BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1929.

General, Physical, and Inorganic Chemistry.

Monochromatic light filters. II. Use of Goldberg's spectrodensograph. E. Elvegard, W. Staude, and F. Weigert (Z. physikal. Chem., 1929, B, 2, 149—160; cf. Weigert and Staude, A., 1928, 40).—The principle of autocollimation is applied to the method of producing a strong beam of monochromatic light described previously. The purity of the light was tested by means of Goldberg's "spectrodensograph," the spectral intensity curve of the light source being determined. The method of using the instrument for this purpose is described.

A. J. Mee.

Para- and ortho-hydrogen. K. F. Bonhoeffer and P. Harteck (Naturwiss., 1929, 17, 182).—According to Heisenberg's theory, two modifications of molecular hydrogen should occur. Dennison concludes that ordinary hydrogen contains para- and ortho-hydrogen in the ratio 1 : 3. Heat conductivity measurements at low pressures show that the transformation is incomplete at the end of a year, but at high pressures (350 atm.) in metal vessels at the temperature of liquid air practically the theoretical quantity of parahydrogen can be obtained in a week. At the ordinary temperature parahydrogen is a gas which is fairly stable for a week in glass vessels. At 100 atm. it slowly reverts to ordinary hydrogen in metal vessels, but in the presence of platinised asbestos the change occurs at once. Adsorption on charcoal at the temperature of liquid air gives practically pure parahydrogen. After one day, liquid hydrogen contains about 10% of the equilibrium quantity of parahydrogen. Freshly-solidified hydrogen contains parahydrogen in the proportion 1 : 3. R. A. Morton.

Perturbations in the band spectrum of helium. G. H. Dieke (Nature, 1929, 123, 446—447).—Kronig's theory of perturbations in band spectra (A., 1928, 1067) is illustrated by the band spectrum of helium.

A. A. Eldridge.

Stark effect of helium $2P-6D$ line by quantum mechanics. Y. Fujioka (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 99—106).—The theoretical displacements and intensities due to the Stark effect on the $2P-6D$ line have been calculated. The effect has been examined experimentally and found to be in fair agreement with the predictions.

W. E. Downey.

Simple relations between the most intense radiations and the highest chemical elements in the luminous atmosphere of the sun. H. Deslandres (Compt. rend., 1929, 188, 669—673).—Further examples are provided of the rule proposed by the author (this vol., 223), 21 elements, of which 10 have atomic numbers higher than 20, now being included. Apparent exceptions may be explained, *e.g.*, by the effect on the observed line spectra of hydrogen or helium in the chromosphere. Differences between the intensities of the lines of the same elements in the chromosphere and those obtained in the laboratory are also discussed. J. Grant.

Absorption measurements in the cæsium principal series. Widening due to vapour pressure. F. Waibel (Z. Physik, 1929, 53, 459—482).—The intensities of the 5th to 14th members of the principal series of cæsium and the widening due to vapour pressures of 10—32 mm. were determined. There is an appreciable asymmetry in the absorption edges for the lower members of the series. This disappears gradually with the higher members. The widening of the lines is approximately proportional to the square root of the vapour density. The half-value widening increases with the higher members of the series, ultimately becoming constant. The half-value widening of the stronger components is considerably larger than that of the weaker. The ratio of intensities of the components was determined for the 5th and 6th doublets. The total absorption and the number of resonators per atom were determined for the 5th to 14th members of the series, inclusive. The apparatus is described and a table of vapour pressures of cæsium from 6·65 mm. at 355·5° to 760 mm. at 670° is given. A. J. Mee.

Series in the As VI spectrum. P. Pattabhiramiah and A. S. Rao (Z. Physik, 1929, 53, 587—591).—The As VI spectrum has been investigated in the usual way. It is found that the singlet and triplet P, D, and S terms of the d^9p order are strongly combined with the a^3D and a^1D terms of the d^9s order, in agreement with Hund's theory. A. J. Mee.

Effect of resistance on spark spectra. O. Occhialini (Atti R. Accad. Lincei, [vi], 8, 579—584).—A continuation of the author's work to perfect a method of quantitative spectroscopic analysis (this vol., 374). Using apparatus described previously, the effect of variable resistance, in the discharge circuit, on the spark spectrum of lead is demonstrated.

G. E. Wentworth.

Arc spectrum of samarium. Measurements at normal pressure between 3100 and 2750 X. S. Piña de Rubies (Compt. rend., 1929, 188, 780—781).—The lines and their intensities are tabulated together with those ascribed to impurities.

J. Grant.

Measurement of the relative intensities of two emission lines ($1S-3P$ and $2S-3P$) from sodium atoms, arising from the same initial state, as regards the ratio of the corresponding transition probabilities. C. Weiss (Ann. Physik, 1929, [v], **1**, 565—612).—The intensity of an emission line arising from the spontaneous transition of an atom from a state k to a state i is given by $J\nu_{ki}=N_k a_{ki} h\nu_{ki}$, N_k being the number of atoms in the state k, h Planck's constant, and ν_{ki} the frequency of the line, whilst a_{ki} is the transition probability. Bohr has shown that the transition from $3P$ to $2S$ (for sodium atom) should occur much more frequently than that from $3P$ to $1S$. Detailed experiments on the intensities of the lines 3302·6 and 22070 Å. have shown that the ratio $a_{2S-3P}/a_{1S-3P}=25$ with a maximum error of 50% and a mean error of ±15%. An exact determination of a_{3D-3P} was not possible, but it is certainly smaller than a_{2S-3P}. R. A. Morton.

Singlets and triplets in the spectra of two-electron systems. W. V. Houston (Physical Rev., 1929, [ii], **33**, 297—304).—Theoretical. The Darwin–Pauli treatment of the electron is applied to the Schrödinger equation for a two-electron system, with the restriction that one electron must be in an s-orbit. The results show that the division into singlets and triplets is justified only as a limiting case. Expressions are derived which give the position of the levels, the Zeeman effect, and the intensities of the lines when the division into singlet and triplet cannot strictly be made, and also give the observed facts of several spectra. N. M. Bligh.

Stark effect for the diffuse lines of silver and lithium. R. H. Snyder (Physical Rev., 1929, [ii], **33**, 354—360).—The Stark effects on the $5^2P_2-6^2D$ and $5^2P_1-6^2D$ groups of silver lines were studied experimentally by the Lo Surdo method. In the former group the violet s-component was split into two branches, the stronger outer one being designated the $^2D_3$ branch and the weak inner one the F branch. The red s-component had only one, the $^2D_2$ branch. Both the violet and red p-components showed only one branch, the $^2D_3$ violet and $^2D_2$ red branch. In the second group the violet s-component was also split into a strong inner F branch and a weak outer G branch. The single red s-component was designated the $^2D_2$ branch. Both the violet and red had only a single branch, the violet F and the red $^2D_2$ branch (cf. Fujioka and Nakamura, A., 1928, 2). The lithium line 4602·51 Å. was resolved into three s- and three p-components in an electric field, with the violet side having a stronger outer and a weaker inner component for the p-vibration, and a weaker outer and a stronger inner component for the s-vibration. The line 4132·93 Å. was resolved into three s- and three p-components. N. M. Bligh.

Tables of theoretical Zeeman effects. C. C. Keiss and W. F. Meggers (Bur. Stand. J. Res., 1928, **1**, 641—684).—The splitting of spectrum lines into components, when the source is in a magnetic field, furnishes theoretically an absolute identification of the terms involved in the production of the lines. The Zeeman effects of various term combinations have been computed on the basis of Landé's work, and are presented in tables giving results for terms from S to I in the doublet, quadruplet, sextet, and octet systems, in the triplet, quintuplet, and septet systems, and in the doublet–quadruplet, quadruplet–sextet, sextet–octet, singlet–triplet, triplet–quintuplet, and quintuplet–septet intersystems.

C. J. Smithells.

Excitation of sodium by ionised mercury vapour. H. W. Webb and S. C. Wang (Physical Rev., 1929, [ii], **33**, 329—340).—The method used allowed a comparison of the spectrum produced by excited mercury atoms with that due to the ions. The former showed marked resonance and the latter also showed excitation corresponding with the excitation energy of the metastable mercury atom. Theoretical explanations are proposed. Data from photomicrometric measurements on typical spectrograms and from the behaviour of mercury and sodium lines with varying amounts of sodium vapour present are fully tabulated. The spectrum excited by ionised mercury resembled the chemiluminescence spectrum resulting from mixing sodium and mercuric chloride vapours. The spark line of mercury 3984 Å., not previously found in the luminous mercury stream, was found when sodium was present. N. M. Bligh.

Persistence of λ 2537 in mercury at low pressures. H. W. Webb and (Miss) H. A. Messenger (Physical Rev., 1929, [ii], **33**, 319—328).—The persistence of this line excited by electron impact was measured for vapour pressures corresponding with the temperature range 78° to −19° (cf. Zemansky, A., 1927, 491), using an alternating-potential method (cf. A., 1927, 85). Between 78° and 17° the persistence varied inversely as the first power of the pressure, and was much too small to be explained as depending on the life of the metastable atoms; it approached a limiting value of the order of 10^{-7} sec. as the pressure was lowered. The life of 1849 Å. was found to be less than 3×10^{-9} sec. A radiation process probably associated with the 7·1 break in the critical potential curves had a life of 1/470,000 sec., which is suggested as the life of an infra-red transition to the 6·7 volt level, followed by the radiation of 1849 Å. A process associated with an excitation potential between 5 and 6 volts had a life of about 1/120,000 sec. N. M. Bligh.

Transition of excited 2^3P_1 mercury atoms to the metastable state 2^3P_0. H. Klumb and P. Pringsheim (Z. Physik, 1929, **52**, 610—626).—Data are given for the absorption of the line 4047 Å. in mercury vapour as a function of the partial pressure of added gas and the effects produced by helium–neon mixture, argon, nitrogen, carbon monoxide and dioxide, and water vapour have been examined. The results are discussed in relation to the authors' theory and to that of Foote (A., 1927, 999). All the above gases facilitate the transition $2^3P_1\longrightarrow2^3P_0$; nitrogen, however, has an abnormally great influence.

R. W. Lunt.

Excitation of mercury vapour by the resonance line. (Lord) Rayleigh (Nature, 1929, **123**, 488, 569).—Experiments show that with a blast of mercury vapour the source of re-emitted radiation of wave-length 2537 Å. can be observed separated in space from the source of the continuous bands which are of molecular origin. It appears that the interval between excitation and emission may be considerably greater than 10^{-7} sec. As the temperature of the mercury vapour is progressively raised, and a rapid stream of vapour is generated, the secondary source, originally symmetrical on either side of the primary beam, elongates on, and is finally wholly on, the down-stream side. A. A. ELDRIDGE.

Energies of dissociation of cadmium and zinc molecules from an interpretation of their band spectra. J. G. WINANS (Phil. Mag., 1929, [vii], 7, 555—565).—New observations have been made on the absorption spectrum in cadmium vapour. At low pressure the cadmium resonance line at 2288 Å. appears as a narrow absorption line which broadens symmetrically to the limits 2207—2800 Å. with increasing pressure. At pressures above 130 mm. a set of broad and diffuse flutings over the range 2650—2780 Å. develop on this band. The bands at 2212 and 2114 Å. appear at a pressure of 7 mm., the former broadening slightly towards longer wavelengths and the latter increasing symmetrically with increasing pressure. The electrodeless discharge in cadmium vapour exhibits a continuous spectrum with maxima at 2288, 2980, 3000, and 4400 Å. The band at 2212 Å. does not appear. The absorption band 2207—2800 Å. is attributed to the absorption of light by the collision of two atoms to produce a stable excited molecule. The energy of dissociation of the cadmium molecule calculated from the main absorption band is 0·200 volt. Similar measurements on the absorption spectrum of zinc vapour lead to the value of 0·246 volt for the energy of dissociation of the zinc molecule. The dissociation energies of cadmium, zinc, and mercury molecules are shown to be proportional to their atomic heats of fusion. The flutings observed in the main absorption band of cadmium are attributed to the absorption of light by colliding atoms to form an excited molecule and the subsequent emission of this light when the excited molecule returns to the normal state. The fluctuations of intensity arising from this are shown by the flutings in the spectrum. A. E. MITCHELL.

Flutings in the absorption spectrum of a mixture of mercury and cadmium vapours. J. G. WINANS (Phil. Mag., 1929, [vii], 7, 565—566; cf. preceding abstract).—The absorption spectrum of a mixture of cadmium and mercury vapour behaves similarly to that of pure cadmium vapour under changes in pressure. A new set of flutings extending from 2488·6 to 2406·8 Å. appears. These are not present in the spectrum of pure cadmium or pure mercury vapour and are attributed to HgCd molecules.
A. E. MITCHELL.

Resonance as a result of collisions and its bearing on fluorescence and chemiluminescence. H. BEUTLER and B. JOSEPHY (Z. Physik, 1929, 53, 747—765; cf. A., 1928, 459).—Irradiation of a sodium–mercury vapour mixture by the mercury line 2537 Å. causes resonance of the sodium atoms by collisions with mercury atoms excited to the transition $2^3P_1-1^1S_0$. The resonance of the sodium atoms results in the transition 1^2S-7^2S. Admixture of nitrogen causes a rearrangement of 2^3P_1 state of the mercury atoms to the 2^3P_0 state, with a consequent change in the resonance transition of the sodium atoms to 1^2S-5^2S, in agreement with the $2^3P_0-1^1S_0$ transition of the mercury atoms. Similar resonance effects are observed in the chemiluminescence of dilute gas reactions. W. E. DOWNEY.

Second spark spectrum of potassium, K III. T. L. DE BRUIN (Z. Physik, 1929, 53, 658—664).—Making use of the chlorine arc spectrum, Cl I, and the first argon spark spectrum, A II, and with the aid of the law of irregular and regular doublets, the principal terms in the second spark spectrum of potassium, K III, are identified. A doublet and quadruplet system are found. A. J. MEE.

Spectrum of ionised rubidium. R. MAJUMDER (Naturwiss., 1929, 12, 198—199).—By comparison of the spectra of the group Ge^+ to Sr^+ the lines in the spectrum of Rb^+ have been classified.
R. N. KERR.

Spark producer as atomiser of salt solutions for flame spectra and the photography of their spark spectra. W. HIRSCHEL (Chem.-Ztg., 1929, 53, 218—219).—See A., 1928, 449.

Anomalous terms in the spectrum of doubly-ionised lead. S. SMITH (Nature, 1929, 123, 566).—In an analysis of the spectrum of doubly-ionised lead, Pb. III, combinations involving the anomalous terms arising from the state of the doubly-ionised atom of lead when both the two remaining valency electrons occupy $6p$ orbits were found; these are: 995·75, 1165·05 Å. ($6^3P_{1\,2}-6^1D_2$), 4004·16, 3925·23 Å. ($6^1\bar{D}_2-6^3F_{32}$), 1439·42, 3832·83 Å. ($6^1P_1-6^1D_2$ and $6^1\bar{D}_2-6^1F_3$, respectively). In the first spark spectrum of thallium, Tl II, the lines $6^3P_{1\,2}-6^1\bar{D}_2$ and $6^1P_1-6^1\bar{D}_2$ have been found. A. A. ELDRIDGE.

Recombination spectra of ions and electrons in cæsium and helium. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1919, 2, 489—500).—Spectrophotometer measurements of intensity distribution were made in connexion with probe wire measurements of electrical conditions. Intensity depends on the ion concentration independent of discharge current and voltage. Measurements of intensity distribution in the $2P$ band of cæsium and electron velocity distribution were made under a variety of discharge conditions. Photographs and approximate intensity measurements on continuous bands of helium show a strong band beyond 2^3P and fainter bands beyond 2^3S, 2^1P, and 2^1S. The cæsium afterglow is characterised by a more rapid decrease in intensity of the continuous bands with decreasing wave-length.
W. E. DOWNEY.

Corona discharge in neon. F. M. PENNING (Phil. Mag., 1929, [vii], 7, 632—633).—Experiments similar to those of Huxley (A., 1928, 567) are described in which it was found that with pure neon the starting potential for the negative discharge (wire cathode and cylinder anode) was less than that for the positive discharge. This result is in opposition to those of Huxley. Small quantities of argon give a reproduction of Huxley's results. It is concluded that Huxley's results offer no evidence against the theory that electrons can be set free from the cathode by the action of positive ions. A. E. Mitchell.

High-frequency discharges in helium and neon. R. L. Hagman (Phil. Mag., 1929, [vii], 7, 586—596).—In cylindrical discharge tubes of constant diameter and with a constant oscillation frequency, at each distance between the electrodes there is a certain pressure at which the starting potential is a minimum. The potential at this minimum increases with the distance between the electrodes. With tubes of different diameters it was found that the starting potential decreases with increasing diameter. Over the wave-length range of 40—640 metres the starting potentials increase with the wave-length for pressures up to 6 mm., above which the potential is approximately constant for all wave-lengths. With each gas there is a certain pressure at which the potential required to maintain the discharge is a minimum. With increasing pressure the maintenance potential increases almost directly proportionally to the increase of pressure. The maintenance potentials vary considerably with the wave-lengths, indicating that the potential comprises two parts, (1) the potential fall in the main column of the gas which is under uniform electric force which is independent of the wave-length, and (2) the potential drop at the electrodes which is independent of the length of the discharge and roughly proportional to the wave-length. All the discharge phenomena in helium and neon are highly sensitive to impurities in the gases. A. E. Mitchell.

High-frequency discharges in gases. J. S. Townsend and W. Nethercot (Phil. Mag., 1929, [vii], 7, 600—616).—Methods for the determination of the relationship between the current and the *E.M.F.* in high-frequency discharges are described. Experiments have been made with high-frequency and continuous-current discharges in nitrogen. The results are in agreement with the theory of Townsend (Compt. rend., 1928, **186**, 55). A. E. Mitchell.

High-frequency discharge in gases. B. C. Mukherjee and A. K. Chatterji (Nature, 1929, **123**, 605).—The striations obtained with internal and external electrodes differ, the former, except at low pressures, having a comb-like appearance. As the pressure is lowered, the thickness of the striæ increases; the glow extends beyond the electrodes, and striations are also observed in this region. The same glow discharge can be obtained with only one external electrode. A. A. Eldridge.

Direct transition from the independent to the dependent conduction of electricity in strongly ionised gases at high pressures. R. Thaller (Physikal. Z., 1929, **30**, 59—61).—The normal current–voltage characteristic curve of a gas ionised by means of *X*-rays, β- and α-rays, or ultra-violet light shows (*a*) an increase of current proportional to the voltage, (*b*) at higher voltage the current increases more slowly and reaches a saturation value maintained until the saturation voltage has been exceeded several times over, when (*c*) a very sudden increase in current makes its appearance. An arrangement is described whereby the transition from the stage where Ohm's law is obeyed (*a*) to the third stage (*c*) occurs without the appearance of the saturation stage (*b*) (cf. this vol., 114). R. A. Morton.

Thermionic emission of copper tubes filled with salts. T. Pecsalski and J. Chichocki (Compt. rend., 1929, **188**, 699—701).—The positive thermionic current obtained from a copper tube filled with nickel, chromium, or calcium chloride and heated electrically at a pressure of 10^{-6} mm. increases with time more rapidly than the negative emission and exists even when the tube is at zero potential. The phenomena are most marked with nickel salts. J. Grant.

Photo-electric effect with change of state of the cathode. A. Goetz (Z. Physik, 1929, **53**, 494—525).—In order to examine the change in the photo-electric effect caused by change of state of the cathode, and to see whether the change is analogous to that in the thermionic emission, the photo-electric effect with molten tin and two of its allotropes has been investigated. The metal tin alone possesses the properties required of an element for this work. An apparatus is described by means of which both the thermal progress of the phase change and the electric effect can be observed simultaneously. The photo-electric emission was measured by a Hoffmann electrometer of extreme sensitiveness. The temperature range used was 50—550°, and the wave-length range 2300—2900 Å. Within these ranges the photo-electric emission is independent of the temperature for the three phases examined, provided there is no change in the phase. The three phases have different wave-length limits, the emission energy increasing with decreasing energy content of the metal. A change in phase alters the intensity of the emission. The wave-length limits are: for liquid tin 2925±10, for hexagonal (γ) tin 2820±10, for tetragonal (β) tin 2740±10 Å. The transition point from γ- to β-tin determined by this method is 200±2°, but the velocity of transition is very small. The emission for short wave-lengths follows an exponential law, involving two constants, from one of which the capacity of the surface for optical absorption and the photo-electric quantum equivalent can be found. It is probable that the quantum equivalent changes with the phase, the modification with the denser packing (*i.e.*, β-tin) having a larger equivalent than that with the less dense packing (*i.e.*, γ-tin). There is a parallelism between thermionic and photo-electric phenomena for the three phases. A. J. Mee.

Photo-electric emission and thermionic emission. E. H. Hall (Proc. Nat. Acad. Sci., 1929, 15, 126—127).—It is shown that it does not follow from the experiments of Du Bridge on platinum (cf. A., 1928, 340) and of Warner on tungsten (cf. A., 1927, 391) that the amount of work required to overcome resisting forces is the same for an electron taken from the free state within to the free state outside the metal as for an electron taken by photo-electric action out of the metal. The values of the constants in the thermionic emission formula are discussed. N. M. Bligh.

Temperature dependence of electron emission under high fields. W. V. Houston (Physical Rev., 1929, [ii], **33**, 361—363).—Theoretical. N. M. Bligh.

Photo-electric effect and the continuous X-spectrum. E. Sevin (Compt. rend., 1929, **188**, 911—912; cf. Décombe, *ibid.*, 1927, **185**, 1265).—The photo-electric law and the maximum frequency of the continuous X-spectrum resulting from the law of Duane and Hunt are deduced from the author's theory of light (*ibid.*, 1929, **188**, 290). J. Grant.

Photo-electric effect of ultra-violet rays on gases. R. Dantinne and P. Lenaerts (Arch. Sci. Phys. Nat., 1929, [v], **11**, 5—14).—The photo-electric action of ultra-violet rays on gases depends on the nature of the gas, the frequency of the light, and probably to a considerable degree on the pressure. It is a volume effect in contradistinction to the photo-electric effect on solids, which is a surface effect. The characteristics of the photo-electric effect with solids lead to the view that it is the adsorbed gas and not the solid which furnishes the photo-electrons. This view implies a parallelism between the relative intensities of the effects with different gases and the relative intensities of the effects brought about by the same radiation on a metallic surface surrounded by the same gases. A special apparatus has been constructed for measuring the photo-electric effect caused by the light from an aluminium spark on oxygen, air, carbon dioxide, and sulphur dioxide. The relative values of the ionisations produced in the different gases agree well with the data for the photo-electric effect at a metallic surface in the same gases. The active element (for the frequencies used) appears to be oxygen. R. A. Morton.

Form and structure of sparks. V. Long sparks in different gases. T. Terada, U. Nakaya, and R. Yamamoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 43—68).—The sparking potential in sulphur dioxide at normal pressure is three times that in air. Long sparks in acetylene and in carbon dioxide have an afterglow of 10^{-4} sec. duration. W. E. Downey.

Average "forward" momentum of photo-electrons. E. J. Williams (Nature, 1929, **123**, 565—566).

Astrophysical estimate of the ionisation potential of vanadium. A. V. Douglas (Nature, 1929, **123**, 606—607; cf. A., 1928, 682).—From periodic intensity changes the value of the ionisation potential of vanadium is estimated to be 6·74 volts, in agreement with Russell's value from spectroscopic data of 6·76 (Astrophys. J., 1927). A. A. Eldridge.

Polarisation of electron waves. E. Rupp (Z. Physik, 1929, **53**, 548—552; cf. Davisson and Germer, this vol., 7).—A beam of electrons was twice reflected from the surface of a copper crystal. The number of electrons reflected showed no selective reflexion maxima depending on the rotation of the two reflectors about the axis of the beam. A homogeneous external magnetic field has no effect on the reflexion. A selective maximum was obtained for electrons of velocity 150 volts when reflected from the {111} face of copper, which might be attributed to polarisation, but the angle of the beam with the reflector for this was small (12°) and there are many experimental difficulties involved in finding out whether it is a case of real polarisation. A. J. Mee.

Effects of an homologous series of amines on the mobilities of ions in hydrogen gas. L. B. Loeb and K. Dyk (Proc. Nat. Acad. Sci., 1929, **15**, 146—156; cf. A., 1928, 932, 809, 609).—Following a study of the effect of ammonia (cf. A., 1927, 181), that of the amines was investigated, as the size of the molecule could be varied without markedly changing the electro-chemical properties of the gas. The reciprocal mobility for positive and negative ions is plotted against the percentage of amine present, and compared with Blanc's law. For pure methylamine, the mobilities in the amine were somewhat less than in ammonia; for methylamine and hydrogen mixtures the negative ion showed a marked departure from Blanc's law for small percentages of amine; for mixtures of propylamine and hydrogen the smallest trace of amine reduced the mobility; for methylamine–hydrogen–ammonia mixtures the mobilities were decreased slightly more by the ammonia in accordance with Blanc's law. Theoretical explanations are given. N. M. Bligh.

Ionisation of gases by positive ions. R. M. Sutton (Physical Rev., 1929, [ii], **33**, 364—372).—Using a simple tube, positive potassium ions were driven by controllable accelerating potentials up to 750 volts into neon and argon. Curves are given showing the variation of ionisation with pressure over a range of 0·05—1 mm., and the number of new ions formed per positive ion per cm. path reduced to 1 mm. pressure. The efficiency of the effect is less than for electron bombardment, and had not reached a maximum at 750 volts. The pressure range showing ionisation effect is higher than expected from kinetic theory, and indicates the presence of long mean free paths for the positive ions (cf. Kennard, A., 1928, 453; Durbin, *ibid.*, 103). N. M. Bligh.

Nature of the ions in air. H. A. Erikson (Physical Rev., 1929, [ii], **33**, 403—411; cf. A., 1927, 1002; this vol., 114).—The transference of an electron from an H_2O molecule to the final positive air ion is further studied and results are given showing the production and ageing of the initial positive ion in dried air and nitrogen. When the final positive air ion of mobility 1·36 is passed into moist air the final ions disappear and a swifter 1·87 ion appears; these in turn change back into a 1·36 ion. This is interpreted as due to a neutral H_2O molecule giving up an electron to the final 1·36 two-molecule positive ion, thus giving a one-molecule positive ion having a higher mobility. This H_2O^+ ion ages by attaching itself to another molecule forming a slower 1·36 ion. The initial and final positive ions are considered to be one and two molecules large, respectively. N. M. Bligh.

Formation of monatomic hydrogen by collisions with slowly moving electrons. K. E. Dorsch and H. Kallmann (Z. Physik, 1929, **53**, 80—91).—Experiments are described in which electrons of energy from 7 to 16 volts are allowed to collide with hydrogen molecules; the blackening of lead chloride in the hydrogen stream was used as an index of the formation of monatomic hydrogen. In

accordance with theory and the earlier experiments of Hughes and Skellett (A., 1927, 811), appreciable dissociation takes place only above the first resonance potential, 10·8 volts, and increases greatly when the potential is 16 volts corresponding with ionisation. Evidence has been obtained that with 7-volt electrons a small formation of monatomic hydrogen occurs, probably due to absorption of the electron energy as nuclear vibrational energy, since the dissociation energy corresponds with 4·3 volts. Under such conditions not more than 1 in 4×10^5 collisions results in dissociation. Experiments are also described which establish that monatomic hydrogen is also formed by a secondary process in which hydrogen ions react.
R. W. Lunt.

Electron- and ion-streams in gases at low pressures. G. Spiwak (Z. Physik, 1929, 53, 805—839).—Mathematical. W. E. Downey.

Electronic charge *e*. J. H. J. Poole (Nature, 1929, **123**, 530).—The possibility that a new value of π should be used in obtaining the value of $hc/2\pi e^2$ is suggested (cf. Birge, this vol., 368; Bäcklin, *ibid.*, 369). A. A. Eldridge.

Electromagnetic field of an electron. The electron as a gravitational phenomenon. D. Meksyn (Phil. Mag., 1929, [vii], 7, 425—433).—Mathematical. An electron is assumed to represent the same entity as a neutral mass in which the matter or energy is spread throughout the space instead of being located in a small region. The electron is thus a gravitational field of potential m/r^2. It is shown that there are no stresses in such a field.
A. E. Mitchell.

Phenomena of projected electrons. T. J. I. Bromwich (Phil. Mag., 1929, [vii], 7, 470—476).—A definite statement of the deductions from the author's previous treatment (*ibid.*, 1928, [vii], 5, 636) of the Einstein theory of relativity is given.
A. E. Mitchell.

Thermodynamical properties of the electron and atomic theory. R. D. Kleeman (Phil. Mag., 1929, [vii], 7, 493—504; cf. this vol., 379).—The equation of state of electron gas is shown to be $pv=RT\xi$, where ξ is less than unity and decreases as v increases. This result combined with kinetic deductions is used to show that the velocity of an electron in an electron gas gradually decreases between two consecutive collisions and increases during a collision, whilst the internal energy of an electron under the same conditions increases between consecutive collisions and decreases during collisions. Since these changes can be achieved only by changes in the electric fields of the colliding electrons, it is concluded that decreases in internal energy must result in radiation into space. These results are employed in the discussion of the formation of atoms.
A. E. Mitchell.

Vapour-pressure separation of isotopes by fractional distillation. I. Distillation experiments with carbon tetrachloride. H. G. Grimm (Z. physikal. Chem., 1929, **B**, 2, 181—199).—In the hope of separating two different carbon tetrachlorides containing the two isotopes of chlorine, the pure liquid was subjected to extensive fractional distillation. The densities of the fractions were found, and were shown not to differ within the experimental error of 2×10^{-5}. Using this estimated error it is possible to calculate the upper limit for the density difference between the compounds containing neighbouring isotopes. Using an empirical formula due to F. D. Brown, it is shown that the difference in b. p. between the two forms of carbon tetrachloride differing in mol. wt. by two units cannot exceed 10^{-3}°, and the vapour pressures cannot differ by more than 0·03 mm. Calculations using this value point to the existence of energy at 0° Abs. A. J. Mee.

Vapour-pressure separation of isotopes by fractional distillation. II. Experiments in the fractionation of chlorine on the large scale. H. G. Grimm and L. Braun (Z. physikal. Chem., 1929, **B**, 2, 200—206).—When 60,000 kg. of chlorine were fractionally distilled, the fractions converted into ammonium chloride, and the densities of the saturated solutions of the salt determined, the results were the same for all the fractions within the experimental error. Any possible at. wt. difference of the fractions must be smaller than 0·002% of the at. wt. of chlorine. A. J. Mee.

Constitution of oxygen. F. W. Aston (Nature, 1929, **123**, 488—489).—There is no evidence that oxygen is other than a simple element (cf. Giauque and Johnston, this vol., 369). Faint lines which might be ascribed to the existence of O^{18} are capable of other interpretations. A. A. Eldridge.

Separation of isotopes. J. N. Brönsted and G. Hevesy (Phil. Mag., 1929, [vii], 7, 631—632).—Exception is taken to the view expressed by Harkins and Mortimer (A., 1928, 1301) that the mercury used by Brönsted and Hevesy in their work on the separation of the isotopes of mercury was impure. An outline of the methods used to establish the purity of their material is given. A. E. Mitchell.

Quantum theory of radioactive disintegration. G. Gamow (Z. Physik, 1929, 53, 601—604).—Mathematical. Earlier work on the solution of the wave equations (cf. this vol., 7) is further discussed in connexion with the views of Laue. A. J. Mee.

Adsorption of radium emanation. A. Becker and K. H. Stehberger (Ann. Physik, 1929, [v], 1, 529—555).—The adsorption of emanation by carbon and silica gel has been investigated by a static method. Adsorption on solids, like absorption by liquids, is characterised by the appearance of stationary equilibrium states determined solely by the concentration ratio of emanation in the solid or liquid and in the surroundings, this ratio depending on the temperature. The law governing adsorption of ordinary gases is thus confirmed at partial pressures of a very low order. The equilibrium distribution of emanation is independent of the nature and pressure of the accompanying gas, of the amount of adsorbing solid, of the volume of the container, and of the partial pressure of emanation; it depends solely on the adsorbing material and the temperature. The adsorption coefficient has been measured over the temperature range —80° to 100°, and the validity of the thermodynamic equation for the reaction isochore is demonstrated. The specimen of carbon exhibited a high absolute value for the adsorption coefficient which varied greatly with temperature. The silica gel was less effective, since the adsorption coefficient at the temperature of solid carbon dioxide was equal only to that of carbon at the ordinary temperature. The reason for the difference between the two substances is not clear.

The dynamic method of investigating the adsorption of emanation in a gas stream is attended by special difficulties, but quantitative data can be obtained if due precautions are taken.

R. A. Morton.

Straggling of α-particles from polonium in passing through gases. H. Eyring (Physical Rev., 1929, [ii], **33**, 386—388; cf. A., 1928, 4).—The straggling coefficients in the gases ethylene, air, nitrous oxide, carbon dioxide, methyl iodide, ethyl bromide, and ethyl iodide have been determined from the ends of the Bragg ionisation curve. The average values are found to be greater than those calculated theoretically, except in the case of methyl iodide.

N. M. Bligh.

Volatilisation of polonium. P. Bonét-Maury (Ann. Physique, 1929, [x], **11**, 253—341).—The concept of temperature of vaporisation as applied to the radio-elements is examined critically and abandoned. A method is described of investigating the distribution in space of the active atoms vaporised, and Lambert's law of cosines is verified. A detailed study is made by an improved experimental method of the vaporisation of polonium deposited electrochemically or by condensation on platinum or nickel. Curves are given showing the quantity of polonium vaporised as a function of time at a number of different temperatures. The quantity vaporised is independent of the time, and is a simple function of the temperature. A reverse phenomenon is indicated, and is presumed to be a thermal diffusion tending to cause polonium to penetrate into the surface on which it is deposited. The removal of a polonium atom from platinum requires more energy than its removal from nickel. Results from condensed polonium are less regular than from samples deposited electrochemically.

N. M. Bligh.

Counting of scintillations produced by α-particles. I. II. Determination of the efficiency of transformation of the kinetic energy of α-particles into radiant energy. III. Practical applications. J. Chariton and C. A. Lea (Proc. Roy. Soc., 1929, **A**, **122**, 304—319, 320—334, 335—352).—I. A systematic investigation has been made of the factors involved in the scintillation method of counting α-particles and of its limitations. An apparatus is described for producing regular point flashes of light of known spectral constitution, the conditions under which scintillations are observed being imitated as closely as possible.

II. A determination of the luminous efficiency of the process of scintillation formation necessitates the measurement of the candle-power of a zinc sulphide screen when bombarded by a known number of α-particles of known energy. To obtain the spectral distribution, spectrograms were taken of various zinc sulphides when bombarded by α-particles, using an α-ray tube filled with radon which could be covered with different preparations of zinc sulphide. The numbers and energies of the α-particles producing the radiation could not be determined with precision, owing to irregularities of the glass walls of the tube. The brightness of the α-ray tube was therefore compared with that of a plane screen of the same zinc sulphide bombarded by a known number of α-particles of known energy. Since the spectral distributions of the light were the same in both cases, the intensities could be compared by comparing the blackening produced in a photographic plate illuminated directly by light from the two sources. The values obtained for the radiant and luminous efficiencies of various zinc sulphides when bombarded by α-particles are surprisingly high—viz., about 25 and 12%, respectively—whilst the value obtained by Marsden for the radiant efficiency was 1·5%. The high values, however, are in agreement with those calculated from data for radioactive luminous paints.

III. An investigation of the influence of the numerical aperture of the microscope employed on the results of counting showed that, when scintillations produced by α-particles of 2·7 cm. range are observed with a microscope of magnification 50 and of variable numerical aperture, the scintillations become invisible when the numerical aperture is reduced below 0·08. For this value of the numerical aperture the energy entering the eye from a single scintillation evaluated as green light (λ=0·505 μ) is 290 quanta. Scintillations observed with the eye placed at varying distances from the screen become invisible when the eye receives less than 30 quanta per scintillation. The velocity of the slowest α-particles capable of producing a scintillation observable in a microscope of magnification 50 and numerical aperture 0·45 was found to be $2{\cdot}7\times10^8$ cm./sec. The energy entering the eye from such a scintillation, using the value previously obtained for the efficiency of the zinc sulphide employed, is 300 quanta of green light (λ=0·505 μ).

The experimental results obtained in the three parts of the paper are interpreted and discussed. It is considered that the explanation of the fact that a smaller fraction of the light from a scintillation produces a visual sensation when the eye is unaided than when a microscope is used lies in the optical properties of zinc sulphide crystals. If the "size" of a scintillation is the same as that of a crystal of zinc sulphide, then the dimensions of the retinal image will be greatly increased when a microscope is used. The mechanism of the scintillation process is discussed, with special reference to the high values obtained for the radiant efficiencies.

L. L. Bircumshaw.

γ-Radiation of radioactive elements. E. Chalfin (Z. Physik, 1929, **53**, 130—133).—Polemical.

Quantum mechanics and radioactivity. II. J. Kudar (Z. Physik, 1929, **53**, 134—137).

Course of the α-change. D. Enskog (Z. Physik, 1929, **53**, 639—645).—The assumption that through a quantum switch there is a decrease in the number of magnetons from the two which the α-particle is supposed to possess in the normal state, to one, is further examined. The calculations show that the quantum switch for fast rays occurs with an increase in energy, and for the slower rays with a decrease. The calculated velocity range for rays of the former type agrees with observed values.

A. J. MEE.

Ionisation method for the examination of corpuscular rays and its application to the detection of atomic particles. A. WEGERICH (Z. Physik, 1929, **53**, 729—746).—The construction of an ionisation cell filled with helium–neon mixture is described. The cell is used to examine corpuscular rays, in particular the atomic particles resulting from the bombardment of certain elements with α-particles. In the direction 130—150° with respect to the direction of the α-particles, H-particles were emitted from carbon, aluminium, iron, copper, and zinc.

W. E. DOWNEY.

Range of fluctuations of α-rays. P. PREISLER (Z. Physik, 1929, **53**, 857—886).—The fluctuations in range of α-particles from thorium-*C′* in air, mica, and bismuth have been measured. W. E. DOWNEY.

Internal absorption of γ-rays. J. A. GRAY and A. J. O'LEARY (Nature, 1929, **123**, 568).—A previous estimate (A., 1925, ii, 84) of the internal absorption of the γ-rays of radium-*D* and the fraction of the atoms emitting γ-rays is revised. Of 43 atoms disintegrating, 24 emit γ-rays, and of these 24 γ-rays, 19 suffer internal absorption. Less than one atom of radium-*E* in 25,000 atoms emits a β-ray of energy 2×10^6 volts. A. A. ELDRIDGE.

Successive α-transformations. G. GAMOW (Nature, 1929, **123**, 606).—The paradox that, although the probability of emission increases enormously with the energy, the slowest α-particles are the first to be emitted, is explained if it is assumed that all the α-particles are originally in the same quantum state. A. A. ELDRIDGE.

Duration of elementary light emission. J. STARK (Ann. Physik, 1929, [v], **1**, 323—340).—The oscillation period is defined as the time occupied in the transition between a higher and a lower equilibrium position of an atomic electron with respect to the atomic ion. For the line H_γ, Traubenberg and Gebauer (A., 1927, 1002) obtained an experimental value of 10^{-9} sec. The author's views (cf. this vol., 223) now indicate a theoretical value of 10^{-13} sec. The experimental work on the luminescence of canal rays has therefore been repeated under improved conditions. It is shown that the effect of an electric field on the lines H_α, H_β, and H_γ arising from particles moving at about 7×10^7 cm. sec.$^{-1}$, is restricted to the first 0·1 mm., from which result it is concluded that the emission process for the three lines, and therefore the time occupied in the transitions between equilibrium positions, must be less than 10^{-10} sec. A suggestion is made that the discrepancy between this result and the work of Traubenberg and Gebauer (which can be confirmed if glass tubes are used instead of fused quartz tubes) arises from an electric field between the cathode and the wall of the tube. The earlier observations on the time factor in light emission from canal rays are reconsidered and it is concluded that the moving atoms are characterised by outer electrons distributed over a series of energy levels. R. A. MORTON.

Structure of the solar chromosphere. L. D'AZAMBUJA (Compt. rend., 1929, **188**, 773—775).—The granular structure of the monochromatic solar spectrographs has been examined by simultaneous photography of the two couples of lines Ca 4227—Fe 4384 and Ca 4227—Fe 4202, but no appreciable difference in the form and distribution of the grains was detected, and the difference between the heights of the two iron rays (1200 and 700 km., respectively) is apparently too small to affect them. A similar granulation was observed for the H_α ray, which occurs at a higher level. J. GRANT.

Energy transference in nuclear collisions. W. KUHN (Z. Physik, 1928, **52**, 151—157).—In the collision between an α-particle and an atomic nucleus only a fraction of the energy is transferred to the latter. The energy required for the disruption of the nucleus is considered a measure of the nuclear stability. The astrophysical significance of this is discussed with reference to the elements occurring under the conditions which exist in the fixed stars.

G. E. WENTWORTH.

Efficiency of quenching collisions and the radius of the excited mercury atom. E. GAVIOLA (Physical Rev., 1929, [ii], **33**, 309—318).—The assumption of Foote (cf. A., 1927, 999) that every collision of a foreign gas molecule with an excited mercury atom is efficient in quenching the resonance radiation is discussed critically. A new calculation of the efficiency of collisions leads to the value unity for carbon monoxide, hydrogen, and perhaps oxygen, and less than unity for water vapour, nitrogen, argon, and helium. The radius of the excited mercury atom is calculated using an improved value for the amount of resonance radiation re-absorbed in the resonance vessel and found to be $2{\cdot}91\times10^{-8}$ cm., or 1·62 times as large as for the normal atom, for the case of hydrogen, and $5{\cdot}5\times10^{-8}$ cm. or three times the normal for the case of carbon monoxide. Actually carbon monoxide has a greater quenching efficiency than hydrogen. N. M. BLIGH.

Evaporation of thorium from tungsten. (MISS) M. R. ANDREWS (Physical Rev., 1929, [ii], **33**, 454—458).—The rate of evaporation from pure and from carbonised tungsten, of thorium deposited by evaporation either from thoriated filaments or from metallic thorium was measured between 2000° and 2500° Abs. Evaporation from both surfaces was found to vary directly with the fraction covered, and was more rapid from pure than from carbonised tungsten, the respective heats of evaporation being calculated as 177,000 and 202,000 g.-cal./g.-atom.

N. M. BLIGH.

Polarisation of the Compton scattering according to the Dirac theory. Y. NISHINA (Z. Physik, 1929, **52**, 869—877).—Mathematical.

R. W. LUNT.

Nuclear levels and artificial disintegration. R. W. GURNEY (Nature, 1929, **123**, 565).—Attention is directed to the possibility of resonance phenomena if the solutions of the Schrödinger equation which for certain ranges of energy give ψ-functions the amplitude of which inside the nucleus is large compared with that outside, are taken into account.

A. A. Eldridge.

Boundary of the solar chromosphere. W. H. McCrea (Nature, 1929, **123**, 527—528).

Quantum mechanics of energy transfers between atoms. H. Kallmann and F. London (Z. physikal. Chem., 1929, **B**, 2, 207—243).—The transfer of excitation energy between atoms can be interpreted as a resonance phenomenon. The amounts of energy that an atom can take up or lose are not optically "sharp," but distributed over a range. A resonance curve could be drawn to express the probability of transfer of each given energy. This is analogous to the shortened life period of an oscillator (and consequent broadening of a zone of anomalous dispersion) when the radiation forcing it is intense. The sharpness of resonance between an atomic "resonator" and a light wave will depend on the strength of the atomic field; the stronger the field the broader is the resonance. Quantum mechanics is applied to such a resonance, and the modification of stationary states when two atoms approach adiabatically is calculated. Consideration is given to the elementary processes involved and to the kinetics in the case of an excited gas. The effective cross-section for collisions in which energy transfer takes place depends on the sharpness of resonance. The limiting case of sharp resonance is considered separately, and the effect of velocity of the gas atoms discussed. The effective cross-section for a transfer corresponding with a "permitted transition" is very great. These ideas are applied to some special cases of collisions of the second kind: (1) the production of the ultraviolet bands observed by Lyman in hydrogen mixed with argon, (2) the calculation of intensities of the sodium lines produced in a mixture of sodium atoms with mercury atoms excited to the 2^3P_0 and 2^3P_1 states, (3) resonance by the switch $2^3P_1 \longrightarrow 2^3P_0$ in mercury itself, and (4) the quenching of fluorescence of sodium vapour by nitrogen and hydrogen. Further application is made in the case where a transfer of excitation energy occurs in one atom only, and to the various ways in which the degree of polarisation of resonance radiation can be influenced. The simple formulæ will explain the excitation of the two *D* lines by the radiation of one, and the results of iodine vapour resonance experiments. The possibilities of energy transfer in chemical reactions, particularly catalytic reactions and the dissociation of hydrogen molecules by excited mercury atoms, are discussed. The broadening of spectral lines by collisions is examined in the light of the supposed transfer mechanism.

A. J. Mee.

Quantum laws and the uncertainty principle of Heisenberg. G. N. Lewis and J. E. Mayer (Proc. Nat. Acad. Sci., 1929, **15**, 127—139).—Mathematical.

Doubling of *X*-ray and optical terms through electronic rotation, and the intensity of the cæsium lines. G. Gentile and E. Majorana (Atti R. Accad. Lincei, 1928, [vi], 8, 229—233).—Theoretical. It is shown that the potential of Fermi not only allows of the satisfactory *a priori* determination of the energy levels of the heavy atoms, but also gives derived values of great accuracy, considering the statistical nature of this theory of the atom, for the doubling of the *X*-ray and optical terms.

F. G. Tryhorn.

Theory of electron emission of metals. L. Nordheim (Physikal. Z., 1929, **30**, 177—196).—A review.

Transmutation of the lighter elements in stars. R. d'E. Atkinson and F. G. Houtermans (Nature, 1929, **123**, 567—568).

Beryllium and helium. (Lord) Rayleigh (Nature, 1929, **123**, 607).—Since beryl contains helium but no appreciable quantities of radioactive substances (A., 1908, ii, 649), the isotope Be^8 may have existed and have broken up as suggested by Atkinson and Houtermans (preceding). A. A. Eldridge.

Distribution of electrons in atoms. L. M. Alexander (Phil. Mag., 1929, [vii], **7**, 517—522).—It is assumed that the electronic relationships between sublevels of a group are similar to the relationships postulated by Bohr for the principal groups. The suggestion of Stoner (A., 1925, ii, 85) that the number of electrons in an atom associated with each sublevel is equal to double the inner quantum number, is discarded. A classification of the electron distribution in the *K*, *L*, *M*, *N*, *O*, and *P* levels of thirty atoms with atomic numbers from 1 to 85 is given.

