid and its reduction products. H. Burton and C. S. Gibson (J.C.S., 1927, 2386—2387).—3-Amino-9-methylcarbazole has been converted by the usual procedure into 9-*methylcarbazole*-3-*arsinic acid*, m. p. above 300°, 9-*methylcarbazole*-3-*arsenious chloride*, m. p. 121—122°, and 9-*methylcarbazole*-3-*arsenious oxide*, m. p. 182—185° (decomp.). 9-*Methylcarbazole*-3-*azo*-β-*naphthol* has m. p. 212° (decomp.). M. Clark.

Syntheses by means of magnesylpyrroles. Series II, Note X. B. Oddo and Q. Mingoia (Gazzetta, 1927, **57**, 473—479).—The action of carbonyl chloride on magnesylmethylketole yields: (1) principally 3 : 3-*carbonyldimethylketole*,  $CO\left(\cdot C\ll\substack{C_6H_4\\CMe}>NH\right)_2$, m. p. 290°, which forms a *diacetyl* derivative, m. p. 230°; (2) 1 : 1-*carbonyldimethylketole*,  $CO\left(\cdot N<\substack{C_6H_4\\CMe}\gg CH\right)_2$, m. p. 180°; (3) 1 : 3-*carbonyldimethylketole*,  $CH\ll\substack{C_6H_4\\CMe}>N\cdot CO\cdot C\ll\substack{C_6H_4\\CMe}>NH$, m. p. 135°. The products of the interaction of carbonyl chloride and magnesylindole are: 3 : 3-*carbonyldi-indole*, $C_{17}H_{12}ON_2$, m. p. 280°, which forms a silver derivative, but yields no phenylhydrazone, oxime, or semicarbazone; 2 : 2-*carbonyldi-indole*, m. p. 198°; and 1 : 1-*carbonyldi-indole*, m. p. 245°. In contradiction to the statement of Majima and Kotake (A., 1923, i, 150), the formation of indole-1-carboxylic acid by the action of carbon dioxide on magnesium indolyl iodide in ethereal or anisole solution (A., 1911, i, 486) is confirmed. T. H. Pope.

Mechanism of the Grignard reaction in the indole series. R. Majima and T. Hoshino (Proc. Imp. Acad. Tokyo, 1927, **3**, 339—341).—When magnesium indolyl iodide reacts with an alkyl (or acyl) halide, the active halogen of the latter first removes the magnesium iodide group, and, the free indolyl radical immediately changing to the form (I), the alkyl group enters the 3-position. In warm solutions a similar course is followed in the reaction with a carbonyl-containing compound, and, after hydrolysis in this case, an aldehyde group remains in the 3-position. In the cold, however, the tautomeric change to (I) does not take place with sufficient rapidity, and the aldehyde group assumes the 1-position. B. W. Anderson.



(I.)

Position occupied by acetatomercuric groups, Hg·OAc, in anilines having in the nucleus a halogen group or a hydrocarbon residue. I. L. Vecchiotti (Gazzetta, 1927, **57**, 485—497).—Previous results (cf. Jackson and Peakes, A., 1908, i, 523; Schoeller and Schrauth, Ber., 1912, **45**, 2812; Vecchiotti, A., 1924, i, 957) show that when, in a substituted aniline, the *meta*-position to the amino-group is occupied by a halogen atom or a hydrocarbon residue, the action of mercuric acetate gives rise to a monomercuri-compound in which the acetato-mercuric group always occupies the *para*-position to the amino-group and to a dimercuri-compound having the two mercuri-groups in the 2 : 5- or, more usually, in the 4 : 6-positions.

Treatment of *m*-chloroaniline in alcoholic solution with aqueous-alcoholic mercuric acid gives: (1) 4-*Acetatomercuri*-3-*chloroaniline*, $NH_2\cdot C_6H_3Cl\cdot Hg\cdot OAc$, m. p. 155°; the corresponding *hydroxymercuri*-compound, decomp. 210°, *chloromercuri*-compound, decomp. 202°, *acetyl* derivative, m. p. 205°, and *mercury di*-o-*chloro*-p-*aminophenyl*, $(NH_2\cdot C_6H_3Cl)_2Hg$, m. p. 162°, were prepared. Treatment of the acetyl derivative in acetic acid solution containing calcium chloride, with a current of chlorine yields 3 : 4-dichloroacetanilide. (2) 4 : 5-*Diacetatomercuri*-m-*chloroaniline*, $NH_2\cdot C_6H_2Cl(Hg\cdot OAc)_2$, m. p. 190°, which forms an *acetyl* derivative, m. p. 245°, convertible into 3 : 4 : 6-trichloroacetanilide.

The action of aqueous alcoholic mercuric acetate solution on *m*-iodoaniline (2 mols.) gives 4(?)-*acetatomercuri*-m-*iodoaniline*, m. p. 176°, which forms the corresponding *hydroxy*-, m. p. 172°, *iodo*-, m. p. 193° (decomp.), and *acetyl* compounds, m. p. 192°, the latter being convertible into 3 : 4(?)-*di-iodoacetanilide*, m. p. 167°. In aqueous solution this reaction gives 2 : 4 : 6(?)-*triacetatomercuri*-m-*iodoaniline*, m. p. 190° (decomp.). T. H. Pope.

Preparation of lead tetraphenyl. H. Gilman and J. Robinson (J. Amer. Chem. Soc., 1927, **49**, 2315—2317).—Detail improvements are described in the preparation of lead tetraphenyl from lead chloride and magnesium phenyl bromide (cf. Pfeiffer and Truskier, A., 1904, i, 544). F. G. Willson.

Effect of alkali, acid, and enzymes on proteins, peptones, polypeptides, 2 : 5-diketopiperazines, and related compounds. E. Abderhalden and H. Mahn (Z. physiol. Chem., 1927, **169**, 196—222).—Experiments similar to those carried out previously on silk peptone (Abderhalden and Schnitzler, this vol., 686) have been made with elastin. A solution has been obtained by heating dried defatted powdered elastin with *N*-hydrochloric acid for 5—6 hrs. at 70—75° and in some cases by the action of pepsin in acid solution. The hydrolysis of the dissolved elastin by *N*-hydrochloric acid and by *N*-sodium hydroxide at various temperatures has been followed by Sörensen " formol " titrations or by Willstätter's methods, and by measurements of the optical rotation of the peptone solution and its copper salts. The hydrolysis of dipeptides and anhydrides by various amounts of acid and alkali at different temperatures has been measured by amino-nitrogen determinations; it is found that certain polypeptides are not hydrolysed by *N*-hydrochloric acid at the ordinary temperature, but are attacked by *N*-sodium hydroxide under similar conditions. The bearing of these results on the theories of protein structure is discussed and the conclusion is reached that linkings other than those of polypeptide and 2 : 5-diketopiperazine nature are present. A. Wormall.

Blood pigments. VII. Behaviour of prosthetic groups in different solvents. F. Haurowitz (Z. physiol. Chem., 1927, **169**, 235—262).—Spectrophotometric measurements of the spectra of hæmin, mesohæmin, dimethylmesohæmin, and ætiohæmin and the corresponding hæmochromogens have been made in the presence and absence of pyridine and cyanides. The spectrum of hæmin in pyridine differs significantly from that of hæmochromogen, The preparation of trimethylhæmatin from methylhæmatin and methyl sulphate results in the change : C:C ⟶ CH·C(OMe) in the unsaturated side-chain, the Fe·OH grouping not being methylated. In all the solvents used, the chlorine atom of hæmin chloride dissociates as the anion, and in acid solution the coloured residue behaves as cation. In alkaline solutions both hydrogen and chlorine are dissociated, even with a preparation esterified at both carboxyl groups. Thus hæmin contains a third acid group (cf. this vol., 1092). Hydrogen cyanide is not bound by hæmin in the same way as chlorine, bromine, or hydroxyl groups. The action of hydrogen cyanide on hæmin chloride is similar to that of pyridine or aniline; the coloured portion of the compound behaves, however, as cation with pyridine or aniline and as anion with hydrogen cyanide. Pyridine resolves hæmoglobin into globin and pyridine-hæmochromogen, oxyhæmoglobin into the same products together with oxygen, and methæmoglobin into globin and pyridine-oxyhæmin. The constitution of the different hæmins is discussed. A. Wormall.

Effect of irradiation on the tyrosine and tryptophan contained in protein. F. Lieben (Biochem. Z., 1927, **187**, 307—314).—Tyrosine and tryptophan, when forming part of a protein molecule, are oxidatively destroyed when irradiated both in diffused daylight (in presence of a sensitiser) and with the mercury lamp, the destruction not being as rapid, however, as when these acids are free. Addition of alkali increases the action and of formaldehyde accelerates the attack on tryptophan. P. W. Clutterbuck.

Catalytic hydrogenation of hæmateric acid and hæmin. A. Papendieck (Z. physiol. Chem., 1927, **169**, 59—63).—Hæmateric acid in acetic acid solution is catalytically hydrogenated (cf. A., 1926, 631) to a porphyrin not distinguishable from mesoporphyrin. The maximum amount of hydrogen absorbed is equivalent to 6 atoms of hydrogen per mol. of hæmateric acid; no decolorisation occurs. Mesoporphyrin solutions absorb hydrogen irregularly, and are not decolorised. Appreciable hydrogenation of hæmin occurs in acid solution with the formation of mesohæmin and mesoporphyrin. In alkaline solution, approximately 6 atoms of hydrogen are absorbed per mol. of hæmin, but spectroscopical examination reveals no mesohæmin. A. Wormall.

Determination of active hydrogen in hæmin, in some of its derivatives, and in pyrroles. II. H. Fischer and E. Walter (Ber., 1927, **60**, [*B*], 1987—1995; cf. A., 1926, 630).—Determinations are recorded of the number of atoms of active hydrogen per molecule of the following substances, using the method of Zerewitinov (A., 1907, ii, 509; 1908, i, 593; 1911, i, 101) as modified by Flaschenträger (A., 1925, ii, 999). The results are expressed in parentheses after the name of the compound : bis-(3-carbethoxy-2 : 4-dimethyl-5-pyrryl)methane (2·11); bis-(3-carbethoxy-2 : 4-dimethyl-5-pyrryl)methene (1·13); bis-(4-carbethoxy-2 : 3-dimethyl-5-pyrryl)methane (1·94); bis-(4-carbethoxy-2 : 3-dimethyl-5-pyrryl)-methene (0·81); bis-(2-bromo-4-carbethoxy-3-methyl-5-pyrryl)methane (1·01); bis-(2-bromo-4-carbethoxy-3-methyl-5-pyrryl)methene (1·08); product of the condensation of benzaldehyde with 3-acetyl-2 : 4-dimethylpyrrole (2·21); bis-(5-carbethoxy-3-(β-methylmalonic ester)-4-methyl-2-pyrryl)methane (5·3); ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrryl-β-methylmalonate (2·31); ethyl 2 : 5-dimethyl-4-ethyl-3-pyrryl-β-methylmalonate (1·7); ethyl malonate (1·1); triphenylmethyl chloride (—); *cyclo*pentadiene (0·86); ethyl β-methoxymethylmalonate (0·95); hæmin (3·02—5·11 according to temperature); dihydrohæmin (4·06—4·49); *meso*hæmin ester, $C_{36}H_{40}O_4N_4FeCl$ (2·1); ætiohæmin (1·64—1·98); *iso*ætiohæmin (2·37); protohæmin (4·82, 4·68); coproporphyrin ester (3·82, 4·46); *iso*coproporphyrin ester (4·22, 4·3); β-*iso*coproporphyrin ester (3·72); ætioporphyrin (2·03, 2·09); protoporphyrin diester (1·93); *iso*ætioporphyrin (4·08, 4·32); 1 : 3 : 5 : 7-tetramethyl-2 : 4 : 6 : 8-tetraethylporphin (2·1); 2 : 3 : 6 : 7-tetramethyl-1 : 4 : 5 : 8-tetraethylporphin (2·05, 2·2); 1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetraethylporphin (2·1); coproporphyrin ester (synthetic) (4·32); iron complex salt of tetramethylhæmatoporphyrin (5·82); uroporphyrin ester (9·46); *iso*uroporphyrin ester (7·37). From the results, it appears that either the experimental material is insufficient to allow deductions with regard to the constitution of the blood pigments or that the porphyrins and hæmins are able to unite with hydrogen in such a manner that production of methane ensues with Grignard's reagents, particularly in the presence of pyridine. Possibly the Zerewitinov method is not applicable to complex unsaturated systems. H. Wren.

Pyridine-hæmins. A. Hamsík (Z. physiol. Chem., 1927, **169**, 64—72).—From a solution of hæmin chloride in pyridine, ether slowly precipitates large crystals and it is suggested that a pyridine–hæmin chloride compound has been formed. These crystals become much smaller when washed with ether or alcohol and hæmin chloride is regenerated. Hæmin acetate forms a partly crystalline similar precipitate which, with ether and alcohol, yields a mixture of oxyhæmin and oxyhæmin anhydride. This accounts for the high iron content of hæmin acetate preparations (cf. Küster and Gerlach, A., 1922, i, 596) and their incomplete solubility in pyridine. Hæmin formate, acetate, oxalate, and sulphate, but not hæmin chloride, decompose when heated in pyridine–chloroform solution, giving oxyhæmin and oxyhæmin anhydride. A. Wormall.

Blood pigments. VI. Relation between hæmin, hæmochromogen, and porphyrin. F. Haurowitz (Z. physiol. Chem., 1927, **169**, 91—101; cf. this vol., 686).—Porphyrins can be converted into the corresponding hæmins by ferrous or ferric salts in presence of acetic acid, but with butyric and valeric acids ferrous iron only is introduced. It is concluded that in the acetic acid solution a reduction occurs which is not effected primarily on the ferric salt, but probably on a loose intermediate compound of iron and porphyrin. Hæmatin is not formed on acidification of a solution of hæmochromogen in absence of oxidising agents. Hæmin chloride in pyridine solution can be reduced to hæmochromogen by sodium in the absence of oxygen or compounds containing oxygen, and the hæmochromogen formed contains 4O per mol. The formulæ of porphyrin and hæmin are discussed in relation to the active hydrogen atoms present and the combination of bi- or tervalent iron. A. Wormall.

Electrodialysis of proteins. W. Pauli (Biochem. Z., 1927, **187**, 403—409).—A reply to Dhéré (this vol., 423). P. W. Clutterbuck.

Phosphorus nucleus of ovovitellin. S. Posternak and T. Posternak (Compt. rend., 1927, **185**, 615—617; cf. this vol., 273, 582).—β_1-Ovotyrin, $C_{72}H_{144}O_{78}N_{24}P_{12}$, is hydrolysed by boiling 25% hydrochloric acid to phosphoric acid (12 mols.), pyruvic acid (1·6 mols.), histidine (0·7 mol.), arginine (0·62 mol.), lysine (0·75 mols.), *l*-serine, $[\alpha]_D^{22}$ −6·67° (7·9 mols.), and ammonia (4·9 mols.). The ammonia and pyruvic acid are probably produced by deamination of part of the serine, and when allowance is made for this, serine and phosphoric acid appear in almost equimolecular amounts. Hydrolysis of β_1-ovotyrin with 15% sulphuric acid affords polypeptides with N : P ratios of 1·1—1·3 together with phosphoric acid, serine, and its deamination products. Serine has not previously been isolated directly from a protein hydrolysate. G. A. C. Gough.

Determination of organic material by oxidation with chromic acid. T. von Fellenberg (Biochem. Z., 1927, **188**, 365—391).—An attempt to extend the use of Bang's micro-determination of fat by combustion with dichromate and sulphuric acid to a large number of organic substances gives the following results. Formic acid yields quantitatively carbon dioxide, acetic acid is not attacked, whilst with propionic and butyric acids more oxygen is used than is required to convert them into acetic acid. Higher fatty acids give very complex results. Malic, tartaric, and citric acids give carbon dioxide quantitatively. Oxalic acid is not attacked and succinic acid only slightly so. Soluble carbohydrates and polyhydric alcohols are oxidised quantitatively, but ethyl, propyl, and *iso*butyl alcohols form one molecule of acetic acid and dimethylethylenecarbinol forms two molecules. Benzoic acid is oxidised quantitatively and salicylic acid almost so. Glycine and alanine are scarcely attacked, whilst tyrosine is oxidised almost completely. Proteins give different values, the smallest being that of gelatin (glycine-rich). The method is adapted for determination of alcohol in acetic acid and of methyl alcohol mixed with a small amount of ethyl alcohol. P. W. Clutterbuck.

Determination of phenylacetylene. F. Hein and A. Meyer (Z. anal. Chem., 1927, **72**, 30—31).—Phenylacetylene is precipitated from an alcoholic solution as its copper compound by an ammoniacal solution of cuprous chloride. The precipitate is filtered into a glass Gooch crucible, washed with water, alcohol, and ether, and dried in a vacuum over concentrated sulphuric acid. This determination can be checked by treating the precipitate with a solution of ferric ammonium sulphate in dilute sulphuric acid, and titrating the ferrous sulphate formed with permanganate. The error is less than 1%. F. S. Hawkins.

Volumetric determination of hydroxyl groups in organic compounds. V. L. Peterson and E. S. West (J. Biol. Chem., 1927, **74**, 379—383).—Hydroxyl groups in sugars and other organic compounds may be determined by heating the compound with a known amount of acetic anhydride and pyridine until acetylation is complete, dilution of the reaction mixture with water, and titration of the excess acetic acid. C. R. Harington.

Determination of *iso*propyl alcohol in presence of acetone, and of methylethyl ketone in presence of *sec.*-butyl alcohol. H. A. Cassar (Ind. Eng. Chem., 1927, **19**, 1061—1062).—Rapid determinations of *iso*propyl alcohol in presence of acetone are effected by quantitative oxidation of the alcohol to acetone with chromic acid solution and back-titration of the excess of chromic acid. The acetone is determined by Messinger's method (J.S.C.I., 1920, 280A), applying a correction of 1—2% for the *iso*propyl alcohol present. *sec.*-Butyl alcohol may be determined in presence of methyl ethyl ketone by this method, but for the determination of methyl ethyl ketone Messinger's method gives high results and a modification thereof is suggested. R. Brightman.

Determination of diacetyl and acetylmethylcarbinol. C. B. van Niel (Biochem. Z., 1927, **187**, 472—478).—A slight modification of the usual method for determination of diacetyl and acetyl methylcarbinol as nickel dimethylglyoxime is described.

P. W. Clutterbuck.

Determination of the methoxyl content of volatile substances in dilute aqueous solutions containing aldehydes. K. Wiesler (Z. angew. Chem., 1927, **40**, 975).—The ordinary Zeisel method for the determination of the methoxyl group fails in the presence of aldehydes but good results are obtained by the following modification: The solution is mixed with freshly-precipitated silver oxide and distilled to two thirds its volume, the distillate being collected in a second distillation flask containing 10 c.c. of hydriodic acid (*d* 1·96). The latter flask is heated gently on the water-bath and is provided with a reflux air condenser connected at its upper end to a small washing flask containing a suspension of red phosphorus in water, whence the vapours pass into a measured volume of 0·1*N*-alcoholic silver nitrate. Carbon dioxide is passed through the apparatus throughout the determination. The deposited silver iodide is collected and weighed as usual.

A. R. Powell.

Detection of chlorophyll by means of the analytical quartz lamp. P. W. Danckwortt and E. Pfau (Arch. Pharm., 1927, **265**, 560—562).—Small quantities of powdered drugs or tinctures are treated with water and ether and the mixture is illuminated by the quartz lamp. If chlorophyll is present, even in small quantities, the ethereal solution shows a vivid, red fluorescence. The red colour is not given by carotin or xanthophyll. It is suggested that this reaction might be utilised in separating the two components of chlorophyll (cf. Willstätter and Hug, A., 1911, i, 393), since on treating a methyl-alcoholic solution of crude chlorophyll with light petroleum, the latter shows a gradually increasing fluorescence, whilst the fluorescence of the alcoholic solution gradually diminishes.

S. Coffey.

Determination of selenium in organic compounds. E. H. Shaw and E. E. Reid (J. Amer. Chem. Soc., 1927, **49**, 2330—2334).—The sample (0·2—0·4 g.) is mixed with sucrose (0·4 g.), potassium nitrate (0·2 g.), and sodium peroxide (14 g.), the mixture covered with a thin layer of sodium peroxide, and the whole burnt in the Parr bomb in the usual manner. The mass is dissolved in water and the solution boiled, cooled, acidified with hydrochloric acid, filtered, and diluted to 350 c.c. The selenium is then precipitated (*a*) by adding 200 c.c. of hydrochloric acid, heating the mixture not quite to the b. p., and passing in a rapid stream of sulphur dioxide, or (*b*) by adding 50 c.c. of hydrochloric acid and 3 g. of potassium iodide, and gently boiling the mixture, with replacement of evaporated water, until the excess of iodine is volatilised. The selenium is collected on a Gooch crucible, washed with alcohol and water, and dried at 110—120°. The greatest errors recorded in 25 analyses are +0·17% and −0·33%.

F. G. Willson.

Biochemistry.

Regulation of respiration. IX. Relation of tissue acidity and blood acidity to volume flow of blood as illustrated by hæmorrhage and re-injection. A. B. Hertzman and R. Gesell (Amer. J. Physiol., 1927, **81**, 563—578).—The changes in acidity of the circulating arterial and venous blood were determined by the manganese dioxide electrode and checked by the hydrogen electrode. Hæmorrhage elicited increased alkalinity of the arterial blood and increased acidity of the venous, decreased oxygen consumption, and increased pulmonary ventilation. Reinjection reversed all these changes. The importance of volume flow of blood and acidity in the control of the normal acid-base equilibrium is emphasised.

R. K. Cannan.

Effects of respiratory gases on density of blood and other fluids. W. F. Hamilton and H. G. Barbour (J. Biol. Chem., 1927, **74**, 553—556).—Dissolution of carbon dioxide in water, alkaline salt solution, blood-serum, and whole blood increases the density of these liquids, the increases being in ascending order of magnitude owing to the effect of chemical reactions in causing the increase of volume per c.c. of carbon dioxide to be progressively less. In the case of oxygen, the dissolution of which in whole blood is accompanied by actual diminution in volume, the effect on the density is very much greater.

C. R. Harington.

Effect of asphyxia on blood. J. B. Collip (Trans. Roy. Soc. Canada, 1927, [iii], **21**, V, 151).—Asphyxia produces a slight but definite increase in the serum-calcium and in the inorganic phosphorus content of the blood, and a decrease in blood-p_H of from 0·15 to 0·35 of a unit.

H. D. Kay.

Micro-determination of carbon dioxide in blood and other solutions. Efficiency of paraffin in preventing loss of carbon dioxide. D. Raffel (J. Biol. Chem., 1927, **74**, 839—849).—An apparatus is described in which the carbon dioxide in a small amount of liquid is liberated and aspirated into standard barium hydroxide solution, the excess of which is then titrated with the aid of a micro-titration syringe. The method is applicable to determination of 0·1—0·5 c.c. of carbon dioxide with a maximum error of ±2%. The loss of carbon dioxide from normal blood-serum kept under liquid paraffin does not exceed 2% in 24 hrs., although in presence of higher concentrations of carbon dioxide the loss may be 10%.

C. R. Harington.

Oxidation processes in blood-serum. T. R. Parsons and W. Parsons (Biochem. J., 1927, **21**, 1194—1205).—In the presence of certain oxidising agents such as potassium ferricyanide and potassium permanganate, human blood-serum absorbs oxygen at the rate of about 0·25 c.c. per c.c. per hour when shaken with air at the ordinary temperature. The same effect is observed in the presence of ferric salts in alkaline solution, but not with ferric salts in acid solution nor with dichromate at any reaction. Extraction with ether reduces the rate at which the serum will absorb oxygen in this way, but this can be restored in some measure by the re-addition of the extracted material, provided that this is recovered by evaporation of the ether extract in an oxygen-free atmosphere. The oxidisable substances are precipitated completely by full saturation with ammonium sulphates, partly by half saturation, and scarcely at all by one third saturation with ammonium sulphate. The substances primarily responsible for the effect are therefore most probably lipins. S. S. Zilva.

Action of essential oils on the formation of methæmoglobin. E. Dessemontet (J. Pharm. Exp. Ther., 1927, **31**, 377—386).—The formation of methæmoglobin in a mixture of defibrinated blood and various essential oils has been studied. Oils containing eugenol, safrole, *iso*safrole, linalool, anethole, anisole, and carvene induce the formation of methæmoglobin within 24 hrs., whilst menthol, thymol, borneol, oil of cloves (eugenol-free), methyl salicylate, and camphor produce no reaction. It is therefore suggested that this property of the alcoholic constituents of essential oils depends on the presence of unsaturated side-chains and on the position of the ethylenic linkings. No relation between velocity of formation of methæmoglobin and degree of unsaturation has been detected in carvene, carvone, pinene, vanillin, and cineole. There appears to be a definite pressure of oxygen specific for linalool, for carvene, and for pinene, at which the formation of methæmoglobin is an optimum. E. A. Lunt.

Calcium and potassium content of the blood. E. Kylin (Acta med. Scand., Suppl., 1927, [xix], 1—112).—The normal calcium content of the blood is 10·6—12·0 (average 11·13) mg. %; below 21 years the average is 11·6 mg., and above 41 years 10·83 mg. %. The regulation of the calcium content is hormonal. The normal potassium content of the blood is 18—24 (average 20·7) mg. %; in pathological conditions the calcium content is usually diminished and the potassium content increased, but in diabetes high blood-calcium values are observed. The response of the human organism to adrenaline is largely dependent on the potassium : calcium ratio.

Chemical Abstracts.

Calcium content of blood-serum of rat. A. T. Cameron and J. E. Williamson (Trans. Roy. Soc. Canada, 1927, [iii], **21**, V, 139—145).—The calcium content of the serum of the normal white rat (on a mixed diet), determined during summer or winter, shows an average value corresponding with that of other mammals, but with greater individual variations. No difference for sex is observable. Values determined in late spring are definitely lower (average 2 mg. lower) while still showing about the same degree of variation. H. D. Kay.

Determination of calcium in blood and urine. J. S. Sharpe (Edinburgh Med. J., 1926, **33**, 27—30). —The cloudiness produced by ammonium oxalate in a protein-free solution in glycerol is compared nephelometrically with a standard. The method is accurate to 0·5 mg. for 10—15 mg. in 100 c.c.

Chemical Abstracts.

Effects of dialysis and of ether extraction on diffusibility of calcium in human blood-serum. R. F. Loeb and E. G. Nichols (J. Biol. Chem., 1927, **74**, 645—649).—Normal human blood-serum, the same serum dialysed until free from calcium, and the same serum extracted with ether, were dialysed under similar conditions against calcium chloride solution; in all cases the equilibrium concentration of calcium attained in the serum was higher than expected from the Donnan equilibrium, the deviation being greatest in the serum extracted with ether and least in the dialysed serum. The view is therefore supported that un-ionised compounds of calcium with protein account for the unequal distribution of calcium attained on dialysing blood-serum against water.

C. R. Harington.

Free sugar of the blood-plasma. E. J. Bigwood and A. Wuillot (Bull. Soc. chim., 1927, **9**, 867—883).—When blood-plasma or -serum is incubated with yeast for ½—1 hr., the reducing power of the deproteinised fluid, determined by the method of Hagedorn and Jensen (cf. A., 1923, ii, 265, 440) does not completely disappear, but becomes approximately constant at a value corresponding with 0·0—0·03% of dextrose. The residual reducing power of the serum of rabbits, dogs, and man is on the average 13·3%, 13·5%, and 14·3%, respectively, of the original reducing power. The total sugar of the cerebrospinal fluid is on the average 67% of that of the blood, but the fermentable sugar of the cerebrospinal fluid is 75% of that of the blood. Conclusive evidence as to the nature of the non-fermentable reducing material was not obtained, but the possibility that it may be uric acid has been excluded, although uric acid may be responsible for the abnormally high values obtained in cases of nephritis.