A. E. Mitchell.

New regularities in the series of the elementary ionic radii. A. M. Berkenheim (Z. physikal. Chem., 1929, **141**, 35—40; cf. A., 1928, 1191).—The ionic radii of the elements in any horizontal row of the periodic table can be arranged as an arithmetical series with a constant difference which is different for each series. Taking the radius of the positive carbon ion as unity, the radii of the positive and negative ions can be arranged in regular series of simple numbers; *e.g.*, the ions C^{++++}, B^{+++}, Be^{++}, Li^{+} have radii represented by the numbers 1, 2, 3, 4; the ions C^{++++}, Si^{++++}, Ti^{++++}, Zr^{++++}, Ce^{++++} have the radii 1, 2½, 4, 5½, 6½, and the neon atom with the negative ions F^{-} and O^{--} form the series 10, 9½, 8½. The absolute values of the ionic radii calculated by this method agree well with the values of Goldschmidt. O. J. Walker.

Optical experiments with perylene and its derivatives. II. Visible absorption spectra of some di-derivatives. A. Dadieu (Z. physikal. Chem., 1929, **B**, 2, 253—261; cf. A., 1928, 1071).—The absorption spectra of the following di-derivatives have been investigated: 3 : 9-dipropionyl-, 3 : 9-dibutyryl-, 3 : 9-di-*o*-toluoyl-, 3 : 9-dianisoyl-, 3 : 10-dinitro-, and 3 : 10-diamino-perylene, perylene-3 : 10- and -1 : 12-quinone. The influence of the substituents is to displace, widen, and alter the intensity of the bands. The results are discussed on the basis of the electronic theory. A. J. Mee.

Absorption spectra of pyrrole and its derivatives. IV. Ethyl and methyl esters of 1-anilino-2-phenyl-5-methylpyrrole-4-carboxylic acid. V. Certain pyrrolecarboxylic acids and their ethyl esters. VI. Ethyl 2 : 5-dimethyl-

pyrrole-3 : 4-dicarboxylate and 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate. VII. Ethyl 1-phenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate and 1-anilino-2-phenyl-5-methylpyrrole-carboxylate. VIII. Ethyl 2 : 5 : 2′ : 5′-bispyrrole-3 : 4 : 3′ : 4′-tetracarboxylate. G. Korschun and (Mme.) C. Roll (Bull. Soc. chim., 1928, [iv], 43, 1075—1085).—IV. The absorption spectra of these two esters are nearly identical, each consisting of a single band, the intensity of which is a little stronger for the ethyl than for the methyl ester. The *methyl* ester was prepared from methyl phenacylacetoacetate (from methyl acetoacetate and phenacyl bromide) and phenylhydrazine, the *monohydrazide*, m. p. 113° (indef.), being obtained as an intermediate.

V. The absorption spectra of the following have been examined: 1 : 2 : 5-trimethylpyrrole-3 : 4-dicarboxylic acid and its monoethyl ester, mono- and diethyl esters of 1-phenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid, 1-anilino-2-phenyl-5-methylpyrrole-4-carboxylic acid, the diethyl and 3-monoethyl esters of 2 : 4-dimethylpyrrole-3 : 5-dicarboxylic acid, 1-carbamido-2 : 5-dimethylpyrrole-3-carboxylic acid and its ethyl ester. The general conclusion is reached that the effect of the replacement of a carbethoxyl by a carboxyl group depends on intramolecular compound formation. If the latter does not occur, the nature of the curve is unaltered. Where complex formation is probable between the nuclear pyrrole nitrogen atom and the carboxyl group, a displacement of the curve towards the red and an increase in the intensity of the absorption occur. On the other hand, if the complex is formed between the nitrogen atom of a substituent in position 1 and the carboxyl group, displacement towards the ultra-violet and a decrease in the intensity are produced. When the saturation of a substituent in position 1 is increased, in addition to the displacement to the ultra-violet previously noted (A., 1925, ii, 258), a decrease in intensity occurs.

VI. The curves for these two ethyl esters are nearly coincident, the intensity of the asymmetric ester being a little stronger than that of the symmetrical one.

VII. Replacement of a methyl group in position 1 by a phenyl group has very little effect on the absorption curve, but when a methyl group attached to a nuclear carbon atom is replaced by phenyl displacement towards the red occurs.

VIII. A displacement towards the ultra-violet is noticed when the absorption spectrum of this ester is compared with that of the ester of 2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid. Two feeble absorption bands can be distinguished in the curve for the bispyrrole derivative. R. N. Kerr.

Absorption spectrum of fluorspar. S. van der Lingen (Z. Physik, 1929, 53, 581—586).—The absorption spectra of various specimens of fluorspar were investigated by means of a Hilger infra-red spectrometer. The different specimens gave different spectra, but some general features are to be noted. In order to discover whether the presence of any gas was the cause of the colour of some fluorspars, some broken mineral was placed in a dried evacuated tube. The emission spectrum of the gas in the tube was found to give only a trace of the strong ultra-violet hydrogen band and the carbon monoxide lines. A. J. Mee.

Polarised fluorescence. (Frl.) E. Hakenbeck (Ann. Physik, 1929, [v], 1, 457—496).—The absorptive properties and the polarised fluorescence of sodium fluorescein (uranine) in glycerol or aqueous glycerol have been studied. A formula has been deduced and confirmed experimentally for the degree of polarisation as a function of the direction of vibration of the incident light. Values for the molecular radius, correct as regards order of magnitude, have been obtained from the degree of polarisation as a function of the viscosity of the solvent, using Perrin's formula. The hitherto accepted mechanism of the fluorescence does not suffice for the explanation of the observations. The mean constants for the quasi-elastic forces have been determined approximately from refractive indices. Beer's law is not obeyed.

R. A. Morton.

Ultra-violet absorption spectra of *o*-, *m*-, and *p*-cresol. J. Savard (Compt. rend., 1929, 188, 782—783).—The energy of electronic activation of the cresols decreases in the order, *o*-, *m*-, *p*-, the *o*- and *m*-compounds having two states of activation and the *p*- only one. The results are compared with those for the dihalogen compounds of benzene, to which they are similar, and with those for benzene, toluene, and phenol. It is shown that the molecular deformability calculated from the frequencies in the active and normal states is increased by the introduction of a methyl group into the benzene nucleus, and that when two substituents are present the deformability is least for the *p*-compound.

J. Grant.

Transformation spectrum of the ruby. E. L. Nichols and H. L. Howes (Proc. Nat. Acad. Sci., 1929, 15, 139—146).—The spectrum of an incandescent ruby heated in a hydrogen flame was found to have superimposed upon the general radiation 21 narrow emission bands termed transformation bands, and visible for a temperature range, 600—775°, which corresponds with profound changes in the absorption of light by the ruby. The wave numbers of the bands and also of the absorption and fluorescence bands are tabulated and shown to occur in sets having a constant frequency interval of 36·7. The phenomena are analogous to those observed in the incandescence of solids containing various rare earths as activators.

N. M. Bligh.

Molecular spectrum of ammonia. I. Two types of infra-red vibration bands. G. A. Stinchcomb and E. F. Barker (Physical Rev., 1929, [ii], 33, 305—308).—The infra-red spectrum of ammonia (cf. Robertson and Fox, A., 1928, 1073) was studied, and the absorption bands at 3·0 and 1·9 μ were examined, using ruled gratings, and their fine structures shown to be of different character. The 3 μ band is associated with a vibration of the electric moment parallel to the symmetry axis of the molecule, yielding one zero branch and a simple rotation series. The vibration giving rise to the 1·9 μ band is normal to the symmetry axis. The band probably corresponds with one of the four fundamental frequencies.

N. M. Bligh.

Zeeman effect in the Ångström carbon monoxide bands. II. F. H. Crawford (Physical Rev., 1929, [ii], 33, 341—353).—A continuation, with improved experimental methods, of previous work (cf. A., 1927, 1119). Observations of the Zeeman effect were extended from the bands at 5610, 5198, and 4835 to include 4511 and 4394 Å. For fields from 18,000 to 36,000 gauss the widths of the Zeeman patterns were proportional to the field strengths. The weighted average of the pattern widths for M (the ordinal number of the line in a branch)$=1$ is 97·7% $\Delta\nu_n$, and $M=2$, 66·3% $\Delta\nu_n$, where $\Delta\nu_n$ is the normal Lorentz triplet half width. The new quantum mechanics predicts 100% $\Delta\nu_n$ and 66·7% $\Delta\nu_n$ for these widths, respectively, as against 88·9% and 64% on the old quantum theory. Thirteen out of eighteen patterns predicted for the first two lines of the P, Q, and R branches were resolved and measured in agreement with theory. Intensity asymmetries were found to behave qualitatively, but not quantitatively, in accordance with Kronig's treatment (cf. A., 1928, 340). Three, and possibly four, new bands of the Ångström group were observed. N. M. Bligh.

Enlargement and displacement of spectral lines by molecular diffusion. J. Cabannes and P. Salvaire (Compt. rend., 1929, 188, 907—908; cf. A., 1928, 812).—The displacements obtained by the lateral diffusion of the mercury line 4358 Å. with alcohols, acetic acid, *cyclo*hexane, benzene, and phosphorus tribromide and studied by means of a Perot–Fabry interferometer, are of the order of 0·05 Å. in the direction of the red, and are accompanied by an enlargement of the radiation due to fluctuations in density of less than 0·1 Å. These phenomena, which are comparable with the Compton effect, are not to be confused with the Raman effect (*loc. cit.*). J. Grant.

Study of the absorption of a sample of blue rock salt. P. Leroux (Compt. rend., 1929, 188, 904—907).—The absorption coefficient (K) at 18° of a cleavage plane about 0·1 cm. thick of blue salt from Stassfurt increases with the wave-length of the source (3655—5790 Å.), but is decreased for each wave-length after heating at 220—250° and cooling to 18°. The absorption minimum is displaced towards the higher wave-lengths, and the salt appears colourless. A colourless sample showed effects of the same order except that above 4358 Å. K was less both before and after heating than for the blue salt. J. Grant.

Influence of boric acid on the phosphorescence of zinc sulphides prepared by the explosion method. F. Prevet (Compt. rend., 1929, 188, 903—904).—Boric acid decreases the violence of the explosive reaction of zinc and sulphur, but to a smaller extent than other substances (this vol., 524), and the resulting sulphide increases in hardness and stability with the amount used. Between 5 and 20% of boric acid produces an increased intensity of phosphorescence, the actual optimum depending on the size of the grains, whilst the permanence of the phosphorescence is slightly higher than that of the best commercial products. J. Grant.

Use of crystalline quartz for spectrographic work. J. W. Ellis (J. Opt. Soc. Amer., 1929, 18, 82—88).—In the study of the infra-red absorption of a solution of benzophenone in chloroform, using a cell having quartz end-plates, spurious effects in the absorption record were observed. These were found to be due to a polarisation phenomenon in the quartz plate and to a slight departure from parallelism between the optic axis and surfaces of the plate. The errors due to these causes and practical methods for their elimination are discussed. N. M. Bligh.

Structure and activation of the molecules of aliphatic aldehydes. II. Formaldehyde, acetaldehyde, propaldehyde, and chloral. S. A. Schou (J. Chim. phys., 1929, 26, 1—43; cf. this vol., 236).—From its moments of inertia the formaldehyde molecule is concluded to be Y-shaped, the distances C—O, C—H, and H—H having the values $1{\cdot}09\times10^{-8}$, $1{\cdot}3\times10^{-8}$, and $1{\cdot}3\times10^{-8}$ cm., respectively. The normal molecule probably possesses 4 valency electrons and is in the state $3p^3P_{0,1,2}$; it has the fundamental frequencies 1572·3 and 441 cm.$^{-1}$, the former of which corresponds with the vibration of the carbon and oxygen atoms and the latter with the vibration of the hydrogen atoms. On activation, the molecule passes into the state $4s^3P_{0,1,2}$ and the vibration frequencies fall to 1231·3 and 398 cm.$^{-1}$, showing that the distances between the atoms have increased. The limit for the predissociation of the molecule is at 2670 Å. at the ordinary temperature, but at higher temperatures is shifted towards the red. In the absorption spectrum of acetaldehyde vapour 60 bands have been detected, the fundamental frequency for the normal molecule being 825 and for the activated molecule 517 cm.$^{-1}$ From the fine structure the moment of inertia is $2{\cdot}43\times10^{-40}$, from which it is concluded that the atoms C·C:O lie in a straight line. The vapour of propaldehyde shows discontinuous absorption. Chloral, on the other hand, shows two regions of continuous absorption. A new triple absorption band at 2060 Å. has been found in the absorption spectrum of carbon monoxide. R. Cuthill.

Band spectra of carbon monoxide in the electrodeless discharge. G. Herzberg (Z. Physik, 1929, 52, 815—845).—Following a description of the various forms and colours which characterise the electrodeless discharge in carbon monoxide, the spectroscopic data are discussed in detail, and it is shown that the distribution of intensity in the various band systems is very similar to that observed in the case of nitrogen. The data are thought to indicate that the dissociation of CO^+ takes place thus: $CO^+=C^++O$. A similar mechanism appears to hold for the dissociation of CN. R. W. Lunt.

Life period of excited molecules in aqueous fluorescing solutions. S. I. Vavilov (Z. Physik, 1929, 53, 665—674).—The extinction of fluorescence by the addition of foreign substances is examined. The theory of extinction due to collisions of the second kind is applied to the observations of Jette and West (this vol., 8) on the extinction of fluorescence in various solutions by addition of potassium iodide. The effect of temperature on the extinction phenomena is investigated. Results agree with the theory. The mean value for the life period is in agreement with the direct value obtained by Gaviola (A., 1927, 712). The life period is independent of the exciting wave-length. The polarisation of fluorescence also gives a method of determining the life period. The depolarisation of fluorescence with decreasing exciting wave-length is discussed. A. J. Mee.

Intensity measurements of molecular rays in gases. F. Knauer and O. Stern (Z. Physik, 1929, **53**, 766—778).—The stream of molecules passes through an opening into an otherwise closed vessel, setting up a pressure therein which is measured by means of a hot-wire manometer. W. E. Downey.

Reflexion of molecular rays. F. Knauer and O. Stern (Z. Physik, 1929, **53**, 779—791).—Molecular streams from hydrogen and helium are reflected from highly-polished surfaces on which they fall at grazing incidence. The power of reflexion is in accordance with the de Broglie wave theory. W. E. Downey.

New phenomenon of diffusion: Raman effect. A. Carrelli (Atti R. Accad. Lincei, 1929, [vi], **9**, 165—169).—Mathematical. The Raman effect is discussed on the basis of the dispersion formula derived from the Schrödinger wave theory. The ratio of the intensities of the two radiations of frequency $\nu+\nu_{lk}$ and $\nu-\nu_{lk}$ is calculated, and is shown to be of the right order of magnitude. The degree of depolarisation of the Raman light is calculated and compared with that of the Tyndall light. The intensity of the Raman light is directly proportional to the fourth power of the frequency emitted, but depends also on certain factors, which are characteristic for each line in the dispersion formula of the substance considered. O. J. Walker.

Difference between the absorption and the Raman spectrum. G. H. Dieke (Nature, 1929, **123**, 564).—The fact that some Raman lines do not correspond with infra-red absorption frequencies supports the validity of Kramers' theory of dispersion (cf. Langer, this vol., 379). A. A. Eldridge.

Raman effect in some organic liquids. S. Venkateswaran (Phil. Mag., 1929, [vii], **7**, 597—600).—The Raman spectra of acetic, butyric, and propionic acids have been determined and the results employed in the calculation of the characteristic infra-red frequencies of the acids. The values so obtained for acetic and butyric acids agree closely with those obtained by Coblentz and Weniger. In addition to the Raman lines, the spectrum of light scattering in the three acids shows a continuous spectrum the intensity of which is approximately the same in acetic and propionic acids, but is greater in butyric acid. This greater intensity is attributed to the greater viscosity of butyric acid. A. E. Mitchell.

Raman effect and fluorescence. P. Das (Nature, 1929, **123**, 607).—A relation is revealed by probability considerations. A. A. Eldridge.

Line absorption spectra in solids at low temperatures in the visible and ultra-violet regions of the spectrum. S. Freed and F. H. Spedding (Nature, 1929, **123**, 525—526).—The absorption spectra of gadolinium, samarium, and erbium chloride hexahydrates from the ordinary temperature to that of liquid hydrogen have been studied. At the ordinary temperature the entire spectrum (about 60 lines) of gadolinium was in the ultra-violet extending to about 2350 Å.; on lowering the temperature new faint lines appeared in the visible portion and most of the original lines shifted slightly towards the red. Many of the closely-spaced lines appear to have originated by the splitting up of a "normal" energy level because of the influence of the electrostatic fields of the neighbours of the gadolinium ions, principally water molecules. With samarium, the spectrum consisted of diffuse lines and bands chiefly between 3000 and 5000 Å.; on lowering the temperature the lines sharpened and the bands became narrower, some lines disappeared and others appeared. The samarium ion in the solid state is a mixture of electronic isomerides. With erbium, the spectrum at the ordinary temperature consisted of very diffuse bands, the bands being resolved into lines at low temperatures. The structure of the groups of lines suggested the multiplets of gaseous atoms under the influence of external fields. Few lines were found below 3000 Å. A. A. Eldridge.

Origin of the ultra-violet beryllium hydride band spectrum. E. Bengtsson (Nature, 1929, **123**, 529).—The two band systems of the beryllium arc in hydrogen are emitted by two different molecules. The ionised BeH^+ molecule is the only possible origin of the ultra-violet bands. A. A. Eldridge.

Spectral absorption of monoazo-dyes. I. Effect of position isomerism on the spectral absorption of methyl derivatives of benzeneazophenol. W. R. Brode (Bur. Stand. J. Res., 1929, **2**, 501—540; cf. A., 1926, 884).—Solutions of azobenzene, benzeneazophenol, and the mono- and di-methyl derivatives of benzeneazophenol in alcohol, aqueous hydrochloric acid, and aqueous sodium hydroxide were examined. The differences found in the spectral absorption of alcohol solutions or of hydrochloric acid solutions of the position isomerides studied were small. Marked differences were found in the absorption of 3% aqueous sodium hydroxide solutions. W. E. Downey.

Magnetic susceptibilities of several organic gases. F. Bitter (Physical Rev., 1929, [ii], **33**, 389—397).—Using an improved method in which the investigated gas was diluted with hydrogen and the concentration determined for which the volume susceptibility of the mixture was equal to that of nitrogen, the following results given in molecular susceptibility $\times 10^6$ were obtained: methane $-12{\cdot}2$; ethane $-27{\cdot}3$; propane $-40{\cdot}5$, butane $-57{\cdot}4$, *iso*butane $-56{\cdot}3$, ethylene $-12{\cdot}0$, acetylene $-12{\cdot}5$, using as standards hydrogen $-3{\cdot}94$ and nitrogen $-11{\cdot}8$. It is shown that the results cannot be reconciled with the assumption that the susceptibilities of the constituent atoms are additive. It is suggested that the susceptibilities of the substances are determined by the binding electrons. N. M. Bligh.

Electrical dipole moment of pentaerythritol by the method of molecular rays. J. Estermann (Z. physikal. Chem., 1929, **B**, **2**, 287—288).—By measurement of the deviation of a molecular ray in a non-homogeneous electric field, the free molecules of pentaerythritol have been shown to possess a dipole moment estimated at about 2×10^{-18} c.g.s. unit (cf. A., 1928, 1309). R. CUTHILL.

Magnetic moment of lithium. J. B. TAYLOR (Z. Physik, 1929, 52, 846—852).—The magnetic moment of lithium has been determined by the molecular streaming method; the value found is of the order of one third of a Bohr magneton. R. W. LUNT.

Electric polarisation in insulators. E. BRODY (Z. Physik, 1929, 52, 884—889).—A mathematical analysis shows that the application of an accelerating field to an insulator containing ions of widely differing mobilities will produce an electric moment in the material. The possibility of experimentally investigating the matter is discussed. R. W. LUNT.

Chemical phenomena connected with the contraction of hydrogen in discharge tubes. R. DELAPLACE (Compt. rend., 1929, **188**, 708—710).—The observed contraction in volume of hydrogen and the appearance of carbon monoxide and methane (A., 1928, 933) are not due to gases contained in the aluminium electrodes or to the state of the walls of the discharge tube, but may be explained partly by the oxidation of adsorbed mercury vapour which is subsequently reduced by the hydrogen, and by the fact that Pyrex glass emits small quantities of hydrogen, oxides of carbon, and methane after bombardment by cathode rays. Oxygen would thus be available from dissociation of the carbon dioxide. J. GRANT.

Magnetic rotatory power in an anisotropic medium. R. DE MALLEMANN (Compt. rend., 1929, **188**, 863—865).—The molecular theory of magnetic rotation in a homogeneous medium is analogous to that of the natural rotation (this vol., 495). The normal magnetic rotatory power is therefore defined by the projection of the rotation vector on the normal to the wave, and its anisotropy is a result of the refringence anisotropy of the electrons, atoms, or molecules. The ratios of the three principal rotations are a function of the intramolecular birefringence. J. GRANT.

Super-dispersion. T. TAKEUCHI (Z. Physik, 1929, **53**, 148—150).

Microscopic images. C. LAKEMAN and J. T. GROOSMULLER (Z. Physik, 1929, **53**, 628—638).—An arrangement of apparatus is described by means of which it is possible to project on a screen images of microscopic objects. A parallel beam of light is diffracted by the object, and the spectra of the various orders are later recombined. The working of the apparatus with different kinds of illumination and structures of different sizes is shown. A. J. MEE.

Molecular refraction and number of molecules in unit volume. W. HERTZ (Z. anorg. Chem., 1929, **179**, 211—214).—The product of the molecular refraction and the number of molecules per unit volume at the b. p. has an approximately constant value, viz., $1\cdot2-2\times10^{23}$, for all substances except a few elements of very low b. p. The value holds more closely for groups of analogously constituted substances. H. F. GILLBE.

Modification of Baeyer's strain theory. E. E. AYLING (Chem. News, 1929, **138**, 164—165).—Short's expression for the tertiary carbon atom (cf. A., 1926, 1028) is shown to be identical with one of the equations derived by Ingold, whilst the expression for the secondary carbon atom yields results identical with those obtained from Ingold's expression. The differences between the results of Short and Ingold arise from the use of different atomic volumes. The use of Le Bas' atomic volumes in place of Traube's in calculating valency angles is suggested, and Ingold's expressions are preferred, since in this way uniformity can be preserved with the case of a carbon atom included in a polymethylene ring. R. A. MORTON.

Quantum mechanical theory of the natural optical activity of liquids and gases. L. ROSENFELD (Z. Physik, 1928, **52**, 161—174).—Mathematical. G. E. WENTWORTH.

Boric acids. L. F. GILBERT and (MISS) M. LEVI (J.C.S., 1929, 527—535).—From vapour-pressure measurements evidence is brought forward to show that eight boric acids exist, $n\mathrm{B_2O_3,H_2O}$, where $n=1-8$. The heat of hydration of boric oxide to orthoboric acid is approx. 54,363 g.-cal. F. J. WILKINS.

Surface energy and the orientation of molecules in surfaces as revealed by surface energy relations. W. D. HARKINS [with B. GINSBERG, R. W. WAMPLER, T. F. YOUNG, J. W. MORGAN, and N. BEEMAN] (Z. physikal. Chem., 1928, **139**, 647—691).—A summary. The principle that the molecules in a surface are always oriented so that the change from one phase to the next is as continuous as possible is treated from the thermodynamical aspect. Application of the second law leads to the general entropy principle that in a one-component system the average molecular kinetic energy which is converted into molecular potential energy, when molecules move from one region to another, depends merely on the change of state. From consideration of the evidence for the orientation of molecules in the surface of a pure liquid, with respect to molecular symmetry and evaporation, it is stated, given complete orientation, that the value of e/j (e=mean total surface energy per molecule, j=energy of thermal emission) should be a criterion of symmetry of the molecule, and hence of the orientation. Evidence is also adduced for orientation from the energy of adhesion as related to the energy of cohesion. Films, the spreading of liquids and the spreading coefficient, the surface film on an aqueous solution of an organic substance, the thickness of water films on salt solutions, and the stabilisation of emulsions by unimolecular soap films are also discussed. G. E. WENTWORTH.

Chemical combination as an electrostatic phenomenon. IV. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, **26**, 182—184).—The measurements of the distances between the oppositely-charged ions in the alkali halide salts are arranged to show that these distances are additive properties of the ions, as would be expected if atoms and ions could be regarded as hard balls. Differences in volatility of similar compounds of elements of increasing at. wt. in a family of the periodic table are ascribed to the degree to which the central atom (*e.g.*, boron or aluminium in the fluorides) is enveloped by the surrounding atoms, which is regarded as determined by the relative sizes of the atoms. Other properties are considered similarly. S. I. Levy.

Electron exchange and the formation of molecules. W. Heitler (Nachr. Ges. Wiss. Göttingen, 1927, 368—374; Chem. Zentr., 1928, ii, 1523).—A preliminary discussion of the statistics whereby the stationary state of an electronic system arises. A. A. Eldridge.

Constitution of boron hydrides. E. Wiberg (Helv. Chim. Acta, 1929, **12**, 225—227).—The fact that pentaborane can take up four molecules of ammonia is difficult to explain by means of Ephraim's structure for the boron hydrides (cf. this vol., 123), but is readily accounted for by means of the author's more unsymmetrical formula (A., 1928, 936). O. J. Walker.

Capillary-tube method for the simultaneous determination of surface tension and density. A. Ferguson and J. A. Hakes (Proc. Physical Soc., 1929, **41**, 214—223).—An apparatus is described for measuring the surface tension of liquids by forcing the meniscus down to the end of a capillary immersed in the liquid. By varying the depth of immersion the density of the liquid can also be measured. It is shown how the results should be calculated from the shape of the meniscus. J. L. Buchan.

Surface tension. A. W. Porter (Phil. Mag., 1929, [vii], 7, 624—630).—The validity of the assumptions of Rayleigh (Proc. Roy. Soc., 1915, **A**, **92**, 184) in his treatment of the rise of liquids in a capillary tube has been established from an analysis of the curvature of the vertex of the liquid. The weights of liquid drops from tubes of various diameters have been examined and it is concluded that the viscosity of the liquid has little influence on the weight. The problem of vanishing of surface tension close to the critical point has been examined and it is shown that if it be recognised that the molecules cannot approach nearer to one another than their diameter it is not necessary to accept Laplace's deduction that vanishing of the surface tension can take place only when the densities of the two phases are the same. This result is offered in confirmation of the observations of Callendar (A., 1928, 1179) on the vanishing of the surface tension of water at a temperature 6° below the critical. A. E. Mitchell.

"Resistance" limits, peaks in conductivity curves, and *X*-ray interferences in metallic mixed crystals. G. Tammann (Ann. Physik, 1929, [v], **1**, 309—317, 321—322).—The existence of sharp "resistance" limits to the action of reagents on metallic mixed crystals is re-affirmed. Good agreement obtains between the results of *X*-ray spectroscopy and chemical reactivity in mixed-crystal series as well as in systems showing compound formation. "Resistance" limits and peaks in the conductivity curves are not related phenomena, the latter possessing neither precise physical significance nor certain value as a test for compound formation. The criticism of the author's theory (A., 1919, ii, 398, 406) by Le Blanc, Richter, and Schiebold (A., 1928, 1082) based on the copper–gold mixed crystals is refuted and the data are stated to show no essential discrepancy with either the work of Tammann or the interpretation. R. A. Morton.

"Resistance" limits, peaks in conductivity curves, and *X*-ray interferences in metallic mixed crystals. M. Le Blanc, K. Richter, and E. Schiebold (Ann. Physik, 1929, [v], **1**, 318—320).—A reply to Tammann (cf. preceding abstract). R. A. Morton.

Fine structure of the *K*-edge. V. Dolejsek and K. Pestrecov (Z. Physik, 1929, **53**, 566—573).—The limit of the *K*-series for the free elements in the first halves of the short periods of the periodic system has been investigated, thus completing earlier values. The frequency values for all such elements are in agreement with the equation $\nu/R=a+bN+cN^2+dN^3+eN^4$. The difference between the observed and calculated values of ν/R, when plotted against the atomic number, N, shows periodic fluctuations. A. J. Mee.

Character of interference lines in *X*-ray diagrams of highly crystalline material. II. H. Möller and A. Reis (Z. physikal. Chem., 1929, B, 2, 317—339; cf. this vol., 246).—The relation of the effective width of the focus of the primary radiation and the variation of intensity across it to the character of the lines obtained in the Debye–Scherrer method of *X*-ray investigation, using non-parallel radiation, has been examined theoretically. The various arrangements to secure sharpness and accuracy are described. R. Cuthill.

Origin of soft *X*-rays with the lighter elements. B. B. Ray and R. C. Mazumdar (Z. Physik, 1929, **53**, 646—657).—On the assumption that an atom loses two electrons from the same or different energy levels, it is possible that besides the ordinary types of radiation a new one occurs, which is caused by the simultaneous switch of both electrons. The frequency of the radiation emitted is equal to the sum of the frequencies of the single switches. Both electrons can thus combine to give monochromatic radiation. This assumption of simultaneous switch can be applied to a large number of unexplained experimental determinations of critical potentials. The existence of critical potentials for the excitation of *X*-rays in the range 40—200 volts for the elements iron, cobalt, nickel, and copper is thus explained. It is shown that the critical potentials of manganese and chromium can be treated in the same way. A. J. Mee.

Polarisation from the Compton effect. P. Lukirsky (Z. Physik, 1929, **53**, 792—804).—Examination of the distribution of the directions of the scattered secondary rays shows that the emission is polarised. W. E. Downey.

Fine structure of absorption edges in metals. B. B. Ray and P. C. Mahanti (Nature, 1929, **123**, 528—529).—The non-appearance of fine structure edges when metallic plates or crystals (powder) are used as absorption screens can be explained on the hypothesis of the existence of free electrons in metals. A. A. Eldridge.

Diffraction of *X*-rays by a two-dimensional crystal lattice. W. Linnick (Nature, 1929, **123**, 604—605).—When mica is cleft into thin layers by heating and cooling, and a thin beam of *X*-rays is passed through the plate, a system of spectra corresponding with a series of two-dimensional lattices is obtained. The spectra obtained accord with the assumption that the molecules are distributed at the summits of equilateral triangles of side 5·2 Å. More diffuse photographs are obtainable with gypsum and Iceland spar. A. A. Eldridge.

Photographic measurement of the relative intensities of the $L\alpha_1$, α_2, α_3 lines of silver. H. C. Webster (Proc. Physical. Soc. 1929, **41**, 181—191).—The crystal was rocked so that the reflexion angles of the three lines $L\alpha_1$, α_2, α_3 were covered by its sweep. The exposure was taken on a standard film which was developed under specified conditions and the lines were measured on a Moll type micro-photometer. The interpretation of the curves so obtained is discussed, and it is shown that *D*, the density of the part of the film under consideration, is a function of *Nt*, where *N* is the number of quanta absorbed per second by the emulsion and *t* is the time of exposure. The relative intensities of the lines are $L\alpha_1 : L\alpha_2 : L\alpha_3 : : 100 : 12 : 4{\cdot}6$ to 7·3, it being found that the intensity of $L\alpha_3$ varies with the tube voltage. The ratio $L\alpha_1 : L\beta_1$ has also been determined and found to be 100 : 40.

J. L. Buchan.

Spark satellites of the $L\alpha$ lines of silver. H. C. Webster (Proc. Physical Soc., 1929, **41**, 192—193; cf. preceding abstract).—Spark satellites have been observed on the hard side of $L\alpha_1$. Their wavelengths were found to be $a_2'=4134{\cdot}7$ X, a_1'(or a_3)$=4130{\cdot}5$ X, $a_2''=4125{\cdot}6$ X, and a_1''(or a_4)$=4119{\cdot}0$ X, whilst the decreasing order of intensities of the lines is a_1', a_1'', a_2'', a_2'. J. L. Buchan.

Precision measurements of *X*-ray reflexions from crystal powders. Lattice constants of zinc carbonate, manganese carbonate, and cadmium oxide. J. Brentano and J. Adamson (Phil. Mag., 1929, [vii], 7, 507—517).—Exact determinations of the spacing and of the rhombohedral angle of zinc carbonate and of manganese carbonate have been derived from *X*-ray measurements on the crystal powders mixed with cadmium oxide as a reference substance. The rhombohedral angle of zinc carbonate is found to be 103° 27′, in agreement with the usually accepted value of 103° 28′ of Rose (Pogg. Ann., 1852, **85**, 132). The value of the d_{100} spacing is $5{\cdot}493\pm0{\cdot}005$ Å., as compared with 5·44 Å. obtained by Levi and Ferrari (A., 1924, ii, 760). These values lead to $a=5{\cdot}928\pm0{\cdot}005$ Å., and $v=1{\cdot}877\pm0{\cdot}015\times10^{-22}$ cm.³, whence $d=4{\cdot}406$ as compared with $d=4{\cdot}51$ obtained by Levi and Ferrari. For manganese carbonate $\alpha=102°\ 50'$, in agreement with $\alpha=102°\ 50{\cdot}3'$ obtained from goniometric measurements, $d_{100}=5{\cdot}666\pm0{\cdot}005$ Å., $a=6{\cdot}064\pm0{\cdot}005$ Å., and $v=2{\cdot}039\pm0{\cdot}015\times10^{-22}$ cm.³, whence $d=3{\cdot}747$. These values are used in conjunction with the analogous measurements of Brentano and Dawson (A., 1927, 297) on magnesium carbonate to verify calculated lattice constants of the isomorphous carbonate series. When the values are combined with a fixed parameter for the CO_3 group the results are in good approximation to the observed, but are not quite in agreement. It is thus concluded that terms characteristic of the various elements must be included.

A. E. Mitchell.

Distribution of charge in the chlorine ion in rock salt. G. W. Brindley and R. G. Wood (Phil. Mag., 1929, [vii], 7, 616—623).—It is pointed out that the experimental and theoretical values of the *X*-ray scattering factor for the chlorine ion differ by an amount greater than that which can be attributed to experimental error, for values of (sin θ)/λ of the order 0·4—0·5. It is assumed that this difference is due to a change in the radial distribution of the charge on the ion. The difference between the charge distribution in a free chlorine ion, as determined by Hartree and others (A., 1928, 462), and in a chlorine ion in a rock-salt lattice has been calculated from a Fourier analysis of the difference between the experimental and theoretical scattering factors and the result have been employed to determine the charge distribution in a chlorine ion in rock salt. A. E. Mitchell.

Crystal structure of trimethylethylammonium chlorostannate. R. W. G. Wyckoff and R. B. Corey (Amer. J. Sci., 1929, [v], **17**, 239—244).—Trimethylethylammonium chlorostannate, $(NMe_3Et)_2SnCl_6$, has a cubic structure, the length of a unit cube being 13·17 Å. Its density is 1·487. The size, shape, and distribution of the chlorostannate groups are the same as in analogous compounds. The resulting structure resembles that of calcium fluoride. C. W. Gibby.

Crystalline structure, lattice constants, and density of rhenium. V. M. Goldschmidt (Z. physikal. Chem., 1929, **B**, 2, 244—252).—See this vol., 382. A. J. Mee.

[*X*-Ray] structure of crystalline uraninite from Katanga (Belgian Congo). A. Hadding and R. van Aubel (Compt. rend., 1929, **188**, 716—717). Katanga uraninite, which is the primary mineral from which the cryptocrystalline pitchblende of the district is derived, has been shown by Debye's method to have the structure of a face-centred cube of side 4·67 Å. The spectral data are tabulated. J. Grant.

Translation lattice of cellulose hydrate. K. Weissenberg (Naturwiss., 1929, **17**, 181).—By means of an improved focussing method sharp *X*-ray interferences can be obtained with cellulose, cellulose hydrate, and natural silk. The structure hitherto ascribed to the hydrate is probably erroneous. The following dimensions are given: $a=14{\cdot}66$, $b=8{\cdot}89$, $c=10{\cdot}35$ (all $\pm2\%$), $\alpha=90°$, $\beta=90°$, $\gamma=85°\pm5°$. The cell contains eight $C_6H_{10}O_5$ groups (*d* 1·60), whereas the earlier view was in favour of four such groups, *d* 1·46. Natural cellulose appears to have a structure very similar to that suggested for the hydrate.

R. A. Morton.

Domain of the atom of bismuth in its crystal. H. Perlitz (Scientists Soc. Tartu, 1928, **35**, 113—120).—Theoretical. In crystalline bismuth every atom has six neighbours in two triplets. The decrease of volume at fusion suggests that the domains of atoms cannot intersect. From the distribution of the shared electrons it is inferred that the electrons of the outer completed shell, consisting of two sub-shells, occur in pairs, and that diameters of the inner and outer sub-shells are equal to the shorter and longer inter-atomic distances and form the boundaries of Bi^{+} and Bi^{---}, respectively. A distribution of electrons of the outer shell in vertices of two regular tetrahedra is indicated. The observed and calculated rise of conductivity at fusion are in good agreement, assuming that the non-shared electrons in the crystal carry the electric current, and that the shared electrons are liberated on melting. N. M. Bligh.

Structure of artificial ultramarines. IV. Ultramarines of thallium, and the analogous derivatives of the bivalent metals calcium, strontium, barium, zinc, manganese, and lead. F. M. Jaeger (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 156—166; cf. A., 1928, 463).—Thallium, calcium, strontium, barium, zinc, manganese, and lead were substituted for sodium in Guimet's blue, $Na_6Al_4Si_6O_{24}S_3$. The substitution of the sodium (or silver in silver ultramarine) by the bivalent metals took place easily and completely. The method used was to heat the silver ultramarine with five times the theoretical quantity of the iodide of the substituting metal and a little water in sealed tubes for 50 hrs. at 160°. In the case of calcium, strontium, and barium, pure olive-green calcium–, strontium–, and barium–silver ultramarines of the formula $R^{II}Ag_4Al_6Si_6O_{28}S_3$ were formed. By melting with the iodides of the metals colourless ultramarines were produced. *X*-Ray powder spectrograms of all the ultramarines showed the original characteristics of the ultramarines. Although the original character of the ultramarine spectrogram is preserved, the relative intensities of the images are different from those of ordinary ultramarines. Various other ultramarines were prepared and their structure was investigated. A lead–sodium compound, rich in silicon, was prepared by heating Guimet's blue in sealed tubes at 160° for 50 hrs. with five times the theoretical quantity of lead nitrate, and data of its spectrogram are given. By heating silver ultramarine with lead chloride a lead–silver ultramarine was obtained, dark grey in colour. Attempts were made to prepare mercurous and mercuric ultramarines from Guimet's blue by methods similar to the above. The compounds formed, however, were not true ultramarines and the powder spectrogram did not correspond with cubic symmetry. A. J. Mee.

Structure of artificial ultramarines. V. Absorption phenomena with ultramarine, and the structure of nosean, hauyne, and the ultramarines. F. M. Jaeger and F. A. van Melle (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 167—181; cf. preceding abstract).—The progress of the reaction between silver ultramarine and alkali halides used in the preparation of ultramarines is studied. It was found that the substitution took place more rapidly during the early part of the reaction and the more concentrated the reactants. The occurrence of adsorption phenomena is indicated. The structure of nosean and the ultramarines is deduced. The reason why all the ultramarines give inconstant results on analysis appears to be due to a mixture of isomorphous substances. This also explains the identity of the *X*-ray spectrograms. A. J. Mee.

***X*-Ray study of the system palladium–hydrogen.** J. D. Hanawalt (Physical Rev., 1929, [ii], **33**, 444—453).—An *X*-ray study of the lattice parameter of palladium as influenced by hydrogen occluded by electrolysis, from the gas phase, and by sputtering in hydrogen showed, in the first two cases, a unique value $a_0=4{\cdot}017$ stable up to 80°, and associated with the concentration Pd_2H. The effect of the hydrogen on the L_{111} absorption limit of palladium is to cause a shift of the main edge and the occurrence of a secondary absorption towards shorter wave-lengths, suggesting the combination PdH. Impurities in the palladium showed a marked effect on the occlusion of hydrogen. N. M. Bligh.

Electronic analysis; structure of oxides of magnesium, zinc, and cadmium. Louis de Broglie's law. M. Ponte (Compt. rend., 1929, **188**, 909—910).—It is shown that electronic analysis by the author's method (this vol., 367), using electron speeds equivalent to 16670—10870 volts, may be applied to the oxides mentioned with the same degree of accuracy as Bragg's method. The structure of zinc oxide is obtained from de Broglie's law with an accuracy of 1%. J. Grant.

Changes in the crystalline form of sodium nitrate in accordance with the composition of the solution from which it separates. P. P. Orlov (Bull. Acad. Sci. U.R.S.S., 1928, 529—548).—Sodium nitrate crystallised from water in presence of acid amides, *e.g.*, formamide, or hydroxy-acids, *e.g.*, lactic acid, α-hydroxy*iso*butyric acid, glycollic acid, glyceric acid, or if crystallised from concentrated solutions of chromic nitrate changes its usual rhombohedral form. A. Freiman.

***X*-Ray investigation of the structure of hardened carbon steels.** G. Kurdjumow and E. Kaminsky (Z. Physik, 1929, **53**, 696—707).—The effect of carbon content on the value of the ratio of the axes and the parameter in the tetragonal lattice in carbon steels is investigated. The tetragonal lattice was found, by careful polishing, to exist throughout the steel, and not only on the surface as has been previously stated. The ratio of the axes increases linearly with the carbon content; the parameter *c* increases with the carbon content, whilst the parameter *a* decreases somewhat. Austenite was found in all the types of steel dealt with; its quantity increased with increasing carbon content. The asymmetry of the tetragonal structure is one of the causes of the indefiniteness of the lines in the diagram. Tempering at 100° changes the tetragonal structure to cubic. A. J. Mee.

***X*-Ray structure and magnetic properties of single crystals of Heusler alloy.** H. H. Potter (Proc. Physical Soc., 1929, **41**, 135—142).—Using the single-crystal rotation method, Heusler alloy has been found to crystallise as a body-centred cube with lattice constant 2·95 Å. The aluminium atoms are distributed so as to lie on a face-centred cube of lattice constant 5·9 Å. Directional magnetic properties are found to be identical with those of nickel, which has a face-centred cubic structure. It is suggested that this may be interpreted as indicating that the manganese atoms (the positions of which cannot be determined by *X*-ray analysis) also lie in a face-centred cubic lattice. W. E. Downey.

Structural relationships of rhodonite to other silicates. B. Gossner and K. Brückl (Zentr. Min. Geol., 1928, **A**, 316—322; Chem. Zentr., 1928, ii, 1756).—The constants of the triclinic unit cell of rhodonite are *a* 7·77, *b* 12·45, *c* 6·74 Å., α 85° 10′, β 94° 4′, γ 111° 29′, whence the axial ratios are $a:b:c=0{\cdot}624:1:0{\cdot}541$. The units of the cell are very similar to those of babingtonite and anorthite, whilst the angles are interchanged. The unit cell contains 2 mols. of $MnSiO_3,Mn_3CaSi_4O_{12}$. A. A. Eldridge.

Spiral markings on carborundum crystals. W. Hughes (Nature, 1929, **123**, 603—604).—When a film of molten sulphur on clean glass cools, centres of crystallisation appear, and rings grow outwards in succession from these points. When the logarithm of the number of rings counted from a centre is plotted against the logarithm of the distance of the rings, a straight line is obtained. The formation of the rings is ascribed to the evolution of latent heat on crystallisation diminishing the surface tension of the surrounding sulphur, which is then drawn outwards to form a circular ridge, this quickly crystallising and continuing the effect. The rings observed on carborundum crystals by Menzies and Sloat (this vol., 381) also give straight lines when the above data are plotted, and may have a similar origin. No particular significance is ascribed to the spiral nature of the markings. A. A. Eldridge.

Crystal structure of *n*-butyl-, amyl-, hexyl-, and heptyl-ammonium halides. S. B. Hendricks (Z. Krist., 1928, **68**, 189—203; Chem. Zentr., 1928, ii, 1858).—The structures of the above compounds are similar to that of methylammonium iodide. The space-group is $4D-2$, $4d-3$, $4Di-7$, $4c-1$, $4e-1$, or $4C-1$. Measurements of the dimensions of the unit cell are recorded. A. A. Eldridge.

Artificial preparation of diamonds. L. Sesta (Phil. Mag., 1929, [vii], **7**, 488—493).—In reply to a statement that no one has yet succeeded in producing diamonds in the laboratory and that all who have made this claim have been deceived by mistaking crystals of spinel for diamonds, reference is made to the work of La Rosa (A., 1909, ii, 311, 399) and of the author (Trans. Faraday Soc., 1910, **5**). Experimental evidence is produced to show that the author has produced diamonds and that from the nature of the method employed there was no chance of the formation of spinel, as was possible in the original method of Moissan. A. E. Mitchell.

Theory of ferromagnetic crystals. G. S. Mahajani (Phil. Trans., 1929, **A**, **228**, 63—114).—Mathematical. An atomistic theory of ferromagnetism is developed for two types of crystal—iron and pyrrhotite. The results of Webster (A., 1925, ii, 369) are accounted for qualitatively and quantitatively. C. W. Gibby.

Method for measuring Joule magneto-strictive effect in a cold-drawn wire. J. H. Handley (J. Sci. Instr., 1929, **6**, 84—88).

Effect of tension and a longitudinal magnetic field on the thermo-electromotive forces in permalloy. A. W. Smith and J. Dillinger (Physical Rev., 1929, [ii], **33**, 398—402).—The specimens consisted of wires containing 78, 81, and 84% of nickel, the remainder being iron. The effect of tension on the change of thermo-electromotive force produced by a longitudinal magnetic field was, for the three specimens, respectively, to decrease the maximum value, relatively no effect, and a decrease for low, but an increase for higher magnetic fields. In each case there is relatively no effect for tensions beyond about 10 kg./mm.^{2} In all cases the magnetic field produces a decrease in the thermo-electromotive force. N. M. Bligh.

Electrical conductivity of carborundum. H. J. Seemann (Physikal. Z., 1929, **30**, 143—144).—Measurement of the electrical conductivity for six samples of carborundum at 17° and −80° shows that the ratio at these temperatures varies between 4 and 6. No relationship emerges from the presence of impurities. The nature of the conductivity of carborundum is discussed. The specific conductivity is of the order obtained with solid electrolytes, but it is considered that carborundum should be regarded as a half-conductor in the sense of Königsberger's theory. R. A. Morton.