W. O. Kermack.

Blood-sugar. III. Non-dextrose of blood-filtrates. B. Sjollema (Biochem. Z., 1927, **188**, 465—474).—Further investigations (cf. this vol., 476, 789) of the non-dextrose reducing substances of blood show that when blood-filtrates are shaken with charcoal and acetic acid the ergothioneine and glutathione present cause no appreciable error in the blood-sugar determination with ferricyanide. Both dextrose and the non-dextrose reducing substance reduce ferricyanide but little when the p_H is smaller than 9·5. Dextrose remains completely in solution when both trichloroacetic and tungstic acids are used as precipitants, but a non-dextrose reducing substance is precipitated by the former, but not by the latter. Ergothioneine (0·1%) is not precipitated by trichloroacetic acid. Sulphur determinations of the fractions show that blood-corpuscles contain other non-dextrose reducing substances than ergothioneine and glutathione. An adaptation of the Folin–Wu method is given for determination of dextrose in blood-filtrates. P. W. Clutterbuck.

Total sugar of blood and urine. M. R. Everett, H. A. Shoemaker, and F. Sheppard (J. Biol. Chem., 1927, **74**, 739—759).—The low results obtained by

Folin and Berglund (A., 1922, ii, 400) for the total sugar of blood and urine were due to the interfering effect of the hydrochloric acid used in the hydrolysis, and of silicates in the sodium hydroxide employed for neutralisation, on the subsequent colorimetric determination. Satisfactory results are obtained by hydrolysis with sulphuric acid and neutralisation with potassium hydroxide free from silica. C. R. HARINGTON.

Plasma-proteins of normal dogs. C. W. MATTHEW (J. Biol. Chem., 1927, **74**, 557—560).—The blood-plasma of normal dogs contains, on the average, 0·45% of fibrin, 4·64% of albumin, and 2·12% of globulin. For any one animal the figures remain practically constant. C. R. HARINGTON.

Effect of hydrogen-ion concentration and protein concentration on the osmotic pressure of serum-proteins. J. MARRACK and L. F. HEWITT (Biochem. J., 1927, **21**, 1129—1140).—The osmotic pressure of serum-proteins rises with increase of p_H to an extent which is less than that calculated for ideal solutions if the compound of protein and base is fully dissociated. The activity coefficients of anions are slightly reduced by the presence of protein in solution. The excess of diffusible ions in the protein solution, due to the Donnan effect, and deviations from the state of ideal solution cause the osmotic pressures of proteins not to bear a linear relation to the protein concentration. It is not necessary to suppose that proteins in solution occupy a greater bulk than they do when dry (cf. Verney, A., 1926, 856). S. S. ZILVA.

Rôle of tissues in maintaining acid–base equilibrium of blood. I. Effect of isolated muscle-tissue. II. Effect of hind-leg preparation. M. G. BANUS and L. N. KATZ (Amer. J. Physiol., 1927, **81**, 628—643, 644—649).—I. Apparatus is described for the perfusion of isolated organs with oxygenated non-acapnic blood under controlled conditions. The gastrocnemius of the dog was perfused with blood rendered acid by addition of hydrochloric acid and the changes were observed in the p_H, chloride content, and carbon dioxide-combining power at constant carbon dioxide tension. No measurable exchange of chloride or alkaline radicals occurred between blood and tissues, and it is concluded that at constant carbon dioxide tension under the experimental conditions muscle does not increase the buffering power of the blood.

II. When the hind-leg was perfused there was some increase in the p_H and carbon dioxide-combining power of the blood, but no change in the chloride-ion concentration. The nature of this buffering effect of some of the tissues of the hind-leg is unknown.
R. K. CANNAN.

Distribution of nitrogen in the blood and urine of the turtle. F. H. WILEY and H. B. LEWIS (Amer. J. Physiol., 1927, **81**, 692—695).—Determinations of the distribution of the nitrogen of the blood, urine, and tissues of the turtle (*Chrysemys pinta*) are reported. The turtle excreted considerable amounts of both urea and uric acid, so that, as regards nitrogen metabolism, it is intermediate between mammals and the reptiles of arid regions.
R. K. CANNAN.

Action of hirudin on thrombin. J. O. W. BARRATT (J. Physiol., 1927, **64**, 47—53).—From determinations of the amounts of thrombin inactivated when solutions of varying concentrations of thrombin and hirudin are mixed, it is concluded that the reaction is of the same type as that of a weak acid with a weak base. R. K. CANNAN.

Determination of catalase in blood and animal tissues. E. GAGARINA (Biochem. Z., 1927, **188**, 284).—A claim of priority over Golzov and Jankovsky (this vol., 689; cf. J. Exp. Biol. Med., 1926, **7**, 33).
P. W. CLUTTERBUCK.

Immunological behaviour of mucoids. J. H. LEWES and H. G. WELLS (J. Infect. Dis., 1926, **40**, 316).—Various mucoids from eggs and blood are antigenic although less so than most other proteins of equal solubility. The ovomucoids from goose and duck eggs were the most closely related to each other, as were also the hen and guinea-fowl mucoids. Seromucoids from sheep, ox, and dog blood were easily distinguishable from one another and showed but little relationship to the ovomucoids.
CHEMICAL ABSTRACTS.

Isolation of substances with immune properties. A. LOCKE and E. R. MAIN (J. Infect. Dis., 1926, **39**, 848).—Diphtheria antitoxin was purified by isoelectric fractionation of the Ramon toxin-antitoxin precipitate. These preparations contain 0·0005—0·0015 mg. of nitrogen per antitoxin unit, have the anaphylactogenic character of horse-serum protein, and are injured by boiling as well as by ageing.
CHEMICAL ABSTRACTS.

Composition of blood and tissues of fœtal calf. J. B. COLLIP (Trans. Roy. Soc. Canada, 1927, [iii], **21**, V, 147—150).—Very high values for serum-calcium and inorganic phosphorus are found, partly due to asphyxia. Whole blood shows a higher non-protein nitrogen figure than does serum, although the urea values for the two fluids are almost identical. Fœtal serum has a low protein content. Amniotic fluid shows great variation in the calcium content, which is apparently unrelated to the blood-calcium value. The fœtal heart-muscle shows a relatively high glycogen content which diminishes with the age of the fœtus. The glycogen content of the skeletal muscle, on the contrary, increases with the age of the fœtus. H. D. KAY.

Mechanism of the Golgi black reaction [of animal tissues]. A. MOSCHINI (Arch. Farm. sperim. Sci. aff., 1927, **43**, 97—114).—Chemical theories of this reaction, the development of a black colour in sections which have been treated with potassium dichromate solution, kept for a few days, and treated with a silver nitrate solution, and of the modified reaction, in which the second reagent applied is mercuric chloride, followed by ammonia or other reagents, are discussed. It is suggested that, by the reducing action of the tissue, potassium chromite is formed, and that this reacts with reagents subsequently applied. E. W. WIGNALL.

Colloid chemical and morphological study of chromosomes. Y. KUWADA and T. SAKAMURA (Protoplasma, 1926, **1**, 239—254).
CHEMICAL ABSTRACTS.

Iron content of animal tissues. C. A. Elvehjem and W. H. Peterson (J. Biol. Chem., 1927, **74**, 433—441).—Iron is determined directly in a sample of tissue and in a duplicate sample to which a known amount of iron has been added; if the recovery of the added iron in the second case be not quantitative, the determination is repeated after preliminary removal of phosphates (cf. A., 1926, 443). Figures are given for the iron content of various tissues of the ox and for that of the spleen, liver, and kidney of different animals; the latter organs are rich in iron as compared with the other tissues.

C. R. Harington.

Chemical composition of brain. II. G. V. Stuckert (Cordoba Medica, 1927, **2**, 13—19).—Data are given for the chemical composition of the cerebrum, medulla oblongata, and cerebellum of ox-brain. No marked differences exist in respect of their content of total lipins, proteins, and soluble extractives. The individual lipins occur in different proportions. For example, the cerebellum contains twice as much phosphatide as the medulla oblongata, the difference being attributed chiefly to lecithins and kephalins. The medulla oblongata is rich in fats and fatty acids. G. W. Robinson.

Preparation of kephalin. P. A. Levene and I. P. Rolf (J. Biol. Chem., 1927, **74**, 713—714).—Practical details are given for the preparation of kephalin from brain. C. R. Harington.

Iodine content of the thyroid gland of various breeds of ox and its relationship to the condition of these glands. T. von Fellenberg and H. Pacher (Biochem. Z., 1927, **188**, 339—364).—Of 80 ox thyroid glands examined, the weight varied from 8·7 to 130·4 g., the lower values relating predominantly to the English shorthorn variety and the heavier to the Swiss and Austrian (brown, Simmental, etc.) varieties. The relative iodine content is not directly related to the weight of the gland, the brown and shorthorn varieties having a higher iodine content than the heavier glands. The absolute iodine content generally increases with increasing weight. The colloid content and size of follicle is correlated rather with the iodine content than with the weight of gland. It was not possible, however, to establish a definite race variation or variation due to origin and condition.

P. W. Clutterbuck.

Enzymes of the omentum. J. M. Goldberg (Biochem. Z., 1927, **188**, 475—480).—Enzymes possessing proteolytic, lipolytic, and faint amylolytic actions are detected in the omentum of dogs.

P. W. Clutterbuck.

Ultra-violet absorption spectra of certain physiological fluids. M. C. Reinhard (J. Gen. Physiol., 1927, **11**, 1—6).—Ultra-violet absorption curves are given of human bile, saliva, pericardial fluid, urine, and hæmoglobin. W. O. Kermack.

Spectrophotometric determinations of purified bilirubin. C. Sheard, F. C. Mann, and J. L. Bollman (Amer. J. Physiol., 1927, **81**, 774—781).—Spectrophotometric comparison and tests of the solubilities of purified bilirubin and the pigment in the bile and blood of normal and jaundiced animals further confirm their identity. R. K. Cannan.

Surface energy of some physiological fluids. I. N. Vedenski (Biochem. Z., 1927, **188**, 270—278).—Physiological fluids may be surface-inactive (urine, gastric juice), surface-active (blood, milk, bile, saliva), or may hold a mean position (aqueous humour, cerebrospinal fluid). The total surface energy of surface-active liquids shows a maximum at a definite temperature, but of surface-inactive liquids does not change with temperature. The surface tension of the less surface-active physiological liquids decreases directly with the temperature, but that of the surface-active liquids changes according to a typical curve. The total surface energy of milk shows a sharp increase at 60°.

P. W. Clutterbuck.

Measurement of colloid–osmotic pressure in biological fluids. A. Krogh and F. Nakazawa (Biochem. Z., 1927, **188**, 241—258).—Two simple methods, each requiring 0·3—0·5 c.c. of liquid, are described for the determination of colloid-osmotic pressure and are used for human, horse, and frog serum, human urine, etc. The methods are accurate to within 10 mm. pressure of water. The results are not affected by changes in salt concentration from 0·5 to 1·5% and of p_H from 7 to 8, but at a lower p_H the pressure decreases. Carbonic acid does not exert any specific effect on the colloid-osmotic pressure. The latter decreases more quickly on dilution than the colloid concentration. Curves showing the relationship of the pressure per cent. and the percentage protein are almost linear and may be used for the investigation of pathological sera. Addition of caffeine does not affect the colloid-osmotic pressure of serum. P. W. Clutterbuck.

Amylase content of dog saliva and the influence of diet. O. Galehr (Fermentforsch., 1927, **9**, 224—227).—In view of the conflicting reports as to whether dog's saliva contains a diastatic enzyme, investigations have been made on the saliva of three dogs which have been fed almost exclusively on carbohydrates for several months and that of three control dogs fed on a carbohydrate-free diet. It is found that dog saliva has no "dextrinase," but contains very small amounts of a "polyamylase." The amount of this diastase secreted bears no relationship to the diet and no increase of the starch-splitting activity occurs during long carbohydrate feeding. A. Wormall.

Influence of diet on the inorganic constituents of human saliva. G. W. Clark, J. S. Shell, J. B. Josephson, and M. E. Stockle (Dental Cosmos, 1927, **69**, 500—513, 605—617).—The acid–base balance of the ration had little influence on the ability of adults to retain bases. Diets containing green foods increased the retention of calcium, phosphorus, sulphur, and nitrogen. There is no relationship between the quantity of an element ingested or retained and the quantity in the circulating blood or resting saliva, or between the concentrations of inorganic constituents in the blood and in the saliva. The concentration of inorganic phosphorus was 4—5 times as great in the saliva as in blood-plasma. Chemical Abstracts.

Gastric digestion. Relation of volume, hydrogen-ion concentration, and buffer capacity of the test meal to the gastric contents. W. A. Standish, G. R. Cowgill, and A. T. Shohl (Amer. J. Physiol., 1927, **81**, 696—706).—The amount of gastric juice varies with the volume and concentration of the meal. The p_H of the gastric contents remains nearly constant at a value of about 4 throughout the meal. The buffer capacity of the stomach contents likewise remains fairly constant after an initial rise. R. K. Cannan.

Constituents of sweat, urine, and blood. III. Urea. G. A. Talbert, J. R. Finkle, and S. S. Katsuki (Amer. J. Physiol., 1927, **82**, 153—156).—Tables are given of the urea-nitrogen found in the blood, urine, and sweat of 17 subjects.

R. K. Cannan.

Chlorine and sodium in the milk of mammals. L. Barthe and E. Dufilho (Compt. rend., 1927, **185**, 613—615; cf. B., 1926, 644).—The milk of women contains 1·162 g. of chlorine per litre on the 6th day of lactation. This value rises to a maximum of 1·349 g. on the 12th day and falls to 0·923 after 9 months, at which time the milk contains 0·154 g. of sodium per litre. Whilst the amount of chlorine seems to be large during the colostral period, sodium does not appear in considerable amounts until the 45th day. Other elements than sodium are in combination with the chlorine, since the milk of mares, which contains 0·568—1·207 g. of chlorine per litre, contains only traces of sodium.

G. A. C. Gough.

Urinary acidity. Electrometric titration of urine. S. Morgulis and W. R. Hamsa (J. Biol. Chem., 1927, **74**, 851—861).—Urine is titrated electrometrically against a buffer solution of p_H 7·4, using the quinhydrone electrode. Much lower values for the acidity of the urine are thus obtained than by the method of titration with phenolphthalein as indicator, owing to the increasing buffering capacity of urine as the reaction becomes more alkaline than p_H 7·4. C. R. Harington.

Determination of acetone in urine. G. Kleyer (Pharm. Ztg., 1927, **72**, 1262—1263).—Details are given for carrying out adapted Rothera and the more delicate Reichardt and Frommer–Emilewicz (salicylaldehyde) tests. P. W. Clutterbuck.

Nitrogenous constituents of hen urine. R. E. Davis (J. Biol. Chem., 1927, **74**, 509—513).—A technique is described for the collection of hen's urine without contamination with fæces. In such urine there was found, on the average, total nitrogen 100 mg. %, of which 62·9% was uric acid, 10·4% carbamide, 17·3% ammonia, and 8·0% creatinine.

C. R. Harington.

Salicylsulphonic acid as a protein reagent. G. Roche (Pharm. Ztg., 1927, **72**, 1263).—A claim of priority as the first to suggest the use of sodium salicylsulphonate as a test for protein in urine.

P. W. Clutterbuck.

Determination of quinine [in urine] by Hartmann and Zila's method. I. A. Smorodincev and A. N. Adova (Biochem. Z., 1927, **188**, 279—283).—This method (A., 1918, i, 328) does not give accurate results and possesses no advantage over the simple extraction with ether.

P. W. Clutterbuck.

Proteases of urine. II. Proteolytic action of urine in protracted starvation and with experimentally increased protein catabolism. O. Peczenik (Fermentforsch., 1927, **9**, 166—191; cf. A., 1926, 1275).—After prolonged starvation the urine of the rat, guinea-pig, and cat has a proteolytic action which varies with the type of food administered before the fast. Rats which are starved after a long meat diet give a urine which has strong peptic and tryptic activities, and the protein usage, as determined by the total nitrogen of the urine, is much higher than with rats which are starved after a milk diet. After injection of protein (caseinogen and milk), during prolonged starvation, and under experimental influences which lead to an increased cell disintegration, protein derivatives pass into the circulation and cause secretion of pepsinogen.

A. Wormall.

Distribution of protein in blood in experimental anæmia. M. Bodansky, S. W. Morse, V. C. Kiech, and R. B. Bramkamp (J. Biol. Chem., 1927, **74**, 463—471).—Figures are given for the distribution of the various protein fractions in dogs' blood-serum, classified by the method of Howe (A., 1922, ii, 172). More than half of the protein obtained from the red blood-corpuscles by hæmolysis can be salted out within the limits of precipitation of the globulins. In anæmia induced by administration of acetylphenylhydrazine, the albumin : globulin ratio of the serum decreased, whilst the content of fibrinogen, euglobulin, and the protein fraction precipitable by 0·75*M*-sodium sulphate increased.

C. R. Harington.

Pernicious anæmia. III. Contrast of the chloride contents of corpuscles and plasma in pernicious anæmia and other conditions. A. T. Cameron and M. E. Foster (Canad. Med. Assoc. J., 1927, **17**, 670—675).—The plasma-chlorine values in the anæmias are normal; cell-chlorine values in pernicious anæmia are low, but in secondary anæmia are high. Both plasma- and cell-chlorine values are low in diabetes and other conditions where increase of blood constituents requires osmotic compensation, and in acute intestinal obstruction.

Chemical Abstracts.

Glycolysis in leucæmic blood. H. L. Schmitz and E. C. Glover (J. Biol. Chem., 1927, **74**, 761—773).—In normal blood the rate of glycolysis is 15—23 mg. % per hr. and is independent of the initial concentration of dextrose. In cases of myelogenous leucæmia rates of glycolysis of 18—84 mg. % per hr. were observed, with an approximate parallelism between the rate of glycolysis and the leucocyte count. In lymphatic leucæmia, the rate was not increased. Addition of potassium cyanide to the blood accelerates glycolysis markedly in myelogenous leucæmia and slightly in lymphatic leucæmia, but is almost without effect in normal blood.

C. R. Harington.

Cerebral and cardiac glycogen and muscular lactic acid in adrenalectomised rats. B. A. Houssay and P. Mazzocco (Rev. Soc. Argentina

Biol., 1927, **3**, 491—500).—Extirpation of the adrenals in rats is without marked effect on cardiac and cerebral glycogen or on muscular lactic acid and lactacidogen. The increase in muscular lactic acid after 1 min. tetanisation is greater than in the controls. The excess of lactic acid disappears within 5 min., slightly more rapidly in the rats deprived of their adrenals than in the controls.

G. W. Robinson.

Fate of sugar in the animal body. VII. Carbohydrate metabolism of adrenalectomised rats and mice. C. F. Cori and G. T. Cori (J. Biol. Chem., 1927, **74**, 473—494).—In adrenalectomised rats, a starvation period of 24 hrs. caused almost complete disappearance of glycogen from the liver and a marked fall in the blood-sugar, the glycogen of the muscles remaining unchanged. Administration of dextrose to such animals resulted in normal synthesis of glycogen, although the rate of absorption of the dextrose was slower than in the normal animal. The relationship between dextrose oxidised and converted into glycogen after administration of dextrose to adrenalectomised rats with and without insulin was similar to that previously observed for normal rats (A., 1926, 1271); further, the effect of insulin in decreasing the liver-glycogen of normal fasting mice was observed also in adrenalectomised mice. These effects of insulin are therefore to be regarded as specific to this hormone and are independent of the effect of adrenaline. C. R. Harington.

Calcium metabolism in diabetes. E. Kylin (Acta Med. Scand., 1927, **66**, 197—206).—In diabetes of pancreatic origin the blood-calcium is high, falling after injection of insulin with elimination in the urine. Chemical Abstracts.

Acid production in diabetes. M. Odin (Acta Med. Scand., Suppl., 1927, XVIII, 1—573).—In mild diabetes the carbon dioxide capacity of the blood (C), the total acid excretion, and the p_{H} of the urine are normal, but there is increased acetonuria; in severe diabetes C is generally low. The total acidity of the urine is less when C is less than 30 vol.-% than when it is 30—39 vol.-%. In coma, C is always below 30 vol.-%; when it is below 25 vol.-% there is always coma. During coma there is a rise in the blood-sugar value. The urinary acid and acetone excretion often decreases during coma. Coma due to lack of insulin is ascribed to a lag in the production of ammonia. A fat–vegetable diet causes C to rise, until the urine actually becomes alkaline. Œdema is considered to be due to an excessive value of C. Changes in the value of C, the total acidity and p_{H} of the urine following a meal have been followed for normal and diabetic subjects. The effects on acid production of varying the diet have also been investigated.

Chemical Abstracts.

Cholesterol content of the blood-plasma as an index of progress in insulin-treated diabetics. I. M. Rabinowitch (Canad. Med. Assoc. J., 1927, **17**, 171—175).—The blood-lipin is a better index of the course of diabetes than is the blood-sugar. An increased blood-cholesterol value is not compatible with an improvement in pancreatic function.

Chemical Abstracts.

Diagnostic value of the diastatic enzyme of the urine. L. Kreyberg (Norsk Mag. Lægevidenskap., 1926, **24**, 992—1003).—Acute diseases of the pancreas and salivary glands are usually accompanied by a considerable rise in the diastatic index of the urine. The normal index (number of c.c. of 1 in 10^3 starch solution transformed by 1 c.c. of urine) ranges between 4 and 64. Chemical Abstracts.

Experimental lead hæmatoporphyria. H. Liebig (Arch. exp. Path. Pharm., 1927, **125**, 16—28).—The administration of lead by mouth or intraperitoneally to rabbits causes them to excrete hæmatoporphyrin in the urine and fæces. The origin of the pigment appears to be in the bone-marrow and it is not secreted in the bile as is the case in sulphonal poisoning. A method is given for the determination of hæmatoporphyrin in the urine and fæces. W. O. Kermack.

Chemical nature of the serum-globulin of the hæmatoporphyrin rabbit. M. Komatsu (J. Biochem. [Japan], 1927, **7**, 19—26).—The nitrogen : sulphur ratios of normal serum-albumin and -globulin of rabbits are 9·94 and 20·5, respectively. The sulphur content indicates that the globulin, which shows an increase of 50% in hæmatoporphyrin rabbits, retains its normal chemical constitution.

Chemical Abstracts.

Blood-chemistry in leprosy. II. Alkali reserve. E. M. Parás (Philippine J. Sci., 1927, **33**, 155—167).—The Van Slyke method for the determination of carbon dioxide capacity has been performed on 110 specimens of blood-plasma from cases of leprosy classified as follows: (*a*) leprosy without complication; (*b*) lepra reaction without alkali treatment; (*c*) lepra reaction with alkali treatment; (*e*) leprosy with tuberculosis; (*e*) leprosy with nephritis; (*f*) leprosy with miscellaneous complications such as malaria, anæmia, osteoarthritis, etc. The mean value obtained for the normal healthy adult was 70 vol.-% of carbon dioxide. The following results have been obtained respectively: (*a*) no significant variation from the normal mean, mean value for 41 cases 67·9; (*b*) no significant variation, mean value for 19 cases 66·5; (*c*) characteristic indications of alkalosis in some cases, mean value for 16 cases 75·7; (*d*) no significant variation, mean value for 7 cases 72; (*e*) significant reduction, mean value for 8 cases 61; (*f*) significant reduction, mean value for 19 cases 59·6. There appears to be no correlation between the alkali reserve, and the duration, type, or stage of the disease. E. A. Lunt.

Identity of urinary albumin. L. F. Hewitt (Biochem. J., 1927, **21**, 1109—1111).—Purified albumins excreted in the urine of patients with chronic nephritis or albuminuria of pregnancy have been isolated, purified, and examined for their rotatory power and dispersion. They do not differ in these respects from serum-albumin. S. S. Zilva.

Kidney phosphatase. II. The enzyme in disease. R. T. Brain and H. D. Kay (Biochem. J., 1927, **21**, 1104—1108).—Both in chronic nephritis in man and in acute experimental nephritis in rabbits the phosphatase activity of the renal tissue is markedly reduced. S. S. Zilva.

Prevention of tetany by oral administration of ammonium chloride. W. F. Wenner (Amer. J. Physiol., 1927, **81**, 612—619).—Oral administration of ammonium chloride prevents and cures tetany in parathyroidectomised dogs. Its action is due, probably, to an increased acidity of the blood and consequent rise in serum-calcium.

R. K. Cannan.

Decreased nitrogen secretion during pregnancy. S. Stefancsik (Magyar Orvosi Arch., 1927, 28, 156—160).—Accumulation of urea in the liver does not occur. Use of amino-acids by the fœtus accounts for the low concentration of these substances in the blood. Chemical Abstracts.

Theory of muscle contraction with *X*-ray diffraction patterns from relaxed and contracted muscles. J. H. Clark (Amer. J. Physiol., 1927, **82**, 181—194).—It is suggested that lactic acid production leads to contraction by reason of an abrupt conversion of the substance in the anisotropic bands from the liquid crystal into the solid crystal state. It is shown that under the influence of slight increases in acidity the myelin forms of ammonium oleate contract with the formation of acicular crystals. *X*-Ray diffraction patterns of relaxed and contracted muscles show two distinct differences. In the contracted state the zones, representing first, second, and third order reflexion from equidistant molecular planes, show a fairly well-defined ring at the edge and an increase in diameter. These differences suggest an approach to a microcrystalline state. The distance between the molecular planes is 9·5 Å. in the relaxed and 8·5 Å. in the contracted muscle. The distances probably refer to the widths of the molecules forming the equidistant planes. R. K. Cannan.

Dextrose and salt solutions recovered from Thiry-Vella loops. H. L. White and J. Rabinowitch (J. Biol. Chem., 1927, **74**, 449—454).—Solutions of dextrose in water or dilute sodium chloride were introduced into loops of the intestine of dogs with a Thiry-Vella fistula; after removal of the solution no mutarotation was observed. Slight differences which were sometimes observed between the reducing power and rotatory power of such solutions were accounted for by entrance into the solution from the gut of non-reducing lævorotatory or non-dextrose reducing substances. The results of Hewitt and Pryde (A., 1920, i, 508, 648) were therefore not confirmed.

C. R. Harington.

Effect of p_H on the respiratory exchange of the muscle of the frog. M. Comel (Atti R. Accad. Lincei, 1927, [vi], 5, 808—812).—The respiratory exchange in the muscle of the frog has been determined between the values p_H 9·1 and 3·0, using Jarisch's and McIlvaine's solutions for the buffering medium. Slight differences in the values obtained are reported, but in both cases the maximum respiratory exchange takes place at p_H 7·1. The use of McIlvaine's solution brings about a more rapid decrease in the respiratory exchange below p_H 5·3 than the use of Jarisch's solution. Variations in the respiratory quotient are also observed. E. A. Lunt.

Furan compounds derived from sugars. J. Karashima (Z. physiol. Chem., 1927, **169**, 278—296).—The administration of chitose to the dog, hen, frog, and rabbit leads to the excretion in the urine of small amounts of hydroxymethylpyromucic acid, the maximum yield being 6·3% of the chitose administered. That hydroxymethylpyromucic acid is one of the main products of metabolism of chitose appears improbable, however, since feeding with hydroxymethylfurfuraldehyde results in the excretion of 66·7% of the acid as hydroxymethylpyromucic acid. Chitonic acid and chitaric acid yield no hydroxymethylpyromucic acid in these feeding experiments. The preparation of *hydroxymethylpyromucyl chloride* (5-*hydroxymethylfuran*-1-*carboxyl chloride*), b. p. 120°/9 mm., *hydroxymethylpyromucic acid*, m. p. 167° (uncorr.), and *hydroxymethylpyromucylglycine*, $OH{\cdot}CH_2{\cdot}C_4H_2O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, is described.