Magnetic behaviour of organic crystals. C. V. Raman [with S. Bhagavantam] (Nature, 1929, **123**, 605).—The diamagnetic anisotropy of naphthalene is very pronounced (cf. Bragg, Nature, Suppl., May 7, 1927), the susceptibilities along the three magnetic axes of the crystal having the approximate ratio 16 : 7 : 4. The axes of maximum diamagnetic susceptibility and of minimum optical dielectric constant are approximately coincident. The observation explains why aromatic liquids exhibit a strong positive magnetic birefringence. In crystals of aliphatic compounds the anisotropy is less pronounced and the relation between the magnetic and optical characters is more varied; in iodoform the axes are parallel, whilst in carbamide they are crossed. A. A. Eldridge.

Apparent Mie effect and atmospheric optics. G. I. Pokrowski (Z. Physik, 1929, **53**, 67—71).

Theory of optical activity in a homogeneous medium. R. de Mallemann (Compt. rend., 1929, **188**, 705—707).—A mathematical interpretation of the rôle of the "rotation vector" involved in the author's general molecular theory of optical activity (this vol., 13). It is concluded that both the variation of rotatory power and its change of sign are perfectly continuous. J. Grant.

Reflecting power of beryllium, chromium, and several other metals. W. W. Coblentz and R. Stair (Bur. Stand. J. Res., 1929, **2**, 343—354).—Curves are given for the ultra-violet reflecting power of beryllium, chromium, cobalt, nickel, silver, speculum, stellite, and stainless steel. For chromium and beryllium the observations extend into the infra-red. Unlike most metals, beryllium has a high reflectivity at 250 mμ in the ultra-violet, followed by a lower reflectivity with a minimum at 400 mμ in the visible spectrum. Chromium has a higher reflectivity than nickel in the ultra-violet, and is conspicuous for its high maximum (70%) at 425 mμ, followed by a flat minimum extending from 600 to beyond 2000 mμ in the infra-red.

C. J. Smithells.

Elastic constants of unicrystalline aluminium and gold. E. Goens (Naturwiss., 1929, 17, 180).—The elasticity and torsion moduli, E and G, of unicrystalline aluminium and gold have been determined at the ordinary temperature in relation to the crystal orientation. For aluminium, $E_{[111]}:E_{[100]}=1\cdot18$ as against 2·7 for gold, whilst $G_{[111]}:G_{[100]}=1/1\cdot13$ for aluminium and 1/2·2 for gold. The cubic compressibility of unicrystalline aluminium is practically the same as that of the polycrystalline material. The results show gold to be markedly anisotropic in its elastic properties.

R. A. Morton.

Flowing of metallic crystals under torsion. R. Karnop and G. Sachs (Z. Physik, 1929, 53, 605—618).—Experiments were carried out with an aluminium–copper alloy (95% Al, 5% Cu). The force required to produce permanent set varies with the orientation of the crystal in the ratio 2·2 : 1 (cubic : octahedral). Assuming that there is a flowing surface layer the theoretical value 1·85 : 1 is obtained. An attempt is made to explain the effect of orientation on the basis of different slipping ratios for the different forms. The elastic limit of the crystals varies in the ratio 1·73 : 1. The effect of orientation on the elastic constants of the alloy is determined.

A. J. Mee.

Metastability of the elements as a result of enantiotropy or monotropy. XIII. The differential gas dilatometer of C. J. Smith and its accuracy. E. Cohen and H. L. Bredée (Z. physikal. Chem., 1929, 140, 199—222).—The accuracy of Smith's dilatometer (A., 1927, 954) has been tested by determination of the density and coefficient of expansion of mercury. The error for the former is 0·02% and for the latter 0·05%. The transition temperature and volume change in the transition of α- to β-silver iodide have also been determined. The values found are in good agreement with those obtained by other methods (this vol., 22). This dilatometer is therefore considered to be specially suitable for the quantitative study of volume alteration in polymorphous changes.

R. N. Kerr.

Change of volumes and electric resistances of antimony and arsenic at fusion. H. Perlitz (Scientists Soc. Tartu, 1928, 35, 121—125).—Theoretical. Antimony having been proved to expand during solidification, the diameter of the spherical domain of its atom is calculated as 3·09, and from two crystal lattice data as 3·04 and 3·06 Å. The corresponding value for arsenic from its crystal lattice is 2·75 Å. From this value it is deduced that liquid arsenic should expand during solidification by 5·1%, and it is estimated that the electrical resistance at the m. p. of liquid arsenic is about 0·4 of that of the solid phase.

N. M. Bligh.

Electrical resistances of some metals below the b. p. of oxygen. W. Tuyn (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 115—123).—The resistances of cadmium, crystalline copper, gold, indium, lead, platinum, thallium, tin, zinc, and a single crystal of tin were measured at temperatures from 1·40° (or the superconducting temperature) to 90° Abs. Tables of the resistances are given.

A. J. Mee.

Resistance-hysteresis phenomena of tin, lead, indium, and thallium at the temperature of liquid helium. W. J. de Haas and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 206—213).—To ascertain whether the hysteresis phenomena in the change of resistance appearing with the magnetic disturbance of the superconductivity of tin and mercury hold for other superconductors, indium, thallium, and lead were examined. The magnetic transition curve for tin corresponds completely with that for mercury. For the indium used the resistance disappeared with one jump, the curves not being rounded as in other cases. This may be due to the fact that the wire used consisted of a single crystal. It is shown that hysteresis phenomena appear in all superconducting metals, but best only when there are large crystals and the metal is in a homogeneous magnetic field.

A. J. Mee.

New superconductors. E. van Aubel, W. J. de Haas, and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 218—225).—The resistances of compounds of two metals are investigated. The compounds used were Cu_3Sb, Ag_3Sb, Ag_3Sn, Cu_3Sn, Bi_5Tl_3, SbSn, and Sb_2Sn_3. The resistances were determined over the range 0° to −259°. A table showing the specific resistances at 0° is given. The resistances of Cu_3Sb, and Ag_3Sb depend little on temperature, and the resistance of all the compounds decreased less than that of their components. All the resistance curves show a point of inflexion, a phenomenon which is known to occur in some simple conductors. At the temperature of liquid helium it was found that Bi_5Tl_3, SbSn, and Sb_2Sn_3 behave as superconductors. The rod of Bi_5Tl_3 actually became superconducting above the b. p. of helium, although its components themselves have much lower transition points. Cu_3Sn remained a non-superconductor even at the lowest temperatures used.

A. J. Mee.

Superconductivity of gallium. W. J. de Haas and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 214—217).—At the lowest temperatures used (1·1° Abs.) gallium did not become superconducting, but from the appearance of the temperature–resistance curves it may be presumed that at a temperature slightly lower than this it would become so. This phenomenon may be due to the presence of a trace of indium. Certain abnormal phenomena were noted. The fall of the resistance is abnormal. The resistance–temperature graph is very curved at low temperatures, the transition stage (should the metal become superconducting) extending over several degrees. With ordinary superconductors the transition stage occupies only a few hundredths of a degree. The resistances are very sensitive to current.

A. J. Mee.

Electron theory of metals. H. M. Barlow (Phil. Mag., 1929, [vii], 7, 459—470).—Experiments designed to examine the assembly of free electrons in the interior of a conductor are described. The results show that these behave as a perfectly incompressible fluid and offer no confirmation of Sommerfeld's theory (Z. Physik, 1928, 57, 1, 43) of the persistence of an electron gas interpenetrating the atoms of a metal. A. E. Mitchell.

Simple method for determining C_p/C_v. E. Rüchardt (Physikal. Z., 1929, 30, 58—59).—Glass tubing is now available in which the circular cross-section is so accurate that a commercial steel ball used for precision work slides along the tube, maintaining the air-tight condition. If such a tube is inserted in a rubber stopper closing a 5- or 6-litre vessel, the ball undergoes vertical oscillations with a period of the order of 1 sec. The measurement of the period makes possible an instructive lecture experiment for the determination of C_p/C_v for the gas in the large vessel. The adiabatic elasticity of a gas is clearly demonstrated. The method has been applied to carbon dioxide and air.
R. A. Morton.

Triple point of water as a fixed point on the temperature scale. H. Moser (Ann. Physik, 1928, [v], 1, 341—360).—A thermostat is described which allows the temperature of the triple point of water to be established in a volume of about 10 c.c. and maintained for long periods. The precautions necessary for the greatest constancy in temperature are described, special attention being directed to the purity of the water. Refined experimental methods permit the measurement of very small temperature differences, and it is shown that the fluctuations in the thermostat over a period of several hours need not exceed $\pm 0{\cdot}5\times10^{-4}$ degree. The lowering of the m. p. when air-free water is in contact with ice as a result of an increase in pressure from 0 to 1 atm. is $0{\cdot}00748° \pm 0{\cdot}00005$, in agreement with the Clausius–Clapeyron equation. The temperature of the triple point, having regard to the depression of the normal m. p. of ice caused by water saturated with air, is therefore $+0{\cdot}0098°$. In consequence of the great constancy attainable at the triple point of water, it is suggested that for temperature measurements involving the highest accuracy the normal m. p. of ice should be replaced by the triple point as a fixed point on the temperature scale. The zero point should be re-defined as a temperature differing from the triple point by a numerical quantity (about 0·01°). R. A. Morton.

Limiting value of latent heat of vaporisation. J. E. Verschaffelt (Z. physikal. Chem., 1929, 140, 64).—Polemical against Kolosovski (cf. *ibid.*, 1928, 136, 314). H. F. Gillbe.

Detection of the transformation of antisymmetrical to symmetrical hydrogen molecules. A. Eucken (Naturwiss., 1929, 17, 182).—According to the wave-mechanics there are two forms of hydrogen characterised by symmetrical and antisymmetrical functions. At sufficiently low temperatures a gradual change in the relative proportions should occur and be detectable by means of specific heat determinations. The heat capacity of hydrogen in steel vessels at 50 atm. and at 106—149° Abs. has been measured initially, after 6 days and after 12¾ days. The results are in agreement with the assumption that the molecular fraction (γ) of the hydrogen present as the antisymmetrical form changes from 0·750 to 0·689 and then to 0·636. If the limiting value of γ is about 1 at the temperature of liquid air, the change in γ with time should follow the equation $\log(4\gamma-2)=-kt$. This relation is in accord with experience. R. A. Morton.

Constitution of aromatic substances and their chemical and physical properties. VI. Crystalline symmetry. I. Pastak (J. Chim. phys., 1929, 26, 65—68; cf. A., 1925, ii, 759; 1926, 340).—The symmetry of the crystalline forms of aromatic organic substances can be related to the symmetry of the molecules as deduced from melting points and solubilities. For disubstituted benzene derivatives in which the substituents are either the same or belong to the same group, the sequence in which the symmetry varies is $m>o>p$. If the substituents belong to different groups the sequence is $o>m>p$. For diphenyl derivatives the crystalline symmetry of the *oo'*-isomeride is greater than that of the *pp'* and for the substituted naphthalenes that of the α- is greater than that of the β-isomeride.
R. N. Kerr.

Fusion curve of helium. I. F. Simon, M. Ruhemann, and W. A. M. Edwards (Z. physikal. Chem., 1929, B, 2, 340—344).—The fusion curve of helium has been followed from 12° to 20° Abs., corresponding with a range of pressure of 800—1800 kg./cm.^{2} If p is the pressure and T the temperature, the results may be expressed by the equation $\log_{10} p=1{\cdot}5537 \log_{10} T+1{\cdot}233$ (cf. this vol., 386). Measurements of the latent heat of fusion indicate that there is no critical point crystalline–fluid near this temperature region. R. Cuthill.

Corrections to be applied to the platinum scale of temperature. F. E. Hoare (J. Sci. Instr., 1929, 6, 99—102; cf. this vol., 385).—Using the equation $t-pt=d(t-100)t$, where t, pt, are respectively the temperatures on the centigrade and platinum scales, and $d=1{\cdot}50\times10^{-4}$, the corrections to be applied to the platinum scale between 0° and 1000° to convert into gas scale temperature have been tabulated.
F. G. Tryhorn.

Majorana thermal effect. A. L. T. Moesveld (Z. physikal. Chem., 1929, A, 140, 423—428).—A discussion of the temperature difference which was found by Majorana (Atti R. Accad. Lincei, 1926, [vi], 4, 419) to exist between two pieces of the same metal placed in a constant-temperature bath, when one of the pieces had previously been heated. It is considered improbable that this phenomenon is due to the heat developed by a gradual gas adsorption, and it is suggested that the temperature difference is due to the heat evolved during the slow attainment of equilibrium between metastable states in the piece of metal which has been previously heated. Evidence for this view is obtained from the work of Cohen on the metastability of elements and compounds.
O. J. Walker.

B. p. in homologous series. B. Nekrassov (Z. physikal. Chem., 1929, 140, 342—354).—

The b. p. of a series of homologous compounds are considered as a function of two variables, viz., the mass and the volume of the molecules, and the empirical relationship $T\sqrt{MR}/(M-MR)=k$ is derived, which represents the b. p. (T) of such a series in terms of a constant k which is characteristic for each series and involves only the mol. wt., M, and the specific refractivity, R. According to the Clausius–Mosotti theory R is proportional to the actual volume of the molecules in unit mass of the substance. In the simplest case of the saturated hydrocarbons the introduction in the above equation of MR, the molecular refractivity as calculated from optical data in the usual way, gives a constant value of k. With polar compounds, however, for each polar group a certain empirical correction must be applied to MR in order to give a constant value for k, and the possible physical meaning of this correction is discussed. O. J. Walker.

Effect of intensive drying on certain physical properties of benzene. H. V. A. Briscoe, J. B. Peel, and P. L. Robinson (J.C.S., 1929, 368—377).—No material change was observed in the density and surface tension of benzene during drying for 16 months with phosphoric oxide. F. J. Wilkins.

Critical state. II. Limiting curve of ethyl ether. E. Schröer (Z. physikal. Chem., 1929, **140**, 241—253; cf. A., 1927, 1029).—The temperature–density curve of ethyl ether in the critical region has been determined by means of a new apparatus permitting observations for wide volume limits. Within the limits $d=0·23$ to $d=0·29$, change from the two-phase to the one-phase system is independent of the mean density. The following values are found: critical temperature$=193·4°\pm0·15°$, critical pressure$=36·15$ kg./cm.$^2\pm0·05$, critical density$=0·265$ g./cm.$^3\pm0·004$. The influence of stirring and of adiabatic dilatation and compression on the critical opalescence has been studied; the effect is attributed to an emulsion of the two phases formed before the actual temperature of miscibility is reached. The nature of the temperature–density curve is explained by means of the critical isotherm. R. N. Kerr.

Critical state. III. Behaviour of ethyl ether under isothermal compression in the critical and hypercritical region. E. Schröer (Z. physikal. Chem., 1929, **140**, 379—390; cf. preceding abstract).—Using the apparatus described in the previous paper, the isotherms of ethyl ether have been determined from 185° to 250° and 30 to 75 kg./cm.^{2}, and the following values of the critical temperature, pressure, and volume obtained: $t_c=194·6°\pm0·3°$, $p_c=36·7\pm0·2$ kg./cm.^{2}, $v_c=3·77\pm0·02$ cm.^{3} From the diagram of state the coefficient of compressibility (β) of ether is calculated. For each temperature β rises to a sharp maximum at a definite pressure. The maximum becomes flatter with rise of temperature, but is still observable at 250°, and its position alters only slightly with the temperature. An examination of the variation of β with volume shows that it can be represented qualitatively by van der Waals' equation. O. J. Walker.

Maxwell–Clausius and Clapeyron relations. V. Karpen (Compt. rend., 1929, **188**, 778—779).—A generalisation of the author's previous deductions (this vol., 138) in which the Maxwell–Clausius relation is shown to be obtainable for any fluid, independently of Carnot's principle, by replacing the condition imposed by the latter by the condition of equilibrium between the liquid and the saturated vapour above it. J. Grant.

Equation of state for ethylene. L. J. Gillespie (J. Physical Chem., 1929, **33**, 354—360).—Beattie and Bridgeman's equation of state (A., 1927, 819) has been applied to gaseous ethylene. The constants of the equation found from the data of Amagat are $A_0=6·152$, $a=0·04964$, $B_0=0·12156$, $b=0·03597$, and $c=22·68\times10^4$, when $T=273·13+t°$ and $R=0·08206$. Amagat's data are well represented up to a density of 7 mol./litre, and fairly so up to 8, slightly above the critical density, the average deviations being 0·36 and 0·45%, respectively. The calculated normal density, 1·2599, supports the value of Batuecas (1·2604) as against that of Stahrfoss (1·2610). L. S. Theobald.

F. p. of organic compounds. XI. Compounds with 5 and 6 carbon atoms. I. Simon (Bull. Soc. chim. Belg., 1929, **38**, 47—70).—Precise measurements of the f. p., b. p., densities at 0°, 15°, and 30°, viscosities at 15° and 30°, and refractive indices for the red, yellow, and violet helium lines, and the D, $H\alpha$, $H\beta$, and $H\gamma$ lines have been made for a number of derivatives of n-amyl alcohol and n-hexoic acid. By interaction of potassium sulphide and the alkyl iodide in alcoholic solution, n-*amyl sulphide*, m. p. $-51·3°$, b. p. $230·1\pm0·05°/760$ mm., has been prepared. The f. p. of ethyl hexoate is $-67·5°$. Using the new data to supplement existing figures, the relationships existing between the f. p. of the various members in homologous series have been examined. R. Cuthill.

Density, internal friction, dielectric constant, and solvent and ionising powers of hydrogen cyanide. K. Fredenhagen and J. Dahmlos (Z. anorg. Chem., 1929, **179**, 77—88).—The dielectric constant of hydrogen cyanide of specific conductivity $0·60\times10^{-6}$ ohm^{-1} has been determined from $-13·4°$ to $+22·1°$. Considerable divergence from Bredig's figures is observed, especially at the lowest temperatures; the temperature coefficient decreases as the temperature rises. The viscosity from $-7·5°$ to $+20·2°$ has been determined, and is about 20% of that of water. Density measurements from $-13°$ to 0° are in good agreement with those of other observers. A number of Kahlenberg and Schlundt's measurements of the solubilities and conductivities of inorganic salts in hydrogen cyanide have been confirmed, and the conclusion of these authors, that hydrogen cyanide, despite its abnormally high dielectric constant, has only a moderate solvent and ionising power, is supported. H. F. Gillbe.

Metastability of elements and compounds as a result of enantiotropy or monotropy. XIV. Investigation of potassium nitrate by means of the differential gas dilatometer. E. Cohen and H. L. Bredée (Z. physikal. Chem., 1929, **140**, 391—405).—By means of the Smith differential gas dilatometer (cf. Cohen and Bredée, this vol., 496) the densities and expansion coefficients of the rhombic (α) and rhombohedral (β) forms of potassium nitrate have been determined with greater accuracy at temperatures below and above the transition point, which was found to be 127·0°±1°. The volume change in the transition from the α to the β form is very small. A third, γ, form of potassium nitrate has been found which is monotropic and has a higher density than the other two forms.

O. J. Walker.

Physico-chemical investigation of dioxan. W. Herz and E. Lorentz (Z. physikal. Chem., 1929, **140**, 406—422).—A large number of physico-chemical data have been determined for pure dioxan and for mixtures with water and with methyl and ethyl alcohols between 20° and 90°, viz., densities (d^{20} 1·0330); the mixtures with water have higher, those with alcohol lower densities than correspond with the addition law; viscosities ($\phi_{20°}=0·01255$); surface tension ($\gamma_{20°}=35·42$ dynes/cm.^{2}); specific heat, $c_p=0·420$ at 23°. The heat of evaporation, $L=86·2$ g.-cal./g., gives a Trouton's constant of 20·3. Ebullioscopic, cryoscopic, and vapour-pressure data are also given. The critical temperature and pressure are calculated to be 583° and 44 atm., respectively. Dioxan has the normal mol. wt. (found 89·1) in benzene. The heat of combustion is 6602 g.-cal./g. Refractive index measurements have been made for pure dioxan and for aqueous solutions. The molecular refractivity of dioxan is 21·6. The solubilities of the following substances in various dioxan–water mixtures at 25° have been determined: sodium, potassium, and ammonium chlorides; potassium bromide, chromate, and dichromate; oxalic, malonic, succinic, benzoic, and salicylic acids.

O. J. Walker.

Constants of elasticity with respect to the periodic system of the elements. M. Kahanoviez (Atti R. Accad. Lincei, 1929, [vi], 8, 584—590).—Young's modulus and the moduli of rigidity and bulk have been comprehensively studied with regard to the periodic position of the elements. Unlike other physical properties of the elements, elasticity is shown to be a progressive function of the atomic number. In the transition elements, however, as given by the electronic theory, the moduli of bulk and shear show a periodicity. G. E. Wentworth.

Elastic constants of fused quartz. Change of Young's modulus with temperature. H. D. H. Drane (Proc. Roy. Soc., 1929, **A**, **122**, 274—282).—Measurements have been made of the deflexion at a fixed temperature (15°) of a small loaded cantilever of fused quartz and of the changes in deflexion as the temperature of the specimen varied over the range −183° to 700°. Similar results were observed with three specimens of quartz of different geological origin, the general behaviour being a continuous increase in Young's modulus with rise of temperature. The large changes and irregularities reported by Lees (Proc. Physical Soc., 1923, **36**, 405) were not confirmed, but indications were observed of some irregularity of behaviour between −183° and the ordinary temperature. Re-tests of the various specimens showed that heating caused an apparent increase in the viscosity, and semi-permanent changes were also found in the value of the modulus after cooling to the ordinary temperature. It is suggested that a close relation exists between the observed irregularities in mechanical behaviour and the optical anomalies found by Rayleigh in examining specimens of vitreous silica (Proc. Roy. Soc., 1921, **A**, **98**, 284).

L. L. Bircumshaw.

Compressibility of crystals and the exponent of the force of repulsion between atoms. N. Raschevsky (Nature, 1929, **123**, 448—449).—It is considered possible that practically the whole change of volume of a crystal (consisting of a large number of small, perfect crystals with a system of submicroscopic cracks between them) is due to the decrease in size of the cracks. If this is the case, the exponents of the forces of repulsion between the ions are considerably greater than Born's value of 9.

A. A. Eldridge.

Determination of forces of attraction from chemical equilibria. R. Lorenz (Z. physikal. Chem., 1928, **139**, 1—11).—The new mass action law (A., 1926, 126) as developed for condensed systems is further discussed and its significance in determining the forces of attraction between atoms or molecules is pointed out. It is shown that the only unknowns in the expressions connecting α and α′ with the van der Waals constants a and b are the constants $a_{1,2}$ and $a_{3,4}$, which represent, respectively, the attractions of the molecules (or atoms) of the first component for the second, and of the third for the fourth; α and α′, and $a_{1,2}$ and $a_{3,4}$ are not arbitrary, empirical constants, and in general $a_{1,2}>(a_1 . a_2)^{\frac{1}{2}}$. Values of $a_{1,2}$ (metal phase) and of $a_{3,4}$ (salt phase) have been calculated for equilibria of the type $A+BCl_2 \rightleftharpoons B+ACl_2$ and are tabulated for the following pairs of metals: cadmium and lead (600°), tin and cadmium (600°), tin and lead (chloride and bromide, at 400°, 500°, and 600°), zinc and cadmium (600°), copper and silver (900°), and lead and silver (900°). The values of $a_{1,2}$ and $(a_1 . a_2)^{\frac{1}{2}}$, and of $a_{3,4}$, and $(a_3 . a_4)^{\frac{1}{2}}$, respectively, are of the same order of magnitude throughout the series, and for a given equilibrium are approximately equal. The physical significance of these facts is that in a liquid mixture two dissimilar molecules are drawn together by a force approximately equal to that obtaining between two similar molecules. The values of $a_{1,2}-(a_1 . a_2)^{\frac{1}{2}}$ and of $a_{3,4}-(a_3 . a_4)^{\frac{1}{2}}$ are measures of the chemical attraction which for a mixture of two different substances makes itself felt over and above the mutual attraction of the molecules. L. S. Theobald.

Viscosity constants and surface layers. J. Tausz and F. von Körösy (Z. physikal. Chem., 1929, **140**, **A**, 263—272).—The experiments of Traube and Whang have been repeated (this vol., 129). It is shown that the change in rate of flow of water in a capillary tube produced by coating the tube with amyl alcohol or oleic acid is due entirely to a change in the hydrostatic pressure which forces the water through the tube. This change of pressure is caused by the smaller capillary rise of water in the equilibrium position in these cases because of lowering of surface tension. Contrary to the results of Traube and

Whang, the rate of flow is increased by coating the capillary with a film of paraffin; this is due to the smaller capillary rise of water on a paraffin surface than on glass. Traube's viscosimeter had been used to determine the absolute viscosity of water; the value found is 5% too high. Care must be taken in using this viscosimeter for different liquids that the equilibrium position of the liquid in the capillary is always the same. R. N. KERR.

Influence of surface tension on viscosity measurements. S. ERK (Z. physikal. Chem., 1929, **140**, 309—315).—The results of Traube and Whang are criticised on grounds similar to those used by Tausz and Körösy (preceding abstract). An equation is deduced from the Hagen–Poiseuille law which connects the viscosity and the height of the capillary rise at equilibrium. The capillary rise in the different tubes has been measured and the times of flow are calculated from this equation. Good agreement is obtained with those found by Traube and Whang. R. N. KERR.

Thermal conductivity of gas mixtures. T. L. IBBS and A. A. HIRST (Proc. Roy. Soc., 1929, A, **123**, 134—142).—By comparing Wachsmuth's values for the thermal conductivity of helium–argon mixtures (Physikal. Z., 1908, 7, 235) with the catharometer calibration curve for the same pair of gases (Ibbs, A., 1925, ii, 376), a curve is constructed showing the relation between catharometer deflexion and thermal conductivity at 0° over a wide range of values. By interpolation, the conductivity which corresponds with the galvanometer deflexion for any gas or mixture can then be determined. Data are given for the relation between conductivity and composition for the mixtures hydrogen and carbon dioxide, hydrogen and argon, hydrogen and nitrogen, hydrogen and carbon monoxide, and hydrogen and nitrous oxide. The results for hydrogen–carbon dioxide mixtures are in good agreement with those of Weber (Ann. Physik, 1917, [iv], 54, 481). The accuracy and advantages of the method are discussed. L. L. BIRCUMSHAW.

Viscosity formula for binary mixtures taking into account the association of the constituents. II. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, **4**, 25—31; cf. this vol., 387).—A study of the field constant k in the formula previously proposed indicates that its value is characteristic of a given liquid, and, further, that for homologous liquids the value of k is proportional to the product $D\sigma$, where D is the dielectric constant and σ the molecular diameter. Thus, for methyl, ethyl, and *n*-propyl alcohols the values of $D\sigma\times10^8/k$ are respectively 264, 260, 266, and for methyl and ethyl acetates, 15·6 and 15·7. Extended to the case of binary gaseous mixtures the formula becomes $\eta=\eta_1/[1+kz_m/(1-z_m)]+\eta_2/[1+(1-z_m)/kz_m)$.

In the application of the author's formula to binary liquid mixtures in which molecular compounds are formed the deviation of the measured viscosity (η) from that calculated from the formula (η_0) is termed the solvation viscosity, $\delta=\eta-\eta_0$. The magnitude of δ is determined by the extent of the reaction between the two constituents. It is assumed that if reaction occurs between ν_1 and ν_2 molecules of the two components to form a molecular compound, then the solvation viscosity $\delta=c(1-z_m)^{\nu_1}\,.\,z_m^{\nu_1}$, where z_m is the concentration of the second component. This assumption has been tested by reference to the mixtures water–methyl alcohol, water–ethyl alcohol, and water–acetic acid. Evidence is found for the existence of the molecular compounds $AcOH,H_2O$, $MeOH,2H_2O$, $EtOH,3H_2O$ (in solutions up to 40 mol.-% of EtOH), $EtOH,2H_2O$ (in solutions containing more than 40 mol.-% of EtOH). F. G. TRYHORN.

Mixed crystals, solutions, and fusions of the system $(K,NH_4)(Cl,NO_3)$. E. JÄNECKE (Z. angew. Chem., 1929, **42**, 318).—Corrigenda to an earlier paper (cf. A., 1928, 1095).

Logarithmic mixture law. J. DEJMEK (Physikal. Z., 1928, **29**, 907—908).—The relation between the simple and the logarithmic mixture laws is discussed. The latter is applicable to the calculation of electrical and thermal conductivity for alloys of the cadmium–bismuth, aluminium–bismuth, and silver–lead types, and also to the calculation of the viscosity of liquid mixtures. R. A. MORTON.

Crystal form in the production of solid solutions. IV. Analysis of the anhydrous systems $MgCl_2$–$FeCl_2$ and $CdCl_2$–$FeCl_2$. A. FERRARI and M. CARUGATI (Atti R. Accad. Lincei, 1928, [vi], **8**, 306—309; cf. this vol., 388).—The similarity of the crystal lattices of the anhydrous chlorides of magnesium, cobalt, and nickel and bivalent iron and manganese suggests complete miscibility in the solid state. F.-p. determinations demonstrate the formation of a complete series of solid solutions for the two systems examined. G. E. WENTWORTH.

Structure of some ternary alloys of copper, zinc, and aluminium. A. J. BRADLEY and C. H. GREGORY (Mem. Manchester Phil. Soc., 1927—1928, **72**, 91—100).—An attempt is made to elucidate the problem of so-called intermetallic compounds. The resemblance between the structures of analogous phases in the systems Cu–Zn, Cu–Al suggested that ideal solid solutions of a ternary alloy could be produced from binary alloys of similar structure. This has been proved. G. E. WENTWORTH.

Some physical constants of pure, carbon-free chromium–iron and vanadium–iron alloys. K. RUF (Z. Elektrochem., 1928, **34**, 813—818).—For the two kinds of alloy, curves showing the influence of temperature and composition on the specific resistance, on the thermoelectric force against platinum, and on the thermal expansion are reproduced. The specific resistance at 20° of electrolytic chromium, remelted in a vacuum, was found to be 0·284 ohm mm.^{2}/m. For electrolytic iron with less than 0·02% C, d^{20} is 7·876. The density curves are linear for alloys with up to 18% V and for those with up to 50% Cr, and extrapolation of the chromium curve gives d^{20} 7·014 for the pure metal as compared with d^{20} 7·011 found for the electrolytic chromium remelted in a vacuum. The thermal expansion curves are convex to the composition axis, and the temperature–thermal expansion curves show that addition of vanadium causes a disappearance of the change of state observed in pure iron at 850—900°. Alloys containing up to 12% Cr show discontinuities (less marked than in the case of iron) in these curves at temperatures above that of the corresponding discontinuity in electrolytic iron. This effect decreases with an increase in chromium content and disappears with alloys containing 13% Cr or more.

L. S. THEOBALD.

Limits of reactivity of the magnesium–cadmium alloys, and their potential–concentration curves. C. KRÖGER (Z. anorg. Chem., 1929, **179**, 27—48).—The reactivity of the magnesium in the alloys has been determined as a function of the composition by measuring the quantity of hydrogen evolved when the alloy is treated with methyl alcohol; the "reactivity coefficient" α is the fraction of the total magnesium dissolved, and for cadmium concentrations up to about $0{\cdot}25M$ is approximately unity; with increase of cadmium content α decreases very rapidly to zero. Tempering the alloys decreases α between 0·375 and $0{\cdot}5M$, whilst even at a cadmium concentration of $0{\cdot}25M$ α is very small. Treatment of the alloys with ethereal ethyl iodide solutions leads to analogous results. The protective action of the cadmium atoms is explained by consideration of the relative positions of the atoms of the two metals in the mixed crystal lattice. The variation with time of the *E.M.F.* of the cell $Cd|N\text{-}MgSO_4|Cd_xMg_{1-x}$ has been determined for a number of values of x. For alloys of lower cadmium concentration than $0{\cdot}5M$ the *E.M.F.* falls for several hours, remains constant for a lengthy period, and finally falls again, whereas for alloys richer in cadmium the *E.M.F.* at first rises rapidly to a maximum and then decreases somewhat to a steady value. The significance of these results for the fine structure of the alloy is discussed.

H. F. GILLBE.

Aluminium and the formation of mixed crystals with silicon. L. ANASTASIADIS (Z. anorg. Chem., 1929, **179**, 145—154).—At the eutectic temperature the specific resistance curve shows that the terminal point of the mixed crystals series lies at 1·48% Si. Aluminium seems to undergo no transition, for its resistance is not influenced by prolonged cooling or by suddenly cooling from 630°. Aluminium containing 0·31% Si exhibits an increase of resistance after chilling, and even with 0·18% Si a small effect is to be observed. It follows that mixed crystals are formed between these concentrations at the ordinary temperature. The value $36{\cdot}8\times10^{-4}$ is recorded for the electrical conductivity of (99·94%) aluminium. H. F. GILLBE.

Deviations from Dalton's partial pressure law and their chemical significance. M. TRAUTZ and M. GÜRSCHING (Z. anorg. Chem., 1929, **179**, 1—26).—Accurate measurements have been made of the changes of pressure which occur when equal volumes of pairs of gases are mixed at constant pressure. Primary deviations from the simple laws in the case of pure gases and binary mixtures are attributed to the formation of associated molecules which in the case of mixtures may contain two similar or two different molecules. For such systems equations of state corresponding with that of van der Waals have been derived, wherein the constant a is replaced by a dimerisation constant. The Berthelot equation $a_{1,2}=\sqrt{a_1a_2}$ assumes the form $a_{1,2}=\frac{1}{2}\sqrt{K'}\sqrt{a_1a_2}$, where K' is the equilibrium constant of the process $A_2+B_2=2AB$, A and B being the component gases. On the basis of this theory and of the measurements which have been made, the gaseous compounds Me_2O,CO_2, Me_2O,SO_2, and $Me_2O,MeCl$ have been detected. The thermal changes with dimethyl ether indicate the formation of the known compound between methyl ether and hydrogen chloride. The association of ethylene and hydrogen is not the same as the hydrogenation of ethylene to ethane. The degree of association may be calculated simply from equilibrium considerations if the pressure change on mixing exceeds about 2% of the initial pressure; with smaller pressure changes the newly-derived equations are more readily applicable, since account is therein taken of association in the component gases. The significance of the duration of collision between gas molecules which is involved in the theory of binary association is considered in reference to the internal friction of gases. H. F. GILLBE.

Diffusion coefficients of gases in water, and their temperature relationships. G. TAMMANN and V. JESSEN (Z. anorg. Chem., 1929, **179**, 125—144).—The diffusion coefficients K and their variations with temperature have been measured for carbon dioxide, acetylene, hydrogen, nitrogen, and oxygen diffusing through agar-agar solutions. Excepting for oxygen the value of K increases linearly with rise of temperature. The anomalous behaviour of oxygen is due to absorption of the gas by the agar-agar solutions. H. F. GILLBE.

Dissolution of silver in water. H. KŘEPELKA and F. TOUL (J. Czechoslov. Chem. Comm., 1929, **1**, 155—164).—By accurate nephelometric determinations and measurements of the *P.D.* of the electrode Ag|pure conductivity water, it was found that the solubility of pure silver in pure water in the dark, out of contact with air, at 18—20° is 0·037 mg./litre. The silver passes into solution as the ion, dissolution being due to surface oxide, to oxygen absorbed on the surface, or to oxygen dissolved in the water. When the surface of the silver has been previously reduced in pure dry hydrogen at 400°, the metal does not dissolve in pure water carefully freed from dissolved gases. Solubility measurements made in glass vessels are, on the average, 0·003 mg. higher than those obtained in silver vessels, this difference being due, probably, to the effect of alkali dissolved from the glass. J. W. BAKER.

Solubility of iodine in solutions of halides. J. S. CARTER and C. R. HOSKINS (J.C.S., 1929, 580—585).—The solubility of iodine in solutions of halides has been measured at 25°. Owing to the reaction between iodine and fluorides in aqueous solution, the solubility in the case of fluoride solution could not be determined. Over the very large range of concentrations investigated it is shown that the solubility of iodine can be simply expressed in terms of two opposing factors, (*a*) the salting-out effect and (*b*) the tendency to form perhalides. With iodides the former is negligible, but with bromides and chlorides it is of considerable importance. F. J. Wilkins.

Diffusion in hydrotropic solutions. H. Freundlich and D. Krüger (Biochem. Z., 1929, 205, 186—193).—The diffusion of benzoic acid in pure water and in solutions of hydrotropic salts (sodium benzenesulphonate and *p*-toluenesulphonate) is measured by Ocholm's method. The diffusion coefficient in hydrotropic solutions is as great as or greater than in pure water but is not constant. The diffusion coefficient of brucine both in aqueous solution and in solutions of sodium benzenesulphonate is not constant, but is rather smaller in hydrotropic solutions than in pure water.

P. W. Clutterbuck.

Distribution of acetone through a rubber membrane. D. S. Morton (J. Physical Chem., 1929, 33, 384—397).—The distribution of acetone between methyl alcohol and water separated by a rubber membrane at the ordinary temperature over a composition range of 0—70%, can be represented by the equation $G_1/G_2=2{\cdot}24(G_1/G_3)^{1{\cdot}09}$, where G_1, G_2, and G_3 are the mol fractions of acetone, alcohol, and water, respectively. The results have been checked by a deduction of the distribution curve from measurements of the vapour pressures of the three pairs of binary mixtures; these were made by means of an interferometer at 20°. Equations representing the partial pressure of acetone for acetone–methyl alcohol solutions and for acetone–water solutions are given. The results indicate that distribution of a solute between two phases is primarily a function of mass concentrations. L. S. Theobald.

Adsorption isothermals for a plane platinum surface. W. G. Palmer (Proc. Roy. Soc., 1929, A, 122, 487—497; cf. A., 1927, 722).—Petrol of b. p. 40—60° was purified by shaking with saturated alkaline permanganate and dried over sodium wire. A fraction of the product, b. p. 40—44°, gave a film only with difficulty and showed a cohering voltage of $<0{\cdot}2$. The adsorption on a plane platinum surface of benzene, ethyl alcohol, and acetic acid has been studied by the coherer method (*loc. cit.*), using the above hydrocarbon as diluent. The results confirmed Langmuir's formula $a=a_\infty[pc/(1+pc)]$, where p is a constant representing the average life of a molecule of adsorptive in the film. The similarity in the values of p for the three adsorptives indicates that the lives of the adsorbed molecules on the surface are almost equal. The variation in the apparent area available for the adsorption of different substances is discussed in relation to the mechanism of adsorption and catalytic action.

L. L. Bircumshaw.

Formation of sulphur films on a mercury surface. A. Frumkin (Kolloid-Z., 1929, 47, 229—231).—When drops of a solution of sulphur in a volatile solvent (ethyl ether, benzene, light petroleum) are dropped on to a surface of clean mercury, the first drops spread out very rapidly and subsequent drops more slowly until finally a stage is reached where addition of another drop does not cause further spreading. It is shown that at this stage the mercury is covered with a unimolecular layer of sulphur and that the area of the surface occupied by each sulphur atom is of the order of magnitude of the cross-section of a mercury atom. The linking between the mercury and sulphur atoms would therefore seem to be of the same type as in a chemical compound of these elements. A similar effect cannot be obtained with solutions of iodine, but the effect is produced by drops of solutions of iodoform. E. S. Hedges.

Formation of thin films of organic colloids on mercury surfaces. R. L. Keenan (J. Physical Chem., 1929, 33, 371—380; cf. A., 1928, 702).—A technique for obtaining thin films of organic colloids on mercury is described. Cellulose esters and isoelectric gelatin form rigid films of an irregular shape. Data for cellulose acetates of varying viscosities and in different solvents are given, and with cellulose nitrates the limiting film thickness, which is independent of dilution, varies inversely as the viscosity. Films of rubber are elastic. The limiting thickness increases with increasing complexity of the atom groups; thus rubber, cellulose, and gelatin have the values 1·5, 2·5—5·0, and 7·0 Å., respectively. The results indicate that the films consist of long chains or ribbon-like molecules which lie flat on the mercury surface or have an open-work, net-like structure. L. S. Theobald.

Reversal of Traube's rule in adsorption of homologous compounds by sugar charcoal. T. Sabalitschka (Pharm. Ztg., 1929, 74, 382—384).—Whilst the degree of adsorption of organic acids from aqueous solutions by blood charcoal, bone charcoal, and vegetable charcoal increases with the mol. wt. of the solute, the reverse is found to be the case with sugar charcoal. This reversal is observed with both monobasic and dibasic acids.

S. I. Levy.

Hydrolytic adsorption by humic acid. A. Ganguli (Phil. Mag., 1929, [vii], 7, 317—322).—The adsorption of electrolytes by humic acid causes a liberation of free acid in direct proportion to the concentration of the electrolyte. The change in hydrogen-ion concentration is due to the adsorption of the cations to form a complex electrolyte. There is a marked effect of valency and for a common anion cations give the regular order $Al>Ba>K>Na$, whilst for anions $Cl<SO_4$. The results are in agreement with those of Michaelis and Rona (Biochem. Z., 1914, 94, 240) and offer a confirmation of Mukherjee's theory of the acidity of soils (A., 1923, i, 79).

A. E. Mitchell.

Adsorption. (Frl.) M. T. Isselstein (Physikal. Z., 1928, 29, 873—878).—The adsorption of carbon disulphide, pentane, and chloroform on powdered glass has been studied. The area of glass was measured by the methods of Schmidt and Durau (A., 1924, ii, 238) and of Schelte (A., 1925, ii, 286). Adsorbed layers up to 35 molecules in thickness have been observed, the thickness decreasing, however, with decreasing pressure. When the temperature is well above the condensation point there is little tendency towards the formation of even a unimolecular adsorbed layer, but as the conditions for condensation are approached the adsorption increases.

R. A. Morton.

Adsorption of carbon dioxide and ammonia by silica gel. A. Magnus and R. Kieffer (Z. anorg. Chem., 1929, **179**, 215—232).—The adsorption of carbon dioxide by silica gel has been determined at temperatures between —21·2° and 100° and at pressures between 0·1 and 760 mm. The heat of adsorption, calculated from the isotherms, is an approximately linear function of the temperature, whilst the repulsion constant of Magnus' equation of state has at the higher pressures a constant value at each temperature. Variation of the water content of the gel has but little influence on the isotherms. Experiments have been made with titanium and zinc oxides, calcium and barium fluorides, barium sulphate, and nickel bromide with the object of finding other adsorbents which would behave in the same manner as silica gel, but in each case the drying and degassing processes appear to render the adsorbent chemically active towards the gas. The influence of water on the adsorption of ammonia by silica gel has been determined. The heat of adsorption has been determined from the isotherms for a nearly water-free gel as a function of the pressure, and by extrapolation to zero pressure the value of Q is found to be about 12,000 kg.-cal., which agrees with the value obtained by calorimetric measurements using an almost water-free gel. H. F. Gillbe.

Absorption of dextrose by protein precipitates. J. H. Cascao de Anciaes and C. Trincao (Compt. rend. Soc. Biol., 1928, **98**, 1003—1004, 1586—1588; Chem. Zentr., 1928, ii, 1700).—Absorption of dissolved dextrose by albumin is prevented by addition of sodium chloride. A. A. Eldridge.

Optical study of adsorbed films. J. H. Frazer (Physical Rev., 1929, [ii], **33**, 97—104).—Rayleigh and Drude's method for the study of surface transition layers has been applied in the investigation of adsorption on glass. Only water and methyl alcohol show definite adsorption, and two successive unimolecular layers are indicated. The method is applicable to the study of surface conditions at the interface between any two phases. N. M. Bligh.

Invisible oxide films on metals. F. H. Constable (Nature, 1929, **123**, 569).—If reduced copper is acted on by a mixture of hydrogen sulphide (1 vol.) and air (5 vols.), two complete colour sequences are produced in a few minutes; if, however, the copper surface is left exposed to air for some hours, and then subjected to the action of hydrogen sulphide and air, the interference colours are developed very slowly. The results support Evans' conclusion that a thin film of oxide is formed when copper is exposed to air at the ordinary temperature.

A. A. Eldridge.

Elliptical polarisation produced by reflexion at the surface of solutions of fatty acids in water. C. Bouhet (Compt. rend., 1929, **188**, 59—61).—Earlier experiments (*ibid.*, 1927, **185**, 200) have been extended to the measurement at 15—21° of the ellipticities (K) of solutions in water of fatty acids of the series acetic to myristic acid. The curves connecting K (as ordinates) with the concentration of acid show minimum values of the former which decrease as the carbon content of the acid increases, and in the case of the higher acids these correspond with saturated solutions. It is inferred that although a layer of acid molecules may be adsorbed on the surface of the solution, its orientation in the case of solutions showing minimum ellipticities differs completely from that for the pure acid. J. Grant.

Interfacial tension between mineral oils and aqueous solutions. Influence of time and p_H. H. Weiss and E. Vellinger (Compt. rend., 1929, **188**, 901—903).—The interfacial tension between a mineral oil and a solution of an electrolyte increases or decreases with the time to an extent which depends on the p_H value of the latter, and the value obtained by extrapolation to zero time is the most trustworthy. The interfacial tension–p_H curves are of two characteristic types, one almost parallel with the p_H-axis but having slight maxima at p_H 6 and 11, and the other showing a rapid fall in interfacial tension above p_H 7. Smaller variations are due to the nature of the buffer substances used. J. Grant.

Creeping of crystals. II. H. Erlenmeyer (Helv. Chim. Acta, 1929, **12**, 264—269; cf. A., 1928, 12).—Further observations are recorded. The addition of 1% of glycerol almost entirely prevents creeping in a saturated solution of potassium chloride. Sucrose and thymol have a similar effect. This is not due to a decrease in evaporation. Experiments are also described relating to the factors which influence the height to which crystals will creep up a glass rod placed in a saturated solution of a salt.

O. J. Walker.

Synthetic kidneys. W. D. Bancroft and R. L. Nugent (5th Coll. Symp. Mon., 1928, 149—158).—The kidney glomerulus is not a simple ultra-filter, since changes occur in the concentration of solutes, due to some form of dialysis or electrical endosmosis. If manganese sulphate is added to aqueous acetone on one side of a rubber membrane, the acetone content of a similar mixture on the other side is considerably increased. The concentration effects in *Valonia* and in the kidney are discussed.

Chemical Abstracts.