A. Wormall.

Behaviour of *iso*quinoline in the animal organism. M. Takahashi (Z. physiol. Chem., 1927, **169**, 297—299).—After subcutaneous injection of *iso*quinoline, the methylated compound has been isolated in small quantities from the urine of the dog and the hen, but not of the rabbit. A. Wormall.

Detoxication of benzoic acid in man. J. L. Brakefield (J. Biol. Chem., 1927, **74**, 783—785).—After administration of 5—6 g. of benzoic acid to human subjects, more than 90% was recovered from the urine as hippuric acid; a trace of free benzoic, but no benzoylglycuronic acid was detected.

C. R. Harington.

Utilisation of calcium of spinach. L. McLaughlin (J. Biol. Chem., 1927, **74**, 455—462).—Storage of calcium in adult women was not impaired when 70% of the total intake of this element was supplied in the form of spinach.

C. R. Harington.

Growth and reproduction on synthetic diets. II. G. A. Hartwell (Biochem. J., 1927, 21, 1076—1086).—Three generations of rats have been reared on a synthetic diet of butter, caseinogen, potato starch, salt mixture, marmite, and distilled water. The substitution of cod-liver oil for butter in this diet produces less good growth and causes sterility. Synthetic diets are described which produce good growth in young rats, but cause inability of the young to be born and consequent death of the doe. The dietary requirements of the rat vary at different phases of its existence. S. S. Zilva.

Physiology of reproduction in birds. XXII. Blood-fat and -phosphorus in the sexes. O. Riddle and F. H. Burns (Amer. J. Physiol., 1927, **81**, 711—724).—During the ovulation cycle in female ring-doves there is a notable increase in the fat and lipoid phosphorus of the blood. The relation of the ovary to this increase is discussed and the question of sex inequalities in fat metabolism reviewed.

R. K. Cannan.

Nitrogen equilibrium and nitrogen balance. Experiments with rye bread. A. Putter (Z. Biol., 1927, 86, 317—344).—A discussion, based on experimental evidence, of the preliminary conditions necessary for the attainment of suitable basal conditions for feeding experiments. Experiments on nitrogen equilibrium in which these conditions are not fulfilled give too high values for the nitrogen administration with which equilibrium is reached.

W. Robson.

Rôle of the lungs in intermediary nitrogenous metabolism. I. Total and residual nitrogen content of arterial blood and of blood from the right heart in the normal animal and after intravenous injections of serum. II. [With S. Krassovitzkaja.] **Residual nitrogen content of the defibrinated blood flowing to and from the isolated lung.** A. M. Tscharny (Biochem. Z., 1927, 188, 372—377; 378—380).—I. In dogs, the arterial blood flowing from the lungs contains much less residual nitrogen than the blood flowing to the lungs from the right heart. This decrease is still greater after injection of serum. Some of the residual nitrogen is therefore retained by the lung.

II. Experiments with the isolated organ confirm the view that nitrogen accumulation takes place in the lung.

P. W. Clutterbuck.

Amino-nitrogen in the egg of *Bombix mori*. M. Tirelli (Arch. Farm. sperim. Sci. aff., 1927, 43, 115—128).—The determination by Monzini (Ann. R. Staz. Bac. Padova, 1921, [v], 43, [2]) showed that the amino-nitrogen in the eggs of the silkworm moth increases during incubation, but in a slight and transient amount. It is now found that the amino-nitrogen is greater in the fresh or hibernated eggs than in those which have been incubated, in which the values oscillate, decreasing during the first phase and subsequently increasing. Variations in the nitrogen in eggs of the "yellow native" and "white Chinese" moths, and of crosses, are discussed.

E. W. Wignall.

Influence of fat and carbohydrate diets on uric acid of blood. V. J. Harding, K. D. Allin, and B. A. Eagles (J. Biol. Chem., 1927, 74, 631—643).—The increase in the uric acid of the blood, previously observed (A., 1925, i, 604) to result from a diet rich in fat, is accompanied by decreased excretion of uric acid. During the normal puerperium the uric acid of the blood is not increased by a diet low in protein and rich in carbohydrate, although in the puerperium following toxæmia such diets do cause an increase in the uric acid.

C. R. Harington.

Metabolism of uric acid in the living animal. V. S. J. Przylecki (Arch. int. Physiol., 1926, 27, 159—202).—The invertebrates are classified (*a*) according as they excrete (or contain) uric acid, or not (uricopositive, uriconegative), and (*b*) according as they decompose uric acid, or not (uricolytic, uricostatic). Unlike the higher vertebrates, certain invertebrates lack purine oxydases, whilst others readily oxidise endogenous or exogenous purines to uric acid. The decomposition, with vertebrates and invertebrates, of uric acid by uricase proceeds only in the presence of oxygen, and terminates with allantoin. The invertebrates do not contain allantoinase. Some can synthesise uric acid from acyclic compounds; the invertebrates cannot decompose allantoin, alloxan, dialuric acid, or barbituric acid to urea or ammonia. Whilst the first stage in the catabolism of uric acid involves the elimination of carbon dioxide, the last stage is the addition of a molecule of carbamide to the pyrimidine nucleus. The two reactions are biologically irreversible. In the invertebrates no species can form uric acid from purines which cannot convert it into allantoin except those which do not contain it and those which form it from acyclic compounds.

Chemical Abstracts.

Purine metabolism. III. Basal metabolism and purine content. IV. The nuclear-plasmic ratio in dogs in carbohydrate and protein feeding and in starvation. R. Truszkowski (Biochem. J., 1927, 21, 1040—1046, 1047—1053).—III. The chemical nuclear-plasmic ratios of whole rats and guinea-pigs differ little from one another. The values obtained for purine- and total nitrogen and for the nuclear-plasmic ratios of liver and of skeletal muscle of rats, rabbits, dogs, horses, and cattle vary within wide limits, but are in no way connected with the basal metabolism of the animals in question. The purine content of animals cannot therefore be identified with the intensity of the metabolism.

IV. The total nitrogen and purine contents of the liver of the dog are respectively 43 and 47% higher when the animal is fed on meat than when carbohydrates are consumed. The nuclear-plasmic ratio of the liver tissue in meat-fed dogs is almost the same as on a carbohydrate diet. The total solids of the skeletal muscle of dogs fed on meat are 14% higher than on carbohydrate diet. The total nitrogen and purine contents of skeletal muscle are respectively 35 and 49% higher in dogs fed with meat than in those fed on carbohydrates. The nuclear-plasmic ratio of skeletal muscle in meat-fed dogs is slightly higher than that found in carbohydrate feeding. In starvation, the nuclear-plasmic ratio of the liver is 10% above normal, whilst that of skeletal muscle is unchanged. These experiments do not support the view of protein storage.

S. S. Zilva.

Metabolism of sulphur. XIII. Effect of elementary sulphur on growth of white rat. G. T. Lewis and H. B. Lewis (J. Biol. Chem., 1927, 74, 515—523).—Addition of flowers of sulphur to a diet deficient in cystine was not only unable to replace the latter, but also caused actual retardation of growth, when given in small amounts. Addition of larger amounts of sulphur, even in presence of an adequate supply of cystine, caused toxic effects, presumably due to formation of hydrogen sulphide in the intestine.

C. R. Harington.

Rôle of lipins in biology and immunology. L. Suranyi (Magyar Orvosi Arch., 1927, 28, 125—137).—It is suggested that lipins, and especially cholesterol, play an important part in the neutralisation of the normal products of assimilation, whether poisonous or not, and probably in their transport and elimination.

Chemical Abstracts.

Effect of fasting on the urine of steers. T. M. Carpenter (Amer. J. Physiol., 1927, 81, 519—551).—Comparative analyses are reported of the urine of steers before, during, and after fasting periods of from 5 to 14 days.

R. K. Cannan.

Kinetics of the swelling of cells and tissues. J. H. Northrop (J. Gen. Physiol., 1927, 11, 43—56).

—The rates of swelling of *Arbacia* eggs and of slices of carrot and potato conform to the formulæ previously developed (cf. this vol., 825) for the increase in volume of a gelatin solution within a collodion membrane and for the swelling of blocks of gelatin.

W. O. Kermack.

Influence of external osmotic pressure and disturbance of the cell surface on the permeability of *Spirogyra* for acid dyes. G. W. Scarth (Protoplasma, 1926, 1, 204—213).—The cells of *Spirogyra* are normally highly impermeable to acid dyes, the permeability increasing with the osmotic pressure of the medium in which the dye is applied. It is suggested that the permeability is regulated by an organised film on the surface of the cytoplasm.

Chemical Abstracts.

Permeability of living cells. VII. Effects of light of different wave-lengths on the penetration of 2 : 6-dibromophenolindophenol into *Valonia*. M. M. Brooks (Protoplasma, 1926, 1, 305—312).—Between 300 and 700 μ the amount of 2 : 6-dibromophenolindophenol penetrating the sap of *Valonia* from a 0·00035*M*-solution in sea-water increased as the wave-length decreased. Chemical Abstracts.

Bioelectrical phenomena. W. J. V. Osterhout (J. Gen. Physiol., 1927, **11**, 83—99).—A discussion of bioelectrical phenomena preliminary to the publication of experimental results. The advantage of using single large cells as of *Valonia* and *Nitella* is emphasised. W. O. Kermack.

Properties of radiation-substances with weak irradiation. H. Zwaardemaker (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 420—422).—Perfusion of a heart with Ringer's solution deficient in potassium causes its action to cease, but on irradiation the beat recommences after a latent period of ½—1 hr. The perfusion liquid is then capable of regenerating the beat of another heart which has been similarly treated but not irradiated. The active substance has not been isolated, but is soluble in alcohol, stable when the solution is heated, and adsorbed by charcoal and magnesium silicate; it may be dialysed and is ultrafilterable, but does not appear to lower the surface tension of water. H. F. Gillbe.

Relationship between structure and action of cardiac glucosides. W. A. Jacobs and A. Hoffmann (J. Biol. Chem., 1927, **74**, 787—794).—Saturation of the double linking associated with the lactone group in the cardiac glucosides reduces, but does not abolish, the physiological activity, which is therefore a property of the molecule as a whole. Cymarin, on hydrogenation, gave *dihydrocymarin*, $C_{30}H_{46}O_9,H_2O$, m. p. 128° and 190°, $[\alpha]_D^{22}$ +17·8° in pyridine, of which the toxicity was 1/16 of that of cymarin. Ouabain gave *dihydro-ouabain*, $C_{30}H_{48}O_{12}$, m. p. 105°, $[\alpha]_D^{30}$ −47·4° in water; toxicity 1/23 of that of ouabain. Digitoxin yielded *dihydrodigitoxin*, m. p. 202—204°, $[\alpha]_D^{23}$ +2·4° in pyridine. C. R. Harington.

Pharmacology of galegine. H. Müller and H. Reinwein (Arch. exp. Path. Pharm., 1927, **125**, 212—227).—Galegine raises the blood-sugar when administered to rabbits or when given in large doses to dogs, but small doses given to dogs lower the blood-sugar. Also when given to depancreatised dogs it causes a decrease in the concentration of sugar in the blood and in the urine. The hyperglycæmic action of galegine is antagonised by ergotamine. When galegine and ergotamine are administered together, hypoglycæmic convulsions may be produced in the rabbit and the dog. W. O. Kermack.

Physico-chemical causes of the behaviour of the phenol–camphor medicament. P. Günther and M. Peiser (Z. physikal. Chem., 1927, **128**, 189—202).—The fact that an equimolecular mixture of phenol and camphor does not exert any corrosive action on the mucous membrane of the mouth cannot be attributed to compound formation, since f.-p. curves for phenol–camphor mixtures indicate only the existence of an extremely loose compound, and the densities and refractive indices of the mixture are very nearly additively constituted of those of the components. A distribution of the phenol between the camphor and water in favour of the camphor phase is not a possible explanation, for addition of a little water to a mixture containing 15 mols. % of camphor causes the separation of a solid which is nearly pure camphor. With the mixture used medicinally, however, addition of a little more water results in the appearance of a third phase, consisting of an approximately 1·3% aqueous solution of phenol. The efficacy of the mixture is therefore due to the addition of water causing the deposition of finely-divided and nearly pure camphor with subsequent formation of an aqueous solution of phenol which has a bactericidal but not a corrosive action.

R. Cuthill.

Phenylalanine series. IX. Pharmacological action of hexahydrophenylalanine and hexahydrotyrosine, and of the related amine and its derivatives. E. Waser (Arch. exp. Path. Pharm., 1927, **125**, 129—139).—The pharmacological activity of the following compounds has been investigated; hexahydrophenylalanine, hexahydrotyrosine, and the hydrochlorides of their ethyl esters; hexahydrophenylethylamine hydrochloride; hexahydrotyramine hydrochloride, *N*-methylhexahydrotyramine hydrochloride and *ON*-diacetylhexahydrotyramine. Their toxicity and their action on the pupil, heart, respiration, intestine, and temperature are small, but hexahydrophenylethylamine, hexahydrotyramine, and *N*-methylhexahydrotyramine markedly raise the blood-pressure.

W. O. Kermack.

Preparation of dibismuthyl monosodium citrate. W. F. von Oettingen, Y. Ishikawa, and T. Sollmann (J. Pharm. Exp. Ther., 1927, **31**, 353—360).—Dibismuthyl monosodium citrate has been prepared by dissolving monobismuthyl citrate in sodium hydroxide. The formation of a pure product depends on the final p_H of the solution, which should not exceed 7·6, and on the amount of alcohol used to precipitate the dibismuthyl salt. The therapeutic advantages claimed for this substance over the bismuth citrates now in use are that, prepared in this way, the bismuth content is constant, the substance is stable in aqueous solution, and can be readily sterilised.