Artificial membranes electively permeable to anions. R. Mond and F. Hoffmann (Pflüger's Archiv, 1928, **220**, 194—202; Chem. Zentr., 1928, ii, 1659).—The membranes were obtained by deposition of rhodamine-B in the pores of collodion membranes. *E.M.F.* determinations with 0·1N-sodium chloride on one side and 0·1N-sodium thiocyanate, nitrate, iodide, bromide (chloride), acetate, sulphate, and with potassium chloride and nitrate, showed that only the anions are electromotively active in the above order. The *P.D.* between potassium nitrate solutions (1 : 10) diminish with the absolute concentrations; the more dilute solution is negative towards the more concentrated. A. A. Eldridge.

Electrolyte equilibria at elective ion-permeable membranes and its biological significance. H. Netter (Pflüger's Archiv, 1928, **220**, 107—123; Chem. Zentr., 1928, ii, 1576).—From thermodynamic and statistical considerations it is inferred that all permeating ions on both sides of an elective cation- or anion-impermeable membrane must become distributed in equal ratio. Experiments with anion-

impermeable collodion membranes illustrate the effect, the biological significance of which is considered.
A. A. Eldridge.

Refraction constants and solution volumes of some organic compounds in aqueous solution. E. Berner (Z. physikal. Chem., 1929, **141**, 91—124).—The refractive indices and densities of dilute aqueous solutions of ethyl alcohol, *n*- and *sec.*-propyl and butyl alcohols, acetone, methyl ethyl ketone, and the methyl esters of the isomeric tartaric acids have been measured at 20°. The molecular refractivities of the solutes agree well with the values for the pure substances, and are therefore additive. The molecular solution volumes, however, are dependent on the structure and configuration of the compounds.

The hydration of the anhydrides of succinic, methylsuccinic, and glutaric acids has been followed by dilatometric and interferometric measurements, and the molecular refractivities and solution volumes of the anhydrides and of the corresponding free acids have been calculated. The oxygen ring in glutaric anhydride has a larger refractivity and a smaller solution volume than in succinic and methylsuccinic anhydrides.
O. J. Walker.

Effect of ionisation on optical rotation. IV. Amino-acids and peptides. P. A. Levene, L. W. Bass, A. Rothen, and R. E. Steiger (J. Biol. Chem., 1929, **81**, 687—695).—Figures are given for the optical rotations of *l*-valine, *l*-leucine, glycyl-*d*-valine, glycyl-*l*-valine, and glycyl-*d*-*iso*valine in presence of varying amounts of acid or base. The results confirm the previous conclusion (A., 1927, 625) that such measurements afford a satisfactory means of determining the dissociation constants.
C. R. Harington.

Ebullioscopic researches on mixtures of salt solutions. G. Proniewski (Rocz. Chem., 1929, **9**, 115—130).—The b. p. of mixtures of equimolecular solutions of the chlorides of ammonium, sodium, potassium, magnesium, calcium, barium, zinc, cadmium, and mercury have been measured. Deviations from the theoretical value are given by all pairs consisting of one alkali or alkaline-earth chloride and of zinc, cadmium, and mercuric chlorides; in the case of cadmium and zinc, the b.-p. deviation curves exhibit a maximum at 60% of alkali or alkaline-earth salt solution, and the position of this maximum is little affected if solutions other than equimolecular are used. Maximum deviations of b. p. appear at about 50% of 3*M*-alkali salts on progressive dilution. On similarly diluting solutions of cadmium, zinc, and mercuric chlorides both negative and positive deviations are obtained, according to the salt in question and its initial concentration. It follows from the above results that the b.-p. deviation maxima obtained at about equimolecular proportions of pairs of salts do not necessarily indicate the formation of double salt, as was assumed by Bourion and Rouyer (A., 1927, 415). No combinations of the nitrates of sodium, magnesium, and zinc give mixtures with anomalous b. p., whilst in the case of sulphates the b. p. is raised only for the pair sodium sulphate–zinc sulphate.
R. Truszkowski.

Measurements of albedo in artificial layers of fog. E. Regener (Z. physikal. Chem., 1928, **139**, 416—244).—An investigation has been made to determine the maximum value to which the diffuse reflecting power of a layer of fog can be raised by increasing the concentration of the particles. The fog was illuminated by parallel rays from the sun at a height of 28—44° and the light reflected perpendicularly to the surface was measured by means of a photometer. Comparison was made with a gypsum plate with an albedo approximately equal to that of an absolutely white body. Fogs of sulphur trioxide, paraffin oil, and ammonium chloride were investigated. In order to obtain fogs with a sharp, flat surface it was found necessary to use carbon dioxide instead of air for their production.
R. N. Kerr.

Dispersoidal synthesis of gold by means of alkaline formaldehyde solutions. I. P. P. von Weimarn (Bull. Chem. Soc. Japan, 1929, **4**, 35—47).—In accordance with the author's theory of dispersoidal synthesis it has been found possible to prepare reproducible gold sols of red or orange colour by reducing gold chloride solutions with formaldehyde rendered alkaline by the addition of potassium hydroxide or carbonate. Under suitable conditions these stable sols may be obtained without rigorous purification of the water or reagents employed. The effect of increasing purity of the reactants is to yield sols which may be concentrated to a greater degree without the development of a blue colour on cooling.
F. G. Tryhorn.

Colloidal solutions of practically insoluble gold compounds and their transformation to gold sols. P. P. von Weimarn (Kolloid-Z., 1929, **47**, 231—235).—Colloidal solutions of gold iodide may be prepared by adding a very dilute solution of chloroauric acid to a boiling dilute aqueous solution of iodine, or by mixing dilute solutions of chloroauric acid and potassium iodide in presence of potassium hydroxide. Using potassium thiocyanate in place of potassium iodide, sols of gold thiocyanate are produced. The properties of these sols depend on the concentration of the reagents, temperature, etc.; they change spontaneously to gold sols, thus casting doubt on the usual simple explanation of the production of gold sols.
E. S. Hedges.

Production of colloidal solutions of lead or lead salts. M. C. Reinhard, K. W. Buchwald, and K. P. Tucker (J. Cancer Res., 1928, **2**, 160—165).—Lead acetate in gelatin and 10% sodium orthophosphate are used; the influence of p_H and of protective colloids, and the microscopical characters of the products, were studied.
Chemical Abstracts.

Colloidal potassium ferrocyanide solutions. A. Kutzlnigg (Kolloid-Z., 1929, **47**, 221—222).—Colloidal solutions of potassium ferrocyanide are obtained when the solid salt is shaken with water to which has been added ethyl, methyl, or propyl alcohol, or acetone. The best condition is to shake 0·1 g. of the salt with 100 c.c. of ethyl alcohol and 50 c.c. of water. The sols are much deeper in colour than a true solution of the same concentration, they sometimes show a yellow, blue, or red opalescence, and exhibit the Tyndall phenomenon. Addition of more alcohol causes the precipitation of a white amorphous mass or gel of potassium ferrocyanide. The more concentrated sols are sensitive to light.

E. S. HEDGES.

Colloidal behaviour of antimony pentoxide. S. GHOSH and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 17—25).—By dialysing a mixture of potassium antimonate and dilute nitric acid a negatively charged sol of antimony pentoxide has been obtained, which behaves normally towards dilution and mixtures of electrolytes, and follows the Schulze–Hardy law. The viscosity, electrical conductivity, acidity, and stability towards electrolytes change slightly on ageing or on boiling. A coagulum of antimonic acid can be repeptised very easily by washing when the sol has been precipitated by univalent ions, but with difficulty when coagulated by multivalent ions. It is a reversible colloid, and the hydrate $Sb_2O_5,4{\cdot}7H_2O$, obtained by drying the sol at the ordinary temperature, passes into the colloidal state on the addition of water. About 0·5% of the colloid is in the dissolved condition.

O. J. WALKER.

Colloid types. E. G. BINGHAM (5th Coll. Symp. Mon., 1928, 219—228).—From the point of view of plastic flow, colloids are differentiated as polar, emulsions, and non-polar. Measurement of the "solubility" of polar colloids is discussed.

CHEMICAL ABSTRACTS.

Tactosols. H. ZOCHER and K. JACOBSOHN (Kolloidchem. Beih., 1929, 28, 167—206).—The term "tactosols" is given to sols containing non-spherical particles which have the property of spontaneously arranging themselves in parallel order. This property has been studied with sols of vanadium pentoxide, benzopurpurin, ferric oxide, tungsten trioxide, and chrysophenin. Vanadium pentoxide separates on ageing into a concentrated anisotropic phase—the tactosol—which later precipitates out, and a dilute isotropic phase, which is termed the atactosol. This process has been followed microscopically. Addition of arsenic acid retards the process greatly, whilst addition of other electrolytes does not affect the ageing, but produces different forms of tactoids in the sense of a closer crowding of the particles. When an electrical *P.D.* is applied, the particles arrange themselves with their long axes parallel to the direction of the current, but if an alternating current is applied the orientation of the particles is perpendicular to the current. In a magnetic field, the particles are arranged parallel to the lines of force. Tactoids are readily produced by cooling a 2% boiling sol of benzopurpurin-4B, and with difficulty from 1·5 or 1% sols. Benzopurpurin-6B exhibits the effect better, even in a 1% sol. Addition of electrolytes has an effect similar to that observed in the case of vanadium pentoxide. In a magnetic field, the particles become arranged with their long axes perpendicular to the lines of force. Measurements have been made of the concentration and conductivity of the atactosol remaining after the separation of the tactosol from tactosols of aged ferric oxide sols. Tactosols of tungsten trioxide have disc-like particles bearing a negative charge, and evidence is given that the particles consist of a number of parallel platelets having a constant "period" or distance apart. A method is given for preparing tactosols the particles of which have different periods. Measurements of conductivity show that the period is smaller the higher is the electrolyte content of the sol. It is also possible to diminish the periodicity of the layering by direct addition of hydrochloric acid, sodium hydroxide, sodium tungstate, or sodium chloride. The gelatinous precipitate from heated chrysophenin solutions of various concentrations and electrolyte content has been studied microscopically. At certain concentrations the tactoids attain macroscopic dimensions. Unshaken solutions of this concentration show negative streaming-double refraction, whilst shaken solutions are positive. The tactoids of chrysophenin consist of long, lamellar, negative anisotropic crystals.

E. S. HEDGES.

Dispersity of dissolved cellulose. H. ZEISE (Kolloid-Z., 1929, 47, 248—251).—A criticism of papers by Hess and others (B., 1924, 88) and by Baur (A., 1925, ii, 662) on the state of cellulose dissolved in cuprammonium hydroxide solution.

E. S. HEDGES.

Number of nuclei formed during crystallisation of gels. P. A. THIESSEN and E. TRIEBEL (Z. anorg. Chem., 1929, 179, 267—276).—The relation between the degree and period of supercooling and the number of centres of crystallisation in dilute sodium oleate gels is analogous to that observed in single-component systems. The number of such centres varies linearly with the concentration.

H. F. GILLBE.

Characterisation of colloidal solutions by the degree of polarisation of Tyndall light. R. O. HERZOG and B. LANGE (Ber., 1929, 62, [*B*], 491—495).—Parallel rays from an arc lamp pass through a slit into the solution under investigation. At right angles to the incident ray the emergent beam passes through a doubly-refracting Wollaston prism and monochromator. The intensities of the two components are determined by a half-shadow apparatus with Nicol prism. The depolarisation is calculated from the formula $\Delta=\tan^2\alpha$. Spherical particles, small in comparison with the wave-length of light, cause complete polarisation of the Tyndall light ($\Delta=0$). Increase in α is observed with increasing size of particles. Observations are recorded for cellulose trinitrate in methyl acetate and acetone, glycogen and inulin in water, cellulose acetate in methyl acetate and acetone, "total caoutchouc" and polystyrene in benzene, gelatin in water and cresol. Congo-red and vanadium pentoxide in water.

H. WREN.

Optical properties of turbid solutions containing non-metallic particles and the Pulfrich step-photometer. (FRL.) U. MILTHALER (Ann. Physik, 1929, [v], 1, 229—259).—The application of the Pulfrich photometer to the measurement of absorption, Tyndall effect, and depolarisation in turbid media has been investigated. Beer's law is shown to hold for gamboge solutions provided the initial solution is not too concentrated. The optical properties of mastic solutions have also been studied.

R. A. MORTON.

Double refraction of bentonite. R. Bradfield and H. Zocher (Kolloid-Z., 1929, 47, 223).—The streaming-double refraction of natural bentonite is negative, but is positive after electrodialysis. It is possible that the change of sign through electrodialysis is due to an alteration in the constitution of the anisotropic colloidal particles, which lose their bases. The constitution of the particles is analogous to that of zeolite crystals, both allowing of exchange of bases. E. S. Hedges.

Streaming-double refraction and thixotropy of bentonite suspensions. A. von Buzágh (Kolloid-Z., 1929, 47, 223—229).—Bentonite, from which coarsely disperse particles have been removed, is peptised by water in two fractions. The more readily peptisable part contains considerably less alkali and alkaline earths than the other fraction and is positively doubly refracting, whilst the more difficultly peptisable part exhibits negative streaming-double refraction. The negative doubly refractive bentonite can be made positive doubly refracting by electrodialysis. This can be intensified by adding potassium hydroxide, but addition of calcium hydroxide produces weak negative streaming-double refraction. The original bentonite gives with certain proportions of water thixotropic pastes, the time of setting of which decreases greatly with increasing content of bentonite. Electrodialysed bentonite does not behave in this way, but gives thixotropic pastes when dilute alkali solutions are employed instead of water. The time course of the peptisation of natural bentonite with water and of electrodialysed bentonite and of kaolin with alkali has been followed. In each case the curve passes through a maximum. E. S. Hedges.

Effect of electrolytes on emulsions. H. V. Tartar, C. W. Duncan, T. F. Shea, and W. K. Ferrier (J. Physical Chem., 1929, 33, 435—446).—The effect of acids, bases, and sodium chloride on the stability of benzene–water emulsions stabilised by sodium oleate has been investigated. These emulsions are destroyed by hydrochloric, acetic, and oxalic acids when approximately sufficient acid is present to decompose the soap. A high concentration of oleic acid inverts the benzene-in-water emulsion, but sodium hydroxide does not increase its stability. Emulsions of benzene, toluene, or xylene in water, with sodium oleate as stabiliser and containing small amounts of sodium hydroxide, are inverted by sodium chloride. With benzene-in-water emulsions, there exists a well-defined zone of instability between concentrations 0·25 and 0·45N with respect to sodium chloride, and the point of inversion varies slightly with the concentration of sodium hydroxide in the system. With the toluene and xylene emulsions, the inversion point lies at 0·35—0·40N-sodium chloride and is independent of the concentration of hydroxide. Similar emulsions in which potassium stearate replaces sodium oleate are more easily prepared, are more stable, and are not inverted by the addition of potassium chloride. Nitrobenzene readily gives stable emulsions which are of the oil-in-water type at all concentrations of sodium chloride with sodium oleate as stabilising agent; with potassium stearate, the emulsions are even more stable. Dimethylaniline is emulsified readily with both soaps, giving the oil-in-water type; *o*-toluidine also gives stable emulsions of the same type, but these are not formed in the presence of small amounts of sodium and potassium hydroxide, and chlorides. Discussion of the results is reserved for a future communication. L. S. Theobald.

Coagulation of blood and milk by electrolytes and the similarity between the clotting of blood and the formation of jellies. N. R. Dhar and S. Prakash (J. Physical Chem., 1929, 33, 459—466).—Blood and milk belong to that class of colloids which absorb ions bearing the same charge as the sols. On dilution they are less readily coagulated by sodium citrate, tartrate, and acetate, potassium fluoride and oxalate, ammonium nitrate, and hydrochloric acid. The addition of saponin and gelatin (less than 1%) renders blood and milk less stable towards salts. Saponin only has a sensitising effect in the case of hydrochloric acid. The action of gelatin is attributed to the presence of hydrogen ions. In the presence of small amounts of the above salts and of potassium hydroxide, blood and milk are stabilised with respect to the coagulating action of ammonium nitrate and copper sulphate; this is attributed to the adsorption of negative ions from the salt solutions. The clotting of blood is analogous to the formation of gels of vanadium pentoxide and silicic acid. L. S. Theobald.

Kinetics of coagulation of colloids of the second order. K. Jabłczyński and H. Jaszczołtówna (Rocz. Chem., 1929, 9, 111—114).—The expressions derived previously (Jabłczyński and Soroczyński, A., 1928, 360) for the kinetics of coagulation of ferric hydroxide sols are shown to hold also for suspensions of silver bromide and chloride, in the presence or absence of protective colloids. R. Truszkowski.

Change of precipitating concentrations of electrolytes with the purity and temperature of some hydroxide sols. N. R. Dhar and V. Gore (J. Indian Chem. Soc., 1929, 6, 31—43).—Sols of ferric, chromium, and zirconium hydroxides of different degrees of purity have been prepared, and it is shown that the ratio of the precipitating concentrations of uni-, bi-, and ter-valent ions decreases considerably as the purity of the sol is increased. The viscosity of a sol increases with its purity even when its concentration is constant. The ratios of the precipitating concentrations of uni- and bi-valent ions measured with stannic, zirconium, and ceric hydroxide sols are smaller at 60° than at 30°. The precipitating concentrations of uni-, bi-, and ter-valent ions are very seldom in the ratio $1 : x : x^2$, as demanded by Whetham's rule, and tend towards the ratio $1 : \frac{1}{2} : \frac{1}{3}$ in the case of sols which are not hydrolysed. The ratios of the precipitating concentrations are always smaller in the cases of those sols which can be obtained readily in the pure state without peptisation by means of large quantities of electrolytes, and also smaller in the case of sols which have been exposed to light. The difference in the coagulating powers of different ions towards the same sol prepared by different investigators is mainly due to the difference in the peptising agents retained by the sol. The difference in the precipitating concentrations is more marked with univalent ions than with multivalent ions. O. J. Walker.

Coagulation of strongly solvated sols by organic substances and salts. III. B. Jirgensons (Kolloid-Z., 1929, 47, 236—243).—Experiments on the coagulation of sols of casein, hæmoglobin, and albumin by high concentrations of salts in presence of varying amounts of capillary-active organic substances (ethyl alcohol, acetone, *iso*propyl alcohol) have given the following results. The organic substance has a sensitising effect when present in concentrations between 30 and 40 vol.-%, but a stabilising effect at concentrations of 40—60 vol.-%; coagulation is observed at still higher concentrations of the organic substance. In some cases, the curves connecting the coagulation number with the concentration of the organic substance exhibit a maximum or a minimum. For substances having a very small dielectric constant the coagulation minimum lies nearer to the ordinate than for substances of higher dielectric constant. The stabilisation is always in direct relation to the concentration of salt and in inverse ratio to the concentration of colloid. In the coagulation of casein and hæmoglobin sols in presence of capillary-inactive organic substances, the results are not of so general a nature. Ethylene glycol has a sensitising effect on the coagulation of both casein and hæmoglobin, but stabilises at high concentrations of the organic substance or of the salt. At relatively small concentrations, dextrose has a weak stabilising effect and carbamide is strongly stabilising. The results are discussed from the point of view of the dipole theory. E. S. Hedges.

Periodic precipitation. F. E. Lloyd and V. Moravek (Plant Physiol., 1928, 3, 101—130).—Photographic records were obtained of precipitation resulting from the action (in tubes, or between glass slides and cover glasses) of ammonium sulphide or hydroxide on sodium cobaltinitrite or cobalt nitrate in gelatin. The surface of the enclosing vessel gives rise to a ring and disc structure. In tubes of a certain diameter the precipitate is attached to the walls as a ring, no disc being observed. This critical diameter is related to the rate of movement of the ions concerned. Bradford's view, that the precipitate furnishes surfaces towards which the surrounding solute moves, is supported. Chemical Abstracts.

Sensitisation of sols of mastic, gum dammar, and Odén sulphur in presence of gelatin and some carbohydrates. L. S. Bhatia, S. Ghosh, and N. R. Dhar (J. Indian Chem. Soc., 1929, 6, 129—142; cf. A., 1927, 414).—Gelatin sensitises dialysed and undialysed sols of mastic, gum dammar, and sulphur towards potassium chloride; with larger amounts of gelatin the sols are stabilised. These sols are acidic, and when increasing amounts of gelatin are added the p_H increases to a maximum and then decreases. The amount of gelatin which produces maximum sensitisation is that which corresponds with the maximum p_H value. Sols exposed to sunlight are more readily sensitised by gelatin than sols which are kept in diffused daylight. It is suggested that the sensitisation observed with proteins and some negatively charged sols is due to neutralisation of the charge of the colloid particles by positively charged proteins which have been formed by the adsorption of hydrogen ions. Carbohydrates in small amounts sensitise mastic and gum dammar sols and increase their p_H values, and in larger amounts stabilise the sols and decrease their p_H values. Odén sulphur sol is neither sensitised nor protected by carbohydrates, but is stabilised by tannic acid. O. J. Walker.

Dispersoidological investigations on proteins. I. Influence of temperature on the dispersion and coagulation of egg-albumin. S. Utzino (Kolloid-Z., 1929, 47, 244—248).—The system albumin–water–alcohol, with and without addition of sodium chloride, has been studied. In absence of sodium chloride very stable dispersoid systems are produced, the opalescence and turbidity being more intense the higher is the temperature of preparation and the greater the amount of alcohol. With addition of sodium chloride, coagulation is the more complete the higher is the concentration of the salt. The turbidity is greater in systems prepared at higher temperatures, but, so long as the amount of sodium chloride is not too great, such systems are more stable than those prepared at lower temperatures. The solutions remain stable only at very low salt concentrations. E. S. Hedges.

Proteins. III. Proteins and the lyotropic series. R. A. Gortner, W. F. Hoffman, and W. B. Sinclair (5th Coll. Symp. Mon., 1928, 179—198).—In order of ascending peptising effect on the proteins of wheat flour the following series were observed: fluoride, sulphate, chloride, tartrate, bromide, iodide, and (less pronounced) sodium, potassium, lithium, barium, strontium, magnesium, calcium. Alkali halides cause decreased, and alkaline-earth halides increased, peptisation with increasing concentration of salt. In neutral salt solutions, protein "solubility" is in reality peptisation. Chemical Abstracts.

Colloid chemical reactions between sols of albumins and polymerised carbohydrates. I. Wo. Ostwald and R. H. Hertel (Kolloid-Z., 1929, 47, 258—268).—A study has been made of the precipitation reactions between gelatin sols and sols of maize-, rice-, wheat-, and potato-starch, agar, and inulin. Potato-starch gives with certain concentrations of gelatin a liquid–liquid system, whilst the other starches and agar give a solid–liquid system. The influence of concentration and the relative proportions of the components has been investigated, and also the effect of time. In the formation of the solid–liquid system an optimum concentration of gelatin occurs at 2%, whilst in the liquid–liquid system (potato-starch) an optimum occurs at 5% of gelatin. Whilst the liquid–liquid system does not separate out until after about 3 hrs., separation of the solid–liquid system occurs in a few minutes after mixing. E. S. Hedges.

Caseinates and the theory of lyophilic colloids. M. H. Fischer and M. O. Hooker (Kolloid-Z., 1929, 47, 193—206).—The system casein–water has been studied with the object of applying a theory of lyophilic colloids previously advanced (cf. A., 1920, i, 215). The gels formed by the action of acids and bases of varying concentration on neutral casein are described. This action is specific and bears no relation to the hydrogen-ion or hydroxyl-ion concentration of the solutions. The substances formed are salts of the type of casein chloride or potassium caseinate, and their colloidal properties are conditioned by their solubility in water and their water-binding capacity. The effect of addition of a number of electrolytes to aqueous solutions of casein chloride and of sodium and potassium caseinate has been studied and two effects have been observed: (*a*) the electrolyte reacts with the casein compound to form a new substance with different solubility or degree of hydration; (*b*) a direct effect is excluded and the electrolyte combines with the solvent. These facts are considered to offer an explanation of the increase in viscosity, gelatinisation, syneresis, and final separation into solid and liquid phases.

E. S. Hedges.

Denaturation of proteins. VIII. Effect of denaturation and coagulation on acid- and base-binding power of proteins. H. Wu and T. T. Chen (Chinese J. Physiol., 1929, 3, 7—27).—A solution of denatured egg-albumin containing sufficient acid to be on the acid side of the isoelectric point has a p_H greater than a solution of the native protein containing the same quantity of acid. Similarly, a solution of denatured egg-albumin containing alkali has a lower p_H than a solution of native protein containing the same quantity of alkali. Similar results are obtained with serum-globulin and hæmoglobin. The greater buffering action of denatured as compared with native protein may be due to hydrolytic fission during denaturation. Coagulated protein has less buffering action than native protein. This may be due to molecular condensation during coagulation, but other possible explanations are given.

W. O. Kermack.

Capillary structure of soft woods. A. J. Stamm (J. Agric. Res., 1929, 38, 23—67).—The limitations of microscopical methods for studying the structure of wood are indicated. Four dynamic physical methods have been developed and applied to the structure of soft woods. By the method of electro-endosmotic flow the total effective capillary cross-sections have been measured for sections cut in each of the three structural directions. Further information on structure can be obtained by the method of hydrostatic flow, the method of overcoming surface tension of water in the capillary structure, and lastly the method of measuring the permeability to colloidal solutions.

R. A. Morton.

Deduction of Einstein's formula for the Brownian movement from impulses of molecular collisions. V. Pospíšil (Physikal. Z., 1929, 30, 82—83).—The method used by Einstein in his later work in conjunction with the principle of superposition of motions leads to a deduction of the formula for the Brownian movement which is regarded as clear, brief, and suitable for teaching purposes.

R. A. Morton.

Equilibrium in the system methyl alcohol–hydrogen–carbon monoxide. D. M. Newitt, B. J. Byrne, and H. W. Strong (Proc. Roy. Soc., 1929, A, 123, 236—252).—Discrepancies between the recorded equilibrium data for the system methyl alcohol–hydrogen–carbon monoxide are discussed, and details are given of (*a*) a static method, and (*b*) an intermittent-flow method, by means of which the equilibrium constant K_p has been determined at eight temperatures within the range 280—340°, for pressures of about 100 atm. In each case, equilibrium was approached from opposite sides. The static method consists essentially in introducing an approximate equilibrium mixture into an evacuated vessel containing basic zinc chromate as catalyst. The rate of change of pressure is followed by a specially devised manometer until the attainment of equilibrium, when a sample of the contents of the vessel is analysed. Known quantities of the components are then added to displace the equilibrium in the required direction, and the pressure change is again followed until constant conditions are reached. In the intermittent-flow method, a mixture of the three components, in nearly equilibrium proportions, is passed over the catalyst maintained at the desired temperature, and the change in composition of the mixture determined by analysis. By varying the rate of flow from fast to slow through a series of experiments with a mixture of given composition, a series of apparent equilibrium constants is obtained approaching more closely to the true value as the velocity decreases. By plotting the apparent K_p values (obtained by synthesis and by decomposition) and the corresponding rates of gas flow two curves are obtained which meet at the true equilibrium value. The values obtained by the two methods show fair agreement among themselves, and when plotted against the absolute temperature lie on a curve rising steeply in the neighbourhood of 290°. The experimental figures are considerably lower than those found by calculation. The linear relation $\Delta F = 70{\cdot}5T - 30500$ is found to hold between the free energy, calculated from the experimental K_p values, and the absolute temperature over the range studied. The following values of K_p are tabulated: $1{\cdot}2\times10^{-3}$ (260°), $4{\cdot}5\times10^{-4}$ (280°), $1{\cdot}6\times10^{-4}$ (300°), $6{\cdot}7\times10^{-5}$ (320°), $2{\cdot}9\times10^{-5}$ (340°), $1{\cdot}3\times10^{-5}$ (360°), $6{\cdot}3\times10^{-6}$ (380°).

L. L. Bircumshaw.

Heitler's theory of concentrated solutions. L. Vieth (Physikal. Z., 1929, 30, 126—139).—Heitler's theory has been subjected to a critical examination. Various assumptions, explicit and implicit, are not quantitatively in accord with experience. The theory nevertheless possesses great advantages, and the degree of agreement between experiment and theory in some instances lends support to the view that revision of the simple theory will lead to better agreement in other cases.

R. A. Morton.

Equilibrium law for electrolytes. Association. K. Jabłczyński (Rocz. Chem., 1929, 9, 97—110).—A study of the equilibrium constants given by various authors for concentrated solutions of alkali nitrates shows that K diminishes with increasing concentration, whence it is concluded that the anion to a certain extent combines with undissociated molecules to give rise to complex ions of the type $(R\cdot N_2O_6)'$. The expressions $K_1=(n_1P)^{2/3}/(N-2n_1)$, and $K_2=(n_1-P)^{2/3}/P^{2/3}(N-2n)$ are derived, where K_1 and K_2 are respectively the dissociation constants of the nitrate in question and of the complex anion $(RN_2O_6)'$, n_1 is the concentration of the cation in each case, P the concentration of nitrate ions, and N the total number of molecules. In the case of nitric acid and of lithium nitrate association does not occur. K_1 decreases and K_2 increases along the series H, Li, Na, K, Rb, Cs. The cations are hydrated to the same extent in solutions of the alkali chlorides and nitrates.

R. Truszkowski.

Effect of position of substitution on apparent dissociation constants of some amino-acids. C. L. A. Schmidt, W. K. Appleman, and P. L. Kirk (J. Biol. Chem., 1929, **81**, 723—726).—β-Aminopropionic acid has K_a' $6\cdot45\times10^{-11}$, K_b' $3\cdot98\times10^{-11}$; α-amino-*n*-valeric acid K_a' $1\cdot9\times10^{-10}$, K_b' $2\cdot3\times10^{-12}$; γ-amino-*n*-valeric acid K_a' $3\cdot99\times10^{-11}$, K_b' $1\cdot06\times10^{-10}$; δ-amino-*n*-valeric acid K_a' $2\cdot04\times10^{-11}$, K_b' $1\cdot62\times10^{-10}$. Curves obtained by plotting the negative logarithms of the above figures against the reciprocal of the distance between the carboxyl and amino-groups are straight lines (cf. MacInnes, A., 1928, 1326).

C. R. Harington.

Classical thermodynamics and the new problems of chemical dynamics. H. Damianovich (Anal. Soc. Cient. Argentina, 1928, **105**, 255—271; Chem. Zentr., 1928, ii, 1067).

Entropy and heat of evaporation. W. Hertz (Z. anorg. Chem., 1929, **179**, 277—278).—The product of the entropy and the cube root of the latent heat of evaporation of the elements has an approximately constant value for each group of the periodic table, and also for certain groups of metallic halides.

H. F. Gillbe.

Thermodynamics of mixtures. V. Fischer (Z. Physik, 1929, **53**, 138—147; cf. A., 1928, 241).—Mathematical. The latent heat of fusion and of vaporisation of a binary mixture is calculated in terms of the latent heats of the pure materials. A general type of equation is derived for the equilibrium conditions for a binary mixture. An equation relating the m. p. of a liquid with the applied pressure is also developed, and the results deduced therefrom for the case of mercury were found to be in good agreement with the values measured by Bridgeman (Proc. Amer. Acad., 1911, **47**, 432). J. W. Smith.

Equilibria in systems containing surface distributed phases. N. von Raschevsky (Z. Physik, 1928, **51**, 571—583).—The thermodynamics of the unimolecular films which form on the surface of some solutions has been developed by treating such films as separate phases. R. W. Lunt.

Hysteresis phenomena in physico-chemical systems. N. von Raschevsky (Z. Physik, 1929, **53**, 102—106).—It is shown that the state of any physico-chemical system which has several equilibrium states with fixed external conditions depends on the previous history of the system. Moreover, the state of such a system depends, not only on the path followed by such external conditions, but also on the velocity with which the changes are carried out. J. W. Smith.

Equilibrium and reactions in systems with very large specific surface. N. von Raschevsky (Z. Physik, 1929, **53**, 107—129; cf. A., 1928, 474, 690; and preceding abstracts).—The deductions drawn in previous papers concerning the conditions which exist in drops which gradually increase in size and then split are extended. It is also shown that in any system in which the surface energy is not negligible, the limitation of the number of phases demanded by the phase rule does not hold. Various general properties of such systems are treated, special reference being made to the case where the system has several equilibrium conditions and hence shows hysteresis phenomena. J. W. Smith.

Metastability of elements and compounds as a consequence of enantiotropy or monotropy. XII. Heat of dissolution. I. E. Cohen and J. Kooy (Z. physikal. Chem., 1928, **139**, 273—350; cf. Person, Ann. Chim. Phys., 1851, **33**, 437; Berthelot and Ilosvay, A., 1884, 704).—The effect of previous thermal history on the heat of dissolution of sodium and potassium chlorides, potassium sulphate and nitrate, and thallium sulphate has been investigated, the heats of dissolution being determined at 20·00° in the adiabatic calorimeter previously described (A., 1925, ii, 402). Details of the method and full data after various heat treatments and cooling are given, together with a discussion of previous investigations on each of the salts used.

Kahlbaum's potassium sulphate, dried at 300—350°, showed no change in the value of the heat of dissolution when recrystallised from water or when repeatedly heated below its transition temperature. Other heat treatments, however, show that potassium sulphate exists in two modifications, and the heat of dissolution of the α-form when diluted with 400 mols. of water is -6284 ± 4 g.-cal./mol. When heated above the transition temperature, initial deviations from this value occur to an extent which depends on the rate of cooling. The salt which had been melted and reacted neutral showed a deviation equal to that of the calcined salt, and potassium sulphate which reacted alkaline also showed a marked change in the heat of dissolution. Since deviation and decomposition do not run parallel, this behaviour cannot be ascribed to the presence, by itself, of the corresponding base, but it can be explained by the retarding influence of the base on the velocity of the change $\beta\text{-}\longrightarrow\alpha\text{-}K_2SO_4$. On keeping, spontaneous stabilisation to the α-form occurs in all the cases examined.

Potassium nitrate also shows enantiotropy. The heat of dissolution of the form stable at the ordinary temperature and pressure on dilution to 200 mols. of water is -8336 ± 2 g.-cal./mol. at 20·00° and on dilution to 359 mols. of water -8426 ± 2 g.-cal. at 20·5° (cf. Roth, A., 1928, 22). When heated above the transition temperature, anomalous values, which return to the normal on stabilisation of the salt, are obtained. Melting and rapid cooling of the salt changes the heat of dissolution only slightly.

Thallium sulphate, prepared from Kahlbaum's pure metal and pure sulphuric acid with platinum as catalyst, recrystallised from water and dried at 170° had d_4^{30} 6·765 and after melting, pulverisation, and heating at 170°, 6·771. The heat of dissolution of the rhombic form, diluted to 3200 mols. of water, is -7940 ± 60 g.-cal./mol., and in agreement with Tammann and von Sahmen (A., 1903, ii, 356) more than one modification of the salt is considered to exist. Crystallisation from aqueous or from pyridine–water solutions, melting, and subsequent quenching or slow cooling always yields a product which has the same heat of dissolution as that of the salt prepared by crystallisation from water and dried at 170°. Precipitation from aqueous solution by the addition of methyl or ethyl alcohol yields a product which gives a value initially different from the original. This product is concluded to be a mixture of polymorphic forms of thallium sulphate.

The heat of dissolution of potassium chloride diluted to 200 mols. of water is -4373 ± 2 g.-cal./mol. at 20·00° and -4191 ± 2 g.-cal. at 25·00°, and the former value is quite unchanged by various heat treatments. For sodium chloride diluted to 100 mols. of water, the values at the corresponding temperatures are -1100 ± 4 and -965 ± 2 g.-cal./mol., respectively, and, contrary to Person (*loc. cit.*) and Berthelot (*loc. cit.*), they are unaffected by the previous heat treatment. In both cases, the deviations from the values of other workers are so large that standard values for the heat of dissolution of these two salts cannot be given, but calorimetric processes and not polymorphism must be regarded as responsible for the lack of agreement between the published values.

Finally, it is re-emphasised that many physical constants are invalidated by insufficient physical purification of the substance investigated. This applies especially to potassium sulphate and nitrate, and to a smaller extent to thallium sulphate, and data relating to these substances have no significance unless the previous history of the salt has been taken into account. L. S. THEOBALD.

Transformation of the β-phase in zinc–copper alloys. Causes of the disagreement in the results of different investigators. P. SALDAU (Z. Metallk., 1929, 21, 97—98).—The widely different positions of the boundary line between the β_1 and $\beta_1+\gamma$ fields in copper–zinc alloys found by various investigators are ascribed to insufficient annealing; in the author's work (J. Inst. Metals, 1925, **34**, 258) annealing was continued for 84 days at 440° (cf. also A., 1928, 955). A. R. POWELL.

System ferric oxide–water. G. F. HÜTTIG and H. GARSIDE (Z. anorg. Chem., 1929, **179**, 49—76).—A study has been made of the vapour-pressure curves, *X*-ray diagrams, specific heats, chemical reaction velocities, velocities of dissolution, and catalytic activities of a number of preparations of hydrated ferric oxide, and the following conclusions are reached. The freshly-prepared hydrogel is amorphous, and although as regards the total composition the whole of the ferric oxide is chemically combined with water, probably as $Fe(OH)_3$ or $Fe(OH)_3,H_2O$, at any given moment a certain fraction of the water molecules is mobile within the colloid and unattached to definite ferric oxide molecules. Careful desiccation of the gel until the composition Fe_2O_3,H_2O is reached results in an amorphous substance in which the greater number of molecules are of identical composition. Removal of the residual water is very difficult, and although this may be effected by warming, a partial conversion of the material into the crystalline form is unavoidable. The hydrogels may be kept for several months without crystallisation setting in, although changes take place in the activity and specific heat. The final product of ageing is goethite or crystalline ferric oxide with uncombined water; in presence of free water below a temperature somewhere between 77° and 228°, the former is the stable phase, whilst above this temperature the latter is stable. No crystalline hydrate other than goethite has been observed in an ageing gel. Although ageing at the ordinary temperature tends to the production of goethite, a certain fraction of the gel is converted into crystalline ferric oxide. Although the ferric oxide–water system is not stable at the ordinary temperature the velocity of formation of goethite is too slow to be observed in the laboratory. H. F. GILLBE.

Double sulphates of the rare-earth metals and the alkali metals. XII. Sulphates of cerium (cerous) and cæsium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1929, **9**, 131—133; cf. A., 1928, 957).—The system $Ce_2(SO_4)_3$–Cs_2SO_4–H_2O has been investigated at 25°. Only one compound was obtained, viz., $Ce_2(SO_4)_3,Cs_2SO_4,8H_2O$, which is stable at 25° in contact with solutions containing from 1·5% Cs_2SO_4 and 5·4% $Ce_2(SO_4)_3$ to about 46% Cs_2SO_4. Some crystallographic data are given. O. J. WALKER.

Ternary system mercuric chloride–mercuric iodide–water. (MISS) R. SUGDEN (J.C.S., 1929, 488—491).—The system has been examined at 30° and 70°. The two salts are mutually soluble in the solid state. At the iodide end, two series of mixed crystals are obtained, corresponding with the two forms of the simple iodide. Their stability is dependent on temperature and chloride content. There is no evidence of compound formation (cf. Köhler, A., 1879, 1017). F. J. WILKINS.

Ternary system water–sodium nitrate–potassium nitrate. E. CORNEC and H. KROMBACH (Compt. rend., 1929, **188**, 788—790).—Solubility measurements show the absence of mixed crystals between the ordinary temperature and 100°; mixed crystals appear to be formed at 105°. J. GRANT.

Equilibria between metals and salts in fused masses. XVI. Disturbances of equilibria by additions, and their calculation by the new mass action law. R. LORENZ and G. SCHULZ [with M. HERING, P. WOLFF, and J. SILBERSTEIN] (Z. anorg. Chem., 1929, **179**, 97—110).—Addition of inert miscible substances such as sodium chloride or antimony to the equilibrium $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ causes a displacement of the equilibrium which increases up to a certain limit as the quantity added increases. This limiting concentration is analogous to the infinite dilution of solutions, when the added substance is considered as the diluent, but the actual concentrations involved are much greater, and although with increase of displacement the equilibrium isotherms approach those for an ideal system, there is always a certain deviation. The new mass action law, however, gives satisfactory results for such systems. H. F. Gillbe.

Indirect analysis of a chemically single phase in a system composed of two phases. E. Weitz [with H. Stamm] (Z. anorg. Chem., 1929, **179**, 193—210).—The composition of a compound A which constitutes phase A in a two-phase system, the other phase B being chemically complex, may be graphically determined by analysis of phase B and of a mixture of A and B if the number of components is not less than three. H. F. Gillbe.

Heat of neutralisation of acetic acid. T. W. Richards and B. J. Mair (J. Amer. Chem. Soc., 1929, **51**, 737—740).—The heat of neutralisation of acetic acid with sodium hydroxide, each substance being at a dilution of 1 mol. in 100 mols. of water, was measured directly at 20°. With the aid of previously published data, the values at other concentrations were calculated. Graphical extrapolation yields the value 13,650 g.-cal./mol. at infinite dilution.

S. K. Tweedy.

Thermochemical behaviour of sodium hydroxide solutions. T. W. Richards and L. P. Hall (J. Amer. Chem. Soc., 1929, **51**, 731—736).—The heat of dilution of $NaOH,10H_2O$ was determined at 16° and 20°. At 20° heat is evolved until the concentration $NaOH,17{\cdot}5H_2O$ is reached, after which heat is absorbed. The specific heats of some concentrated solutions are calculated. The earlier thermochemical data on sodium hydroxide solutions obtained by Richards and his co-workers are recalculated. Calculation yields the value 13,650 g.-cal./mol. as the heat of neutralisation of hydrochloric acid with sodium hydroxide at 20° at infinite dilution.

S. K. Tweedy.

Heats of dissolution of some salts in water and ethyl alcohol solutions. J. R. Partington and W. E. Soper (Phil. Mag., 1929, [vii], 7, 209—247).—The heats of dissolution and dilution of potassium chloride, potassium thiocyanate, sodium thiocyanate, anhydrous cupric chloride, and anhydrous calcium nitrate in water, and of sodium thiocyanate, anhydrous cupric chloride, and anhydrous calcium nitrate in ethyl alcohol have been determined. The values for potassium chloride in water were determined to check the accuracy of the method adopted.

A. E. Mitchell.

Heats of combustion of organic compounds. M. S. Kharasch (Bur. Stand. J. Res., 1929, 2, 359—430).—The literature on the heats of combustion of organic compounds is critically reviewed, and a table of best values compiled, containing all available data. The tables are arranged according to the types of the organic substances, and compounds are also indexed by formula. A full bibliography is given. A method for calculating the heats of combustion of organic compounds from the structural formulæ is described. It is assumed that the heat generated is due to the displacement of the electrons between the carbon and oxygen atoms. When the initial and final states of the carbon atom correspond with methane and carbon dioxide the net energy liberated is taken as 26·05 kg.-cal.$_{15}$/electron/mole. The general formula for the heat of combustion, Q, is $Q=26{\cdot}05N$, where N is the number of electrons, plus a structural correction factor when the electrons are displaced as compared with their position in methane. These correction factors are tabulated. The calculated values are given in the tables for comparison with the observed values.

C. J. Smithells.

Specific heats and vapour pressures of systems formed from water and the oxides of zirconium, thorium, and tin. G. F. Hüttig, S. Magierkiewicz, and J. Fichmann (Z. physikal. Chem., 1929, **141**, 1—34).—Changes in such systems which are usually attributed to "ageing" may be followed by means of specific heat measurements. Measurements made with preparations of varying water content in the systems ZrO_2–H_2O, ThO_2–H_2O, and SnO_2–H_2O by the method of Hüttig and Wehling (A., 1926, 1103) show that the relation between the specific heat and the water content is given as a first approximation by $\log_e c_0/c=k/N$, where c_0 is the molecular heat of pure water, c is the molecular heat of the hydrate containing N mols. of water to 1 mol. of oxide, and k is an empirical constant. Vapour-pressure measurements have also been made and a similar connexion is found to hold between the vapour pressure and water content. The changes in the "ageing" process are discussed. O. J. Walker.

Entropy decrease of a thermodynamic system by the intervention of an intelligent being. L. Szilard (Z. Physik, 1929, 53, 840—856).—Theoretical. W. E. Downey.

Electrolytic transport of water in 0·1N-solutions of hydrobromic acid. J. Baborovský and A. Wagner (Chem. Listy, 1929, **23**, 97—98).—When 96,490 coulombs are passed through a 0·1N-solution of hydrobromic acid 0·860 g.-mol. of water is transported. The transport number of the cation is 0·867. The value obtained is greater in the presence of a parchment-paper membrane than in its absence. R. Truszkowski.

Calibration of conductivity cells for use with dilute solutions. I. At 18°. C. W. Davies (Trans. Faraday Soc., 1929, **25**, 129—133).—The equation $\Lambda=129{\cdot}85-79{\cdot}8C^{1/2}$, where C is the equivalent concentration, is suggested for the determination of conductivity cell constants at 18° for concentrations up to 0·001N. Kohlrausch and Maltby's solvent correction for the conductivity data for potassium chloride is modified to take into account the interionic forces, and the conductivity values are thereby reduced by 0·06 unit or more. The differences between the calculated and the corrected experimental results are of the order of 0·02% (cf. following abstract).

J. Grant.

Calibration of conductivity cells. II. Conductivity of potassium chloride at 25°. J. Grindley and C. W. Davies (Trans. Faraday Soc., 1929, **25**, 133—137).—Corrected conductivity determinations (cf. preceding abstract) of aqueous potassium chloride solutions up to 0·0015N at 25° show an average deviation of 0·025% from the equation

$\Lambda=150{\cdot}59-109{\cdot}0C^{1/2}$, where C is the equivalent concentration. The equation may therefore be used for cell constant determinations at 25°. J. Grant.

Measurements of conductivities by means of oscillating circuits. S. D. Gehman and B. B. Weatherby (Phil. Mag., 1929, [vii], 7, 567—569).—The results of Burton and Pitt (A., 1928, 712) for the conductivities of various solutions by means of an oscillating valve circuit are vitiated by the changes in distributed capacity caused by the insertion of the tubes containing the liquids into the coils of the oscillating system; such capacity changes produce serious frequency changes in the circuit. Experimental results are described which indicate that the effects obtained by Burton and Pitt are due primarily to the dielectric constants of the liquids and not to their conductivities. A. E. Mitchell.

Calculation of the conductivity of water. J. L. Linschoten (Chem. Weekblad, 1929, 26, 198—202).—Two methods are given for the construction of nomograms which permit the required conductivities to be obtained without calculation. S. I. Levy.

Conductivity of strong electrolytes for high-frequency currents. H. Zahn (Z. Physik, 1928, **51**, 350—354).—The conductivities of magnesium sulphate and copper sulphate solutions for high-frequency current ($\lambda=1$ metre) have been compared with the conductivities for direct current by determining the concentration of potassium chloride solution which has the same conductivity for the high-frequency current as the solution under investigation. The conductivities for direct current being known, and assuming the change for potassium chloride which was derived by Debye and Falkenhagen (A., 1928, 957), the changes in the conductivities of the other salts are deduced and found to be in good agreement with the theoretical values. J. W. Smith.

High-frequency conductivity of aqueous solutions of electrolytes. H. Rieckhoff and H. Zahn (Z. Physik, 1929, **53**, 619—627).—The increase in conductivity for alternating currents of high frequency of aqueous electrolytes has been further investigated over an extended range of concentrations. There is good agreement with the theory of Debye and Falkenhagen. A. J. Mee.

Conductance of mixed solutions of lead nitrate and ammonium nitrate. G. Malquori (Atti R. Accad. Lincei, 1929, [vi], 9, 231—233; cf. this vol., 141).—The conductance, corrected for viscosity effects, of lead nitrate solutions increases with rise of temperature from 10° to 60° for concentrations between 0·45 and 1·35 equiv./litre. The increase is rapid between 50° and 60°. For solutions of ammonium nitrate under similar conditions the conductance decreases. The conductance of mixed solutions with moderately high concentrations of ammonium nitrate decreases with temperature. A decrease is found also with solutions rich in lead nitrate excepting when the concentration of ammonium nitrate is rather low. In the latter case, $Pb(NO_3)_2$ 1·3525, NH_4NO_3 0·4773 equiv./litre, the conductance decreases up to 35°, and passes through a maximum at about 50°. This behaviour is attributed to complex salt formation with the probable existence of a $Pb(NO_3)_4''$ ion. F. G. Tryhorn.

Electrochemistry of ethereal solutions. II. System arsenic trichloride–ethyl ether. M. Ussanovitsch (Z. physikal. Chem., 1929, **140**, 429—434; cf. A., 1927, 315).—The electrical conductivities of 0—100% solutions of arsenic trichloride in ethyl ether have been determined at 18°. Up to 40% $AsCl_3$ the specific conductance is very small; the increased conductivity at higher concentrations shows a maximum at 94% $AsCl_3$. The temperature coefficient of the conductivity is negative at all concentrations. The variation of the molecular conductivity with the dilution is abnormal when referred to arsenic trichloride as the electrolyte; taking ethyl ether as the electrolyte there is a steady rise in the conductivity with dilution. The conductivity curves are analogous to those of the system $AsBr_3$–Et_2O. The decomposition potential of a 68·81% solution of arsenic trichloride in ether at 18° is 1·22 volts. On electrolysis arsenic is deposited at the cathode in quantitative agreement with Faraday's law.

O. J. Walker.

Wien's voltage effect in electrolytes. M. Blumentritt (Ann. Physik, 1929, [v], 1, 195—215).—Onsager's improved form of the Debye–Hückel theory has been applied to Wien's voltage effect, and good agreement with the experimental data is obtained for field strengths up to 25,000 volts/cm., the only exceptions being with ions of very high valency.

R. A. Morton.

Dielectric measurements as a rapid means of water determination. E. Berliner and R. Rüter (Kolloid-Z., 1929, 47, 251—257).—A simple apparatus for the measurement of dielectric constants is described and it is shown that the measurement of dielectric properties can serve as a rapid means of determining water in other substances. The apparatus has been applied to the measurement of the dielectric constants of binary non-conducting liquid mixtures and aqueous solutions over a wide range of composition and results are given for aqueous solutions of methyl, ethyl, and *iso*propyl alcohols, glycol, glycerol, dextrose, sucrose, carbamide, acetone, and for the systems benzene–ethyl alcohol and benzene–nitrobenzene. E. S. Hedges.

Deposition of radium and other alkaline-earth metals at the dropping mercury cathode. J. Heyrovský and S. Berezický (J. Czechoslov. Chem. Comm., 1929, 1, 19—46).—Measurements of deposition potentials (*i.e.*, the cathodic potentials, calomel electrode being zero, at which the slopes of the current–voltage curves are all 45°) during electrolysis, using a dropping mercury cathode (cf. A., 1923, ii, 119), have been increased in sensitivity partly by the introduction of an auto-registering apparatus (the "polarograph") and partly by other mechanical refinements.

The following deposition potentials for normal ionic concentrations are found: radium, −1·718; barium, −1·761; strontium, −1·964; magnesium, −1·996; calcium, −2·047 volts. Differences in the deposition potentials of alkaline-earth metals are large enough for the deposition of each of them from a mixture to be followed. Thus the deposition of radium may be followed quantitatively for mixtures with barium when the ratio radium : barium falls between the limits 1 : 10 and 25 : 1 in $10^{-4}M$ concentrations. Traces down to 10^{-5} g.-equiv. per litre of radium or barium are likewise determinable in admixture with alkalis or alkaline earths, but strontium only in mixtures with alkaline earths or lithium.

The polarographic method has been used to obtain the solubilities of sparingly soluble salts; even in the presence of excess of other electrolytes it enables the concentrations of small quantities of certain ions to be determined. The following measurements are recorded: barium sulphate in $0{\cdot}001N$-lithium chloride, 3×10^{-5} g.-equiv. per litre (a marked ageing effect is observed, freshly-precipitated barium sulphate being eight times as soluble as a specimen 30 hrs. old); barium carbonate in $0{\cdot}1N$-lithium chloride, $8{\cdot}2\times10^{-4}$ g.-equiv. per litre, in water $5{\cdot}7\times10^{-4}N$; strontium sulphate in $0{\cdot}001N$- and $0{\cdot}01N$-lithium chloride $1{\cdot}1\times10^{-3}N$ and $1{\cdot}8\times10^{-3}N$, respectively, in water $1{\cdot}5\times10^{-3}N$; strontium carbonate in water $2{\cdot}8\times10^{-4}N$; strontium oxalate in water $5{\cdot}6\times10^{-4}N$; calcium oxalate in water $1\times10^{-4}N$ (all at 18°).

Evolution of hydrogen accompanies the deposition of magnesium and beryllium; by this means small quantities of magnesium can be determined.

"Adsorption currents" due to ionic adsorption at the cathodic mercury–solution interface were observed in all solutions more concentrated than $0{\cdot}001N$ and were plainly indicated on current–voltage curves of solutions of the heavy alkaline earths. Illustrations of polarographic titrations of barium, strontium, and calcium ions are given. R. J. W. Le Fèvre.

Electrolytic solution tension and the ionic state. V. Calculation of electrolytic solution tension. Mechanism of electrolytic dissociation. Nature of the ionic state. K. Fredenhagen (Z. physikal. Chem., 1929, **140**, 435—474; cf. A., 1928, 1316; this vol., 397).—A theoretical discussion of the causes of electrolytic dissociation and of the nature of the ionic state. The thermodynamic treatment of electrolytic solution forces given in the previous papers is summarised and a mechanism of electrolytic dissociation is put forward. If KA represents a molecule of the solvent, then the chemical affinities of the two components K and A are not completely saturated by their union to form a molecule. The molecule KA will be partly dissociated into its constituents K and A, each of which will have a certain affinity for the dissolved substance and thereby decrease its chemical "activity." The solution tension of a substance depends on the difference of its affinities for the two constituents K and A, becoming zero when they are equal, and is therefore a function of the internal forces in the solvent molecule. The experimentally determined electrolytic solution tensions are of the order of magnitude required by the preceding assumptions. Further evidence for the theory is obtained from a consideration of the potential series of the elements in various solvents, of the dissociation of water and molten salts, and of the variation of solution tension and dissociation with the temperature. O. J. Walker.

_E.M.F._ of uni-univalent halides in concentrated aqueous solutions. H. S. Harned (J. Amer. Chem. Soc., 1929, **51**, 416—427).—The *E.M.F.* at 25° are recorded for flowing amalgam cells of the type $Ag|AgX|MX(c)|M_xHg|MX(0{\cdot}1M)|AgX|Ag$ in which M=K, Na, Li, X=Cl, Br and c varies between 0·05 and $4M$. For the less concentrated solutions, the results deviate uniformly from the additive relationship postulated by MacInnes and by Harned (A., 1920, ii, 664). The observed activity coefficients for the sodium and potassium salts agree well up to $2M$ with those calculated by Hückel's equation; above this concentration the calculated values become progressively smaller than the observed. The activity coefficients for the lithium salts are also recorded. A comparison of the activity coefficients obtained with those calculated from vapour pressure data is considered to confirm the accuracy of the *E.M.F.* method here employed. S. K. Tweedy.

Oxidation–reduction potentials. I. Ferric–ferrous [iron] electrode. S. Popov and A. H. Kunz (J. Amer. Chem. Soc., 1929, **51**, 382—394).—*E.M.F.* measurements were made on the cell $Pt,H_2|HCl|HCl+FeCl_3+FeCl_2|Pt$, the liquid junction potential being kept constant by the use of a flowing junction. By plotting a function of the potential against the concentration of the ferrous chloride for several values of the latter and extrapolating to zero concentration the junction potential is eliminated, and by plotting the potential for various acidities against the acid concentration and again extrapolating to zero concentration the influence of the acid is eliminated. The value obtained for the normal oxidation–reduction potential of the ferric–ferrous iron electrode is −0·7477 volt, in substantial agreement with the value derived from equilibrium measurements (cf. Noyes and Brann, A., 1912, ii, 916) and with the value calculated on the basis of ionic strength. S. K. Tweedy.

Oxidation potentials of some hypochlorite solutions. V. H. Remington and H. M. Trimble (J. Physical Chem., 1929, **33**, 424—434).—The oxidation potentials of hypochlorous acid and sodium hypochlorite solutions in various solutions have been determined. Reproducible results with smooth platinum wire electrodes could be obtained only after treating the electrode with hot, concentrated nitric acid for 10—15 min., cooling and washing with conductivity water, drying, and heating the wire electrically to dull redness for 1—2 min. and placing at once in the electrolyte. The passage of a current of carbon dioxide through sodium hypochlorite solution markedly increases the oxidation potential and even traces of this gas cause an increase of 0·05—0·1 volt. The oxidising power of hypochlorites in solution as measured potentiometrically increases with an increase in hydrogen-ion concentration, and the amount of added acid or base as well as the hypochlorite content can be approximately determined by electrometric titration. Solutions buffered with alkali phosphate, carbonate, or hydrogen carbonate are more stable and give potentials which are more readily reproduced than those of unbuffered solutions. L. S. Theobald.

Oxidation–reduction systems of biological significance. III. Mechanism of the cysteine potential at the mercury electrode. E. S. G. Barron, L. B. Flexner, and L. Michaelis (J. Biol. Chem., 1929, **81**, 743—754).—The behaviour of the mercury electrode in a solution of cyanide is closely similar to its behaviour in one of cysteine (cf. A., 1928, 1330); this is due to the fact that cysteine reacts with metallic mercury to form an undissociated compound which is apparently identical with that described by Brenzinger (A., 1892, 1111) in the same way that it reacts with cyanide to form undissociated mercuric cyanide. This accounts for the hitherto unexplained fact that the potential established at the mercury electrode in a solution of cysteine is independent of the concentration of the latter; it indicates further that observations made on the "cystine–cysteine" system at the mercury electrode are in reality applicable only to the "cysteine–mercuric cysteinate" system, and may not bear any relationship to the properties of the cystine–cysteine system under physiological conditions.

C. R. Harington.

Maxima on the current–voltage curves. III. Electrolysis of mercury salt solutions with dropping and steady mercury cathodes. P. Herasymenko, J. Heyrovský, and K. Tančakivský (Trans. Faraday Soc., 1929, **25**, 152—159).—Determinations of the current–voltage curve maxima and the corresponding changes in interfacial tension during the electrodeposition of mercury at a dropping mercury cathode (A., 1928, 372, 596) and at a stationary cathode formed by a large drop of mercury in the bottom of the cell, gave analogous results for both cathodes, but were least reproducible for the latter. According to Heyrovský's theory (*loc. cit.*) the discontinuous decrease in current shown by the curves and the associated concentration polarisation are due to the formation of an interfacial layer free from mercury salts which prevents further adsorption at the cathode interface. Preferential adsorption is considered to explain the suppression of the maxima on the addition of adsorptive matter or of an indifferent electrolyte.

J. Grant.

Inversion of the photovoltaic effect by hydroxyl and hydrogen ions. G. Athanasiu (Compt. rend., 1929, **188**, 786—788).—Addition of hydroxyl ions to photo-electric cells containing neutral potassium chloride as electrolyte destroys or inverts the positive photo-electric effect shown by the electrodes Ag|AgI, Ag|AgBr, Cu|Cu_2I_2, Cu|Cu_2Br_2, and Hg|Hg_2I_2, and increase the negative effect shown by the Ag|Ag_2S electrode. The positive effect of the oxidised copper electrode is increased by the addition of hydrogen ions. Halogens liberated at the electrode by the action of light are probably removed from the sphere of action by interaction with the ions of the electrolyte.

J. Grant.

Becquerel effect. II. I. Lifschitz and S. B. Hooghoudt (Z. physikal. Chem., 1929, **141**, 52—70; cf. A., 1927, 423, 942).—The Becquerel effect is discussed from the point of view of Winther (A., 1928, 247), who suggested the necessity of distinguishing between the surface effects at light-sensitive electrodes (effect of the first kind) and the volume effects in the electrolytic solution (effect of the second kind). It is shown that it is not easy to distinguish between these two effects. The effect of the second kind does not depend on a simple photochemical displacement of an equilibrium such as occurs in a cerous–ceric salt solution, for in the latter the changes in photochemical potential do not represent a true Becquerel effect.

The Becquerel effect occurs also with non-aqueous solutions, and is greatly dependent on the wavelength of the radiation and on the nature of the solvent and of the ions present, but the nature and size of the electrode have no appreciable influence. Measurements of the effect with open circuit give only the sign and order of magnitude of the effect. The mechanism of the Becquerel effect is discussed.

O. J. Walker.

Theory of chemical reaction velocity. N. Semenov (Z. physikal. Chem., 1929, **B**, **2**, 161—168).—Mathematical. The kinetics of chain reactions are considered, taking into account secondary activation of molecules taking part, as well as the primary activation. From the equations the theoretical conditions for explosion are calculated. Where experimental results are available they are in agreement with theory. A. J. Mee.

Kinetics of combination of hydrogen and oxygen. N. Semenov (Z. physikal. Chem., 1929, **B**, **2**, 169—180).—Mathematical. The kinetics of the reaction are developed on somewhat different lines from the treatment of Gibson and Hinshelwood (A., 1928, 960), use being made of the Einstein–Smoluchowski formula for calculating the length of the chain. The reactions which are supposed to occur are $H+O_2=HO_2$; $HO_2+H_2=H_2O_2+H$; $2H_2O_2=2H_2O+O_2$. The average number of elementary reactions in the chain is calculated when an inert gas is present, an increase in the reaction velocity being indicated in agreement with the experimental results of Gibson and Hinshelwood. The relationship between the number of elementary reactions and the partial pressure of the inert gas is calculated. It is necessary to make two assumptions, viz., that the diameters of all molecules concerned except HO_2 are equal, and that the diameter of the HO_2 molecule is much larger than that of the other molecules. With these assumptions, the relationship is calculated for nitrogen and helium. It is concluded that the effect of the inert gas is to increase the length of the chain. The temperature coefficient of the reaction and the conditions for explosion are worked out. The latter agree with experiment. The order of the reaction is also investigated. There are three ways in which the hydrogen molecule may be broken down into atoms: (1) by the absorption of radiation, (2) by collision with another molecule moving sufficiently rapidly, (3) by rebounding from the wall of the vessel with sufficient energy. These three are examined, and the first two are found to be insufficient to explain the reaction. Using the third method, the equation for the reaction velocity obtained is $w=c[H_2]^2([H_2]+[O_2])$, where w is the reaction velocity and $[H_2]$ and $[O_2]$ are the partial pressures of the gases. This is in fairly good agreement with experiment. The effect of the addition of an inert gas on the secondary activation is also considered. The experimental curve between log p and $1/T$, where p is the minimum explosion pressure at a temperature T, is given and it is shown that below a certain temperature the curve can be explained on theoretical grounds.

A. J. MEE.

Thermal decomposition of ozone at low pressures. L. S. KASSEL (Z. physikal. Chem., 1929, **B**, 2, 264—265; cf. Riesenfeld and Schumacher, this vol., 146).—It has been shown that reactions which are of the second order at high pressures agree with the first order equations at low pressures, and for yet smaller pressures with the second order equations with increased velocity coefficient. Ozone shows this phenomenon in its decomposition at low pressures. The homogeneity of the reaction is still uncertain.

A. J. MEE.

Retardation period in spontaneous ignitions and explosions. M. BRUNNER (Helv. Chim. Acta, 1929, **12**, 295—304).—The cause of the induction period, which is found to occur with certain gaseous mixtures before ignition or explosion after the ignition temperature has been reached, is discussed and an explanation is proposed based on recent theories of the mechanism of chain reactions (Semenov, Hinshelwood). During the retardation period ignition or explosion does not take place, because owing to the deactivating action of the walls of the vessel a sufficient number of reaction centres is not formed. The activity of the deactivating centres is gradually diminished through adsorption of the slowly-formed reaction products, until finally the formation of new reaction centres predominates, and ignition or explosion can occur. Experimental data on the effect of various factors on the induction period (*e.g.*, temperature, pressure, composition of the gaseous mixture, and nature of the surface of the vessel) support the proposed mechanism.

O. J. WALKER.

Kinetics of combustion of carbon monoxide. V. S. FINKELSTEIN and V. P. MASCHOVETZ (J. Russ. Phys. Chem. Soc., 1928, **60**, 1601—1628).—The catalytic activity of oxides and silicates of iron, aluminium, and of other metals was investigated. The first silicate investigated was glass, either in the form of the walls of the containing vessel or as thin-walled tubes contained in a flask. All experiments were carried out at 500°, except those with ferric oxide, which was investigated at 300°. Results were calculated from a termolecular reaction equation, the concentrations being expressed in partial pressures. The velocity of the reaction was found to diminish, even under constant conditions, in successive experiments. The same was observed when carbon dioxide was passed through the reaction vessel for some time before combustion began. The surface could be re-activated by treating with nitric acid; exposure to air or washing with water is not so effective. Fall in activity is explained by assuming adsorption of the carbon dioxide by the glass surface on which it is held by chemical forces. All the results, together with those obtained with alumina, indicate termolecular reactions. The reaction mechanism assumed is that suggested by Langmuir (A., 1922, ii, 629), but it is assumed that two molecules of carbon monoxide collide with one molecule of oxygen adsorbed on the glass. Ferric oxide as a catalyst was investigated with the view of determining the effect of temperature on the kinetics of the reaction. From k determined at different temperatures for the same composition of the reaction mixture, the mean energy of activation is determined and is found to be 23·9 kg.-cal. per mol.

A. FREIMAN.

Combustion of well-dried carbon monoxide and oxygen mixtures. III. W. A. BONE, F. R. WESTON, and D. A. WINTER (Proc. Roy. Soc., 1929, **A**, **123**, 285—291).—In continuation of previous work (Bone and Weston, A., 1926, 480) a study has been made of the ignitibility of mixtures of (approximately) 2 vols. of carbon monoxide and 1 vol. of oxygen, dried over phosphorus pentoxide for 550—1000 days. The fact that practically no difference is observed between the present results and those recorded for a drying period of 120—240 days (*loc. cit.*) indicates that, under the given experimental conditions, the utmost limits of phosphorus pentoxide drying can be reached in about 6 months, and it is concluded that a highly purified, rigidly dried $2CO+O_2$ mixture will still explode and propagate flame if a sufficiently powerful igniting spark be used. The minimum spark energy required in any given case depends, not only on the character of the discharge, but also on the material and shape of the electrodes; with " pointed " platinum electrodes, a spark of smaller energy sufficed than when " balled " electrodes were used.

L. L. BIRCUMSHAW.

Kinetics in streaming reaction systems. H. SCHMID (Z. physikal. Chem., 1929, **141**, 41—51).—A method of determining the speed of a chemical reaction in streaming reaction systems based on the procedure of Hartridge and Roughton (A., 1925, ii, 47; 1926, 1213) is described. The course of the reaction is followed, not by physical methods, but by " quenching " and subsequent analysis of the reaction mixture. It is claimed that the method is applicable to the investigation of the kinetics of rapid reactions in general and is not limited to a small number of relatively simple reactions. The accuracy of the method is illustrated from a study of the decomposition of nitrous acid in time intervals of less than 1 sec.

O. J. WALKER.

Decomposition of nitrogen pentoxide. II. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1929, **140**, 281—290; cf. A., 1928, 1099).—Contrary to the results of Daniels, Wulf, and Karrer (A., 1923, ii, 24), ozone is found to have no retarding effect on the decomposition of nitrogen pentoxide. The formation of nitrogen pentoxide from nitrogen peroxide and ozone has been investigated and the results support the following mechanism: $NO_2+O_3=NO_3+O_2$, $NO_3+NO_2=N_2O_5$. It is shown that the oxide NO_3 is not formed as an intermediate product in the decomposition of nitrogen pentoxide.

R. N. KERR.

Reaction between nitrogen pentoxide and ozone. II. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1929, **B**, 2, 267—281; cf. A., 1928, 1100).—The rate of the reaction between nitrogen pentoxide and ozone at 20° and 36° is given, over a wide range of concentrations, by the equation $dp/dt=k[N_2O_5]^{2/3}[O_3]^{2/3}$, where k has the value $5{\cdot}57\times10^{-3}$ at 20° and $31{\cdot}2\times10^{-3}$ at 36°. This equation may be derived theoretically by postulating the following reaction mechanism: (1) $N_2O_5 \longrightarrow 2NO_2+0{\cdot}5O_2$; (2) $NO_2+O_3 \longrightarrow NO_3+O_2$; (3) $NO_3+NO_3 \longrightarrow 2NO_2+O_2$; (4) $NO_3+NO_2 \longrightarrow N_2O_5$. The results of Tolman and White (A., 1925, ii, 682) may be accounted for in the same way. It thus follows that the oxide of nitrogen which gives a characteristic absorption spectrum when nitrogen pentoxide and ozone are mixed (cf. Hautefeuille and Chappuis, A., 1882, 927) has the formula NO_3. R. CUTHILL.

Reduction of permanganate ion by chromic ion in acid solution. H. A. FALES and P. S. ROLLER (J. Amer. Chem. Soc., 1929, **51**, 345—359).—The above reduction was investigated at 25·1° in sulphuric acid solution. The initial slow oxidation is rapidly autocatalysed to an almost linear rate, which diminishes rapidly near the end of the reaction (cf. Schiloff, A., 1903, ii, 720). When the chromic ion is in excess the reaction is bimolecular: $MnO_4'+Cr^{\cdot\cdot\cdot}=CrO_4''+Mn^{\cdot\cdot\cdot\cdot}$. In the presence of manganous ions the rate depends on the ratio $Mn^{\cdot\cdot}/MnO_4'$; the ions $Mn^{\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot\cdot}$ are formed [see eqn. (3) below], which, and especially the $Mn^{\cdot\cdot\cdot\cdot}$ ion, oxidise the chromic ion more rapidly than the permanganate ion. With decrease in the ratio $Mn^{\cdot\cdot}/MnO_4'$ there is a large increase in the ratio $Mn^{\cdot\cdot\cdot\cdot}/Mn^{\cdot\cdot\cdot}$. The $Mn^{\cdot\cdot\cdot}$ ions are probably present in the form of complexes with sulphuric acid, and they oxidise indirectly through $Mn^{\cdot\cdot\cdot\cdot}$, *e.g.*, (1) $Mn(HSO_4)_3 \rightleftharpoons Mn^{\cdot\cdot\cdot}+3HSO_4'$; (2) $Mn^{\cdot\cdot\cdot}+Mn(HSO_4)_3=Mn^{\cdot\cdot\cdot\cdot}+Mn^{\cdot\cdot}+3(HSO_4)'$; (3) $2Mn^{\cdot\cdot\cdot}=Mn^{\cdot\cdot\cdot\cdot}+Mn^{\cdot\cdot}$; (4) $Mn^{\cdot\cdot\cdot\cdot}+Mn^{\cdot\cdot\cdot}+Cr^{\cdot\cdot\cdot}+4H_2O=CrO_4'+2Mn^{\cdot\cdot}+8H^{\cdot}$. The unimolecular nature of (1) is demonstrated and its velocity coefficient calculated. S. K. TWEEDY.

Kinetics, quantum efficiency, and temperature coefficients of the decomposition of ferric thiocyanate and the bleaching of neocyanine and some other photochemical reactions in radiations of different frequencies. A. K. BHATTACHARYYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 143—154; cf. this vol., 37).—The order of reaction, temperature coefficient, and quantum efficiency of the following reactions have been determined in radiations of different wave-length: decomposition of ferric thiocyanate, bleaching of neocyanine by air, and reactions between sodium lactate and iodine, sodium tartrate and iodine, chromic acid and citric acid, chromic acid and tartaric acid, and chromic acid and lactic acid. The first two reactions are unimolecular and the two reactions with iodine are bimolecular. The Einstein photochemical equivalence law is not exactly applicable to these reactions. The quantum yield increases with the concentrations and temperature of the systems and with the frequency of the incident radiations. All these reactions are accelerated by radiations of wave-length 7304 Å. due to appreciable absorption of radiations around this wave-length. The temperature coefficients behave as in the case of the previous reactions studied. O. J. WALKER.

Kinetic salt effect. II. Velocity of ionic reactions at great dilutions. A. N. KAPPANNA (J. Indian Chem. Soc., 1929, 6, 45—52; cf. A., 1928, 962).—In order to test the validity of the Debye–Hückel equation for the activity coefficient of an ion as modified by Brönsted and by Soper, the velocity of reaction of sodium bromoacetate with sodium thiosulphate has been studied at 30°, 40°, and 50° over the range of total ionic concentration between 0·0025 and 0·10 μ. So far as the ions involved in this reaction are concerned the Debye–Hückel equation accurately predicts the course of the reaction for ionic concentrations up to 0·015 μ. The temperature coefficient of the velocity has been found to be the same at all ionic concentrations, and this is in accordance with the equations of Debye and of Ghosh. O. J. WALKER.

Kinetic studies on ethylene oxides. J. N. BRÖNSTED, (MISS) M. KILPATRICK, and M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1929, **51**, 428—461).—Ethylene oxide may react with aqueous acid (*e.g.*, HX) as follows: (I) $C_2H_4O+H_2O \longrightarrow (CH_2{\cdot}OH)_2$; (II) $C_2H_4O+H_3O^+ \longrightarrow (CH_2{\cdot}OH)_2$; (III) $C_2H_4O+X'+H_2O \longrightarrow XC_2H_4{\cdot}OH+OH'$; (IV) $C_2H_4O+X'+H_3O^+ \longrightarrow XC_2H_4{\cdot}OH+H_2O$. The kinetics of reactions I and II were investigated dilatometrically in solutions of perchloric acid, and the analogous reactions involving glycide and epichlorohydrin were also examined in phosphate buffers, sodium hydroxide solutions, nitric acid, etc. In some of these cases reactions III and IV vitiated the results. In perchloric acid solutions the salt effect is positive and rather large; reaction II is determined by the hydrogen-ion concentration. *cyclo*Hexene oxide also takes up water rapidly. The apparent basicity of ethylene oxides is due to reaction III and not to reaction IV. Titrimetric methods which permit these reactions to be separately followed are described, although reaction IV is best followed by conductivity measurements. Reaction III exhibits a slight negative salt effect and proceeds at a rate which is proportional to the anion concentration; this rate increases in the order chloride, bromide, thiocyanate, iodide, and formate, benzoate, acetate, trimethylacetate. Reaction IV was investigated in detail for the addition of hydrobromic acid to glycide. The general results indicate that the "basicity" of ethylene oxides is not a property inherent in the oxide molecule, but is exhibited in solutions of the substance under certain conditions, *e.g.*, when acids are present (reaction III). Bases likewise are taken up from solution and the oxides then exhibit "acidity." Brönsted's general theory of reaction velocity is followed very closely by all four reactions. The velocity coefficients of the respective reactions, k_1, k_2, k_3, k_4, are approximately related as follows: $k_1/k_2=k_3/k_4$, and this is explained in terms of a mechanism which is suggested as the basis of all four reactions.

S. K. TWEEDY.

Kinetics of the bromination and chlorination of aliphatic nitro-compounds in aqueous solutions of the hydrogen halides. R. JUNELL (Z. physikal. Chem., 1929, **141**, 71—90).—The velocity coefficients have been determined for the bromination of β-nitropropane, dibromonitromethane, monobromonitromethane, and nitromethane in *N*-hydrobromic acid solution, and for the chlorination of nitromethane in N-hydrochloric acid solution. These reactions are all unimolecular with respect to the corresponding nitro-compound. With nitromethane three consecutive unimolecular coefficients have been determined. An electrometric method for the titration of bromine or chlorine in presence of aliphatic nitro-compounds is described. O. J. Walker.

Rate of hydrolysis of ribonucleotides. P. A. Levene and E. Jorpes (J. Biol. Chem., 1929, **81**, 575—580).—In the acid hydrolysis of adenylic and guanylic acids phosphoric acid and the base are liberated at similar rates; the same applies to hydrogenated cytidinephosphoric acid, whilst in cytidinephosphoric acid itself both groups are hydrolysed only with difficulty. In view of these results the earlier conclusion (A., 1920, i, 774) that in the pyrimidine nucleotides the phosphoric acid residue is attached to the terminal carbon atom of the pentose, is abandoned.
C. R. Harington.

Rate of hydrolysis of casein in acid solution from formation of amino-nitrogen. E. S. Nasset and D. M. Greenberg (J. Amer. Chem. Soc., 1929, **51**, 836—841).—The hydrolysis of casein in 2·5% solution in 0·5—1·0N-hydrochloric, 0·5—2·5N-sulphuric, and 2·5—3·0N-phosphoric acids at 105·5—127·5° has been followed by Van Slyke determinations of the amino-nitrogen. The results are in accordance with a reaction of the second order (cf. Dunn, A., 1925, i, 1477; Carpenter, A., 1926, 631) and the catalytic effect of the acid is proportional to its hydrogen-ion activity. An expression is given for the effect of temperature on the reaction velocity (cf. A., 1927, 213). H. E. F. Notton.

Formation and decomposition of gallic acid, pyrogallolcarboxylic acid, phloroglucinolcarboxylic acid, and their potassium salts. O. Widmer (Z. physikal. Chem., 1929, **140**, 161—193).—The rate of decomposition of pyrogallolcarboxylic acid and gallic acid by boiling with water has been measured. Both decompositions are first-order reactions. The thermal decomposition of both these acids in the dry state has also been studied; the pressure of carbon dioxide obtained is plotted against the time. The shape of the curve is dependent on the temperature, the preliminary treatment of the acid, the amount of acid present, and the addition of foreign substances. The decomposition is strongly accelerated by the products of decomposition and by impurities. The equilibrium constants for the reaction pyrogallol + $KHCO_3 \rightleftharpoons$ potassium pyrogallolcarboxylate + H_2O at 80° and 95° and for the reaction phloroglucinol + $KHCO_3 \rightleftharpoons$ potassium phloroglucinolcarboxylate + H_2O at 40°, 49°, and 60° have been determined. The rates of formation and decomposition of the potassium salts of pyrogallol- and phloroglucinol-carboxylic acids have also been measured. At equal stages from the equilibrium point the formation proceeds more quickly than the decomposition.
R. N. Kerr.

Relation of structure to rate of hydrolysis of diketopiperazines. I. Hydrolysis of N-methyldiketopiperazine by alkali. P. A. Levene, L. W. Bass, and R. E. Steiger (J. Biol. Chem., 1929, **81**, 697—702).—Whilst glycine anhydride, glycylsarcosine anhydride, and sarcosylsarcosine anhydride are hydrolysed by sodium hydroxide at similar (rapid) rates, the hydrolysis, under similar conditions, of the anhydrides of N-methylalanylsarcosine, and still more of N-methylvalylsarcosine, proceeds much more slowly. C. R. Harington.

Some forms of carbon and their reactivity. R. V. Wheeler.—See B., 1929, 309.

Combustion of platinum. E. K. Rideal and O. H. Wansbrough-Jones (Proc. Roy. Soc., 1929, **A**, **123**, 202—216).—An investigation has been made of the loss of weight of platinum wire, enclosed in a bulb immersed in liquid air, when heated for different lengths of time over the temperature range 1400—1900° Abs. in varying pressures of oxygen (100—200 bars). At high temperatures, the loss of weight in oxygen is greater than in a vacuum (cf. Langmuir, A., 1915, ii, 467). The kinetics of the reaction were studied at various pressures and temperatures. The results are most readily interpreted by assuming a surface reaction of which the rate is proportional to the pressure and a zero order bulk phase reaction which occurs simultaneously, the combined effect being denoted by an equation of the type $-bt=\log_e(a+bp)/(a+bP_0)$, P_0 being the initial pressure. From the experimental data a and b are found, and from Langmuir's values for the rate of evaporation of platinum in a vacuum values for a are calculated (subject to certain assumptions) which agree well with those obtained in the present experiments. From the "clean up" of oxygen, and by actual analysis, the deposit on the bulb was found to be PtO_2. From these results it appears that below 1700° Abs., and even above this temperature for pressures below 50 bars, the bulk reaction between platinum vapour and oxygen predominates. No experimental evidence could be found for Langmuir's suggestion that the alteration of reaction rate at high pressures and temperatures is due to the concentration of ozone or oxygen atoms, and it is considered that a surface reaction is more probable. A hypothesis is suggested for the mechanism of the surface action based on the thermionic work function of platinum, and it is shown that the oxidation of carbon and the catalytic decomposition of ammonia on certain metal surfaces are in accordance with this scheme. L. L. Bircumshaw.

Oxidation of copper at high temperatures. W. Feitknecht (Z. Elektrochem., 1929, **35**, 142—151).—The velocity of oxidation of copper depends on the rate at which oxygen can diffuse through the surface film of oxide that is formed. The nature of the layer, produced at different temperatures, was investigated by means of X-rays, using the Debye–Scherrer method, and also with the microscope. The copper becomes covered with a cuprous oxide layer, having a structure similar to that of a metal, which is subsequently covered with a thin film of cupric oxide. For temperatures of 850—1020° the expression $x^2=Kt$ (x being the amount of oxygen taken up by the copper in t min. and K a constant) held only after some time had elapsed. The variation in the velocity coefficient, K, with temperature, T (Abs.), could not be satisfactorily represented by $K=Ae^{-E/RT}$, A and E being constants, for it was found that K became smaller than that given by the formula for falling temperatures (cf. Dunn, A, 1926, 692). Experiments using oxygen–nitrogen and oxygen–carbon dioxide mixtures showed that, provided the partial pressure of the oxygen was greater than the dissociation pressure of copper oxide at the particular temperature, the velocity coefficient was independent of the oxygen pressure, but became approximately proportional to the logarithm of the partial pressure when it fell below the dissociation pressure. H. T. S. BRITTON.

Corrosion of iron in sodium chloride solution. W. VAN WÜLLEN-SCHOLTEN.—See B., 1929, 285.

Oxidation of ferrous hydroxide by air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1929, 4, 65—68; cf. A., 1927, 425).—The disparity between the results obtained for the velocity coefficient of the above reaction by the author and those found by Krause (A., 1928, 1202) is attributed to the fact that whereas the coefficient measured by Krause refers to the rate of disappearance of ferrous iron, that of the author is in effect the velocity of dissolution of oxygen into the reaction mixture. According to the latter, the oxidation of the ferrous iron is an induced reaction, of which the velocity is dependent on the rate of dissolution of oxygen in the reaction mixture. F. G. TRYHORN.

Acid and salt effects in catalysed reactions. XIX. Catalytic activity of chloroacetic acid in the hydrolysis of ethyl acetate. H. M. DAWSON and W. LOWSON (J.C.S., 1929, 393—401; cf. A., 1927, 1150).—In a study of the catalytic effect of chloroacetic acid and the corresponding acid–salt mixtures three factors have to be taken into account: (*a*) the chlorine hydrolysis of the catalyst, and the influence of ionic environment on (*b*) the catalytic coefficients and (*c*) the ionisation constant of chloroacetic acid. The disturbing effect of the first can be eliminated by suitable choice of the experimental conditions, and it is shown that the catalytic effect of the chloroacetic acid can be expressed by the formula $v=k_h[H^+]+k_m[HA]$, provided that suitable allowance is made for the factors (*b*) and (*c*). The chloroacetate ion has a negligible catalytic effect. In sodium chloride solutions of gradually increasing concentration, k_h increases continuously, whilst the ionisation constant of the acid passes through a maximum at about 0·5M-concentration. F. J. WILKINS.

Activation of chemical reactions by neutral salts. III. Activation of dissolution of nickel [in sulphuric acid]. N. ISGARISCHEV and S. SCHAPIRO (Z. physikal. Chem., 1929, **140**, 223—226; cf. A., 1927, 945; 1928, 374).—The effect of various chlorides and potassium salts on the rate of dissolution of nickel in sulphuric acid has been studied. All salts accelerate the reaction and a highly specific action of the different ions is obtained. The order in which the bromate, iodate, and chlorate ions accelerate this reaction is the same as that found for the dissolution of aluminium (A., 1928, 486), but no connexion exists between the effect of the simple halide ions on the two reactions. R. N. KERR.

Activation of chemical reactions by neutral salts. IV. Action of neutral salts on the potential of oxidation–reduction reactions. N. ISGARISCHEV and A. TURKOVSKAJA (Z. physikal. Chem., 1929, **140**, 227—234; cf. preceding abstract).—The oxidation–reduction potentials of the system $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ in presence of the chlorides and the nitrates of metals of the first two periodic groups and of sodium salts with different anions have been measured. The chlorides with the exception of those of zinc and cadmium lower, and the nitrates raise, the potential. For the cations of metals of the first group, the sequence is the same with the chlorides and the nitrates. The alteration of potential cannot be explained by the change in acidity of the solution or by the occurrence of complex formation with the ferric or ferrous ions. A parallelism exists between the sequence of the cations in their action on the potential and on the velocity coefficient of the oxidation of stannous chloride by ferric chloride (A., 1925, ii, 586). R. N. KERR.

Activation of chemical reactions by neutral salts. V. Action of neutral salts on cathodic polarisation. N. ISGARISCHEV and H. RAVIKOVITSCH (Z. physikal. Chem., 1929, **140**, 235—240; cf. preceding abstracts).—The effect of adding salts of metals of the first and second periodic groups and also of cobalt and aluminium on the current density–potential curve for the cathodic deposition of nickel from the chloride has been determined. A marked effect on the shape of the curve is obtained. The effect of the cation rises with the at.wt. throughout each periodic group. The polarisation changes are considered with reference to (*a*) the acidity of the solution and (*b*) the dehydrating action of the salt on the nickel ion. The action of the added salt on the yield and properties of the precipitated nickel has also been investigated. R. N. KERR.

Catalytic effect of ruthenium salts on the reduction of perchloric acid by hydrobromic acid. W. R. CROWELL, D. M. YOST, and J. M. CARTER (J. Amer. Chem. Soc., 1929, **51**, 786—794).—The reaction $ClO_4'+8Br'+8H^{\cdot}=Cl'+4Br_2+4H_2O$, which proceeds only in the presence of ruthenium, was investigated. Tervalent ruthenium is far more effective catalytically than the quadrivalent form; the catalytic effect progressively slackens as the reaction proceeds, since the bromine liberated slowly oxidises tervalent ruthenium to the quadrivalent form. It is suggested that the perchloric acid first slowly oxidises the ruthenium from the tervalent to the sexa- or septavalent state, and that the latter is then almost instantaneously reduced by the bromide to the tervalent state. S. K. TWEEDY.

Catalytic power of medicinal mineral waters. O. FERNÁNDEZ (Anal. Fís. Quím., 1929, **27**, 45—48).—Theories of the catalytic activity of mineral waters in decomposing hydrogen peroxide are reviewed. Bacteriological examination indicates that this effect is sufficiently explained by the catalase activity of bacteria originally present or acquired by contamination. R. K. CALLOW.

Autoracemisation. E. WEDEKIND (Naturwiss., 1929, **12**, 199; cf. Kuhn and Wagner-Jauregg, this vol., 425).—Examples in which autoracemisation is a catalytic process have already been quoted by Wedekind and Maiser (A., 1928, 898; this vol., 194).

R. N. KERR.

Theory of catalysis. A. BERTHOUD (J. Chim. phys., 1929, **26**, 120—124).—A criticism of Dubrisay's thermodynamic theory of catalysis as applied to the Arrhenius conception of activated molecules (cf. A., 1928, 1334). The introduction of a small amount of a foreign substance into a chemical system cannot bring about a change in the concentration of the active molecules. Even if such a change is assumed it does not follow that the rate of the chemical reaction will be accelerated.

O. J. WALKER.

Theory of heterogeneous catalysed reactions. Multiplet hypothesis. Model of dehydrogenation catalysis. A. A. BALANDIN (Z. physikal. Chem., 1929, **B**, **2**, 289—316).—Assuming that catalysed reactions at surfaces occur at active centres, the author suggests that in general such a centre will not attract every part of the reacting molecule with the same intensity, but will exert a preferential attraction on some part or parts of it. If all the centres attract by preference the same part of the molecule, there will be no tendency for the molecule to be broken up, and adsorption without reaction will occur. On the other hand, if there are present various types of centres, some attracting one part of the molecule and some attracting another part, decomposition becomes possible. For actual fission to take place, however, the different centres must not be too remote from each other, but should rather be arranged in groups, each group containing one or more centres of each type, and for such groups the term "multiplets" is proposed. Since catalysed reactions usually involve a synthesis as well as a decomposition, it is suggested that some centres may simultaneously attract two or more parts of the same molecule, or the same part of several molecules, and if decomposition occurs cause these fragments to unite by directing their valencies one to another. Thus in the reaction $C_2H_5\cdot OH = C_2H_4 + H_2O$ it may be supposed that active centres of one kind preferentially attract the carbon atoms of $\cdot CH_2\cdot CH_2\cdot$ groups, whilst those of another kind attract both hydrogen and hydroxyl oxygen, which then unite to form water. If a foreign substance is adsorbed by one kind of centre only, leaving the others free, the surface will be largely poisoned without its adsorptive power being very much affected, whereas a substance which is able to give rise to active centres of a type in which the surface is deficient will act as a promoter. It is considered probable that the groups of active centres are densely packed, constituting small surface elements which are to be identified with crystallisation nuclei. If it is assumed that the arrangement of centres must be such as to correspond with the symmetry of the molecule in order for reaction to take place, it becomes possible to predict what kind of crystal lattice will catalyse a particular reaction and to calculate the extreme values of the distance between the various centres in order for the attractions to be great enough to dismember the molecule. In this way the theory becomes capable of accounting for many of the observations made in investigations of the catalytic hydrogenation and dehydrogenation of organic compounds, and its application to the reactions of *cyclo*hexane is discussed in detail.

R. CUTHILL.

Extension of the intermediate-compound theory of catalysis in gas reactions. H. H. STORCH (J. Physical Chem., 1929, **33**, 456—458).—The function of intermediate compounds in gas-phase catalysis is to provide a complex, containing reactants and catalyst, of a sufficiently large number of degrees of freedom, so that the energy of these may be available for contribution to the energy of activation. The decomposition of hydrogen iodide at the surface of platinum, the catalytic effect of water vapour, and catalysis by gaseous ions are discussed in the light of this extension of the intermediate-compound theory.

L. S. THEOBALD.

Topochemistry of contact catalysis. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1928, **B**, **1**, 385—408).—Theoretical. An attempt has been made to evolve a theory of the surface catalysis of gas reactions which shall in itself achieve all that Langmuir's theory of a unimolecular adsorbed film and of reaction at a homogeneous surface and Taylor's theory of "active centres" (A., 1926, 365) achieve together. For this purpose, it is suggested that the centres of reaction are not distributed over the whole surface, or located at "active points," but rather lie on lines which are phase boundaries. The adsorbed molecules are assumed to be free to move over the surface (cf. Volmer, A., 1925, ii, 539), but they also undergo "adlineation," *i.e.*, they crowd together at phase boundary lines in the surface in the same way as molecules in free space crowd together at a surface where they are adsorbed. By applying the methods of the kinetic theory it is possible to deduce an expression for the number of molecules adsorbed on the surface which impinge on unit length of a line in unit time, and this in its turn leads to the "adlineation isotherm." The same equations may be arrived at from thermodynamical considerations, which also afford a proof of the Langmuir adsorption isotherm, which, unlike that obtained by Volmer (*loc. cit.*), is quite rigid. By means of the new system of equations, formulæ for the velocities of the various types of gas reactions have been derived, and as these prove to be of the same form as those which are applicable to reactions at bounding surfaces, the new assumption as to the seat of reaction appears to be justified, and may be regarded as the basis of a truly comprehensive theory of surface catalysis.

R. CUTHILL.

Topochemistry of contact catalysis. II. Experimental case of alinement. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1929, **B**, **2**, 262—263; cf. preceding abstract).—Eisner's work on the adsorption of heavy metal ions on the edges of crystals (*e.g.*, on crocoisite) and not on the whole surface is used as evidence for the theory of contact catalysis put forward in a previous paper.

A. J. MEE.

Topochemistry of contact catalysis. G. M. SCHWAB and E. PIETSCH (Z. Elektrochem., 1929, **35**, 135—141).—An outline of a new theory of catalysis (cf. preceding abstracts) in which lines which are phase boundaries in the catalyst are considered to be the seats of the reactions as the result of "adlineation" of the reacting molecules. The conceptions of heat of "adlineation" and the relative lengths of these lines of catalytic activity are believed to furnish a basis for the quantitative co-ordination of the various measurable properties of catalysts, *e.g.*, the increase or decrease in activity. H. T. S. Britton.

Catalysis of decomposition of carbon monoxide. I. Iron as catalyst. H. Tutiya (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 69—82).—Iron and carbon have no catalytic action on the thermal decomposition of carbon monoxide; this reaction is, however, powerfully catalysed by ferric carbide formed in the presence of iron. The reactions taking place are: $3Fe+2CO=Fe_3C+CO_2$ and $2CO=C+CO_2$. The carbon formed in the latter reaction acts anti-catalytically by covering the carbide surface. This carbon contains iron from which it is difficultly separable, even by prolonged extraction with concentrated acids. An *X*-ray examination of the deposit forming on iron wire shows that the "*X*-carbide" of Hofmann (A., 1928, 853) is in reality iron oxide. R. Truszkowski.