E. A. Lunt.

Colloidal lead phosphate for use in cancer therapy. F. Bischoff and N. R. Blatherwick (J. Pharm. Exp. Ther., 1927, **31**, 361—375).—Colloidal lead phosphate is prepared by adding sodium phosphate solution to a hot solution of lead chloride in water containing 4% of gelatin. When administered thus it is relatively non-toxic to rats and rabbits, and it does not affect the fragility of red blood-corpuscles (human) *in vitro*. The rate of excretion by the rabbit of lead given as phosphate is the same as that for lead administered in other forms. Ionic lead, buffered with serum containing enough phosphate to react completely with the lead, is also non-toxic.
E. A. Lunt.

Synthetic medicinals. II. Theory of laxatives. H. P. Kaufmann.—See this vol., 1075.

Physiological action of two disulphones. A. Récsei (Biochem. Z., 1927, **188**, 405—408).—Butyrone diethylsulphone, with tadpoles, is, with respect to concentration 20 times and with respect to time 30 times as active as sulphonal and the animals recover twice as quickly. *cyclo*Hexanone diethylsulphone is 10 and 20 times as active, respectively, as sulphonal and the animals recover more quickly. A larger concentration acting for a shorter time is less injurious than a more dilute solution for a longer time. With guinea-pigs the lethal dose is about 1 g. per kg. body-weight and the narcotic dose is very near this. This substance is also powerfully antipyretic.
P. W. Clutterbuck.

Localisation of veronal and phenylethyl- and diallyl-barbituric acids in the brain (the problem of sleep). E. Keeser and J. Keeser (Arch. exp. Path. Pharm., 1927, **125**, 251—256).—Phenylethylbarbituric acid, veronal, or diallylbarbituric acid when injected intravenously into rabbits could be recovered from the thalamus and corpus striatum, but not from the great hemispheres, the mesencephalon, the cerebellum, the pons, or the medulla oblongata.
W. O. Kermack.

Utilisation of carbohydrate in the non-diabetic organism. II. Respiratory exchange after administration of carbohydrate under the influence of adrenaline and substances with adrenaline-like action (pituitary extract, ephedrine, and "ephetonine" [synthetic *dl*-ephedrine]). A. Lublin (Arch. exp. Path. Pharm., 1927, **125**, 229—241).—Adrenaline, pituitary extract, and particularly ephedrine and "ephetonine" retard the conversion of carbohydrate into fat, a process which the authors consider is favoured by the action of insulin.
W. O. Kermack.

Carbon monoxide as a tissue poison. J. B. S. Haldane (Biochem. J., 1927, **21**, 1068—1075).—The movements of a moth and the germination of cress seed are inhibited by carbon monoxide. The greater the partial pressure of oxygen the more carbon monoxide is required. Rats living on oxygen dissolved in their blood under pressure in presence of sufficient carbon monoxide to combine with almost all their hæmoglobin are killed by the addition of more carbon monoxide. It is concluded that cells contain a catalyst of oxidation which is poisoned by carbon monoxide (cf. Warburg, A., 1926, 1277). Its affinity for carbon monoxide was determined in the case of the moth. Its affinities differ in different species and perhaps in different tissues. The toxic effect is not due to any impurities in the gas.
S. S. Zilva.

Nitrogenous metabolism in experimental subacute arsenic and antimony poisoning. E. Pribyl (J. Biol. Chem., 1927, **74**, 775—781).—Subacute poisoning of rabbits with sodium arsenite and with antimony potassium tartrate causes an increase in the non-protein nitrogen of the blood, which is more marked in the case of the arsenite and is chiefly due to an increase in carbamide nitrogen. In the urine, there is an increase in the total nitrogen excreted.
C. R. Harington.

Inhibitory effect of metallic salts on bacterial growth. I. Silver salts. P. H. Andresen (Dansk Tids. Farm., 1927, **16**, 471—489).—In a medium containing peptone, the amount of ionic silver required to inhibit bacterial growth cannot be determined exactly, since the ionic concentration of added silver does not remain constant. If, however, to a synthetic medium containing aspartic acid and a mixture of inorganic salts sodium thiosulphate is added, a culture fluid is obtained which on the addition of silver nitrate displays a definite and constant silver-ion concentration for at least 48 hrs. at 37° (silver-ion concentration measured electrometrically). In such a medium, at p_{H} 7·2 growth of *B. coli* is prevented at an $\text{Ag}^{\cdot}$ as low as $0{\cdot}16\times10^{-11}$. Similar minimum inhibiting values were found for certain other bacteria, which, in absence of silver, grow readily in this medium. The silver-ion concentration is the governing factor in growth inhibition and, no matter how much total silver be present in the medium, the ionic concentration must be maintained at or over the above minimum to ensure complete inhibition.
H. D. Kay.

Antagonism of glucosone and cyanides *in vivo*. A. Hynd (Biochem. J., 1927, **21**, 1094—1101).—In the case of mice and rats, a subcutaneous injection of dextrose or of dextrose plus insulin affords no protection against toxic action following either the subsequent subcutaneous injection of either alkali or methyl cyanide or of the inhalation of gaseous hydrogen cyanide. Glucosone, on the other hand, exerts a definite antagonistic action towards cyanides in these circumstances, but is less efficient than cystine. The previous, or simultaneous, intravenous administration of glucosone or of dextrose plus insulin appears to be protective against the intravenous injection of alkali cyanide into rabbits, but the results obtained are somewhat variable.
S. S. Zilva.

Effect of ethyl cyanide and ethyl carbylamine on biological oxidations. O. H. Emerson and J. W. Buchanan (J. Pharm. Exp. Ther., 1927, **31**, 387—392).—In solutions of the same molar concentration ethyl carbylamine is a more powerful depressant of the oxygen consumption of *Planaria dorotocephala* and *P. maculata* than ethyl cyanide; its action is similar to that of potassium cyanide.
E. A. Lunt.

Purification of malt amylase. E. Glimm and W. Sommer (Biochem. Z., 1927, **188**, 290—325).—

A method is described depending on a charcoal treatment of dilute solutions of diastase (Merck) after 3 days' aseptic autolysis (in presence of toluene) at 40°. The original diastase solution contained 9% of carbohydrate (erythrodextrin) and 8% of total nitrogen, readily reduced Fehling's solution, gave strong ninhydrin and peroxidase (with benzidine–hydrogen peroxide) reactions, and had an amylase value of 0·2—0·5. The amylase filtrate obtained after 3 days' aseptic autolysis of this solution at 40° followed by treatment twice with animal charcoal was water-clear, had amylase content 5·8, nitrogen content only 3·8%, was free from reducing carbohydrates, and gave a very faint ninhydrin reaction.

Amylase may be adsorbed by aluminium hydroxide and eluted without loss by means of secondary phosphate solution, 50% of inactive material being separated. Adsorption by stannic acid separated 70% of inactive material, but elution from kaolin, and still more so from stannic acid, caused considerable inactivation of the enzyme, these acid colloids separating the enzyme from its protective agent. Adsorption on gelatinous zinc phosphate succeeded only in presence of 20% alcohol, and since the conversion into crystalline phosphate took some time, most of the amylase became inactivated. After saccharification of starch, amylase is completely adsorbable from the maltose complex and elutable. Amylase may be heated for a considerable time at 50° without injury and remains adsorbable, but is no longer elutable from the adsorbate.

P. W Clutterbuck.

Taka-diastase. K. Nishikawa (Biochem. Z., 1927, **188**, 386—404).—The p_H optima for the following enzymes of taka-diastase are: for amylase, 6·8—7·2, for tryptase (hydrolysis of gelatin) 7·7—8·3, (hydrolysis of fibrin) 8·2—8·6, and for the milk-clotting enzyme 5·2—6·7. Trypsin, diastase, lipase, and milk-clotting enzyme are adsorbed by fibrin from a taka-diastase solution and may be eluted under suitable conditions by dilute acids and alkalis or by allowing the fibrin–enzyme complex to react with starch solution, when both diastase and trypsin pass into solution. If taka-diastase is heated for 10 min. at 65°, the amylase is considerably inactivated, to a greater extent in presence of sodium or potassium chlorides than in distilled water. Inorganic and organic calcium salts have a protective action on amylase, but barium and magnesium salts are much more injurious. The same applies to tryptase, but the heat action is much more injurious. Zinc is injurious to amylase and zinc and copper to trypsin, but iron, nickel, cobalt, and copper are without effect on amylase. Amylase is inactivated by mercuric chloride and reactivated by adding the corresponding amount of sodium cyanide. Trypsin is similarly inactivated, but requires more cyanide for reactivation. In taka-diastase there is also present a phenoloxidase which oxidises only dihydroxybenzene derivatives (dihydroxyphenylalanine and pyrocatechol) and is without action on tyrosine. Under suitable conditions, taka-diastase converts fibrinogen into fibrin.

P. W. Clutterbuck.

Isolation of diastase from human urine. P. Rostock (Fermentforsch., 1927, 9, 192—194).—The urine of subjects with acute pancreatic necrosis is specially suitable for the preparation of diastase, since the diastatic value is very high in this condition and trypsin and lipase are absent. By dialysis of the urine under sterile conditions and subsequent drying at 37°, a preparation has been obtained which is thirty times as active as the most active commercial preparation (Merck). A. Wormall.

Liver diastase. E. F. Lesser (Biochem. J., 1927, 21, 1128).—Polemical against Eadie (this vol., 482). About two thirds of the liver diastase is adsorbed on the surfaces of the cell and is therefore unable to act on the liver glycogen. This applies also to the parotid gland of the mouse. S. S. Zilva.

Coagulation of egg-yolk by pancreatic diastase. E. Lagrange (Arch. int. Physiol., 1926, 26, 347—361).—Pancreatic juice contains a vitellinase which is more sensitive than lipase to the reaction of the precipitate; its action is prevented by sodium fluoride. Chemical Abstracts.

Influence of thorium-*X* on the activity of emulsin. A. Maubert (Compt. rend., 1927, **185**, 669—671).—The total radiation of thorium-*X* in concentrations down to 0·05 γ per c.c. of liquid, accelerates the action of emulsin on amygdalin, whilst at higher concentrations the reaction is more and more, and with 12 γ per c.c. completely, inhibited. At the latter concentration β- and γ-rays have only a slight effect, and the effect above must therefore be due to the α-radiation (cf. A., 1925, i, 737; 1926, 759; this vol., 483). P. W. Clutterbuck.

Amygdalase, gentiobiase, gentianase. K. Josephson (Z. physiol. Chem., 1927, **169**, 301—304).—The relationship between these enzymes is discussed and it is considered that no definite conclusion can yet be reached as to the identity of gentianase with amygdalase or with gentiobiase.

A. Wormall.

Specific action of plant enzymes. III. Conditions of action of leaf salicinases. A. V. Blagoveschenski and N. I. Sossiedov (Biochem. J., 1927, 21, 1206—1210).—A definite optimal hydrogen-ion concentration exists for the action of salicinases from various species of *Populus* and *Salix*. Different plants contain various amounts of the enzyme. Salicinase is present in *Gossypium hirsutum*; the enzyme is therefore not confined to the Salicaceæ.

S. S. Zilva.

Action of carbon monoxide on certain oxidising enzymes. M. Dixon (Biochem. J., 1927, 21, 1211—1215).—Carbon monoxide has no inhibitory effect on the aërobic oxidation of aldehyde or hypoxanthine by the milk oxidase, or of succinic acid by the succinoxidase of muscle. Its action thus differs from that of cyanide, which strongly inhibits the latter reaction.

S. S. Zilva.

Peroxidase. V. Mathematics of the enzyme action. H. W. Bansi and H. Ucko (Z. physiol. Chem., 1927, **169**, 177—195; cf. this vol., 377).—The oxidation of pyrogallol by peroxidase proceeds according to the equation $u=kt^{1/a}$, where u is the change in time t, k is a constant, and $1/a$ the exponential factor. The calculated values with varying amounts of enzyme, hydrogen peroxide, and pyrogallol, and with variations in the p_H and temperature, agree very well with the experimental results. The factor a is constant for one enzyme preparation with variations in the amount of enzyme and pyrogallol, and, within certain limits, the concentration of hydrogen peroxide; it is influenced chiefly by alterations in p_H and temperature, being increased by a rise in temperature and a rise in C_H. The values for a usually lie between 1 and 2, but with an excess of hydrogen peroxide and a p_H below 4·5 the value rises above 2. The decrease in velocity observed during the course of the oxidation is due to adsorption of the enzyme on the purpurogallin formed, and removal of this product from a reaction mixture, in which the reaction has ceased, leads to a resumption of the oxidation. Hydrogen peroxide inhibits the action of peroxidase only if present in high concentrations. A modification of Willstätter's scheme is suggested for the reactions between hydrogen peroxide and peroxidase, resulting in the formation of an active additive product which gives up oxygen and an inactive product which is dissociated into free peroxidase and hydrogen peroxide under the influence of the substrate. A. WORMALL.

Action of tyrosinase on tyrosine. H. S. RAPER (Fermentforsch., 1927, 9, 206—213).—The mechanism of the oxidation of tyrosine by tyrosinase is discussed (cf. A., 1926, 977; this vol., 278). The first product is 3 : 4-dihydroxyphenylalanine, which is then oxidised to the corresponding quinone; an intramolecular change results in the production of 5 : 6-dihydroxydihydroindole-2-carboxylic acid, which is then oxidised to the corresponding quinone (red compound). This quinone yields 5 : 6-dihydroxyindole and 5 : 6-dihydroxyindole-2-carboxylic acid, the precursors of melanin. From the nitrogen content of melanin (A., 1925, i, 473) it is possible that each molecule of dihydroxyindole oxidised to melanin takes up one atom of oxygen and loses two atoms of hydrogen, and that condensation occurs with the formation of colloidal amorphous melanin. The results do not support the view that melanin production is due to the oxidation of a pyrrole derivative formed from tyrosine. A. WORMALL.