Thermal decomposition of ammonia on iron catalysts. II. C. H. Kunsman (J. Amer. Chem. Soc., 1929, **51**, 688—695; cf. A., 1928, 1101).—The reaction, which was effected at the surface of platinum strips coated with catalyst by an ignition process, is uninfluenced by nitrogen and is retarded by hydrogen. No definite reaction order could be measured. The constants *A* and *E* in the Arrhenius equation vary with temperature for a given catalyst. The presence of a promoter displaces the activity curve towards a lower temperature, whereas a poison, or heat treatment, moves the curve towards a higher temperature, the general shape of the curve remaining unchanged. S. K. Tweedy.

[Platinum] gauze catalyst in ammonia oxidation. G. A. Perley and M. W. Varrell.—See B., 1929, 321.

Decomposition of nitric oxide by platinum at elevated temperatures and its retardation by oxygen. P. W. Bachman and G. B. Taylor (J. Physical Chem., 1929, **33**, 447—455).—The heterogeneous decomposition of nitric oxide on platinum wire at 1035°, and on platinum–rhodium wire at 1035°, 1210°, and 1385° is shown to be bimolecular with respect to nitric oxide (cf. Green and Hinshelwood, A., 1926, 915). It is retarded proportionally to the oxygen concentration. It is pointed out that bimolecular reactions retarded by a reaction product are similar to unretarded unimolecular reactions in that the fraction which reacts in a given time is independent of initial pressure. The apparent heat of activation on platinum–rhodium (10%) is approximately 24,000 g.-cal.; this indicates a large positive value for the heat of adsorption of nitric oxide on the metal. The suggested mechanism of decomposition is that two molecules of nitric oxide are adjacently adsorbed with oxygen towards the catalytic surface; the atoms of nitrogen combine, evaporate, and leave the oxygen to act as a retarding agent. L. S. Theobald.

Topochemistry of catalysis of decomposition of hydrogen peroxide by mercury, and p_H for pulsation. G. Bredig and A. Stark (Z. physikal. Chem., 1929, **B**, **2**, 282—286).—Von Antropoff's investigation of the decomposition of hydrogen peroxide in aqueous solution at a mercury surface (A., 1908, ii, 472) may now be considered to show that this is an example of catalysis at phase boundary lines (Schwab and Pietsch, this vol., 519). The p_H of the solution must lie between 6·65 and 7·05 for pulsations to occur. R. Cuthill.

Kinetics of the hydrogenation of ethylene using a copper catalyst of measurable surface. F. H. Constable (Z. Elektrochem., 1929, **35**, 105—110).—Two series of experiments at 0°, 100°, and 200° on the hydrogenation of ethylene in presence of a copper catalyst, which was prepared by the repeated reduction of copper oxide with hydrogen, are described. In the first, equal volumes of hydrogen and ethylene were employed at pressures of 19, 38, 50, and 76 cm.; and in the second, the volumes of the reacting gases were varied but the pressure was kept constant at 76 cm. The first series showed that the surface of the catalyst was almost saturated with the gases at 0°, but was partly saturated at 100° and was very unsaturated at 200°. According to the second set, and with the particular catalyst used, the rate of production of ethane was at a maximum at 0° when the reaction mixture contained 18 vol.-% of ethylene; at 100°, 42%; and at 200°, approximately 50%.

The kinetics of the reaction at 0° were found to satisfy expressions previously derived (A., 1928, 718). The superficial area of the catalyst was ascertained by means of an interference method after coating the catalyst with a film of oxide by direct oxidation (A., 1928, 832). The interference method was also employed to investigate the nature of the gases adsorbed by the catalyst. At 0° much of the surface appeared to be covered with a unimolecular layer of hydrogen, whilst much of the remaining part was covered with ethylene. H. T. S. Britton.

Indication of hydroxyl in a water–vapour discharge tube. G. I. Lavin and F. B. Stewart (Nature, 1929, **123**, 607).—The gas from a water-vapour discharge tube contains hydroxyl, indicated by the band at 3060 Å., the intensity of which is increased by the addition of a small quantity of oxygen. A larger amount produces the green oxygen afterglow. The active gas reduces copper sulphate and oxidises metallic silver. A. A. Eldridge.

Ozonisation under the action of high-frequency discharges. W. Daniewski (Rocz. Chem., 1929, **9**, 83—96).—The amount of ozone formed employing high-frequency alternating currents in an ozoniser without dielectric is constant at frequencies of 300,000, 1,700,000, and 12,500,000, being about 60 g./kw.-hr. This constancy is ascribed to the disproportion between the number of oscillations and the number of molecular collisions per unit time. The limiting concentration of ozone diminishes with increasing frequency from 6 g./m.^{3} at 300,000 to 14 g./m.^{3} at $12{\cdot}5\times10^6$; this effect is due to the greater density of the sparks at higher frequencies. R. Truszkowski.

Chemical interaction of ions and the "clean up" of gases at glass surfaces under the influence of the electric discharge. J. Taylor (Proc. Roy. Soc., 1929, **A**, **123**, 252—270).—By means of the arrangement previously described (J. Taylor and W. Taylor, A., 1928, 681) experiments have been carried out on the disappearance of gas in the electric discharge. Positive ions, obtained by means of an electrodeless discharge in hydrogen, oxygen, nitrogen, and helium at low pressures (down to 0·001 mm.), were pulled out by the action of an electric field and struck the walls of a thin-walled glass bulb immersed in a sodium nitrate bath maintained at a suitable temperature. A current usually traversed the walls of the bulb and in most cases a progressive diminution of the pressure of the gas in the discharge tube took place. For all the gases except helium, the quantity of gas disappearing was found to be directly proportional to the quantity of electricity transferred through the glass walls. It appears to be dependent on the previous treatment of the glass, but follows laws similar to the Faraday laws of electrolysis. For hydrogen, one molecule frequently disappeared for every electron charge passed, but with continued running one hydrogen atom disappeared for every electron transferred. For oxygen and nitrogen, every two electron charges passed usually involved the disappearance of one atom, but in some cases one oxygen atom disappeared for every four electron charges and one nitrogen atom for every three charges. For helium no progressive disappearance of gas occurred. Experiment showed that the gas which disappeared was not transferred through the glass by diffusion, and that the "clean up" was not of the nature of an occlusion of gas in the glass arising from the ions being driven with high velocity into the surface. Experiments were also made on the nature of the "clean up" in the electrodeless discharge alone and in the combined action of the electrodeless discharge and the direct current discharge through the glass walls. The spectrogram of the condensible product obtained in a liquid air trap was found, in the case of hydrogen, to be identical with the standard spectrum for water at low pressure, whilst with oxygen a condensible product was formed which gave a spectrogram similar to that obtained from a discharge in carbon dioxide. A theory is proposed to account for the observed phenomena. The clean up must be due to chemical interaction of the gaseous ions with the electrolytic products and ions of the glass. Regarding glass as a solution containing Na_2SiO_3 as electrolyte, then for every two electron charges transferred across the glass 2Na is liberated, the SiO_3 radical breaks down into SiO_2+O, and the oxygen atom unites with a hydrogen molecule. Matters are, however, not so simple as this, and glass must be considered as a complex electrolytic solution containing carbon compounds and probably also peroxides. L. L. Bircumshaw.

Decomposition of nitrous oxide in the silent electric discharge. IV. Influence of the addition of foreign gases. S. S. Joshi (Trans. Faraday Soc., 1929, 25, 137—143; cf. this vol., 404).—Measurements by the author's method (A., 1927, 635) of the initial velocity of decomposition of mixtures of nitrous oxide and varying quantities of nitrogen, oxygen, and nitrogen peroxide by a silent discharge of 12·4 kilovolts applied for 50 min. show that the percentage decomposition is diminished by addition of these gases. The mean wattage consumed is also diminished and the minimum potential required to initiate decomposition is increased, the effect of nitrogen peroxide being greatest and that of nitrogen least. The relative influence of the foreign gases is explained in terms of their electron affinities, which follow the order $N_2<N_2O<O_2<NO_2$. Since addition of oxygen increases the nitrogen/oxygen ratio in the final mixture, it is suggested that the equation $4N_2O=3N_2+N_2O_4$ represents the main reaction, whilst oxygen is produced only by either or both of the reactions $N_2O_4=N_2+2O_2$ and $2N_2O=2N_2+O_2$. J. Grant.

Testing of electro-deposits on aluminium. G. B. Brook and G. H. Stott.—See B., 1929, 286.

Cathodic yield in nickel-plating with high current density. Influence of oxidising agents and hydrogen-ion concentration. Ballay.—See B., 1929, 287.

Control of the current density in electrolytic baths. W. Pfanhauser.—See B., 1929, 289.

Anodic behaviour of substituted acetic acids. I. Diphenylacetic acid. H. Katagishi, Y. Ginbayashi, and M. Matsui (Mem. Coll. Sci. Kyōtō, 1929, **A**, **12**, 57—62).—On electrolysis between platinum electrodes of a solution of potassium diphenylacetate of concentration not less than about 35% and acidified with sulphuric or hydrochloric acid, diphenylmethyl alcohol and a little of its diphenylacetic ester are formed with evolution of carbon dioxide. Lead catalyses the formation of alcohol, but not of ester. If an alternating current is employed, the total yield, and also the relative amount of ester are increased. R. Cuthill.

Electrolytic reduction of aldehydes. V. Cinnamaldehyde. VI. Complete reduction of the carbonyl group. G. Shima (Mem. Coll. Sci. Kyōtō, 1929, [*A*], 12, 69—72, 73—80).—V. The best yield (72%) of γ-phenylpropyl alcohol from cinnamaldehyde by electrolytic reduction was obtained by using a mercury cathode and adding the aldehyde slowly to a cathode solution containing saturated sodium hydrogen carbonate solution (50 c.c.) and alcohol (70 c.c.) at 20—22°, with a current density of 6 amp./100 cm.^{2} The results of varying the conditions are tabulated. In alcoholic ethyl acetate solution the maximum yield was 50%.

VI. The use of a zinc amalgam cathode gives better results than cadmium (Schepss, A., 1913, i, 1154) in the complete electrolytic reduction of the aldehydo-group to methyl. The best yields of *p*-tolyl methyl ether from anisaldehyde (68%), and of *o*-cresol from salicylaldehyde (66%), were obtained by using a cathode solution containing 60% sulphuric acid (60 c.c.) and alcohol (20 c.c.) at 35—40° with a current density of 72 amp./100 cm.^{2} The best yields of *p*-cresol from *p*-hydroxybenzaldehyde (58%), and of creosol from vanillin (75%), were obtained under the same conditions, but in the absence of alcohol. The best yield of 3 : 4-methylenedioxytoluene from piperonal (55%) was obtained under the same conditions in a mixture of 60% sulphuric acid (50 c.c.) and alcohol (30 c.c.). The results of varying the conditions are tabulated. The effect of the presence of alcohol is discussed. Müller's theory (A., 1923, i, 90) does not account for the different behaviour of aldehydes and additive products.

R. K. Callow.

Photochemical properties of the halogens. J. Plotnikov (J. Chim. phys., 1929, **26**, 44—58).—From a critical review of the literature relating to the photochemical reactions of iodine and bromine, it is concluded that the experimental data are too incomplete and the discrepancies too pronounced for it to be possible to reach any conclusions as to the reaction mechanism. In experiments of this type, it is essential that monochromatic light shall be employed, and for regulating its intensity thin sheets of metal are recommended, the rotating-sector method being quite useless here. R. Cuthill.

Photosynthesis of hydrochloric acid at low pressures. G. K. Rollefson (J. Amer. Chem. Soc., 1929, **51**, 770—778).—The reaction was studied in white light with excess of chlorine; the equation which holds at high pressures, viz., $d[\mathrm{HCl}]/dt = k[\mathrm{H_2}][\mathrm{Cl_2}]$, remains valid. The experimental results, considered in the light of previously published work, indicate that light dissociates chlorine molecules into chlorine atoms in the ${}^2P_1$ state (cf. Franck, A., 1925, ii, 1077) and also in the normal state. The mechanism of the reaction is discussed in detail and a series of chain reactions which accounts for the influence of water on the reaction is proposed.

S. K. Tweedy.

Coloration of thin layers of silver iodide in light. E. Jenckel (Z. anorg. Chem., 1929, **179**, 89—96).—The alteration of colour exhibited by a thin film of silver iodide when exposed to light is due to the production of fine particles of silver.

H. F. Gillbe.

Inhibition of certain photochemical reactions by oxygen. H. B. Dunnicliff and J. N. Joshi (J. Indian Chem. Soc., 1929, **6**, 121—127).—The following photo-sensitive reactions are inhibited by oxygen or ozone or hydrogen peroxide: action of ammonium oxalate on mercuric chloride, oxidation of lactic acid by bromine water, reduction of ferric oxalate to ferrous oxalate and decomposition of silver halides. The mechanism of the inhibiting action is discussed.

O. J. Walker.

Theory of the photographic process. H. Kieser (Z. wiss. Phot., 1929, **26**, 321—340).—Based on the quantum theory, the secondary reactions produced by the photo-electric effect, and the probable alterations in the structure of the silver bromide crystal which accompany photolysis, a theory has been developed to account for the formation of the latent image. It has been employed to explain the following processes: solarisation, Clayden effect, Schwarzschild and intermittent exposure effects, sensitisation and desensitisation, and the Herschel effect. H. T. S. Britton.

Photographic effects [with silver bromide emulsions]. H. Tollert (Z. physikal. Chem., 1929, **140**, 355—378).—Using a specially prepared silver bromide emulsion in gelatin, determinations were made of (*a*) the amount of silver formed photolytically, (*b*) the amount of silver formed after developing, and (*c*) the amount of "blackening" of the developed silver. In the region of solarisation the amount of silver formed photolytically increases with the quantity of light used, whereas *b* and *c* do not increase. The sensitising action of erythrosin was examined by comparing the number of dye molecules adsorbed by the silver bromide with the number of silver atoms formed photolytically. The number of silver atoms is 64 times the number of adsorbed erythrosin molecules. Some experiments with other sensitisers and desensitisers are described. It is shown that the Herschel effect, *i.e.*, the action of red light on photolytically formed silver before development, is due to a change not in the amount, but in the structure of the silver. A quantitative comparison is made of the energy necessary for direct blackening for blue and red light. O. J. Walker.

Effect of environment on photographic sensitivity. II. Effect of certain salts. S. E. Sheppard and E. P. Wightman.—See B., 1929, 303.

Theory of the hydrogen peroxide effect, of physical development, and of the coloration produced by dyes and silver halides. A. Steigmann (Z. wiss. Phot., 1929, **26**, 341—344).—The hydrogen peroxide effect is briefly discussed on the basis of the author's theory, according to which the number of reduction centres on the surfaces of silver halides diminishes in the order: chloride, bromide, iodide. The insensitivity of silver chloride in presence of silver bromide is considered to be due to the greater number of primary reduction centres on the surface of the chloride, which in the preparation of the plate causes enhanced adsorption to occur and so renders the subsequent action of light difficult. This inactivity to light is accompanied by an inactivity to hydrogen peroxide. Experiments are described on the action of dyes in solutions containing halides of alkali metals on silver halides. Erythrosin became bluish; pinachrome was almost decolorised in concentrated sodium chloride solution; fuchsin became blue and showed dichromatism; methylene-blue, pinakryptol-green, and phenolsafranine were each precipitated and their solutions bleached. Other experiments dealt with the probable chemical combination of methylene-blue with silver halides. H. T. S. Britton.

Photochemical production of optically active substance. W. Kuhn and E. Braun (Naturwiss., 1929, **17**, 227—228).—The rotatory dispersion of ethyl α-bromopropionate in the ultra-violet discloses at first an increased rotation (specific rotation in alcohol of about 4000° at 2450 Å.) followed by a reversal. The absorption bands in the near ultra-violet must therefore influence powerfully the optical activity. Solutions (4—8% in alcohol) of the racemic ester were exposed in quartz flasks to circularly polarised light. Monochromatic light (Mg line 2800 Å.) was used. A solution of the active ester was simultaneously exposed to unpolarised light of corresponding intensity, to provide control for the period of irradiation. The solutions exposed to dextro-circularly polarised light showed dextro-rotation, and *vice versa.* The greatest effect so far obtained is 0·05° on either side. The effect observed agrees in sign with theoretical predictions. R. A. MORTON.

Transformation of cholesterol by *X*-rays. A. H. ROFFO and L. M. CORREA (Bol. Inst. Med. exp., 1925, No. 5, 3 pp.; Chem. Zentr., 1928, ii, 1671—1672).—The products resulting from the action of *X*-rays on cholesterol do not give colour reactions, and are not precipitable with digitonin. The double linking remains unaffected. The action consists in oxidation of the alcoholic carbon atom in Windaus' formula. A. A. ELDRIDGE.

Development of chlorophyll in seedlings in different ranges of wave-lengths of light. J D. SAYRE (Plant Physiol., 1928, **3**, 71—77).—Wave-lengths longer than 680 μμ are not effective in the formation of chlorophyll in maize, wheat, oat, barley, bean, sunflower, or radish seedlings. The effectiveness of radiant energy appears to increase with wave-length to about 680 μμ and then to fall abruptly to zero. CHEMICAL ABSTRACTS.

Change of conductivity of coloured substances during photochemical action. N. ZCHODRO (J. Chim. phys., 1929, **26**, 59—64).—The conductivity of collodion films coloured with cyanine, pinaverdol, or pinachrome increases on illumination with white light; the increase is no longer obtained when the film has become decolorised. The conductivity increases with the duration of exposure until a maximum value is obtained; when illumination ceases the conductivity diminishes gradually. The effect of illumination by monochromatic light has also been studied and curves are given of change of conductivity against wave-length of light used. These curves resemble closely those obtained by Lasareff (Ann. Physik, 1907, **24**. 661) for the energy of light absorbed by these coloured films, and the conclusion is reached that the increase of conductivity of the films during decolorisation is proportional to the energy of the light absorbed. R. N. KERR.

Oxidations promoted by ultrasonic radiation. F. O. SCHMITT, C. H. JOHNSON, and A. R. OLSON (J. Amer. Chem. Soc., 1929, **51**, 370—375).—Some ultrasonic radiation reactions were investigated in presence of oxygen and water, under conditions such that gas bubbles could be formed in the liquid. The reactions included oxidation of halide ions under various conditions, of hydrogen sulphide, and of carbon tetrachloride (chlorine is formed in presence of air and moisture). Some dye molecules are affected by the radiation and give rise to hydrogen ions. The reaction rate of ultrasonic reactions rises as the pressure is increased, but above a certain critical pressure the rate falls again. An explanation is suggested for this behaviour. S. K. TWEEDY.

Is hydrogen peroxide formed in electrolytic gas by α-rays ? B. M. MARKS (J. Physical Chem., 1929, **33**, 381—383).—Contrary to the assumption of Scheuer (A., 1914, ii, 762), no hydrogen peroxide could be detected when electrolytic gas is acted on by α-particles. Tests for ozone were also negative. The excess of hydrogen over that required for the formation of water reported by Scheuer is attributed to reaction of part of the oxygen with the mercury present in the system. L. S. THEOBALD.

Pure hydrogen peroxide. VI. G. L. MATHESON and O. MAASS (J. Amer. Chem. Soc., 1929, **51**, 674—687).—F.-p. curves are recorded for some binary hydrogen peroxide systems. Potassium chloride and sulphate and sodium fluoride are dissociated in solution, but methyl alcohol is associated. The eutectic point was always higher than that for the corresponding water systems; the eutectic for aqueous sodium fluoride solution lies at −2·9°, the composition being 1·4% of salt (cf. Guthrie, Phil. Mag., 1878, **5**, 640). Potassium bromide decomposes hydrogen peroxide rapidly. Ether is only slightly soluble; a compound containing 48—55% of ether was isolated. Sulphur dioxide dissolves even in very cold peroxide to form sulphuric acid; compound formation occurs. Amines and hydrogen peroxide do not interact below 0°, but at the ordinary temperature the amine (*e.g.*, piperidine) is often oxidised to the corresponding nitro-compound. Butylamine–hydrogen peroxide compounds were isolated; they probably represent the first stage in the oxidation to nitro-compounds. Evidence was obtained that the other amines also form compounds; the number of peroxide molecules in the ethylamine compound increases as the hydrogen atoms linked to nitrogen are replaced by ethyl groups. Dimethylaniline differs from aliphatic amines in being less soluble and associated in solution. Direct measurements gave 23,450 g.-cal. at 20° for the heat of the reaction $H_2O_2(l)=H_2O(l)+0{\cdot}5O_2$ (at 1 atm.). Vapour density measurements by the Victor Meyer method gave 34 as the mol. wt. of hydrogen peroxide vapour. The decomposition of the peroxide becomes explosive at 150—153°. This temperature is raised slightly by addition of water or of potassium chloride. S. K. TWEEDY.

Action of helium on platinum. H. DAMIANOVICH (Compt. rend., 1929, **188**, 790—792).—The action of pure helium on platinum under the influence of a moderate electric discharge at 0·75—3·5 mm. for 30 min. to 14 hrs. produces thin brown layers of the metal which is converted by heat into a mirror of ordinary platinum and retains large quantities of helium in the form of adsorption compounds or mixtures of such compounds with excess of metal. J. GRANT.

Action of helium on platinum. H. DAMIANOVICH and J. J. TRILLAT (Compt. rend., 1929, **188**, 991—992).—Products containing helium and platinum (preceding abstract) prepared under various conditions were examined by the Debye–Scherrer method and shown to have the same microcrystalline structure. The deposit obtained by the action of an alternating discharge (0·5 cm. spark) on platinum in helium at 3·5 mm. pressure contained a microcrystalline substance, possibly a compound of helium and platinum, which was not detectable in the other deposits. J. GRANT.

Action of ozone on alkali azides. Pernitrous acid. I. K. GLEU and E. ROELL (Z. anorg. Chem., 1929, **179**, 233—266).—If oxygen containing about 10% of ozone be passed into an *N*-sodium azide solution an orange coloration is at first produced, but later the colour fades and the solution then contains nitrate and nitrite, but no azide. It has not been found possible to isolate the orange substance by freezing out the water, by precipitation with another solvent, or by effecting the reaction in non-aqueous solution; further, ozone does not appear to react with solid sodium azide. The orange substance is stable only in alkaline solution and decomposes below the b. p. with evolution of equal volumes of nitrogen, nitrous oxide, and oxygen; if no azide remains in the solution oxygen alone is evolved. Titrations with stannite, antimonite, and arsenite solutions yield concordant results for the oxidising power of the solution, but with formaldehyde anomalous results are obtained, which lead to the conclusion that this reducing agent is oxidised primarily to performic acid, which is then reduced by the nitrite present. Permanganate is reduced to manganate with vigorous evolution of oxygen. Quantitative titrations show that the nitrate and nitrite contents of the orange solution are equal, that the oxidation titre is equal to the reduction titre, and that the volume of oxygen produced by oxidation is double that resulting from decomposition of the orange substance. The latter is decomposed catalytically by manganese dioxide, and is reduced, although slowly, by hypobromite and hypochlorite solutions. The orange substance thus appears to be a derivative of hydrogen peroxide and is shown to react quantitatively as a pernitrous acid, isomeric with nitric acid, and having the structure O:N·O·OH. Its formation results from the production of an ozonide of azoimide, which then loses one molecule of nitrogen. H. F. Gillbe.

New series of double sulphates of the copper–magnesium group and the phosphonium bases. I. P. C. Rây and N. Rây (J. Indian Chem. Soc., 1929, **6**, 27—30; cf. A., 1928, 505).—The following *magnesium tetraethylphosphonium sulphates* have been obtained ($R=PEt_4$) :—

$MgSO_4,R_2SO_4,8H_2O$; $2MgSO_4,R_2SO_4,H_2SO_4$; $2MgSO_4,R_2SO_4,2H_2SO_4,2H_2O$; $2MgSO_4,R_2SO_4,H_2SO_4,H_2O$, and $2MgSO_4,R_2SO_4,H_2SO_4,2H_2O$. Copper yields only the acid *salt* $2CuSO_4,R_2SO_4,H_2SO_4,4H_2O$.

O. J. Walker.

Spectro-analytical investigation of the dissolution of alloys and the Tammann resistance layer. VI. W. Gerlach (Z. anorg. Chem., 1929, **179**, 111—112).—When alloyed with gold in absence of lead both copper and silver are protected from the action of nitric acid, but if lead be present the copper is dissolved simultaneously with the lead, as a result of compound formation between the two metals.

H. F. Gillbe.

Action of water on tricalcium silicate and β-dicalcium silicate. T. Thorvaldson and V. A. Vigfusson.—See B., 1929, 247.

Preparation of phosphorescent zinc sulphide. R. Coustal and F. Prevet (Compt. rend., 1929, **188**, 703—705).—Phosphorescent zinc sulphide is obtained as a white, spongy mass of wurtzite crystals when intimate and finely-powdered mixtures of zinc (particles of the order of 1 micron) and sulphur are exploded by shock, heat, or friction. In general, an excess of zinc decreases the persistence of the phosphorescence and displaces it towards the higher wave-lengths, the maximum intensity and explosive violence being obtained with 1·5—2 g. and 3·3 g. of zinc/g. of sulphur, respectively. Added copper, halogen, or phosphorus compounds increase or modify the colour of the phosphorescence, but metals (except uranium) have the reverse effect, and all diminish the violence of the explosion. Explosions carried out in nitrogen and sulphur dioxide give a less and more intense phosphorescence, respectively, than that produced in air, and the selenides and tellurides produced by the same method are less phosphorescent than the sulphides.

J. Grant.

Mercurammonium iodides. M. François (Ann. Chim., 1929, [x], **11**, 22—43).—The existence of the two mercurammonium iodides, $HgI_2,2NH_3$ and $3HgI_2,4NH_3$, has been definitely established. Their vapour pressures at a series of temperatures have been measured and the conditions of stability in the dry state and in aqueous solution defined. The reaction between concentrated aqueous ammonia and $HgI_2,2NH_3$ leading to dimercurammonium, Hg_2NI, and $3HgI_2,4NH_3$ leading to $Hg_9N_4I_6$, has been fully investigated and details are given for the preparation of the final products in the pure state. Graphical formulæ for these mercurammonium compounds are described. A. I. Vogel.

Dehydration of kaolin. H. A. J. Pieters.—See B., 1929, 323.

Wöhler's titanium cyanonitride. V. M. Goldschmidt (Nachr. Ges. Wiss. Göttingen, 1927, 390—393; Chem. Zentr., 1928, ii, 1541—1542).—The substance has (E. Brock) a crystal structure analogous to that of sodium chloride. Comparative measurements indicate that it consists of a solid solution of titanium carbide and nitride. A. A. Eldridge.

Compounds of tervalent cerium salts and thorium salts with sodium carbonate (sodium cericarbonate and thoricarbonate). L. Lortie (Compt. rend., 1929, **188**, 915—916).—*Sodium cericarbonate*, $Na_6[Ce(CO_3)_5],12H_2O$, was prepared by gradual addition of a solution of 15 g. of ammonium cerinitrate in 25 c.c. of water to a cold 25% solution of sodium carbonate, the resulting precipitate, probably $CeCO_3(OH)_2$, being filtered. The yellow, prismatic crystals separate after some hours and are filtered and washed in ice water. The salt, which is dehydrated at 200°, is decomposed by water with the formation of the above hydroxycarbonate and by acids with the liberation of carbon dioxide. It is soluble in sodium carbonate solution, gives a blood-red colour with phenolic substances, and is isomorphous with the corresponding thorium salt. Determinations of active oxygen indicate that the cerium is quadrivalent.

J. Grant.

Oxides of nitrogen. F. Raschig and W. Prahl (Z. angew. Chem., 1929, **42**, 253—257).—The evidence for the existence of higher oxides of nitrogen, based on oxidation of stannous chloride, has now been modified by experiments with titanous chloride; the oxidation in this case indicated that no oxide higher than nitrogen peroxide was present, and the phenomena with stannous chloride are attributed to catalytic oxidation by free oxygen in presence of the nitrogen oxides. The dissociation constants of nitrogen peroxide into nitric oxide and oxygen, determined chemically, agree closely with those determined by Bodenstein by physical methods; the apparatus and methods employed are described. By reaction with potassium iodide, it is proved that an equimolecular mixture of nitric oxide and nitrogen peroxide behaves as a mixture, and not as a compound; the peroxide forms potassium nitrite with separation of iodine. S. I. Levy.

Hypophosphoric acid. F. Vogel (Z. angew. Chem., 1929, **42**, 263).—Oxidation of red phosphorus with alkaline permanganate or peroxide yields hypophosphates, the yield being more than 80% on the phosphorus oxidised in the case of peroxide. S. I. Levy.

Preparation of hypophosphoric acid by the action of hypochlorite on red phosphorus. J. Probst (Z. anorg. Chem., 1929, **179**, 155—160).—Red phosphorus is added gradually to a well-stirred solution which is about $0{\cdot}2M$ with regard to alkali and $1{\cdot}5M$ with regard to hypochlorite. The initial temperature should be about 5° and the reaction vessel cooled in ice, when a yield of 25% of the salt $NaHPO_3,3H_2O$, calculated on the phosphorus used, may be obtained. A new method for the determination of the hypophosphate ion is described: silver hypophosphate, quantitatively precipitated from a solution of the sodium hydrogen salt, is washed and dissolved in ammonium hydroxide solution, and the silver is reprecipitated with hydrogen chloride solution. The second precipitation is, when excess of chlorine ion is present, uninfluenced by the presence of hypophosphate ion. H. F. Gillbe.

Sulpho-salts. VII. Polysulphovanadates. L. Fernandes [with C. Orlandi] (Atti R. Accad. Lincei, 1928, [vi], **8**, 234—238).—Polymerisation of normal orthovanadates may occur either as $R_3VS_4 \longrightarrow V_2S_5$ in the presence of a relatively strong acid, or as $R_3VS_4 \longrightarrow RVS_3 \longrightarrow R_4[H_2(VS_3)_6]$ in the presence of hydrogen sulphide. To confirm the latter process the compounds $NH_4VS_3,2H_2O$, $[NH{:}C(NH_2)_2]VS_3,2H_2O$, $(NH_4)_4[H_2(VS_3)_6],18H_2O$, $[NH{:}C(NH_2)_2]_4[H_2(VS_3)_6],18H_2O$, and $Tl_4[H_2(VS_3)_6],18H_2O$ have been prepared. The ammonium salts were obtained by the action of ammonium hydrosulphide and hydrogen sulphide on the orthovanadate, the other compounds being obtained from the corresponding ammonium salts by double decomposition. F. G. Tryhorn.

Reactions in liquid hydrogen sulphide. V. Reaction with furfuraldehyde. R. E. Meints and J. A. Wilkinson (J. Amer. Chem. Soc., 1929, **51**, 803).—A monosulphur *derivative* of furfuraldehyde, $C_4H_3O{\cdot}CHS$, is formed by the spontaneous interaction under pressure of furfuraldehyde and liquid hydrogen sulphide. It forms yellow monoclinic needles, m. p. 95—98°, softening point 80°, soluble in hot ethyl acetate, which are converted in air into a black substance insoluble in liquid hydrogen sulphide. Since furan, furfuryl alcohol, pyromucic acid, and its ethyl and nitroethyl esters do not react analogously with hydrogen sulphide, the sulphur must replace the aldehydic oxygen atom. Aldehydes as a class undergo this substitution when treated with liquid hydrogen sulphide. S. K. Tweedy.

Sulphur. I. System sulphur–chlorine. M. Trautz, H. Acker, (Frl.) L. E. von Broecker, A. Rick, A. Hoffmann, H. Klippel, and O. Loth (Z. Elektrochem., 1929, **35**, 110—132).—Manometric measurements performed on various gaseous equilibria involving sulphur and chlorine at high temperatures indicate that the main reaction is: $S_2Cl_2+Cl_2 \rightleftharpoons 2SCl_2$. Specific heat data show that other polythiochlorides exist in both the gaseous and liquid state, *e.g.*, S_2Cl, S_3Cl_2, and S_4Cl_2. Heats of formation of the various chlorides are given, and equilibrium constants of reactions involving them at various temperatures have been calculated, using Nernst's theorem.

The change in colour, from yellow to red, which occurs when chlorine is passed into sulphur monochloride in the liquid form has been investigated by following changes in colour, in volume, and in the partial pressure of the chlorine in the gaseous phase. Difficulty was experienced in obtaining reproducible results, as the time when the sudden reddening occurred was found to be influenced by several factors, *e.g.*, unless the liquid was "seeded" with sulphur dichloride the colour change did not occur until 3—4 hrs. had elapsed. The absorption of the chlorine by sulphur monochloride is represented by the scheme $S_2Cl_2+Cl_2 \longrightarrow 2SCl_2$, the reaction being very slow except when the sulphur monochloride happens to be in the "active" state, or when a large amount of either sulphur dichloride or sulphur tetrachloride or stannic chloride or iodine has been previously added. The partition coefficients of chlorine between the gas phase and the solution, in both old and freshly-prepared samples of the pure monochloride, have been measured over wide ranges of temperature. Owing to an excess of chlorine being present in the reaction mixture when gaseous chlorine was allowed to act on rhombic sulphur to form sulphur monochloride, it was found necessary to extrapolate the heat of formation, which is given by: $2S$ (rhombic)$+Cl_2$ (gas) $=S_2Cl_2$ (liquid)$+14{\cdot}5\pm0{\cdot}4$ kg.-cal. The heat of dissolution of chlorine in sulphur monochloride was found to be represented by: S_2Cl_2 (liquid)$+Cl_2$ (gas)$=$ $2SCl_2$ (dissolved in S_2Cl_2)$+9{\cdot}8\pm0{\cdot}4$ kg.-cal., whilst $S_2Cl_2+3Cl_2=2SCl_4$ (dissolved in a mixture of S_2Cl_2 and SCl_2)$+12$—14 kg.-cal. Chlorine reacts with sulphur dissolved in sulphur monochloride in accordance with the expression governing the rate of a reaction of the first order. Vapour pressure–temperature curves from 37° to 137° of sulphur monochloride are given, from which a value of 8·5 kg.-cal. for the heat of vaporisation was calculated. By long boiling at temperatures above 100°, but never below 100°, the colour may suddenly become red, through the formation of sulphur dichloride, which is accompanied by a lowering of the b. p. Vapour-pressure curves of sulphur monochloride solutions of sulphur of various concentrations are given, and the possibility of the existence of polythiochlorides is discussed.

The molecular heat of dissolution of sulphur in sulphur monochloride was found to lie between −1·3 and −3 kg.-cal. The specific heats of liquids having widely differing sulphur and chlorine contents were measured, and that of sulphur monochloride is given as 0·22±2·8% at 22°. The sulphur–chlorine system was also studied as regards the composition of the corresponding gaseous and liquid phases, and attempts were made to correlate the vapour pressures with the compositions of the vapours on the supposition that they contained some S_2Cl. Numerous data, referring to the densities and viscosities of sulphur monochloride solutions in which either chlorine or sulphur was dissolved, are recorded. H. T. S. BRITTON.

Action of metals on persulphates. O. ASCHAN [with G. V. PETRELIUS] (Finska Kemistsamf. Medd., 1928, **37**, 40—44; Chem. Zentr., 1928, ii, 1866—1867).—By the action of bivalent metals on cold aqueous solutions of potassium, sodium, or ammonium persulphate, the following double *salts* have been obtained: $M(KO)_2(SO_2{\cdot}O)_2,6H_2O$, where M=Mg, Zn, Cd, Fe^{II}, Ni, or Co; $M(NaO)_2(SO_2{\cdot}O)_2,4H_2O$, where M=Mg, Zn, Cd, or Fe^{II}; $M(NH_4O)_2(SO_2{\cdot}O)_2,6H_2O$, where M=Mg, Zn, Cd, Fe^{II}, Ni, or Co. A. A. ELDRIDGE.

Preparation of stable ammonium molybdate solution. J. P. MEHLIG (Chemist-Analyst, 1928, **17**, No. 4, 6).—A solution of 380 g. of molybdenum trioxide in 550 c.c. of concentrated ammonia solution and 1030 c.c. of water is slowly dropped, through a filter, into 6 litres of 6*N*-nitric acid, which is continuously stirred. CHEMICAL ABSTRACTS.

Oxidations with fluorine. XII. Action of fluorine on nitric acid, perchloric acid, and related compounds. F. FICHTER and E. BRUNNER (Helv. Chim. Acta, 1929, **12**, 305—313; cf. A., 1928, 973).—The action of fluorine on a 10% solution of sodium nitrite is extremely vigorous, but using a 2% solution cooled in ice a solution was obtained which showed the reactions of pernitric acid. Fluorine acts on a dilute solution of nitric acid and gives an appreciable yield of dinitryl peroxide, which is hydrolysed by water in two stages to pernitric acid and hydrogen peroxide. By the action of fluorine on an alkaline solution of potassium chlorate a 25% yield of perchlorate was obtained. With fluorine and an aqueous solution of perchloric acid a solution was obtained which had the characteristic pungent odour of per-acids, liberated iodine from potassium iodide and bromine from potassium bromide, and contained hydrogen peroxide. It is considered probable that the peroxide Cl_2O_8 is first formed, and is then immediately hydrolysed, forming perchloric acid and per-perchloric acid, $HClO_5$, the latter reacting further to form perchloric acid and hydrogen peroxide. O. J. WALKER.

New isomorphous series of fluorine compounds. H. CARON and L. VANBOCKSTAEL (Compt. rend., 1929, **188**, 869—871).—The triple salt $4CaSiF_6,8CaF_2,Al_2(SO_4)_3,45H_2O$ has been prepared by the action of 50 c.c. of hydrofluosilicic acid (*d* 1·075) on 10 c.c. of 10% aluminium sulphate solution, 100 c.c. of 15% calcium chloride solution, and 200 c.c. of alcohol at 60° for 24 hrs. It forms fine octahedra insoluble in alcohol or ether, slightly soluble in water, and easily soluble in warm dilute acids, which lose water and silicon fluoride when heated. Strontium, but not barium, will replace calcium forming an isomorphous salt; iron or chromium will replace aluminium, whilst the sulphur may be replaced by selenium. J. GRANT.

Univalent iron, nickel, and cobalt. V. Formation of nickel carbonyl. W. MANCHOT and H. GALL (Ber., 1929, **62**, [*B*], 678—681; cf. A., 1927, 1157).—Nickel carbonyl is formed when carbon monoxide, saturated with methyl alcohol, is passed over the compound $Ni(NO){\cdot}SEt$ at 100—140°. Preferably, an aqueous solution of nickel sulphate is mixed in an atmosphere of carbon dioxide with potassium hydroxide and ethyl mercaptan; after some time the pressure in the vessel rises owing to the production of nickel carbonyl. The gaseous products are driven successively through an aqueous suspension of mercury acetate and a calcium chloride tube, after which the carbonyl is condensed in acetone–carbon monoxide. The solution is again treated with carbon monoxide and the process repeated. Even better results are obtained by the action of carbon monoxide on nickel sulphate mixed with potassium hydroxide and hydrosulphide. If nickel sulphate is replaced by iron sulphate, the production of small amounts of a volatile iron carbonyl is observed. With cobalt salts a marked absorption of carbon monoxide occurs, but a volatile cobalt carbonyl is not produced; the action may be utilised for the detection of small amounts of nickel in cobalt salts. H. WREN.

Univalent iron, nickel, and cobalt. VI. Compounds of iron, sulphur, and nitric oxide. W. MANCHOT and S. DAVIDSON (Ber., 1929, **62**, [*B*], 681—687; cf. preceding abstract).—A solution of ferrous sulphate in 50% alcohol is saturated with nitric oxide and then treated with potassium xanthate; the brownish-red precipitate, after crystallisation from carbon disulphide, yields almost black crystals of the *compound* $Fe(NO)_2(S{\cdot}CS{\cdot}OEt)_2$, which is readily auto-oxidised in benzene and evolves nitric oxide freely when decomposed with dilute sulphuric acid. The iron therefore appears bivalent.

The assumption of univalent iron, nickel, and cobalt is justified by the following considerations. The arguments on which the bivalency of iron in the xanthate compound is based lead to the hypothesis of the univalent metal in the substances $Fe(NO)_2S{\cdot}R$, $Co(NO)_2S{\cdot}R$, and $Ni(NO)S{\cdot}R$. In these compounds the ability of iron to unite with nitric oxide finds expression. The preparation of these iron, cobalt, and nickel compounds has never been effected from a hyponitrite or a substance, $HS{\cdot}R$. A hyponitrite with tervalent iron should show the instability towards thiosulphate characteristic of ferric salts; actually with potassium thiosulphate the salts $Fe(NO)_2S,SO_3K$ gives an additive compound, $Fe(NO)_2S,SO_3K,K_2S_2O_3$, and analogous compounds, $Co(NO)_2S,SO_3K,K_2S_2O_3$ and $Ni(NO)S,SO_3K,K_2S_2O_3$, have been prepared in well-defined form. The NO group in the sulphur–nitric oxide compounds is characterised as neutral component by direct comparison with hyponitrites, since the former compounds yield nitric oxide with acids, whereas the latter decompose into nitrous oxide and water. The same substance is formed from nitric oxide and the cyanide in which nickel is certainly univalent as from the compounds $Ni(NO)S{\cdot}R$ and potassium cyanide. Equivalent amounts of carbon monoxide and nitric oxide unite with ferrous xanthate. Cobalt and nickel salts with potassium xanthate unite with carbon monoxide and nitric oxide. H. Wren.

Complex oxalates and carbonates of tervalent cobalt. J. Kranig (Ann. Chim., 1929, [x], **11**, 44—103).—The following new complex *compounds* are described: $CoK[Co(NH_3)_2(NO_2)_2C_2O_4]_3,9H_2O$; $Ba[Co(NH_3)_2(C_2O_4)_2]_2,4H_2O$; $Co[Co(NH_3)_2(C_2O_4)_2]_2,7H_2O$; $H[Co(NH_3)_2(C_2O_4)_2],2H_2O$; $Ag_5K[Co(C_2O_4)_3]_2,6—8H_2O$; $PbK[Co(C_2O_4)_3]$; $K[Co(C_2O_4)_3][Co(NH_3)_4C_2O_4]_2,7H_2O$; $K[Co(C_2O_4)_3]_2[Co(NH_3)_4C_2O_4]_5,9H_2O$; $K[Co(C_2O_4)_3][Co(NH_3)_5OH],6H_2O$; $[Co(NH_3)_2(NO_2)_4]_2[Co(NH_3)_5OH],2H_2O$; $K[Co(C_2O_4)_3][Co(NH_3)_4CO_3]_2,4{\cdot}5H_2O$; $[Co(NH_3)_{10}CO_3](SO_4)_2,4H_2O$; $[Co(NH_3)_5CO_3]Cl,H_2O$; $[Co(NH_3)_5CO_3]C_2O_4,3H_2O$; $[Co(NH_3)_2(C_2O_4)_2]_3[Co(NH_3)_6],5H_2O$. New methods of preparation are given for the following compounds: $K[Co(NH_3)_2(NO_2)_2C_2O_4],1{\cdot}5H_2O$; $[Co(NH_3)_5CO_3]Br,H_2O$; $[Co(NH_3)_4C_2O_4]_2C_2O_4,CoC_2O_4,5H_2O$; cobalt oxalate. A new hexamminocobalt trioxalatocobaltiate, $[Co(C_2O_4)_3][Co(NH_3)_6]$, was isolated. The absorption spectra in 0·02*N*-solutions of the following compounds have been studied: $[Co(NH_3)_6]Cl_3$; $[Co(NH_3)_4C_2O_4]Cl$; $NH_4[Co(NH_3)_2(C_2O_4)_2]$; $K_3[Co(C_2O_4)_3]$; $[Co(NH_3)_2(C_2O_4)_2]_3[Co(NH_3)_6],5H_2O$ and $[Co(NH_3)_2(C_2O_4)_2][Co(NH_3)_4C_2O_4],2H_2O$. The conductivities of aqueous solutions of the two last-named compounds were measured. A. I. Vogel.

Ruthenium. H. Remy (Z. angew. Chem., 1929, **42**, 289—290, 291). H. Gall (*ibid.*, 290—291).—Polemical. A discussion of the valency of ruthenium in the blue chloride solution and in solutions obtained by treating the tetroxide with hydrochloric acid (cf. Remy, this vol., 283). A. R. Powell.

Displacement of metals and their oxides by hydrogen under pressure at high temperatures. Action of hydrogen at high temperatures and pressures on solutions of ruthenium salts. V. N. Ipatiev and O. E. Zvjaginstsev (Ber., 1929, **62**, [*B*], 708—710).—The ruthenium compounds investigated were $(NH_4)_2RuCl_5$, K_2RuCl_5, Na_2RuCl_5, and $H_2Ru(OH)_2Cl_4$ in dilute aqueous solution acidified with hydrochloric acid. The same products are derived from all the salts. At 25° and 50 atm., reduction occurs slowly with decolorisation of the solution and formation of a slimy, black precipitate of ruthenium hydroxide which is gradually redissolved under atmospheric pressure. At 85°/65 atm., ruthenium hydroxide is formed as a heavy, black precipitate. At 160°/80 atm., a non-homogeneous precipitate of ruthenium oxide and hydroxide is produced. At 350°/125 atm., ruthenium, mixed with a small proportion of the oxide, is formed. H. Wren.

Iridium fluorides. O. Ruff and J. Fischer (Z. anorg. Chem., 1929, **179**, 161—185).—Fluorine reacts with powdered iridium at 260° with the production solely of the hexafluoride, a yellow, vitreous substance which melts at 44° to a brownish-yellow liquid. After being kept at the ordinary temperature for some months crystal formation is evident, whilst at $-150°$ *X*-ray investigation indicates a tetragonal structure. Approximate values of the density, b. p., heat of vaporisation, and heat of formation are 6·0, 53, 8·5, and 130 kg.-cal., respectively. Iridium hexafluoride is very volatile and highly reactive. Traces of moisture bring about decomposition. In air the substance volatilises completely on account of its high vapour pressure, and fumes are produced of hydrogen fluoride, iridium oxyfluoride, and ultimately lower fluorides. With an excess of water a violet to red colloidal solution of iridium tetrahydroxide is formed. Complex formation has not been observed. If iridium hexafluoride is prepared in glass vessels a greyish substance is formed simultaneously which is probably the oxyfluoride $IrOF_4$; in quartz vessels the oxyfluoride is stable at the ordinary temperature, but when gently heated or kept in glass vessels iridium oxide is produced. Iridium tetrafluoride may be prepared simply by heating powdered iridium with the hexafluoride at 150°. Continued heating removes the excess of hexafluoride, leaving the difficultly volatile tetrafluoride as a brown oil which is easily decomposed by water and, when moderately heated, decomposes with the production of a black, metallic substance. Similar black substances, obtained by reduction of the hexafluoride with excess of iridium, are of indefinite composition and insoluble in water, and are converted into the tetrafluoride when heated in an atmosphere of iridium hexafluoride. They probably consist of a mixture of lower fluorides. H. F. Gillbe.

Physical and chemical properties of the platinocyanides. I. Hydrates of lithium platinocyanide. F. E. E. Germann and O. B. Muench (J. Physical Chem., 1929, **33**, 415—423).—Pure lithium platinocyanide has been prepared from lithium sulphate and barium platinocyanide; its hydrates have been studied by means of the vapour-pressure method previously described (A., 1928, 1203). The tetrahydrate crystallises from aqueous solutions as needles of a grass-green colour, and the equilibrium pressure of the system tetrahydrate–saturated solution at 25° is 14·14 mm. The anhydrous salt is formed at 25° over concentrated sulphuric acid or when the pressure of water vapour is less than 1·02 mm.; it is canary-yellow in colour. Exposure to a pressure of water vapour greater than 1·02 mm. at 25° yields a tan-coloured tetrahydrate. A black modification results, in turn, from this hydrate by exposure to bright sunlight, ultra-violet light, or to water vapour at low pressures above 10·2 mm. At high pressures, light brings about no change. Hydrogen and cyanide ions catalyse the change. The tetrahydrate is the only hydrate which exists. Previous work is summarised and discussed.

L. S. Theobald.

Spectrographic chemical analysis. H. Ramage (Nature, 1929, **123**, 601—602).—By a modification of the method of Hartley and Ramage (J.C.S., 1897, **71**, 583, etc.) whereby the poles of an arc are placed horizontally in the flame above the burning filter-paper containing the material under examination, the delicacy and applicability of the test are increased. Rubidium is widely distributed in soils and in plants, and is particularly concentrated at the growing point; it is also present in most parts of the body, and in human and cow's milk. A. A. Eldridge.

Physical methods in the chemical laboratory. IX. Use of radio-elements as indicators. F. Paneth (Z. angew. Chem., 1929, **42**, 189—192).—A radioactive element when added to its more stable isotope causes no change in chemical properties, and by its radioactivity may be used as a very delicate means of detecting and determining small quantities of the element in question. A number of examples of the application of the method are described.

F. R. Ennos.

Thermometric titration methods. C. Mayr and J. Fisch (Z. anal. Chem., 1929, **76**, 418—438).—By conducting various titrations in small Dewar flasks provided with stirring apparatus and a Beckmann thermometer it is possible to determine the end-point by plotting the temperature against the c.c. of standard solution added; two straight lines are obtained the intersection of which occurs at the end-point. In this way sulphate may be determined by titration with barium chloride, chloride with silver nitrate, calcium, strontium (but not barium), mercurous, and mercuric nitrates with ammonium oxalate, lead with oxalic acid in acetate solution, arsenious acid with potassium bromate, sodium hypochlorite with arsenious acid, and potassium ferrocyanide, hydrogen peroxide, oxalic acid, and ferrous sulphate with potassium permanganate. A. R. Powell.

Glass electrode; its use in determining p_H. A. E. Mirsky and M. L. Anson (J. Biol. Chem., 1929, **81**, 581—587).—A modification of the arrangement of Kerridge (A., 1925, i, 1201) is described.

C. R. Harington.

Effect of the method of preparation of quinhydrone on its value for analytical work. M. Trénel and C. Bischoff (Z. angew. Chem., 1929, **42**, 288—289).—The low p_H value of solutions of some samples of quinhydrone is shown to be due to the presence of iron salts. The following method of preparation is recommended: a solution of 115 g. of iron ammonium alum in 230 c.c. of water at 50° is poured into a solution of 25 g. of quinol in 100 c.c. of water at 60°, the solution is cooled in ice and the precipitate collected, washed seven times with ice-cold water, and recrystallised from water at 80°.

A. R. Powell.

Tödt's simplified electrodes for the electrometric measurement of p_H. L. Köhler (Chem.-Ztg., 1929, **53**, 69—70).—Combined calomel–quinhydrone and calomel–hydrogen electrodes, from which rapid readings may be obtained directly by means of tables supplied with the apparatus, are described. A micro-form of the former is also available.

S. I. Levy.

Comparator for the colorimetric determination of the hydrogen-ion concentrations of coloured solutions. D. McCandlish and G. Hagues.—See B., 1929, 229.

Ultra-violet light in quantitative chemical examination. J. Eisenbrand (Pharm. Ztg., 1929, **74**, 249—252).—Simple substances which show fluorescence in ultra-violet light sometimes show sufficient change in this property under the influence of variations in hydrogen-ion concentration. Both α- and β-naphthol show marked fluorescence in alkaline solutions, but are colourless in acid solutions; the transitions are extremely sharp, and very suitable for acid–alkali titrations. Quinine shows two sharp colour changes (p_H 6 and 9·5) and can be used for titration of strong and weak bases; it is suggested as a universal indicator in ultra-violet light. The changes in fluorescence may also be of use in determinations of dissociation constants. S. I. Levy.

Potential gradient in titrations with acid and alkali and determination of reaction constants. F. L. Hahn (Ber., 1929, **62**, [*B*], 727—736).—Mainly a theoretical paper in which precipitation analyses, titration of mono- and di-basic acids with alkali and ampholytes are considered. The possible accuracy and limits of applicability are discussed in detail. Measurements of the titration of pyridine with hydrochloric acid are cited. The original should be consulted for details. H. Wren.

Determination of water by distillation with hydrocarbons. W. Boller (Chem.-Ztg., 1928, **52**, 721; 1929, **53**, 70).—An apparatus which avoids the difficulty due to adhering droplets of water is described. The vertical reflux condenser is drawn out into a capillary, which reaches to the bottom of the receiver, supported in the neck of the distillation flask, and vacuum-jacketed to prevent redistillation of the condensate by the ascending vapour. The calibrated receiver of the earlier form is later replaced by a detachable measuring vessel held in place by a spring.

S. I. Levy.

Determination of halogen by Gasparini's method. K. Heller (Z. anal. Chem., 1929, **76**, 408—418).—Electrolytic oxidation of organic compounds containing bromine or iodine in concentrated nitric acid containing silver nitrate results in conversion of part of the halogen into silver halide and part into the corresponding halate, whilst some is sublimed in the elementary state. If the electrolysis is conducted in Gasparini's apparatus (cf. A., 1907, ii, 650) absorption bulbs should be provided to collect any bromine or iodine which may distil. After electrolysis for 4 hrs. the contents of the apparatus are treated with sodium sulphite to convert all the halogen into halide, hydrogen peroxide is added to oxidise the excess of sulphite, and the silver halide is collected and weighed or the excess of silver in the filtrate may be determined by Volhard's method. A. R. Powell.

Determination of iodine in urine. H. Bernhardt.—See this vol., 593.

Determination of sulphate in fluorides especially in cryolite. H. Ginsberg [in part with G. Holder] (Z. angew. Chem., 1929, **42**, 314—317).—Digestion of the powdered substance with 10% sodium carbonate solution does not render all the sulphate soluble when aluminium fluoride is present. Methods involving dissolution of the mineral in acids, with or without a previous treatment with alkali, removal of the alumina with ammonia, and precipitation of the sulphate in the usual way usually yield high results, as small amounts of aluminium fluoride escape precipitation with ammonia and subsequently contaminate the barium sulphate precipitate. Ignition of a mixture of the fluoride and zinc dust in hydrogen followed by determination of the sulphide formed by the evolution method gives good results and is the most rapid method available. Good results are also obtained by fusion with sodium carbonate, separation of the alumina with ammonia, expulsion of the fluorine by evaporation with hydrochloric acid and silica, and precipitation of the sulphate with barium chloride.

A. R. Powell.

Determination of fluosilicate and fluorine ions. E. Bayle and L. Amy (Compt. rend., 1929, **188**, 792—794).—The hydrofluosilicic acid is precipitated by addition of a few c.c. of ether and equal volumes of an excess of potassium chloride solution and 95% alcohol, the solution is neutralised to phenolphthalein with potassium hydroxide and heated on the water-bath with a few c.c. of 10% calcium chloride solution. The fluosilicate formed according to the equation $H_2SiF_6+2KOH=K_2SiF_6+2H_2O$ dissolves, and the colour is restored to the phenolphthalein by the addition of a measured amount of standard potassium hydroxide solution, $K_2SiF_6+4KOH=Si(OH)_4+6KF$. Fluorides are heated in a 100 c.c. pyrex flask with a little silica and 10—20 c.c. of sulphuric acid (*d* 1·842) for several hours at 160° in a current of dry air, and the silicon fluoride produced is collected in distilled water and determined as hydrofluosilicic acid in the same way.

J. Grant.

Determination of ozone in air. M. S. Egorov.—See B., 1929, 282.

Automatic apparatus for determination of small concentrations of sulphur dioxide in air. II. M. D. Thomas and J. N. Abersold.—See B., 1929, 282.

Rapid volumetric determination of the sulphate content of drinking water by visual conductometric titration. H. Fehn, G. Jander, and O. Pfundt.—See B., 1929, 342.

Detection of sulphides and thiosulphates by the iodine–sodium azide reaction. L. Metz (Z. anal. Chem., 1929, **76**, 347—348).—Thiosulphates, soluble and insoluble sulphides, tri-, tetra-, and pentathionates, but not dithionates or sulphites, catalyse the reaction between iodine and sodium azide (cf. Feigl, A., 1928, 1106).

A. R. Powell.

Hydrogen peroxide as oxidation catalyst in the determination of nitrogen by Kjeldahl's method. E. Gubarev (J. exp. Biol. Med. [Russia], 1927, 261—266; Chem. Zentr., 1928, ii, 1916).—Hydrogen peroxide is added after the substance has been heated for 10 min. with concentrated sulphuric acid.

A. A. Eldridge.

Quantitative analysis of phosphoric acid. I. Determination as magnesium pyrophosphate. II. Gravimetric and volumetric methods. III. Determination as zinc ammonium phosphate. M. Ishibashi (Mem. Coll. Sci. Kyōto, 1929, **A**, **12**, 23—38, 39—47, 49—56).—I. In the gravimetric determination of phosphate by precipitation as magnesium ammonium phosphate, the magnesia mixture should be adjusted to a p_H of 5—6. The molecular ratio of ammonium chloride to magnesium chloride should be 5—15 : 1, and the ratio of magnesium chloride to phosphoric acid 1·3—10·5 : 1. If the p_H of the phosphate solution is 4·4—8·3, and the precipitation is effected below 35°, the precipitate will settle satisfactorily in 30 min. Sodium acetate, potassium chloride, and ammonium and sodium sulphates interfere.

II. The spontaneous oxidation of manganous ammonium phosphate in alkaline solution may be prevented by addition of hydroxylamine, so that it becomes possible to determine phosphate by precipitation as the double phosphate and weighing as pyrophosphate after ignition. Excess of a solution containing ammonium chloride and manganous chloride in the molecular ratio of 75—125 : 1 and a little hydroxylamine hydrochloride are added to the phosphate solution, which must be not too dilute and of such acidity that only a very slight precipitate results. The solution is then heated nearly at the b. p., precipitated by addition of ammonia, and filtered after 2 hrs. Ammonium citrate, tartrate, and oxalate interfere, and if ammonium molybdate is present it is necessary to precipitate from a strongly ammoniacal solution, then dissolve in acid and reprecipitate. The double phosphate may also be dissolved in acid and titrated with permanganate at 80—90°, the end-point being reached when the colour of the solution does not change for 2—3 min.; 2 g. of sodium acetate must be added for each 10 c.c. of 0·1*N*-permanganate.

III. Phosphate may also be determined by precipitating as zinc ammonium phosphate, igniting, and weighing as pyrophosphate. Excess of a solution containing ammonium chloride and magnesium chloride in the molecular ratio of 50—100 : 1, and 2·0—3·6*N* in respect of the former chloride, is added to the phosphate solution, the acidity of the mixture being so regulated that very little precipitation occurs. The solution is then heated nearly at the b. p., and ammonia slowly added until precipitation is complete, the p_H being kept at 5—6·5 during this process. Ammonium molybdate interferes. Instead of the precipitate being ignited, it may be converted into zinc oxalate by treatment with oxalic acid, and titrated with permanganate.

R. Cuthill.

Determination of borate in natural waters. M. D. Foster.—See B., 1929, 304.

Determination of silicon in ferrosilicon and in other iron alloys. A. Stadeler.—See B., 1929, 326.

Determination of small amounts of silica in orthophosphoric acid. P. Albrecht.—See B., 1929, 281.

Determination of carbon. D. Strohal.—See this vol., 586.

Mercurimetry. E. Votoček and J. Kotrba (J. Czechoslov. Chem. Comm., 1929, **1**, 165—172).—In the authors' mercurimetric method for the determination of cyanide (A., 1921, ii, 238, 272) the action of mercuric cyanide on mercuric nitrate is found to be negligible, and a comparison of the method with gravimetric determinations shows that it is accurate to ±0·25%. The Liebig–Denigès silver method gives results 0·8% low. The application of the method to the determination of chloride and cyanide in the presence of each other by removal of the cyanide with formaldehyde (which itself has no effect on the titration) is described. If at least five times the theoretical quantity of formaldehyde is used removal of the cyanide, as glycollonitrile, is quantitative and rapid (15 min. being allowed for safety) and the chloride is then determined mercurimetrically. Similar titration without the addition of formaldehyde determines the chloride and cyanide present, the latter being then obtained by difference. Alternatively, the cyanide may be determined by the silver method, providing a suitable correction is applied. Determination of alkali nitroprussides may also be effected by precipitation, from the solution acidified with nitric acid, with mercuric nitrate, filtering (with addition of a little infusorial earth) and washing (with water acidified with nitric acid) the precipitated mercuric nitroprusside, dissolving it in a known volume of 0·1N-sodium chloride solution, filtering, making up to 200 c.c., and titrating with 0·1N-mercuric nitrate. The method is not affected by the presence of cyanides, chlorides, and sulphates.

J. W. Baker.

Mixed bromides in place of chlorides in alkali determinations. E. Spencer and K. B. Sen (Analyst, 1929, **54**, 224—226).—If ammonium bromide and hydrobromic acid be substituted for ammonium chloride and hydrochloric acid respectively in the Lawrence Smith method (Amer. J. Sci., 1871, **50**, 269) for determining potassium and sodium in rocks and similar materials, the resulting mixed bromides are purer, less fusible, and less volatile than the mixed chlorides. In Berzelius' method (Pogg. Ann., 1824, **1**, 169) barium bromide may be advantageously substituted for barium chloride for converting the alkali sulphates, and since the alkali platinibromides may be completely separated by 90% ethyl alcohol the above substitution still allows of the determination of potassium, but as platinibromide.

D. G. Hewer.

Separation of calcium and magnesium by the oxalate method. O. Røer (Tidsskr. Kjemi Berg., 1929, **9**, 27—28; cf. Luff, A., 1925, ii, 438).—The usual method of precipitation with a large excess of ammonium oxalate in boiling solution gives a precipitate of calcium oxalate contaminated with magnesium salt. It is claimed that a perfect separation can be effected by a single precipitation according to the following methods, which are based on the stability of a supersaturated solution of magnesium oxalate at 70°. If up to 0·3 g. of lime is present, the feebly ammoniacal solution (containing ammonium chloride and having a volume of 200 c.c. for each 0·25 g. of magnesia present) is heated to boiling and 0·5N-ammonium oxalate solution added from a burette until no further precipitate forms. The solution is then cooled to 70° and an additional 4 c.c. of 0·5N-ammonium oxalate per 100 c.c. of solution are added. With quantities of lime from 0·3 to 0·7 g. the liquid is neutralised with concentrated hydrochloric acid, and 2 c.c. in excess are added. After heating to boiling, a solution of N-oxalic acid in N-hydrochloric acid is added in quantity just equivalent to the lime present. The solution is neutralised with dilute ammonia, added drop by drop, cooled to 70°, and 4 c.c. of 0·5N-ammonium oxalate solution per 100 c.c. of liquid are added as in the previous method. For the determination of magnesia in limestones where very small amounts are present, it is recommended to effect a preliminary concentration of this constituent by boiling a solution of 10 g. of the limestone with 0·2 g. of pure lime, after previous neutralisation with sodium hydroxide. The precipitate, containing the whole of the magnesia together with alumina, ferric oxide, etc., is redissolved and the magnesia in it determined in the usual way.

H. F. Harwood.

Analysis of metals and ores by heating in a current of chlorine. R. Wasmuht.—See B., 1929, 328.

Spectrographic detection of beryllium. H. Fesefeldt (Z. physikal. Chem., 1929, **140**, 254—262).—The beryllium lines given by mixtures of beryllium and aluminium oxides in the carbon arc have been measured. The most sensitive lines are 2348·62, 3130·42, and 3131·06 Å. These lines are obtained with a mixture containing only 0·0001% of beryllium oxide. The influence of adding impurities on the sensitiveness has been investigated. Addition of ferric oxide or a mixture of silica and sodium carbonate has no effect, but sodium carbonate alone or calcium oxide lowers the sensitiveness considerably.

R. N. Kerr.

Detection of magnesium by means of dyes. E. Eegriwe (Z. anal. Chem., 1929, **76**, 354—359).—In the presence of excess of alkali hydroxide magnesium solutions give characteristic colours or, with larger quantities, precipitates with dilute solutions of certain disazo dyes. In the absence of nickel or cobalt the reactions are specific for magnesium and will detect 0·001 mg./c.c. In the presence of chromium the best results are obtained with diamine-blue FF, Chicago-blue 6B, and benzopurpurin 4B.

A. R. Powell.

Quantitative emission spectrum analysis. II. Determination of zinc in solution and of molybdenum in steel by the comparison method. H. Thurnwald (Z. anal. Chem., 1929, **76**, 335—347).—The intensity of the zinc line λ 3345 Å. is compared with that of the silver line λ 3383 Å. in solutions of known silver concentration. The intensities are equal when the zinc solution contains twenty times as much zinc as there is silver in the standard silver solution. For the determination of molybdenum in steel the alkaline molybdate obtained from the steel in the usual way is spectrographed and the intensity of the molybdenum line λ 2816 Å. is compared with that of the lead line λ 2832 Å. obtained with standard lead nitrate solutions; the intensities of these lines are equal when the same concentration of metal is present in each solution.

A. R. Powell.

Analysis by electrolysis with a mercury cathode. W. Moldenhauer [with K. F. A. Ewald and O. Roth] (Z. angew. Chem., 1929, 42, 331—334).—A mercury cathode is conveniently contained in a glass spoon with platinum connexion immersed in the beaker in which electrolysis is carried out. Examples are given of its use in the determination of lead in nitric acid solution, of silver, nickel, and zinc in ammoniacal solution, and of silver in cyanide solution. Separations carried out by varying the *P.D.* include silver and copper or silver and lead in nitric acid solution, copper and nickel in sulphuric acid. Other separations are effected by precipitating one or other metal, *e.g.*, lead as sulphate, and then electrolysing. The use of a mercury electrode makes possible the separation of chromium and other metals which do not form a coherent deposit on platinum, and also the alkali and alkaline-earth metals. It is not suitable for platinum and its allies, antimony, or arsenic. C. Irwin.

Electrometric determination of small quantities of lead ion. H. Millet (Trans. Faraday Soc., 1929, 25, 147—152).—Electromotive measurements at 25° of the cell $\mathrm{Pb}|\mathrm{Pb(NO_3)_2}|$saturated $\mathrm{KCl}|N$-calomel electrode have shown that the lead ion may be determined in concentrations of at least $10^{-8}M$ in solutions as strongly acid as $0{\cdot}1N$-hydrochloric acid. A lead-coated platinum electrode serves for neutral solutions, but in the presence of acid a liquid amalgam is prepared by heating the pure metals in an atmosphere of nitrogen, and oxygen is excluded throughout the determination. The modified Debye–Hückel formula (A., 1923, ii, 724), $-\log \gamma_{\mathrm{Pb}''} = 0{\cdot}48n^2\mu^{\frac{1}{2}}$, is suggested. J. Grant.

Determination of small quantities of mercury in presence of organic and inorganic compounds. R. Robinson (Analyst, 1929, 54, 145—152).—In the presence of impurities such as copper, iron, zinc, sodium, and potassium, mercury may be determined by precipitation with hypophosphorous acid and the use of standard iodine solution. The mercury solution is diluted to 200 c.c. and the acidity adjusted with hydrochloric acid so that an excess of 5 c.c. of $2N$-hydrochloric acid is present. Two g. of sodium chloride are added and 0·01 g. of paper pulp, followed by 30 c.c. of hypophosphorous acid (*d* 1·137), and the mixture is left over-night. After heating for 15 min., keeping for 20 min., and filtering by suction through a paper-pulp filter, the flask and filter are thoroughly washed, and 100 c.c. of water and 2 c.c. of 30% acetic acid are added to the pulp and mercury, followed by excess of $0{\cdot}01N$-iodine solution and 2 g. of potassium iodide. After keeping, $0{\cdot}01N$-sodium thiosulphate is added in excess and titrated with $0{\cdot}01N$ iodine solution. A blank determination is necessary. The results are 0·3 mg. too low on the average, due to volatility of the mercury. The effects of excess of hydrochloric acid, different times of heating, and keeping after heating are discussed. Iron causes low results unless sodium chloride is present; copper does not affect the results unless too small an excess of hypophosphorous acid has been used. When organic compounds are present these may usually be satisfactorily destroyed by heating in a sealed tube at 180° with fuming nitric acid, but where a small amount of sample is available 0·2—0·5 g. may be placed in a Kjeldahl flask connected with two wash-bottles and heated in a paraffin-bath at 130—150° with 10 c.c. of concentrated sulphuric acid with occasional addition of a crystal of potassium nitrate. The contents of the wash-bottles are added to the bulk, the solution is filtered, the filtrate neutralised below 50° with sodium hydroxide and rendered acid, and the original method employed. D. G. Hewer.

Determination of minute amounts of mercury. R. Thilenius and R. Winzer (Z. angew. Chem., 1929, 42, 284—288).—Stock's method (A., 1926, 814) is modified in that the mercury is collected on a gold wire or thin copper strip which is then heated in chlorine in a closed capillary tube at 250° for 2—3 hrs. The resulting mercuric chloride is dissolved in water, the solution treated with alcoholic diphenylcarbazone, and the blue colour compared with that produced by a standard mercuric chloride solution, using a 5% solution of potassium dichromate in a 1 cm. layer as a light filter. The dry chlorination is preferable to the treatment with chlorine water recommended by Stock, as it yields a neutral solution of mercuric chloride which gives the maximum intensity of colour with the reagent without further treatment. A. R. Powell.

Oxidation of mercuric cyanide by sodium hypobromite. Application to the determination of cyanide and oxycyanide of mercury. J. Golse (Bull. Soc. chim., 1929, [iv], 45, 177—183).—Quantitative oxidation of mercuric cyanide occurs in solution on the addition of alkaline sodium hypobromite solution according to the equation $\mathrm{Hg(CN)_2 + 2NaBrO + 2NaOH = HgO + 2NaCNO + 2NaBr + H_2O}$. The primary reaction is the oxidation of the cyanide to mercuric cyanate, which reacts with the free alkali to give mercuric oxide. The technique of the determination consists essentially in the addition of excess of a standard hypobromite solution, the portion remaining unchanged after oxidation of the cyanide being determined by titration with sodium thiosulphate solution, following the addition of excess of potassium iodide. The same reaction may be used for the determination of mercury; in this case the excess of hypobromite solution is decomposed by the addition of ammonia solution, the precipitated mercuric oxide dissolved in an excess of standard potassium cyanide solution, and the excess of the latter determined by titration with silver nitrate. F. G. Tryhorn.

Detection of aluminium by dye reagents. E. Eegriwe (Z. anal. Chem., 1929, 76, 438—443).—The chloride solution is treated with one drop of a 0·1% solution of "eriochromcyanin R conc.," rendered just alkaline with $2N$-sodium hydroxide solution, and reacidified with $0{\cdot}2N$-acetic acid added drop by drop until the colour changes to yellow, then, if aluminium is present, to an intense violet-rose; 0·0005 mg. of aluminium in 2 c.c. of solution produces a distinct colour. The morin test is rendered more sensitive by proceeding as follows: 1—2 drops of the chloride solution are treated with 0·1—0·2 c.c. of a cold saturated solution of morin in methyl alcohol and the mixture is saturated with sodium acetate; a green fluorescence appears if the test solution contains more than 0·0003 mg. of aluminium in 0·5 c.c. These tests are almost as sensitive as the alizarin S and alizarin-red PS tests and are not affected by the presence of 0·1 mg. of cobalt, nickel, zinc, manganese, and chromium. A. R. POWELL.

Determination of aluminium in steel. A. T. ETHERIDGE.—See B., 1929, 326.

Determination of manganese in water. J. DE GRAAF.—See B., 1929, 266.

Determination of iron and aluminium oxides, magnesium oxide, and calcium oxide in Portland cement. J. S. PIERCE and W. C. SETZER.—See B., 1929, 284.

Rapid determination of iron and uranium. G. SCAGLIARINI and P. PRATESI (Annali Chim. Appl., 1929, **19**, 85—90).—Ferric iron is reduced rapidly and quantitatively to the ferrous state by metallic copper in presence of sulphuric acid at the b. p. of the solution, no cuprous salt being formed, so that the iron may be subsequently determined by titration with permanganate solution. The liquid must be free from nitric and hydrochloric acids, and the copper is most conveniently used as a coil of fine electrolytic wire attached to a glass rod passing through a stopper so that it may be raised from the solution. The stopper is provided also with a Bunsen valve, and collapse of the flask by condensation of the steam is prevented by adding to the hot liquid a few crystals of pure sodium carbonate. The results are not affected by the presence of titanium, chromium, manganese, aluminium, or nickel. Uranyl compounds are similarly reduced to salts of quadrivalent uranium, which may be determined by re-oxidation with permanganate. Since ferric salts but not uranyl salts are reduced by hydrogen sulphide, it becomes possible to determine both uranium and iron in their mixtures. T. H. POPE.

Fixation of phosphoric acid by ferric hydroxide in presence of varying amounts of ammonia. E. ANGELESCU and C. BĂLĂNESCU (Kolloid-Z., 1929, **47**, 207—221).—The complete simultaneous precipitation of iron and phosphoric acid is possible only when the ratio of iron to phosphorus is greater than 2 and at a p_H below 7. In acid solution, neither the temperature nor the nature of the anion has any effect. In alkaline solution, the phosphoric acid is incompletely retained by the ferric hydroxide, the amount of phosphoric acid going into solution depending on the ratio of iron to phosphorus and on the initial concentrations. The composition of the precipitate varies with the concentration of the ammonia and with the original iron to phosphorus ratio. In acid solution, various basic phosphates of definite chemical composition are formed, whilst in alkaline solution the fixation of the phosphoric acid proceeds in accordance with the adsorption equation. Two peptisation regions were observed, one in acid solutions at high iron to phosphorus ratios and the other in alkaline solutions at low iron to phosphorus ratios. The phenomena can be explained on the basis of a surface dissociation of the ferric hydroxide, which is influenced by the hydrogen-ion concentration. The results of the investigation are applied to the determination of phosphoric acid, and a method is given for the determination of the oxides of iron, aluminium, and phosphorus in soils. E. S. HEDGES.

Quantitative separation of nickel and calcium. G. W. KÜHL (Chem.-Ztg., 1929, **53**, 279).—Calcium is precipitated as oxalate from boiling ammoniacal solutions containing ammonium chloride and nickel determined in the filtrate as the dimethylglyoxime compound. J. S. CARTER.

Determination of chromium, tungsten, molybdenum, vanadium, nickel, manganese, and cobalt in high-alloy steels. H. MENDE.—See B., 1929, 326.

Determination of molybdenum in steel in presence of tungsten and vanadium. I. KASSLER.—See B., 1929, 249.

Rapid determination of tin in tinplate. W. A. MASEL.—See B., 1929, 286.

Detection of small amounts of vanadium. A. FÖLSNER (Chem.-Ztg., 1929, **53**, 259).—The turbidity given by solutions of lead acetate is a much more sensitive reaction than the hydrogen peroxide test for the detection of vanadium. J. S. CARTER.

Detection of vanadium and cerium by hydrogen peroxide. J. LUKAS and A. JÍLEK (Z. anal. Chem., 1929, **76**, 348—351).—In the colorimetric detection of vanadium by hydrogen peroxide, addition of oxalic acid to the sulphuric acid solution prevents bleaching by excess of hydrogen peroxide (cf. Meyer and Pawletta, A., 1926, 1020). The colour due to molybdenum in this test is bleached entirely by addition of boric acid, which does not affect the vanadium colour. Neutral cerous salt solutions are coloured yellow to orange by addition of quinine hydrochloride and hydrogen peroxide. Titanium and salts of metals which are readily hydrolysed interfere. A. R. POWELL.

Evaluation of stibnite. I. Determination of sulphur. W. M. MCNABB and E. C. WAGNER.—See B., 1929, 286.

Detection of gold and platinum metals [in ores]. SPORCQ.—See B., 1929, 286.

Potentiometric determination of gold and platinum with stannous chloride. E. MÜLLER and R. BENNEWITZ (Z. anorg. Chem., 1929, **179**, 113—124).—The gold is oxidised to the tervalent state by addition of chlorine water until the potential of the indicator electrode is about 1 volt, and the solution is then titrated with stannous chloride; the first break corresponds with the completion of the reaction $Cl_2+Sn^{\cdot\cdot}\longrightarrow 2Cl'+Sn^{\cdot\cdot\cdot\cdot}$, and the second with that of the reaction $2Au^{\cdot\cdot\cdot}+3Sn^{\cdot\cdot}\longrightarrow 2Au+3Sn^{\cdot\cdot\cdot\cdot}$. Platinum may be determined by oxidation to the tervalent state with potassium bromate solution and titration with stannous chloride at 75°; a break occurs when the platinum is reduced to the bivalent state, but no evidence is obtained of a second break such as would be expected if complete reduction to metal occurred; a complex ion is probably formed. If both gold and platinum are present a break occurs only after both metals have been reduced, and for a constant total quantity of gold and platinum the position of the break varies with the ratio between the two metals. H. F. GILLBE.

Modified Pirani gauge for use in corrosive systems. G. K. ROLLEFSON (J. Amer. Chem. Soc., 1929, **51**, 804).—A mercury thread contained in a thin-walled glass capillary is used as the hot filament in the gauge. It is then preferable to use the gauge by measuring the current necessary to keep the temperature of the mercury thread constant. The modified gauge responds to pressure change very rapidly. S. K. TWEEDY.

Sensitive form of Pirani gauge for the measurement of high vacua. L. F. STANLEY (Proc. Physical Soc., 1929, **41**, 194—203).—In a study of the factors affecting the sensitivity of the gauge it was found that the diameter of the manometer is without influence; rise in the temperature of the filament gives greater sensitivity up to about 100°, after which errors are introduced. The most important factor is the temperature of the walls of the manometer; the lower this temperature the more sensitive is the instrument. The construction of a manometer is described in which the length of the loop is 10 cm., the error due to loss of heat by conduction along the leads being minimised by the introduction of a 2 cm. subsidiary loop in both the manometer and the compensator. This gauge was used in conjunction with a Callendar–Griffiths bridge and was capable of measuring pressures between 2×10^{-3} and 4×10^{-6} mm. The accuracy of different forms of the McLeod gauge is discusssed. J. L. BUCHAN.

Laboratory apparatus for producing homogeneity. G. FRANK (Chem.-Ztg., 1929, **53**, 259).—A helical stirrer operates in the vertical portion of a b-shaped vessel. The neck of the apparatus may be closed by a liquid seal. The apparatus is especially designed for producing homogeneity in small quantities of viscid liquids. J. S. CARTER.

Reaction tube. C. DHÉRE (Bull. Soc. chim., 1929, [iv], **45**, 183—184).—The two components of a reaction are separated by placing the one in a small test-tube which rests on three indentations inside a larger tube containing the other reactant. The larger tube is sealed off, and the reaction brought about by inverting the tube. F. G. TRYHORN.

Efficiency of fractional distillation apparatus. I. Application of Brown's law to column distillations. H. G. GRIMM (Z. physikal. Chem., 1929, **140**, 321—341).—The equation which was found by Brown (1879) to represent the course of a distillation of binary liquid mixtures, in which reflux condensation was carefully prevented, has been shown to apply also in the case of distillation with rectifying columns. The three mixtures *i*-amyl bromide+ethyl butyrate, carbon tetrachloride +benzene, and *cyclo*hexane+benzene were fractionally distilled by means of two types of rectifying column, and the weight and composition of the fractions and the speed of distillation determined at intervals. The composition of the mixtures was determined refractometrically. If L and M are the initial amounts of the two components, and ξ and η the respective amounts remaining in the distillation flask at any given time, the course of the distillation is given by the linear relationship $\log \xi/L=(1+k)(P_1-P_2)/P_2 \cdot \log \eta/M$, where P_1 and P_2 are the vapour pressures of the two components at the b. p. of the mixture. The constant k is a direct measure of the efficiency of the distillation apparatus. If k is determined for any given apparatus, the course of the distillation can be predicted by means of the above relationship. A modified form of fractionating column for use with small quantities of liquids is described. O. J. WALKER.

Apparatus for fractional distillation. G. PICHARD (Ann. Sci. Agron. Franç., 1928, **45**, 358—361; Chem. Zentr., 1928, ii, 1911).—The still-head is composed of three concentric tubes, whereby the path of the vapour is trebled. A. A. ELDRIDGE.

Vacuum distillation. C. R. BURCH (Proc. Roy. Soc., 1929, **A**, **123**, 271—284).—An apparatus consisting of an electrically heated copper tray (container) enclosed in a horizontal water-jacketed condensing tube is described. The latter can be evacuated by a mercury condensation pump, and distillations made in this manner are practically equivalent to evaporation into a perfect vacuum. Methods are given for the removal of gas from the apparatus. In most of the distillations an induction coil giving a 1·8 cm. spark between points produced no discharge at the electrode in the receiver chamber (the tray being earthed), this being the point of highest permanent gas pressure in the still. The differences between equilibrant and evaporation distillation are indicated and the theory of the latter is discussed. In the present apparatus the rate of evaporation is given by $0{\cdot}382\sqrt{M}\sqrt{273/T}\,.\,P$ g. per hr., where M is the mol. wt. of the chemical individual distilled at a temperature T° Abs., corresponding with a saturation pressure P microbars. This leads to a choice of about 20 c.c. per hr. as a maximum speed desirable in fractionations. Details are given of the distillation of a number of oils, and graphs showing the temperature–distillate yield relations are reproduced. This method enables distillations to be made which cannot otherwise be accomplished without decomposition and it is shown that a certain degree of fractionation is possible. A substance (grease) was prepared from petroleum jelly which had a vapour pressure as low as 10^{-3} microbar at 70°. Some experiments were made using such material instead of mercury in a condensation pump, and pressures of the order of $<2\times10^{-3}$ dyne/cm.^{2} were obtained. L. L. BIRCUMSHAW.

Shaker for Clark hydrogen electrode vessel. D. M. CAMERON and R. SHEARER (J. Amer. Leather Chem. Assoc., 1929, **24**, 130—133).—Two sheet-metal arms are mounted separately by their lower ends in a slantwise position to the side of a board by means of screws, which serve as pivots. A carriage for an electrode vessel is mounted to the upper end of each arm by means of two pivoting screws. The upper ends of the arms are connected by means of a horizontal rod from the middle of which a cord is attached to an eccentric pin on a pulley, whereby the driving force is applied. D. WOODROFFE.

M.-p. apparatus. F. Kerckow (Chem.-Ztg., 1929, **53**, 219).—The apparatus consists of an L-shaped hard glass tube. The lagged horizontal limb contains an electrical heating spiral and an air inlet. Into the vertical limb, which is air-jacketed, is inserted a thermometer with a capillary m.-p. tube dipping into a small test-tube containing paraffin oil. The small oil-bath is heated by passing a current of air over the hot spiral. With a heating spiral of 7 ohms resistance and an air stream of 950 litres/hr. a temperature of 100° is reached with a current of 2·8 amp. and of 300° with 6 amp. in 4 and 16 min., respectively. F. G. Tryhorn.

Tellurium–bismuth thermo-element and its applications. M. A. Lewitsky and M. E. Lukomsky (Physikal. Z., 1929, **30**, 203—205).—Methods and precautions for obtaining trustworthy data with the tellurium–bismuth thermo-element are indicated. The thermo-element is about six times as sensitive as the iron–constantan combination. For measuring the temperature decreases along an iron bar the ends of which are at 0° and 17·5°, respectively, the tellurium–bismuth thermo-element gives results slightly nearer the theoretical than does the iron–constantan element. R. A. Morton.

***H*-Particles made visible.** H. Pettersson (J. Sci. Instr., 1929, **6**, 130—132).—A modified cloud chamber for the observation of *H*-particles is described. A polonium point is enclosed in a thin glass tube coated inside with paraffin wax, the whole being placed in the cloud chamber. *H*-Particles are liberated from the paraffin wax by the α-particles from the polonium, and produce tracks in the cloud chamber. A spinthariscope may be modified for the same purpose by placing a thin cutting of paraffin wax on a polonium source, and interposing a sheet of mica barely thick enough to stop the α-rays from reaching the zinc sulphide screen. C. W. Gibby.

Optical method for analysing photographs of α-ray tracks. L. F. Curtiss (Nature, 1929, **123**, 529).—Two photographs are taken in directions at right angles; the developed negatives are then replaced in the cameras and images projected on to a screen which is so placed that no part of the composite image appears double. The screen may then be replaced by a photographic plate, whereby there is obtained a photograph of actual size, reproducing all angles of the track in the plane in which they occurred. A. A. Eldridge.

Self-adjusting pipette. E. G. Bilham (J. Sci. Instr., 1929, **6**, 119—120).—The discharge jet of an ordinary pipette is extended upwards inside the bulb, and retains a definite quantity of liquid, which is then poured out through the top of the pipette. C. W. Gibby.

Vacuum arc lamp for spectroscopic work. K. Prosad (J. Sci. Instr., 1929, **6**, 126—130).—The arc, whch is started electromagnetically, is struck inside a brass cylinder and viewed through a quartz window. Vacuum-tightness is secured by wax joints, which are protected by water-cooling. C. W. Gibby.

Spectrography at the temperature of liquid air. G. Beck (Deut. Z. ges. gerichtl. Med., 1928, **12**, 1—4; Chem. Zentr., 1928, ii, 1918).—A tube for the spectrographic examination of alkaloid solution at −180° to −200° is described, and the eutectics of mixtures of ether, propyl alcohol, pentane, methyl*cyclo*hexane, and decahydronaphthalene have been examined in order to select a suitable solvent. A. A. Eldridge.

Measurement of flame temperatures. E. Griffiths and J. H. Awbery (Proc. Roy. Soc., 1929, **A**, **123**, 401—421).—A "wire method" for measuring flame temperatures, in which the condition of thermal equilibrium is identified by the absence of energy interchange between the wire and the flame, has been devised. A platinum wire carrying electric current is immersed in the flame and the apparent temperature of the wire observed by means of a disappearing-filament optical pyrometer. The same wire is then set up in a vacuum and the temperature corresponding with various values of the current is determined. On plotting the data, two curves are obtained which intersect at a point giving the temperature of the flame. The absorption effect of the flame is so small that it may be neglected. The values obtained are independent of the diameter of the wire and agree with those found by the method of spectral line reversal. A description is given of the latter method, in which the source of the continuous spectrum is the incandescent sphere of a tungsten arc, the flame being coloured by sodium or lithium. The current in the arc is adjusted until the sodium or lithium lines just merge into the continuous background, when a reading of the temperature of the incandescent tungsten sphere taken on the optical pyrometer gives the flame temperature. It was found by experiment that the apparent temperature, obtained by the sodium line reversal method, of a column of sodium chloride vapour contained in an electrically heated carbon tube furnace is the same as the "black body" temperature of the furnace. The thickness of the flame has no influence on spectral line reversal, although it is advisable to use a thick flame to ensure sensitivity. This result is shown to be a consequence of theoretical deductions based on certain simplifying assumptions. The method has been successfully applied to the measurement of maximum temperatures in gaseous explosions, using a carbon monoxide, air, and nitrogen mixture; also to the study of combustion, using flames burning mixtures of carbon monoxide and air; and to the measurement of the temperature of the gases between the electrodes of the atomic hydrogen blow-pipe, for which a mean value of 2515° was obtained. L. L. Bircumshaw.

Platinising glass and other substances. G. F. Taylor (J. Opt. Soc. Amer., 1929, **18**, 138—142).—Improved methods are described of preparing and applying a platinising solution of platinic chloride, oil of rosemary, and oil of lavender, so as to obtain either a surface which can be soldered or a fine, flawless mirror. Various properties of the films and applications of the method are described, and other materials which can be similarly treated are mentioned. N. M. Bligh.

Extrusive plastometer. P. M. Giesy and S. Arzoomanian (5th Coll. Symp. Mon., 1928, 253—258).

Falling-sphere viscosimeter and plasticity measurements. H. E. PHIPPS (5th Coll. Symp. Mon., 1928, 259—266).

Manometer for determination of gases in vapours. D. F. OTHMER.—See B., 1929, 267.

Electric resistance furnace. W. ROSENHAIN and W. E. PRYTHERCH.—See B., 1929, 288.

Apparatus for testing liability to corrosion. V. DUFFEK.—See B., 1929, 289.

Improved Czapek apparatus for determining surface tension. V. I. KAMINSKI (Zhur. exp. Biol. Med., 1928, **10**, 21—22). CHEMICAL ABSTRACTS.

Reduction of the time of photographic exposures, especially in *X*-ray work. F. EBERT (Z. anorg. Chem., 1929, **179**, 279—280).—The time of exposure may be reduced by 50—70% by maintaining the film at about 40° during the exposure.
H. F. GILLBE.

Geochemistry.

Radiation in the upper atmosphere, and its bearing on physical and cosmic processes. L. MEITNER (Z. angew. Chem., 1929, **42**, 345—351).—An account of the effects observed, the methods of measurement, and the theoretical significance of the results. S. I. LEVY

Equivalent heights of the atmospheric ionised regions in England and America. E. V. APPLETON (Nature, 1929, **123**, 445).

Earth's age by sodium accumulation. A. C. LANE (Amer. J. Sci., 1929, **17**, [v], 342—346).—In determining solvent denudation by rivers, no account is usually taken of the fact that the greater part of the run-off of a river is in times of flood, when the amount of dissolved matter is much less, and that of sediment greater, than when the river is normal or low. Calculation of the amount of sodium carried off in solution gives lower values if weighted averages of the water analyses are used than if no allowance is made for the different amounts of water flowing at different times of the year. C. W. GIBBY.

Thermal transformation of serpentine. H. HARALDSEN (Zentr. Min. Geol., 1928, **A**, 297—315; Chem. Zentr., 1928, ii, 1757).—When heated at 500—700°, serpentine loses most of its water, and the crystal structure of serpentine gives place at 700° to a structure analogous to that of olivine. At higher temperatures mixtures of olivine, free amorphous silica, and enstatite are obtained; the last increases with rising temperature at the expense of the silicic acid. A. A. ELDRIDGE.

So-called "thermokalite" and the existence of sodium hydrogen carbonate as a mineral. F. A. BANNISTER (Min. Mag., 1929, **22**, 53—64).—A white crystalline saline encrustation was found in 1888 on the walls of a Roman conduit at the Baths of Nero, which was exposed during the construction of the railway line from Baia to Naples. This material was provisionally called "thermokalite," evidently in the belief that it represented the potassium compound corresponding with thermonatrite. It, however, contains no trace of potassium, and analyses show varying amounts of sodium carbonate and sulphate with 7·48—8·45% H_2O. The analyses are interpreted as mixtures of thermonatrite (Na_2CO_3,H_2O), trona ($Na_2CO_3,NaHCO_3,2H_2O$), sodium hydrogen carbonate, and thenardite (Na_2SO_4), and each of these minerals was determined by the optical characters. The sodium hydrogen carbonate, not hitherto definitely recognised as a mineral, is named *nahcolite* (from $NaHCO_3$) to distinguish it from the other sodium carbonate minerals. Its mode of origin and conditions of stability are discussed from a physico-chemical point of view. The reaction $2NaHCO_3 \longrightarrow Na_2CO_3+H_2O+CO_2$ is much retarded by the formation of crusts, and even though it was collected forty years ago the material still contains about 20% of nahcolite. L. J. SPENCER.

Tholeiite dikes of the north of England. A. HOLMES and H. F. HARWOOD (Min. Mag., 1929, **22**, 1—52).—This set of basaltic dikes in the north of England and south of Scotland has a different direction from those associated with the Whin sill (A., 1928, 1211). They are of Tertiary age and radiate from the Mull volcanic centre. Eight detailed analyses of the different types show a range in silica from 50·07 to 57·57%. L. J. SPENCER.

Deposition of sulphur at Monte Solforoso near Scrofano in the province of Rome. E. ONORATO (Atti R. Accad. Lincei, 1928, [vi], **8**, 243—251).—An investigation has been made of the minerals in the old and new workings of the sulphur mines of Monte Solforoso. The tufa above the region of vegetation is clear reddish in colour, has little coherence, and is relatively acid, and probably trachitic, in nature. This type contains SiO_2 47·47, Al_2O_3 23·44%. A second variety which is perfectly white and trachitic in structure has the high silica content of 84·43%. The transformation of the former into the siliceous type is due to the extraction of sulphates by water circulating through the deposits. Goniometric measurements have been made of the sulphur crystals, some millimetres in length, which occur in the rocks. In the abandoned workings, where water has deposited stalactites and crystalline masses of sulphates, sulphur occurs in great masses of fibrous structure. In these deposits alum was recognised in distorted crystals, and alotrichite in a white, fibrous form of composition SO_3 35·10, Al_2O_3 10·61, FeO 9·10, CaO 2·33, MgO trace, H_2O 42·93%. A yellow form of alotrichite, deficient in iron and calcium, was also recognised (SO_3 36·15, Al_2O_3 10·84, FeO 4·98, CaO trace, H_2O, 46·99). Experiments were made on the action of hydrogen sulphide, sulphur trioxide, and sulphur dioxide on the tufa, the results of which appear to support the theory that the Monte Solforoso deposits originated through the action of sulphur dioxide emitted during the acid period in this region.
F. G. TRYHORN.

Cinnabar from Idria. F. Rodolico (Atti R. Accad. Lincei, 1929, [vi], 9, 176—179).—Crystallographic data are given of several samples of cinnabar obtained from Idria. O. J. Walker.

Geology of the ball clays of South Devon. A. Scott (Trans. Ceram. Soc., 1929, 28, 53—61).