Purification of lactic acid-forming enzyme of muscle. O. MEYERHOF and K. MEYER (J. Physiol., 1927, 64, xvi).—The muscle extract is brought to p_H 5 with acetate buffers, thereby precipitating the protein and enzyme. Subsequent elution with phosphate solution effects dissolution of the enzyme with some protein. After a repetition of this process the activity had increased more than tenfold, and may be further increased by adsorption on aluminium hydroxide prepared by Willstätter's method. The co-enzyme and phosphoric esters are removed during the purification so that boiled muscle extract must be added to obtain glycolysis. Besides enzyme and co-enzyme a hydrolysable ester is necessary. This appears to be a hexosediphosphate. On purification the enzyme becomes more stable and may be preserved for several days. R. K. CANNAN.

Influence of some poisons on the serum-lipase of warm-blooded animals. A. KUDRJAVZEVA (Fermentforsch., 1927, 9, 139—145).—In general, the serum-lipase of the carnivorous animal (cat and dog) is more readily inhibited by atoxyl than is that of the herbivora, the rabbit, however, being an exception. Of these animals, the cat, dog, and rabbit are most sensitive to arsenic. Quinine inhibits most strongly the serum-lipases of the dog, sheep, and cow, and the lipase of the horse, hen, and pigeon to a less extent, whilst it has very little action in the case of the guinea-pig, cat, and rabbit. No relationship can be traced between the sensitivity of the lipases to quinine and the type of food eaten. Morphine exerts little inhibitory action on serum-lipase except with the dog, whilst strychnine has even less influence. The sensitivity of the serum-lipases to morphine and strychnine cannot be correlated in any way with the type of food or with the general sensitivity of the animal to the poison. A. WORMALL.

Specificity of proteolytic enzymes. E. WALDSCHMIDT-LEITZ, W. GRASSMANN, and H. SCHLATTER (Ber., 1927, 60, [*B*], 1906—1909; cf. A., 1926, 323).—Enzymic hydrolysis of triglycine, *dl*-alanyldiglycine, tetraglycine, *dl*-leucyltriglycine, pentaglycine, *l*-leucyltriglycyl-*l*-tyrosine, hexaglycine, and *l*-leucylheptaglycine by intestinal erepsin and pancreas-trypsin activated by enterokinase has been investigated. Lengthening of the peptide chain, for example in glycylglycine or leucylglycine by introduction of further glycyl residues up to the octapeptide, is without influence on the specificity of the enzyme, whereas the conversion of leucyltriglycine into leucyltriglycyltyrosine is accompanied by a qualitative change in the specific action, since the peptide is hydrolysed by trypsin but not by erepsin. The nature of the amino-acid component is therefore of primary importance, but the effect of lengthening the chain is shown by comparison of the hydrolysis of leucyltriglycyltyrosine and glycyltyrosine.

The observation that peptides can be hydrolysed by pancreatic trypsin renders unnecessary the formal distinction between the proteases proper, including trypsin, and the peptidases. H. WREN.

Specific adaptation of polypeptidases. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1927, 9, 252—263).—Various polypeptide derivatives have been subjected to the action of polypeptidases, and the nature of the substrate grouping responsible for the affinity for the corresponding enzyme is considered. *dl*-Leucyltyramine is hydrolysed by the erepsin of intestinal and pancreatic press juices, but not by yeast maceration juice. The secondary base, iminodi*iso*hexoyltyramine, is hydrolysed by the yeast juice only, whilst the phenylcarbimides of phenylalanine, leucine, and glycine are unattacked by these juices. Pancreatin hydrolyses benzoyl-*dl*-leucylglycylglycine and benzoyl-*dl*-alanylglycylglycine (cf. Imai, A., 1924, i, 921). Tyramine is condensed with α-bromo*iso*hexoyl bromide to give dl-*α-bromo*iso*hexoyltyramine*, m. p. 113°, and this, when heated with ammonia in a sealed tube at 60—70°, yields dl-*leucyltyramine*, decomp. about 105°, and the secondary base *iminodi*iso*hexoyltyramine*, $NH[CH(C_4H_9)\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OH]_2$.

A. Wormall.

Behaviour of *dl*-alanyl-δ-aminovaleric acid and *dl*-leucyl-δ-aminovaleric acid towards polypeptidases. E. Abderhalden and J. Hartmann (Fermentforsch., 1927, 9, 199—205).—*dl*-α-Bromopropionyl bromide is condensed in an alkaline solution with δ-aminovaleric acid to yield dl-α-*bromopropionyl*-δ-*aminovaleric acid*, m. p. 112°, which is converted by the action of ammonia into dl-*alanyl*-δ-*aminovaleric acid*, m. p. 162°. Similarly, δ-aminovaleric acid condensed with *dl*-α-brom*iso*hexoyl bromide yields dl-α-*brom*iso*hexoyl*-δ-*aminovaleric acid*, m. p. 75—76°, which with ammonia gives dl-*leucyl*-δ-*aminovaleric acid*, m. p. 164—165°. The two dipeptides, *dl*-alanyl- and *dl*-leucyl-δ-aminovaleric acids, unlike *dl*-leucylglycine, are not hydrolysed by yeast maceration juice.

A. Wormall.

Behaviour of *l*-leucylglycyl-*l*-tyrosine and *d*-leucylglycyl-*l*-tyrosine towards yeast maceration juice, pancreatic juice, and intestinal juice. E. Abderhalden and N. Schapiro (Fermentforsch., 1927, 9, 234—237).—These enzyme solutions acting on *l*-leucylglycyl-*l*-tyrosine in a phosphate buffer solution at p_H 8 for 24 hrs., eliminate *l*-tyrosine, which has been isolated in the pure condition, whilst *l*-leucine, glycine, and *l*-leucylglycine are also formed. No action occurs with *d*-leucylglycyl-*l*-tyrosine. *d*-α-Bromo*iso*hexoylglycyl-*l*-tyrosine is condensed with glycyl-*l*-tyrosine to give d-α-*bromo*iso*hexoylglycyl*-l-*tyrosine*, an oil, which when treated with ammonia yields l-*leucylglycyl*-l-*tyrosine*, $[\alpha]_D^{20}$ −30·9°. d-*Leucylglycyl*-l-*tyrosine*, $[\alpha]_D^{20}$ +32·8°, is prepared in a similar manner with the intermediate formation of l-α-*brom*iso*hexoylglycyl*-l-*tyrosine*, an oil.

A. Wormall.

Structure and enzyme reaction. I and II. The systems urea–urease–charcoal and polysaccharide–amylase–charcoal. S. J. Przylecki, H. Niedzwiedzka, and T. Majewski (Biochem. J., 1927, **21**, 1025—1039).—In the system urea–charcoal–urease the enzyme is almost quantitatively adsorbed, whilst the substrate remains almost entirely in solution. The velocity of enzymic reaction in this system is almost the same as in the absence of the adsorbent and is unaffected by the addition of narcotics. Propyl or butyl alcohol does not remove the enzyme from the adsorbent to any appreciable extent. In the system amylase–charcoal–glycogen or -dextrin the enzyme and much of the substrate (50—75%, according to the quantity of charcoal present) are adsorbed. In this case the velocity of hydrolysis is considerably lower than in the absence of an adsorbent, and narcotics can remove the substrate, but not the enzyme, from the charcoal to a great extent. This reduction in the velocity of hydrolysis is due to spatial separation of enzyme and substrate. If the effective concentration of the substrate be taken into consideration, the law of mass action is followed in enzyme reactions in a heterogeneous medium.

S. S. Zilva.

Experiments on bacteria in relation to the mechanism of enzyme action. J. H. Quastel and W. R. Wooldridge (Biochem. J., 1927, **21**, 1224—1251; cf. this vol., 280).—The action of various organic and inorganic reagents on the enzymic activity of *B. coli* has been studied. The evidence obtained militates against the hypothesis that the activity of surfaces is due to their adsorption of specifically active molecules. On the other hand, the results support the conception of "active centres" in the mechanism of enzyme action. This view is developed from the theory previously advanced (Quastel, A., 1926, 434) that dehydrogenations of substrate molecules are induced by electric fields which characterise these "active centres."

S. S. Zilva.

The equation of alcoholic fermentation. A. Harden and F. R. Henley (Biochem. J., 1927, **21**, 1216—1223; cf. Harden and Young, A., 1906, i, 470).—The reaction which occurs when a mixture of a hexose and an inorganic phosphate is fermented by yeast-juice or zymin (yeast treated with acetone) has been re-examined and the amounts of carbon dioxide, hexosemonophosphate, and hexosediphosphate produced have been determined. The ratio carbon dioxide/total phosphorus esterified is on the average 0·9, indicating that if Harden and Young's equation be taken as correct, about 10% of the phosphorus is esterified without evolution of carbon dioxide. The product of this esterification is probably a monophosphate. The ratio carbon dioxide/diphosphate is on the average 2·38, but varies considerably in individual cases. The fact that this ratio is almost invariably somewhat greater than the value 2 required by Harden and Young's equation suggests that the diphosphate is originally produced in accordance with the equation, but that a part of it is subsequently partly hydrolysed with formation of a monophosphate. The ratios carbon dioxide/monophosphate and monophosphate/diphosphate are highly variable and show no definite relations.

S. S. Zilva.

Alcoholic fermentation by yeast-cells under various conditions. VIII. E. Abderhalden (Fermentforsch., 1927, 9, 195—198; cf. A., 1923, i, 519).—Experiments have been carried out to determine whether ultra-violet light has any influence on alcoholic fermentation. Irradiated ergosterol, the alcoholic extract of irradiated yeast, and irradiated yeast maceration juice have no significant influence.

A. Wormall.

Influence of natural and synthetic thyroxines on alcoholic fermentation. E. Abderhalden (Fermentforsch., 1927, 9, 243—245).—Thyroxine has a varying influence on the fermentation of dextrose by bottom yeast in a phosphate buffer solution at p_H 4·5—6·5; usually a definite acceleration is obtained, but often there is no effect or even a very slight inhibition. Natural thyroxine and synthetic thyroxine give identical results with the same yeast.

A. Wormall.

Alcoholic fermentation of solutions of dextrose in water exposed to the radiation of a quartz mercury vapour lamp. R. de Fazi (Atti R. Accad. Lincei, 1927, [vi], 5, 901—905; cf. this vol., 592).—Aqueous dextrose solution, prepared immediately after the water used has been exposed to the radiation from a quartz mercury vapour lamp, is fermented by yeast appreciably more rapidly than one prepared with untreated water. Suspension of the yeast for a time in the irradiated water also enhances the speed of fermentation, but treatment of a highly impure or enfeebled yeast with the irradiated water may result in a considerable lessening in the velocity of fermentation. T. H. POPE.

"Acclimatisation" of fresh culture-yeasts to galactose. H. VON EULER and B. JANSSON (Z. physiol. Chem., 1927, **169**, 226—234).—Top yeast *R* and bottom yeast *H*, previously suspended for long periods in a galactose solution containing phenol, do not acquire the power to ferment galactose. In contrast to earlier experiments (Euler and Nilsson, A., 1925, i, 866), a low phenol concentration, sufficient to prevent any detectable increase in cell count, but not sufficient to prevent fermentation of dextrose, is maintained throughout. Similarly experiments on the fermentation of galactose by fresh bottom yeast *H* at 38° fail to prove that "acclimatisation" can occur without new formation of yeast-cells. "Acclimatisation" to galactose is concerned with the zymase and not with the co-zymase, since "acclimatised" dried bottom yeast washed free from co-zymase ferments galactose on the addition of co-zymase from untreated yeast. A. WORMALL.

Pigment produced by *Chromobacterium violaceum*. J. REILLY and G. PYNE (Biochem. J., 1927, **21**, 1059—1064).—The organism was grown in nutrient lactose broth, filtered, and extracted at 50° with alcohol at reduced pressure. The *pigment* was precipitated from the alcoholic solution by the addition of water. The formula $C_{50}H_{59}O_{15}N_5$ is suggested. One fifth of the total nitrogen is removed by the action of nitrous acid. S. S. ZILVA.

Auto-elimination of ammonia in bacterial cultures. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1927, **9**. 932—934).—Cultures of *B. proteus vulgaris* which normally develop an alkaline reaction as the result of the production of ammonia do not do so in presence of magnesium sulphate and alkali phosphate, since the ammonia is then eliminated from the solution as ammonium magnesium phosphate. W. O. KERMACK.

Production of acetylmethylcarbinol by *Clostridium acetobutylicum*. P. W. WILSON, W. H. PETERSEN, and E. B. FRED (J. Biol. Chem., 1927, **74**, 495—507).—In butyl alcohol fermentation by the above organism, acetylmethylcarbinol is regularly produced in maximum amounts of 0·3—0·4 g. per litre, the production occurring simultaneously with that of acids and acetone. The amount of acetylmethylcarbinol is increased by addition of phosphates and decreased by protein; the effect of such modifications in the medium on the production of acids and of acetone is less marked. C. R. HARINGTON.

Separation of lipin fractions from tubercle bacilli. Phosphatide fraction of tubercle bacilli. R. J. ANDERSON (J. Biol. Chem., 1927, **74**, 525—535, 537—551).—Tubercle bacilli (3868·5 g.) were extracted with a mixture of ether and alcohol and then with chloroform. The latter removed 427 g. of wax, the bacterial residue amounting to 2902 g.; the alcohol-ether extract was separated into ether-soluble and water-soluble fractions, the former yielding 253·1 g. of phosphatides and 240 g. of fat, and the latter 12·5 g. of basic substances and 33·9 g. of a polysaccharide.

The phosphatides, on further purification, yielded 138·3 g. of a fraction having N 0·4%, P 2·3%, m. p. 210°. On hydrolysis with dilute acid, this gave palmitic acid 30·5%, oleic acid 12·8%, a liquid saturated acid, $C_{20}H_{40}O_2$, 20·9%, dextrose 13·9%, a sugar acid 13·8%, and glycerophosphoric acid 5·4%. No choline was found, the nitrogen being apparently present as ammonia. The *acid* $C_{20}H_{40}O_2$ was separated by fractional crystallisation of the *benzyl-ψ-thiocarbamide* salt, m. p. 143—144°, into an optically inactive fraction and one having $[\alpha]_D^{20}$ +3·54°. The sugar acid gave with phenylhydrazine, in the cold, a *substance*, m. p. 194—195°. C. R. HARINGTON.

Soluble specific substance of pneumococcus. V. Aldobionic acid from specific polysaccharide of type III pneumococcus. M. HEIDELBERGER and W. F. GOEBEL (J. Biol. Chem., 1927, **74**, 613—618).—The aldobionic acid obtained by hydrolysis of the specific polysaccharide of pneumococcus (cf. this vol., 77), on oxidation with barium hypoiodite, gave a *dicarboxylic acid*, $C_{10}H_{18}O_9(CO_2H)_2$, *calcium* salt, $[\alpha]_D$ −7·5°; this compound gives the naphthoresorcinol test and yields the same amount of furfuraldehyde, on distillation with hydrochloric acid, as the original aldobionic acid. Further, on hydrolysis with hydrobromic acid in presence of bromine the aldobionic acid yields saccharic acid. The aldobionic acid must therefore be a compound of dextrose and glycuronic acid combined in glucosidic linking through the aldehyde group of the latter. C. R. HARINGTON.

Soluble specific substance of Friedländer's bacillus. IV. Hydrolytic products of specific carbohydrate of type A Friedländer's bacillus. W. F. GOEBEL (J. Biol. Chem., 1927, **74**, 619—629).—On hydrolysis of the specific polysaccharide from Friedländer's bacillus type A with sulphuric acid, there was obtained an aldobionic acid, $C_{12}H_{20}O_{12}$, which is a glucosidic compound of dextrose and glycuronic acid of the same type as and isomeric with the acid obtained similarly from the specific polysaccharide of pneumococcus type III (cf. preceding abstract). C. R. HARINGTON.

Action of free chlorine on micro-organisms. F. DIENERT and P. ETRILLARD (Compt. rend., 1927, **185**, 621—623).—The concentrations of free chlorine required to sterilise aqueous suspensions of micro-organisms, containing about 10^6 per c.c., vary considerably, *e.g.*, *B. coli*, 0·1; *B. subtilis*, 1·0 mg. per litre. Occasionally 4—5 times these concentrations are required to sterilise the suspensions completely. Agitation of the mixture increases the efficiency of the disinfectant since extraneous organic matter shields the organisms to some extent. By adjustment of the concentration of free chlorine it is possible in some cases to obtain a pure culture from a mixed culture. G. A. C. GOUGH.

Functions of the adrenal cortex and mechanism of biological oxidations. A. VON SZENT-GYÖRGYI (Magyar Orvosi Arch., 1927, **28**, 138—143).—

Some biological oxidations require a hydrogen activation as well as an oxygen activation. In the plant the oxygen-activating system has the character of a phenoloxidase. An aromatic substance which is oxidised by the phenoloxidase to a quinone is also present; the quinone is reduced again, thus acting catalytically as a hydrogen carrier. In certain plants there is a second reducing aromatic substance acting as a catalyst in the oxidation system. An analogous substance is present in the adrenal cortex.

Chemical Abstracts.

Effect of the parathyroid hormone on gastric secretion. II. Calcium content of gastric juice. W. C. Austin and S. A. Matthews (Amer. J. Physiol., 1927, **81**, 552—559).—The calcium content of pure gastric juice (dog) is 5—6·5 mg. %. It does not vary greatly during parathyroid hypercalcæmia.

R. K. Cannan.

Application of the axolotl metamorphosis reaction to the assay of thyroid gland hormones. B. M. Zavadovsky and E. V. Zavadovsky (Endocrinol., 1926, **10**, 550—559).—The average velocity of metamorphosis of axolotls varies directly with the concentration of thyroxine solution (0·1—0·001 g. per litre) to which the animals are exposed.

Chemical Abstracts.

Regulation of the production of insulin. I. Dextrose as the hormone liberating insulin. E. Grafe and F. Meythaler (Arch. exp. Path. Pharm., 1927, **125**, 181—192).—From a study of the blood-sugar curves obtained after administration of dextrose by injecting it into the femoral and pancreatico-duodenal arteries, evidence is adduced indicating that the secretion of insulin by the pancreas is the result of direct stimulation by dextrose.

W. O. Kermack.

Behaviour of sugars foreign to the body under the action of insulin. I. Effect of insulin on the degree of assimilation of various sugars. F. Basch and L. Pollak. **II. Resorption of sugars injected intraperitoneally under the influence of insulin.** L. Pollak (Arch. exp. Path. Pharm., 1927, **125**, 89—101, 102—128).—I. Insulin does not appear to influence the permeability of the kidneys of the rabbit to dextrose. On the other hand, it markedly increases the tolerance of the animal towards dextrose, less towards lævulose, very slightly towards galactose, and not at all towards mannose, sucrose, and lactose, when these sugars are administered intravenously.

II. When Ringer solution is injected into the peritoneal cavity of a rabbit, the blood-sugar concentration of the peritoneal fluid gradually becomes equal to that of the blood. The rate at which the process occurs does not appear to be influenced by insulin, except in as far as insulin influences the blood-sugar concentration, and it is probably dependent on simple diffusion. The rates of absorption of dextrose, lævulose, and galactose, but not those of mannose and lactose, when these sugars are introduced into the peritoneal cavity are increased by the action of insulin.

W. O. Kermack.

Effect of certain sugar derivatives on insulinised mice. A. Hynd (Biochem. J., 1927, **21**, 1091—1093).—Glucosimine, glucose ureide, glucosamine hydrochloride, or chitose cannot relieve the symptoms caused by insulin.

S. S. Zilva.

Mechanism of the insulin effect on carbohydrate metabolism. H. Phillips (U.S. Naval Med. Bull., 1927, **25**, 309—314).—Cohnheim's, Collip's, and the γ-glucose theories are discussed.

Chemical Abstracts.

Effect of cobalt on insulin hypoglycæmia in rabbits. N. R. Blatherwick and M. Sahyun (Amer. J. Physiol., 1927, **81**, 560—562).—Contrary to Bertrand and Mâchebœuf (A., 1926, 869), it is found that cobalt is without appreciable influence on insulin hypoglycæmia in rabbits.

R. K. Cannan.

Food requirements for growth of the rat. I. Growth on diet of purified nutrients. L. S. Palmer and C. Kennedy (J. Biol. Chem., 1927, **74**, 591—611).—Normal growth was not obtained in rats (kept from access to their fæces) on a diet of purified caseinogen, dextrin, agar, and salts, with butter fat and wheat embryo extract as sources of vitamins-*A* and -*B*; some hitherto unrecognised factor must therefore be necessary for the growth of these animals.

C. R. Harington.

Phosphorus and calcium metabolism on deficient diets. I. Action of ultra-violet light. II. Action of cod-liver oil. III. Changes of phosphorus or calcium content of the diet. P. Schultzer (Biochem. Z., 1927, **188**, 409—426, 427—434, 435—447).—I. The action of ultra-violet light on the phosphorus and calcium metabolism of young rats on various diets is investigated. On a non-rachitic diet deficient in phosphorus and vitamin-*B*, the rats lost in weight, and irradiation considerably increased phosphorus retention. On a rachitic diet deficient in phosphorus, irradiation caused increased phosphorus and calcium retention due to greater absorption, and the rachitic changes declined. Acid-soluble phosphorus returned to normal and serum-calcium rose above normal. On a diet deficient in calcium, irradiation caused considerable phosphorus and calcium retention and serum-calcium returned to normal.

II. Investigation of the effect of 12 days' treatment with cod-liver oil on the phosphorus and calcium metabolism of young rats on the above diets showed that cod-liver oil had the same effect as ultra-violet light both in respect to phosphorus and calcium retention and to acid-soluble phosphorus and serum-calcium.

III. The phosphorus and calcium metabolism of young rats is investigated on diets the phosphorus and calcium contents of which are changed during the experiment. Addition of phosphate to a diet rich in calcium and relatively poor in phosphorus causes increased phosphorus retention due to greater absorption and an increased calcium retention due to lessened excretion of calcium in the urine. Excretion of calcium in the fæces increased somewhat, acid-soluble phosphorus increased, and serum-calcium remained unchanged. Decreasing the calcium carbonate content of the same diet caused an increase of both phosphorus and calcium retention, due to increased reabsorption. Serum-calcium remained unchanged.

P. W. Clutterbuck.

Physiological equilibrium in plants. III. Connexion between the course of absorption of soil nutrients and their movement in plants. A. Rippel (Biochem. Z., 1927, **187**, 272—282).—With *Helianthus* it is shown that the course of absorption of soil nutrients corresponds with their mobility in the plant. Absorption of readily mobile elements such as nitrogen, potassium, and phosphorus accelerates the formation of dry substance, whilst absorption of less mobile elements such as calcium, sulphur, magnesium, and silicon has a much smaller or no effect. It seems possible that in the young plant, the former, and with increasing age, the latter type of absorption is favoured. P. W. Clutterbuck.

Nature and metabolism of sugars in *Iris*. H. Colin and A. Augem (Compt. rend., 1927, **185**, 475—478).—The sugars occurring in three varieties of *Iris* at various seasons have been investigated. C. W. Gibby.

Enzymic hydrolysis of turanose. M. Bridel and T. Aagaard (Compt. rend., 1927, **184**, 1667—1669).—From the action of various enzymes on turanose it is inferred that this substance is a glucoside of lævulose, and moreover that the constitution of turanose may require revision. W. Robson.

Extraction of asperuloside from *Gallium verum*, L. Probable presence of the glucoside in *Rubiaceæ*. H. Hérissey (Compt. rend., 1927, **184**, 1674—1675).—A method of extraction of this glucoside is described, together with a table showing the results of trial extractions on other members of this family. W. Robson.

Allantoic acid in the leaves of *Acer pseudoplatanus*. R. Fosse and A. Hieulle (Compt. rend., 1927, **184**, 1596—1598).—The dixanthylallantoic acid obtained by the addition of xanthhydrol to extracts of the leaves of *Acer pseudoplatanus* (cf. A., 1926, 548), followed by crystallisation of the crude product from pyridine, is not derived entirely from the allantoic acid in the extract. It appears that the extract contains some uroxanic acid, the xanthyl derivative of which suffers decarboxylation on crystallisation and is converted into dixanthylallantoic acid. The uroxanic acid, together with carbamide, has been directly isolated from the extract. G. A. C. Gough.

ψ-Ephedrine from Chinese *Ephedra*. B. E. Read and C. T. Feng (Chinese J. Physiol., 1927, **1**, 297—304).—Both Chinese and Swiss *Ephedra* contain both ψ-ephedrine and ephedrine. The solubility of ψ-ephedrine hydrochloride in chloroform is 53 times as great as that of ephedrine hydrochloride, and this difference is utilised in the separation of these alkaloids. It is suggested that this difference in solubilities and the inability of a small excess of ammonia to liberate the bases from these salts may account for the many erroneous statements concerning the occurrence of these alkaloids and also for the low assay results reported. W. Robson.

Kentucky coffee nut tree seed-oil. C. Barkenbus and A. J. Zimmerman (J. Amer. Chem. Soc., 1927, **49**, 2061—2064).—The seeds and pods of *Gymnocladus dioica* have, respectively: moisture, 5·98%, 11·41%; ash, 3·85%, 3·18%; protein (N×6·25), 32·30%, 6·50%; crude fibre, 2·01%, 21·12%; free invert-sugar, 0, 3·56%; sugar by inversion, 12·06%, 18·95%; pentosans, 5·67%, 17·29%; and starch (diastase), 13·32%, 18·91%. Light petroleum extracts 19·27% from the seeds, 0·41% from the pods. For ether the corresponding figures are 19·29% and 1·24%, and for 95% alcohol, 49·00% and 42·05%. The oil obtained by ether extraction of the ground seeds deposits a small amount of solid when kept. It is practically odourless, with a bland taste, and has d^{20} 0·9219; n^{20} 1·4769; iodine value (Hanus) 137·5; saponif. value 191·03; Reichert–Meissl value 0·44; acid value 0·39; acetyl value, 11·35; unsaponifiable matter, 1·28%; soluble acids (as butyric acid %), 0·83; insoluble acids, 93·93% (iodine value 132·0); unsaturated acids (corr.), 89·74% (iodine value 145·0); and saturated acids, 4·86% (iodine value 3·4, before correction). The oil contains the glycerides of oleic acid (37·41%), linoleic acid (56·37%), saturated acids (probably stearic and palmitic acid, with a small amount of arachidic acid) (5·08%), whilst a *phytosterol*, m. p. 165—166°, was obtained from the unsaponifiable material. F. G. Willson.

Relative proportions of potassium and sodium in plants. G. Bertrand and D. I. Perietzeanu (Compt. rend., 1927, **184**, 1616—1618).—In terrestrial plants the ratio K/Na is distinctly higher than unity. The ratio, however, is extraordinarily variable, fluctuating from 3 in the case of the mallow to more than 1000 in the elder. In marine plants, preliminary figures yield ratios also greater than unity. W. Robson.

Accuracy obtainable by repetition of simple measurements. A. Krogh (J. Biol. Chem., 1927, **74**, 393—407).—The maximum accuracy obtainable in making simple measurements is given by the average of ten readings, further repetition serving no good purpose. This conclusion is reached both from statistical considerations and from the practical execution of such operations as the measuring of the thickness of needles and cover slips and the use of the polarimeter; in the latter connexion, the degree of accuracy claimed by Lundsgaard and Holbøll (A., 1925, i, 1494; 1926, 861) could not be substantiated. C. R. Harington.

Methods. VIII. L. Pincussen. **Determination of total sulphur in urine and in organs.** A. Konarsky (Biochem. Z., 1927, **187**, 398—402).—A method is described for the determination of sulphur in organic substances, tissue, and urine. P. W. Clutterbuck.

Ceruleomolybdate determination of phosphates. B. E. Gilbert and J. B. Smith (J. Biol. Chem., 1927, **74**, 223—229).—In the method of Denigès (A., 1920, ii, 770) the presence of high concentrations of acid inhibits the development of colour; in such cases, therefore, it is necessary to employ a standard of the same acidity as the unknown solution. The coloured compound formed in the reaction appears to be colloidal. C. R. Harington.