Application of isopyknometric analysis to auriferous rocks. E. Clerici (Atti R. Accad. Lincei, 1928, [vi], 8, 251—254).—The isopyknometric method, employing liquids of *d* 3·03—4·19, is applicable for the separation of gold from auriferous rocks, and has been used successfully with minerals containing gold particles of 2—3 μ diameter. F. G. Tryhorn.

Natural etchings on Japanese pyrite crystals. S. Ichikawa (Amer. J. Sci., 1929, [v], 17, 245—257). —An illustrated description of natural etchings on pyrite crystals from various localities in Japan. The symmetry of the figures corresponds with the hemihedral symmetry of the crystals. C. W. Gibby.

Presence of a variety of jumillite near Calasparra (Murcia). (Mme.) E. Jérémine and P. Fallot (Compt. rend., 1929, 188, 800—802).—The rock, which is black and compact, occurs in thin plates rich in phenocrystals of olivine and biotite, and contains (Raoult) SiO_2 53·90, Al_2O_3 8·88, Fe_2O_3 1·78, FeO 4·16, CaO 3·76, MgO 13·24, Na_2O 1·17, K_2O 7·56, TiO_2 2·26, P_2O_5 0·65, H_2O+ 1·23, H_2O- 1·01, MnO 0·13, CO_2 0·47, Cl 0·04, SO_3 0·24, total 100·48%. Compared with jumillite its silica, potassium, and magnesium contents are somewhat high and the alumina content is low. Unlike jumillite it is holocrystalline and rarely contains leucite. J. Grant.

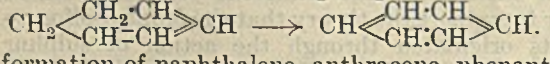
Presence of sulphur in the gaseous nebulæ. I. S. Bowen (Nature, 1929, 123, 450).—Wave-lengths of lines due to transitions in singly-ionised sulphur correspond with those of lines observed in nebulæ. All of the elements so far found in nebulæ are gases or form stable compounds that are gases at low temperatures. A. A. Eldridge.

Organic Chemistry.

Determination of the configuration of mirror-image isomerides. B. Holmberg (Svensk Kem. Tidskr., 1929, 41, 60—73).—A review of the various methods available for determining the configuration of compounds of the above type. The conclusion is reached that there is no general method which can be used in all cases. H. F. Harwood.

Mechanism of thermal decomposition of normal paraffins. E. N. Hague and R. V. Wheeler (J.C.S., 1929, 378—391).—The primary decompositions occasioned by the action of heat on the straight-chain hydrocarbons from ethane to *n*-hexane can be represented by a series of equations indicating the rupture of the chain at any position with production of an olefine and the complementary lower paraffin or, at the limit, hydrogen. As the series is ascended scission at the centre of the chain predominates and the tendency for hydrogen elimination to occur, leaving an olefine with the same number of carbon atoms as the original paraffin, rapidly diminishes.

Methane possesses a higher decomposition point than ethane; at comparatively low temperatures ethylene is formed. As with the other hydrocarbons, ethylene is regarded as the source, through butadiene, of the aromatic hydrocarbons obtained. In the case of methane, optimum benzene formation occurs over the range 1000—1100°; the remaining five hydrocarbons have optimum range 800—850°. The following mechanism is given: $2CH_2{:}CH_2 \longrightarrow$
$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow CH_2{:}CH{\cdot}CH{:}CH_2+H_2$:
$CH_2{:}CH{\cdot}CH{:}CH_2+CH_2{:}CH_2 \longrightarrow$ either
$CH_2{:}CH{:}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ or
$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2+H_2 \longrightarrow$



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH\\CH{=}CH\end{matrix}{\gg}CH \longrightarrow CH{\ll}\begin{matrix}CH{\cdot}CH\\CH{:}CH\end{matrix}{>}CH.$$

The formation of naphthalene, anthracene, phenanthrene, etc. may be analogously formulated by the condensation of benzene with butadiene, naphthalene with butadiene, etc. Except in the cases of pentane and hexane, butadiene has been detected in the gaseous decomposition products obtained between 750° and 950°. The C_2 hydrocarbon which is evidently the precursor of the benzene obtained cannot be acetylene, since (*a*) this gas was absent from the gaseous products, (*b*) treatment of acetylene in a similar manner to the paraffins gave maximum yields of benzene over the range 650—700°, but is probably ethylene, which yields aromatic hydrocarbons above 700°. Further, in the decompositions of the paraffins ethylene yields are proportional to the yields (at a higher temperature) of aromatic hydrocarbons.

Addendum. T. M. Lowry (*ibid.*, 392—393).—The degradation of the paraffins by the reversible elimination of a molecule HX is comparable with the elimination of an acid or water from any other additive compound of an olefine; the decomposition of the paraffins thus conforms to self-established precedents and depends on mechanism of a general character. Similarly, pyrogenic synthesis proceeds according to two well-established processes, viz., polymerisation (ethylene ⟶ butylene) and elimination of hydrogen (butylene ⟶ butadiene $+H_2$). A pyrogenic decomposition is a special case of reversible addition to an olefine of a hydride, either hydrogen or an olefine. R. J. W. Le Fèvre.

Decomposition of methane. I. C. W. H. Jones (J.C.S., 1929, 419—422).—Decomposition of methane by passage through a heated quartz tube is mainly into its elements. The temperature and pressure ranges investigated are 700—1080° and 10—70 cm., respectively. At 800—900° small traces of olefinic hydrocarbons are formed, at 1000° appreciable quantities are obtained (0·13—1·75% according to rate of flow and pressure).

The subjection of methane to the electric spark discharge results in an initially rapid formation of olefines and acetylenes, the percentages of which tend to reach a steady level and the yields are proportional to the pressure of the gas during sparking. The maximum yield of acetylenes is obtained at ½ atm. Small amounts of complex liquid and solid hydrocarbons are also formed. R. J. W. Le Fèvre.

Manufacture of olefines and diolefines [butadiene]. I. G. Farbenind.—See B., 1929, 235.

Aliphatic diolefines. I. Behaviour of $\Delta^{\alpha\epsilon}$-hexadiene towards sulphuric acid. F. Cortese (Ber., 1929, **62**, [*B*], 504—509).—$\Delta^{\alpha\epsilon}$-Hexadiene is treated with 100% sulphuric acid at −15° to +4°, whereby the production of diallyl ether is not noticeable. Addition of ice to the product causes separation of tar and production of a pale pink solution with marked odour of diallyl ether. Addition of ice-water to the tar yields a precipitate of the normal *sulphate* of hexane-βε-diol, m. p. 90° (corr.). The pink solution, containing diallyl ether and a little tar, is neutralised with barium hydroxide, thus leading to the isolation of the very unstable *barium βε-hexyldisulphate*, $[\cdot CH_2\cdot CHMe\cdot O\cdot SO_2\cdot OBa_{0.5}]_2$. If the reaction is effected below −10°, little tar is produced and the normal ester is readily precipitated; at 20—40° diallyl ether and the ester are not produced. With 65% sulphuric acid $\Delta^{\alpha\epsilon}$-hexadiene affords diallyl ether and a *substance*, $C_{12}H_{22}O$, b. p. 65—85°/5 mm., d^{25} 0·865, n 1·4536. 2 : 5-Dimethyltetrahydrofuran is converted by 67% sulphuric acid into a mixture of unsaturated hydrocarbons, the initial phase of the change consisting in the production of methyl *n*-butyl ketone. Similar treatment of acetone, methyl ethyl ketone, diethyl ketone, dipropyl ketone, or methyl *n*-butyl ketone results in the production of oils of agreeable odour and dark red, green, or purple colour, according to the structure of the initial material. H. Wren.

Reactions of olefines of high mol. wt. with sulphuric acid, hydrochloric acid, and air. W. E. Messer (Abst. Thesis Mass. Inst. Tech., No. 3, Jan., 1929, 41—42).—The following olefines are prepared: cetene; Δ^{θ}-heptadecene, f. p. about −50°, b. p. 136°/3·5 mm., 173°/16 mm., d^{25} 0·795, obtained by distilling a mixture of sodium oleate and sodium ethoxide; a mixture of *eicosene* and *docosene* obtained from the mixed alcohols produced by the action of magnesium ethyl bromide on crude methyl stearate; and β-methylnonadecene, m. p. 11—12°, b. p. 146°/2·2 mm., 189°/10 mm., d^{20} 0·795, $n_D^{23.5}$ 1·4504, obtained by dehydrating dimethylheptadecylcarbinol (Ryan and Dillon, A., 1913, i, 583) by oxalic acid Cetene and heptadecene do not react appreciably with concentrated hydrochloric acid, with which, however, dimethylheptadecylcarbinol yields *β-chloro-β-methylnonadecene*, m. p. 19·6—20°, which can be hydrolysed by alcoholic alkali to the olefine and the alcohol. When any one of the above olefines is treated with sulphuric acid, very little organic matter passes into the acid layer; sulphur dioxide is produced in greatest amount with the branched-chain compounds, and when 100% or fuming sulphuric acid is used the formation of sulphur dioxide and tar occurs even at −15° (cf. Brooks and Humphrey, A., 1918, i, 286). Addition of sulphuric acid also occurs; *cetyl* and *heptadecyl hydrogen sulphates*, isolated from their *barium* salts, are found to be very easily hydrolysed, giving rise to alcohols. The alcoholic product from cetene is mainly *hexadecan-β-ol*, m. p. 41·5°; that from heptadecene is a mixture of *heptadecan-θ-* and *-ι-ols*, m. p. 34°; that from β-methylnonadecene has m. p. about 45°.

At the ordinary temperature, β-methylnonadecene is readily oxidised when exposed in a thin layer to the air. At 100° all the above olefines oxidise in the air, yielding acids. E. W. Wignall.

Polymerisation of acetylene by electric discharge. Synthesis of dipropargyl and its isomerides. G. Mignonac and R. V. de Saint-Aunay (Compt. rend., 1929, **188**, 959—961).—When acetylene is subjected to the electric discharge at −60°, a liquid, $d_4^{19.5}$ 0·752, $n_D^{19.5}$ 1·446, corresponding with a trimeride of acetylene, and a hydrocarbon, b. p. −10°/23 mm., are obtained in small amounts. With a current of high frequency (d'Arsonval arrangement) and cooled electrodes a mixture of dipropargyl, γ-methyl-$\Delta^{\alpha\delta}$-pentadi-inene, and diethenylacetylene are formed. These last two hydrocarbons polymerise more readily than dipropargyl. Ethinylethylene is postulated as an intermediate product: addition of acetylene to it occurs in three different ways. H. Burton.

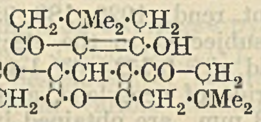
Law of periodicity. IV. P. Petrenko-Kritschenko [with V. Opotzky, M. Diakowa, and A. Losowoy] (Ber., 1929, **62**, [*B*], 581—588; cf. A., 1928, 614).—The action of colloidal silver on halogeno-derivatives of methane which do not contain other different substituents is characterised by a uniform relationship, monohalogen derivative > dihalogen derivative < trihalogen derivative and a less uniform connexion between tri- and tetra-halogen derivatives; the rule $CX > CX_2$ is particularly important. In the presence of substituents (methyl, a different halogen, nitro-, carboxyl, phenyl), the influence of accumulation of the halogen towards silver is marked by the rule $CX < CX_2$. Silver nitrate behaves in the same manner as silver. Towards silver the methyl group changes its usual indifferent character and assumes pronounced chemical character. To eliminate the influence of conditions in the determination of activity coefficients of the dissimilarly substituted derivatives of methane, the ratios CH_2X_2/CH_3X are adopted. The behaviour of a large number of di-derivatives towards silver, potassium hydroxide, piperidine, and silver nitrate has been examined. The graphs appear to fall into two groups; those characteristic of potassium hydroxide and piperidine are characterised by the relationship $CX > CX_2$, whereas with silver and silver nitrate the relationship $CX_2 > CX$ is maintained. Measurements are also recorded for a series of chlorostyrenes, bromoethylenes, chlorobenzene, α- and β-chloronaphthalene, and dichloro*cyclo*propanes. The following relationships appear to be established:

$$\begin{tikzcd}
 & C{:}CX \arrow[r] & C{\vdots}CX \\
\underset{\text{active}}{C\cdot CX} \arrow[ur] \arrow[r] \arrow[dr] & C{:}CX \arrow[r] & C{:}CX_2 \\
 & \underset{\text{passive}}{C\cdot CX_2} \arrow[r] & \underset{\text{active.}}{C\cdot CX_3}
\end{tikzcd}$$

H. Wren.

Reaction of a mixture of methyl chloride and bromide with magnesium in ether. H. Gilman and R. J. Vanderwal (Bull. Soc. chim., 1929, [iv], 45, 135—137).—Contrary to the observation of Rudd and Turner (A., 1928, 504), the authors affirm that a mixture of methyl chloride and bromide with magnesium in ether readily yields magnesium methyl chloride and bromide, the methyl bromide reacting the more rapidly. R. Brightman.

Action of alkali hydroxide on chloroform. D. Vorländer and F. W. Guthke (Ber., 1929, 62, [*B*], 549—554).—The action of potassium hydroxide on chloroform in the presence of methone [5 : 5-dimethylhydroresorcinol] affords *anhydrotrimethonylmethane* (I), m. p about 234° (corr. decomp.) after softening


$$\begin{array}{c}\mathrm{CH_2{\cdot}CMe_2{\cdot}CH_2}\\ \mathrm{CO{-}C{=}C{\cdot}OH}\\ \mathrm{CH_2{-}CO{-}C{\cdot}CH{\cdot}C{\cdot}CO{-}CH_2}\\ \mathrm{CMe_2{\cdot}CH_2{\cdot}C{\cdot}O{-}C{\cdot}CH_2{\cdot}CMe_2}\end{array}$$

(I.)

[*acetyl* compound, m. p. 153°; *benzoyl* derivative, m. p. 258° (decomp.)], and a *substance*, m. p. 175—177°. The compound, m. p. 234°, is also obtained from formic acid but not from alkali formate in neutral or alkaline solution and methone. Since the compound is a derivative of formic acid and not of formaldehyde and methone is a specific reagent for aldehydes, the reducing action of chloroform and alkali hydroxide towards Fehling's solution cannot be attributed to the intermediate production of formaldehyde. The existence of hydroxyformaldehyde in equilibrium with formic acid, $\mathrm{OH{\cdot}(\overset{+}{C}{:}\overset{-}{O}){\cdot}H}$ $\longrightarrow$ $\mathrm{\overset{+}{H}{\cdot}\overset{-}{O}{\cdot}(C{:}O){\cdot}H}$, is therefore postulated. The action cannot be attributed to nascent formic acid, since a similar effect is not observed with formic esters and potassium hydroxide. Bromoform and iodoform (in boiling alcoholic-alkaline solution) and substances which form chloroform (such as chloral and trichloroacetic acid) behave similarly to chloroform towards Fehling's solution. Carbon monoxide or chloroform and alkali hydroxide reduce cold Fehling's solution and ammoniacal silver solution. Reaction does not appear to occur with ethylene chloride or bromide, ethylidene chloride, *s*-tetrachloroethane, or hexachloroethane. Carbon tetrachloride and alkali hydroxide do not produce cuprous oxide, although carbon monoxide and carbylamines are formed. H. Wren.

Manufacture of *iso*propyl alcohol. G. O. Curme, jun., and E. W. Reid.—See B., 1929, 275.

Preparation of allyl alcohol. R. Delaby and P. Dubois (Compt. rend., 1929, 188, 710—711).—The following method is based on the fact that allyl alcohol arises from the pyrolysis of glyceryl diformate (A., 1928, 767). Glycerol (184 g.) and 96% formic acid (300 g.) are heated at 65°/110—120 mm. for 2 hrs., after which the temperature is raised to 110°. After the first hour the pressure is reduced to 40 mm.; 96% formic acid (200 g.) is then added to the residue and the whole subjected to treatment similar to the first. Pyrolysis is effected at 200—250°/760 mm. over a period of 2 hrs. The yield is 435 g. from 1·0 kg. of glycerol. G. A. C. Gough.

Aliphatic [open-chain] hydroterpenes. W. Longuinov and (Mlle.) E. Margoliss (Bull. Soc. chim., 1929, [iv], 45, 156—167).—Geraniol, b. p. 113·5—114°/12 mm., n_D^{20} 1·4762, on hydrogenation in 74% alcohol in presence of platinum-black (Vavon, A., 1914, i, 694) affords tetrahydrogeraniol, the properties of which, b. p. 110·5°/16 mm., b. p. 116—117°/25 mm., d_4^{20} 0·8341—0·8362, n_D^{20} 1·4398—1·4412, varied slightly with different preparations. 50% of the theoretical amount of hydrogen is rapidly absorbed, giving a dihydrogeraniol, b. p. 117—118°/15 mm., d_4^{20} 0·8560, n_D^{20} 1·4543, the remainder being taken up much more slowly, especially in ethereal solution (cf. Grignard and Escourrou, A., 1925, i, 772). In ethereal solution the yield is lower and some βξ-dimethyloctane is formed. Geraniol from essence of palmarosa (Chiris), b. p. 110°/10 mm., d^{15} 0·8835, similarly gave a tetrahydrogeraniol, b. p. 108—109°/10 mm., d_4^{20} 0·8812, n_D^{20} 1·4772. With hydrobromic acid in a sealed tube at 100° tetrahydrogeraniol affords (yield 65—75%) a *bromide*, b. p. 91—92°/10 mm., d_4^{20} 1·0368, n_D^{20} 1·4534, which on distillation with quinoline gives βξ-*dimethyl* Δ^{η}-*octene*, b. p. 154°/738 mm., d_4^{20} 0·7396, n_D^{20} 1·4212. Harries and Neresheimer's methylation method (A., 1911, i, 798) was unsuccessful, the quaternary base undergoing fission on distillation, probably with elimination of methyl alcohol, and not decomposition into trimethylamine and the unsaturated hydrocarbon. The constants of this tetrahydroterpene with a terminal double linking are lower than those of dihydrobupleurolene or γξ-dimethyl-Δ -octene, which possess "internal" double linkings. When heated with hydrobromic acid in a sealed tube at 100°, βξ-dimethyl-Δ^{η}-octene is converted into a *bromide*, b. p. 92°/10 mm., d_4^{20} 1·0743, n_D^{20} 1·4569, which with quinoline gives 70% of βξ-dimethyl-Δ^{ξ}-octene, b. p. 161—162°/753 mm., d_4^{20} 0·7473, n_D^{20} 1·4272. Tetrahydrogeraniol could not be obtained by hydrogenation of citral, only 30% of the theoretical volume of hydrogen being absorbed. R. Brightman.

Pinacols and pinacolins. E. Pace (Atti R. Accad. Lincei, 1928, [vi], 8, 309—314; cf. A., 1928, 1113).—Treatment of diacetyl with magnesium alkyl bromide (2 mols.) and decomposition of the resulting compound with slightly acidified water yields α-ditertiary alcohols (pinacols), which may be converted into the corresponding pinacolins by dehydration with dilute sulphuric acid (1 : 4) followed by steam distillation. αβ-*Dimethylbutane*-αβ-*diol*, m. p. 38°, b. p. 175°, or m. p. 47° (+6H_2O), gives acetone when oxidised with chromic acid mixture and bromoform (iodoform) when treated with alkaline bromine (iodine) solution. γδ-Dimethylhexane-γδ-diol has m. p. 51°, b. p. 216° (cf. Lawrinowitsch, A., 1877, ii, 427). δε-Dimethyloctane-δε-diol has m. p. 62°, b. p. 228—230° (cf. Friedel, Jahresber., 1869, 513). δδ-*Dimethyloctan*-ε-*one*, b. p. 185—187°, gives the iodoform reaction, combines with difficulty with sodium hydrogen sulphite, and forms an *oxime*, m. p. 152°. Acetylacetone fails to react with magnesium alkyl bromides, possibly owing to its existence in desmotropic forms. T. H. Pope.

[Configuration of pentaerythritol.] A. Semenzov (Ber., 1929, 62, [*B*], 514).—The resolution of pentaerythritol derivatives, $\mathrm{C}\left[<^{\mathrm{CH_2{\cdot}O}}_{\mathrm{CH_2{\cdot}O}}>\mathrm{C}<^{\mathrm{R'}}_{\mathrm{R}}\right]_2$, into optical isomerides does not necessarily establish that methane derivatives have a tetrahedral configuration under all conditions, since a plane of symmetry is not present in the *trans*-isomerides (cf. Böeseken and Felix, A., 1928, 1213; Kenner, this vol., 171).

H. Wren.

Catalytic elimination of alcohol from acetals. Preparation of unsaturated ethers. F. Sigmund and R. Uchann (Monatsh., 1929, 51, 234—252).—When acetals are passed over porous earth at 200° or a nickel catalyst (Sigmund and Marchart, A., 1927, 1054) at 160—200° in a current of nitrogen, elimination of alcohol occurs: $R{\cdot}CH_2{\cdot}CH(OR')_2 \longrightarrow R{\cdot}CH{:}CH{\cdot}OR'+R'{\cdot}OH$, and unsaturated ethers are obtained in good yield. Thus, heptaldehyde diethylacetal yields *ethyl Δ^α-heptenyl ether*, b. p. 172—175°, and ethyl alcohol. Similarly, phenylacetaldehyde dimethylacetal gives styryl methyl ether; phenylacetaldehyde di-*n*-propylacetal affords styryl propyl ether; heptaldehyde di-*n*-propylacetal furnishes *propyl Δ^α-heptenyl ether*, b. p. 184—187° (corr.), which does not react with semicarbazide acetate at the ordinary temperature, but after hydrolysis with 2*N*-sulphuric acid forms heptaldehydesemicarbazone (cf. Moureu, A., 1904, i, 285); acetaldehyde diethylacetal yields ethyl vinyl ether at 250°; benzaldehyde diethylacetal is unaltered at 250° owing to there being no available hydrogen atom for the elimination of the alcohol. Acetophenone dimethylacetal and di-*n*-propylacetal give α-methoxystyrene, b. p. 194—196°, and *α-propoxystyrene*, b. p. 214—219° (corr.), respectively. In these last cases hydrogen is eliminated from the methyl group: treatment of the styrenes with semicarbazide acetate yields acetophenonesemicarbazone.

With brass turnings as a catalyst elimination of methyl alcohol from phenylacetaldehyde dimethylacetal is incomplete even at 400—420°. With phenylacetaldehyde di-*n*-propylacetal partial elimination of propyl alcohol occurs and this is further dehydrogenated to propaldehyde. H. Burton.

Enzymic synthesis of β-hydroxyethyl dihydrogen phosphate. H. D. Kay (J.C.S., 1929, 524—527).—Aqueous sodium phosphate and ethylene glycol are smoothly converted at 38° by the catalytic action of a phosphatase preparation derived from duodenal mucosa of a cat into β-hydroxyethyl dihydrogen phosphate (isolated as the barium salt). The sodium salt is hydrolysed by enzymes at the same rate as a sample of the sodium salt isolated by Plimmer and Burch (this vol., 422). R. J. W. Le Fèvre.

Crystalline diglycide and its acetate. M. Battegay, H. Buser, and E. Schlager (Compt. rend., 1929, **188**, 796—798).—Treatment of glycerol with acetic acid and sulphuric acid at 135° affords monomeric acetins and a crystalline diglycide diacetate, $C_6H_{10}O_2(OAc)_2$, m. p. 138°, which, when hydrolysed with alcoholic hydrogen chloride, yields diglycide, $C_6H_{12}O_4$, m. p. 96—97°, b. p. 173°/16 mm.

G. A. C. Gough.

Synthetic glycerides. I. H. P. Averill, J. N. Roche, and C. G. King (J. Amer. Chem. Soc., 1929, 51, 866—872).—In view of the uncertainty attaching to the properties of many glycerides the following pure derivatives have been synthesised by methods which establish their constitutions (cf. Fischer, A., 1920, i, 805, 807): α-monoglycerides: palmito-, m. p. 77·0°; myristo-, m. p. 67·3°; *hexo*-, m. p. 51·4°; lauro-, m. p. 63·0°; stearo-, m. p. 81·1°; αα-diglycerides: lauro-, m. p. 56·6°; stearo-, m. p. 79·1°; palmito-, m. p. 69·5°; myristo-, m. p. 63·8—64·4°; also trilaurin, m. p. 45·6°; β-, m. p. 50·9°, and α-, m. p. 45·4°, -stearodilaurins; β-, m. p. 49·2—49·5°, and α-, m. p. 48·5°, -lauro-, and β-, m. p. 59·8—60·0°, and α-, m. p. 53·0°, -*palmito*-dimyristins; β-, m. p. 64·8°, and α-, m. p. 62·6°, -stearo-; β-, m. p. 54·0°, and α-, m. p. 51—52°, -aceto-; β-, m. p. 66·0°, and α-, m. p. 60·0°, -*hexo*-; β-, m. p. 63·5—64·0°, and α-, m. p. 54·5°, -*lauro*-, and β-, m. p. 58·5—59°, and α-, m. p. 55·5°, -*myristo*-dipalmitins; β-, m. p. 62·7°, and α-, m. p. 56·6°, -aceto-, and α-lauro-, m. p. 50·9°, distearins. *Acetoneglyceryl hexoate*, *α-iododilaurin*, m. p. 23·5°, and *α-iododimyristin* were also obtained. In the nine pairs of isomeric triglycerides examined the symmetrical have all higher m. p. (mean difference, 4·7°) than the corresponding unsymmetrical derivatives. H. E. F. Notton.

Chlorination products of ββ'-dichlorodiethyl sulphide. II. J. W. C. Phillips, J. S. H. Davies, and S. A. Mumford (J.C.S., 1929, 535—549).—Chlorination of ββ'-dichlorodiethyl sulphide by 2 mols. of chlorine results mainly in the formation of ααββ'-tetrachlorodiethyl sulphide (d_4^{20} 1·53), which readily undergoes thermal decomposition, giving β-chloroethyl αβ-dichlorovinyl sulphide, b. p. 107°/15 mm., d_4^{20} 1·4315, n_D^{20} 1·5562. Chlorine reacts additively with the last compound, forming ααβββ'-pentachlorodiethyl sulphide, which easily loses hydrogen chloride, giving β-chloroethyl αββ-trichlorovinyl sulphide, b. p. 122—124°/15 mm., d_4^{20} 1·5425, n_D^{20} 1·5700, from which by further action of chlorine ααββββ'-hexachlorodiethyl sulphide, b. p. 158—159°/15 mm., d_4^{20} 1·6849, n_D^{20} 1·5683, and hexachloroethane are successively obtained.

Treatment of ββ'-dichlorodiethyl sulphide by 3 mols. of chlorine afforded *ααα'ββ'-pentachlorodiethyl sulphide*, d_4^{20} 1·57, which decomposed when heated into β-chloroethyl αββ-trichlorovinyl sulphide and β-(*β-chloroethylthiol*)*ethyl trichlorovinyl sulphide*, m. p. 70·5°. Chlorination of ββ'-dichlorodiethyl sulphide by 3—4 mols. of chlorine led, after similar distillation, to *ααβ-trichloroethyl β-chlorovinyl sulphide*, b. p. 122—123°/15 mm., d_4^{20} 1·5404, n_D^{20} 1·5661. The two isomeric tetrachloro-sulphides have identical b. p.; the densities and physical properties of mixtures are approximately linear functions of the composition. In certain cases, however, a third isomeride appeared to be present, possibly *αβ-dichloroethyl αβ-dichlorovinyl sulphide*, b. p. 120—121°/15 mm., d_4^{20} 1·5378, n_D^{20} 1·5673. Chlorine reacted mainly additively with ααβ-trichloroethyl β-chlorovinyl sulphide, forming *ααα'ββ'β'-hexachlorodiethyl sulphide*, b. p. 159—160°/15 mm., d_4^{20} 1·6841, n_D^{20} 1·5681; the latter when heated lost hydrogen chloride and gave *αββ-trichloroethyl αβ-dichlorovinyl sulphide*, b. p. 134—135°/15 mm., d_4^{20} 1·6293, n_D^{20} 1·5778, from which, by addition of chlorine, *ααα'βββ'β'-heptachlorodiethyl sulphide*, b. p. 170—172°/15 mm., d_4^{20} 1·7473, n_D^{20} 1·5741, was obtained. By a similar sequence of reactions, *αα′α′βββ′-hexachlorodiethyl sulphide*, b. p. 157—159°/15 mm., d_4^{20} 1·6825, n_D^{20} 1·5681, *αβ-dichloroethyl αββ-trichlorovinyl sulphide*, b. p. 133—134°/15 mm., d_4^{20} 1·6190, n_D^{20} 1·5770, and *αα′α′ββββ′-heptachlorodiethyl sulphide*, b. p. 132—134°/*ca.* 2 mm., d_4^{20} 1·743, n_D^{20} 1·5741, were prepared.

Maximum yields in the chlorination of ββ′-dichlorodiethyl sulphide were obtained when 3·5 mols. of chlorine were used. Further chlorination caused partial destruction of the hexachloro-sulphides already formed, chlorinated hydrocarbons of low b. p. and a residual tetrachloro-fraction being obtained on subsequent distillation; *e.g.*, chlorination by 4·1 mols. of chlorine led to αααβ-tetrachloroethane, *trichloroethyl sulphur chloride*, b. p. 53·8°/3·5 mm., and αβ-dichloroethyl αββ-trichlorovinyl sulphide. The last-named by chlorine addition yielded a *heptachlorodiethyl sulphide*, b. p. 144—146°/5·5 mm., d_4^{20} 1·7373, n_D^{20} 1·5739, with a heavier isomeride, possibly either αββ-trichloroethyl αβ-dichlorovinyl sulphide or ααβ-trichloroethyl αβ-dichlorovinyl sulphide or both. The present work confirms the view that the αββ′-trichloro- and αβββ′-tetrachloro-diethyl sulphides of Mann and Pope (J.C.S., 1922, **121**, 594) are β-chloroethyl αβ-dichlorovinyl and αββ-trichlorovinyl sulphides, respectively, and that the formation of chloroethyl chlorovinyl sulphides is in all cases due to the loss of hydrogen chloride from saturated polychlorodiethyl sulphides—the first, but less stable, products of chlorination. Contrary to previous views, chlorination of ββ′-dichlorodiethyl sulphide is not confined to one chain.

In all cases chlorinations were effected in carbon tetrachloride solution and the removals of hydrogen chloride performed by heating at the b. p. under 15—20 mm. pressure. A mechanism of the course of chlorination is suggested. R. J. W. LE FÈVRE.

Modified Curtius reaction. III. Degradation of saturated fatty acids and benzoic acid. C. NAEGELI, L. GRÜNTUCH, and P. LENDORFF (Helv. Chim. Acta, 1929, **12**, 227—261; cf. A., 1928, 881).—In general, the acid chloride is treated, usually in benzene solution, with sodium azide, the course of the reaction being followed by measurement of the volume of nitrogen evolved, and the solution of the carbimide so obtained is treated with hydrochloric acid, calcium hydroxide solution, or acetic acid, and thus converted into the amine hydrochloride, the free base, or its acetyl derivative, respectively, this stage of the reaction being followed by measurement of the volume of carbon dioxide evolved. Thus stearyl chloride is converted into heptadecylamine hydrochloride, m. p. 158° (without decomp.; cf. lit.) (93% yield) (*chloroplatinate*), or *acet-*n*-heptadecylamide*, m. p. 62° (80%) (*hydrochloride*), accompanied by *stearyl-*n*-heptadecylamide*, m. p. 88° (20%), also obtained by the action of stearic acid on heptadecylcarbimide in benzene solution. Palmityl chloride similarly yields pentadecylamine (80%), its hydrochloride, m. p. 199° (without decomp.; cf. lit.) (95%), and *acet-*n*-pentadecylamide*, m. p. 72° (*hydrochloride*), together with palmitic acid. *Palmityl-*n*-pentadecylamide*, m. p. 93°, is obtained by the action of palmitic acid on pentadecylcarbimide. Lauryl chloride yields undecylamine (71%), its hydrochloride, m. p. 190° (without decomp.; cf. lit.) (77—80%), together with a little diundecylcarbamide, and acetundecylamide (76%) (*hydrochloride*, m. p. 65—66°). *iso*Valeryl chloride yields *iso*butylamine hydrochloride (71%) and acet*iso*butylamide (79%), whilst from acetyl chloride is obtained methylamine hydrochloride (50—65%), according to experimental conditions, and acetmethylamide (72%) (*hydrochloride*, which is unstable and slowly loses 50% of its hydrogen chloride). Benzoyl chloride similarly yields aniline (79%), its hydrochloride (74%), and acetanilide (93%), although under certain experimental conditions diphenylcarbamide is the chief product. In no case were secondary or tertiary amines obtained. J. W. BAKER

Action of phosphorus trichloride on formic acid and acetic anhydride. A. VAN DRUTEN (Rec. trav. chim., 1929, **48**, 312—323).—The reaction between formic acid and phosphorus trichloride in an atmosphere of nitrogen or carbon dioxide proceeds: $3H\cdot CO_2H+PCl_3=3CO+3HCl+H_3PO_3$. When phosphorus trichloride reacts with acetic anhydride acetyl chloride is the main product, and after removal of this and any other liquid product by vacuum distillation, a solid product remains. This is hygroscopic, evolves hydrogen chloride when exposed to the air, dissolves in water forming an acid solution which reduces iodine, and from its high oxygen content does not appear to contain either phosphorous or phosphoric acid derivatives. No phosphorus trioxide was obtained in any experiment. H. BURTON.

Chloroacetic acids and zinc. H. W. DOUGHTY and D. A. LACOSS (J. Amer. Chem. Soc., 1929, **51**, 852—855).—Trichloroacetic acid is quantitatively converted in aqueous solution by zinc (1 atom) into zinc dichloroacetate. The mechanism of the strongly exothermic reaction is probably similar to that suggested in the case of copper (cf. A., 1922, i, 427; 1925, i, 628). Dichloroacetic acid reacts less readily, 10% of the carboxylic hydrogen being liberated. Chloroacetic acid reacts slowly, even at 100°, evolving much hydrogen. H. E. F. NOTTON.

Products of the action of chlorosulphonic acid on propionyl chloride at the ordinary temperature. M. KRAJČINOVIĆ (Ber., 1929, **62**, [*B*], 579—581; cf. A., 1926, 1125).—Propionyl chloride is converted by chlorosulphonic acid into α-sulphopropionic acid and 2 : 4-dimethyl-5-ethylpyronone, m. p. 151°. H. WREN.

Configurative relationship of lactic and α-chloropropionic acids; relationship of lactic acid and *n*-pentan-β-ol. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, **81**, 703—709).—Δ^{γ}-*n*-Penten-β-ol was converted into the *hydrogen phthalate*, m. p. 90°, which gave an insoluble *brucine* salt, $[\alpha]_D^{24}$ −13·7°, yielding a hydrogen phthalate, $[\alpha]_D^{24}$ +30·8°; the latter, on hydrolysis, gave the *l*-pentenol, $[\alpha]_D^{22}$ −3·7° in ether (c=24·8) (*α-naphthylcarbamate*, m. p. 130°, $[\alpha]_D^{25}$ +9·2° in alcohol). The *l*-pentenol gave, with pyridine and phosphorus trichloride, l-β-*chloro-Δ^{γ}-pentene*, $[\alpha]_D^{23}$ −9·1° in ether, which, with ozone, yielded *d*-α-chloropropionic acid, $[\alpha]_D^{23}$ +2·0 in water (*sodium* salt, $[\alpha]_D^{23}$ −0·48°). On reduction with hydrogen and palladium the *l*-pentenol gave *d*-*n*-pentan-β-ol, and with ozone it yielded *d*-lactic acid. The latter is therefore configuratively related both to *d*-α-chloropropionic acid and to *d*-*n*-pentan-β-ol. C. R. HARINGTON.

Constitution of glucic acid. E. K. NELSON and C. A. BROWNE (J. Amer. Chem. Soc., 1929, **51**, 830—836).—In 8% aqueous solution dextrose yields with calcium hydroxide in absence of air at 67° a mixture of calcium salts which readily absorbs oxygen and from which formic acid and glucic acid, $C_3H_4O_3$ (optical properties), darkens at 110°, but does not melt at 170°, are separated (cf. Winter, Z. Ver. Rübenzucker Ind., 1874, **44**, 1049). The latter is fairly stable when pure, absorbs 1 mol. of bromine, is readily oxidised to oxalic and formic acids, and shows typical enolic colour reactions. It is therefore probably β-hydroxyacrylic acid (acrolactic acid; cf. Pinner, A., 1875, i, 554). When hydrogenated it appears to undergo polymerisation, yielding amorphous products. Its atmospheric oxidation to formic acid may account for the presence of the latter in molasses. Its transformation into Winter's *apo*glucic acid could not be repeated. H. E. F. NOTTON.

βλ-Dihydroxypalmitic acid from rhamnoconvolvulic acid. E. VOTOČEK and V. PRELOG (J. Czechoslov. Chem. Comm., 1929, **1**, 55—64).—The dihydroxypalmitic acid obtained from commercial convolvuline (this vol., 544) is proved to be βλ-*dihydroxypalmitic acid*, m. p. 83—84° (*methyl* ester, m. p. 81—82°, b. p. 140—150°/0·0001 mm., $[\alpha]_D$ +0·91°; *ethyl* ester, m. p. 72—73°). Reduction by hydriodic acid and red phosphorus gives palmitic acid. Treatment by sulphuric acid–potassium dichromate solution affords, by oxidative scission, acetic acid, *pentadecane*-βλ-*dione*, m. p. 53·5—64° (*disemicarbazone*, m. p. 132—134°), and ι-*ketotetradecoic acid*, m. p. 69°. The *oxime* (an oil) of the last compound undergoes the Beckmann change with sulphuric acid giving, after hydrolysis etc., *n*-valeric acid, *n*-butylamine, sebacic acid, and ι-aminononoic acid.

R. J. W. LE FÈVRE.

"Activated form" of oxalic acid. F. KRAUSS and E. BRUCHHAUS (Ber., 1929, **62**, [*B*], 487—489).—Aqueous solutions of oxalic acid which have been treated with a deficiency of potassium permanganate give a positive reaction for formic acid with mercuric chloride or resorcinol and sulphuric acid. If such solutions are distilled, formic acid may be identified in the distillate by the described tests or, analytically, as sodium formate. Aqueous solutions of oxalic acid do not yield formic acid when distilled under these conditions. The assumption of an activated form of oxalic acid (cf. Oberhauser and Hensinger, A., 1928, 505) appears unnecessary. H. WREN.

Complex scandium oxalates. J. ŠTĚRBA-BÖHM and S. ŠKRAMOVSKÝ (J. Czechoslov. Chem. Comm., 1929, **1**, 1—18).—*Scandium oxalate*, $Sc_2(C_2O_4)_3,6H_2O$, *d* 2·14 (obtained pure only in absence of sodium, potassium, and notably ammonium ions), is prepared by treating an acidified (hydrogen chloride) solution of scandium chloride at 60° with a slight excess of oxalic acid. On drying at 100° this hexahydrate forms a *dihydrate*; it readily absorbs ammonia. Treatment of scandium chloride with slightly acid ammonium oxalate solutions or with oxalic acid in the presence of ammonium salts, or precipitation of scandium oxalate solutions by ammonium carbonate solutions or by ammonium oxalate solutions, results in the formation of *scandium ammonium oxalate dihydrate*, $NH_4Sc(C_2O_4)_2,2H_2O$, *d* 1·75. Exposure of this to an ammoniacal atmosphere gives a *salt*, $(NH_4)_4Sc_2(C_2O_4)_3,8H_2O$. Attempts to repeat preparations of higher complex scandium ammonium oxalates (Meyer and Wassjuchnow, A., 1914, ii, 369; Wirth, *ibid*., 468) have failed.

Analogous procedures with potassium salts give *scandium monopotassium oxalate*, $KSc(C_2O_4)_2,2H_2O$, *d* 1·90, which readily changes into *scandium tripotassium oxalate*, $K_3Sc(C_2O_4)_3,4H_2O$, *d* 2·10, whilst, using sodium salts, *scandium monosodium oxalate*, $NaSc(C_2O_4)_2,3H_2O$, *d* 1·94, and *scandium trisodium oxalate*, $Na_3Sc(C_2O_4)_3,6H_2O$, *d* 1·84, are obtained. The last-named when dried at 100° gives a *monohydrate*.

The sodium salts are less stable than the corresponding potassium salts and these less so than the corresponding ammonium salts.

R. J. W. LE FÈVRE.

Butane-αβδ-tricarboxylic acid. H. KILIANI (Ber., 1929, **62**, [*B*], 640—641).—The crystalline form of the acid is recorded. It does not appear to form well-characterised metallic salts; the barium and calcium compounds are less soluble in hot than in cold water. H. WREN.

Reaction of citric acid and its salts. V. ARREGUINE (Bull. Soc. Chim. biol., 1929, **11**, 242—245).—A dilute solution of citric acid (3—4 c.c.), when oxidised with 5% potassium permanganate, gives rise to acetonedicarboxylic acid, which condenses with resorcinol (0·1 g.) when concentrated sulphuric acid is added until a bright red colour is obtained. The phorone derivative thus formed affords an intensely blue, fluorescent solution in aqueous ammonia.

G. A. C. GOUGH.

Preparation of *d*-gluconic acid. H. KILIANI (Ber., 1929, **62**, [*B*], 588—592).—The following method avoids completely the use of silver or lead compounds. Dextrose in water is oxidised by liquid bromine and the product is treated with barium carbonate. The separation of barium *d*-gluconate from barium bromide is effected by dilute alcohol. The original memoir should be consulted for details.

In the application of oxalic acid to the determination of barium in salts of organic acids (A., 1928, 741) it has been overlooked that oxalic acid is slowly removed from barium oxalate by washing with 50% alcohol so that the filtrate is invariably acidic; the method is still valid if the oxalate is converted into the carbonate by gentle ignition. H. WREN.

***d*-Glycuronic acid. II.** F. EHRLICH and K. REHORST (Ber., 1929, **62**, [*B*], 628—634; cf. A., 1925, i, 1379).—Amended directions are given for the isolation of *d*-glycuronic acid from ammonium mentholglycuronate with the object of avoiding possible contamination of the product with ammonium sulphate and the too protracted action of barium carbonate. For the acid obtained by the action of the requisite amount of sulphuric acid on the sodium salt the initial value $[\alpha]_D^0$ $+3{\cdot}61°$ has been observed, but it has not been found possible to prepare an initially lævorotatory acid. The following data are recorded: anhydrous and monohydrated sodium salt, $[\alpha]_D^{20}$ $-0{\cdot}56°$ to $+22{\cdot}51°$ in water in 1·5 hrs.; anhydrous potassium salt, $[\alpha]_D^{21{\cdot}5}$ $-2{\cdot}78°$ to $+22{\cdot}47°$ in water in 2 hrs., and sesquihydrated salt, $[\alpha]_D^{21}$ $+4{\cdot}53°$ to $+20{\cdot}02°$ in 1·5 hrs.; *ammonium* salt, $[\alpha]_D^{20}$ $-4{\cdot}05°$ to $+23{\cdot}17°$ in water in 1·5 hrs.; barium salt, $[\alpha]_D^{20{\cdot}5}$ $+17{\cdot}45°$ in water (non-mutarotatory); *brucine* salt, $C_6H_{10}O_7,C_{23}H_{26}O_4N_2,H_2O$, m. p. 156—157°, $[\alpha]_D^{20}$ $-15{\cdot}08°$ (non-mutarotatory). H. Wren.

Manufacture of substituted thiolacetic acids. I. G. Farbenind.—See B., 1929, 235.

Use of ozone for the determination of the constitution of unsaturated compounds. J. Dœuvre (Bull. Soc. chim., 1929, [iv], 45, 140—152).—A defence of the ozone method for the determination of the constitution of unsaturated compounds (cf. Verley, A., 1928, 1138, 1139). Samples of methylheptenone and citronellal giving 82% and 78% of acetone, respectively, gave 93% by the permanganate–chromic acid method and 84% by the ozone method, and the isomerising influence of ozone on the position of double linkings is therefore negligible. The failure of the method with eugenol is admitted. The ozonisation results (formaldehyde 25%, formic acid 106%) partly accord with Harries and Haarmann's theory (A., 1915, i, 133) of the formation of an unstable homovanillin peroxide, yielding vanillin and formaldehyde. The presence of acetone peroxide, which would be stable under the experimental conditions, or of pyruvic acid has not been detected in ozonisations by this method, and the formation of acetol in the ozonisation of citronellal dimethylacetal (Harries and Comberg, A., 1915, i, 966) is attributed to the formation of *iso*acetone under the enolising influence of the hexane.

Ozonisation is effected in acetic acid at about 0° with a current of oxygen containing 6—7% of ozone. Fresh controls confirmed the resistance of acetic acid (and acetone) to oxidation under these conditions. After diluting with water and leaving for 12 hrs. the formaldehyde in the decomposition products is determined with Grosse-Bohle's reagent (rosaniline hydrochloride 1 g., sodium sulphite 25 g., hydrochloric acid, d 1·12, 15 c.c., diluted to 1000 c.c.). Results are accurate only to 5—10%, a margin which has little effect on the total results for α- and β-isomerides, since the amount of formaldehyde is usually small. 3 C.c. of reagent are used for the test, the comparison being made 12 hrs. after mixing and diluting to 10 c.c. Formic acid is determined by Liebig's mercuric oxide method, after destroying oxygen present by boiling with sulphurous acid, and acetone by Messinger's method, using 15 min. reaction. In the latter case results are accurate to 5%. Acraldehyde and glyoxylic acid also give a positive result with Grosse-Bohle's reagent and glycollaldehyde a violet coloration. Acetaldehyde, propaldehyde, *iso*butaldehyde, *iso*valeraldehyde, heptaldehyde, lævulaldehyde, βξ-dimethyl-Δ^{ϵ}-heptenal, citral, citronellal, and benzaldehyde give no coloration. R. Brightman.

Citronellal. H. I. Waterman and E. B. Elsbach (Bull. Soc. chim., 1929, [iv], 45, 137—140).—The samples of citronellal examined by Verley (A., 1928, 1138, 1139) are regarded as impure, the density and refractive indices differing consistently from those given by the authors (cf. B., 1928, 654) and other workers, and the value given for the b. p., 82°/2 mm., is inconsistent with the b. p.–pressure curve based on the observations of Tiemann and others, and calculations after Clapeyron or Dühring's equation. Verley's equation, $1/n=k\lambda^2$, 1 is of doubtful value. Attention is directed to the inaccurate data for citronellal in current literature. R. Brightman.

Chemistry of high molecular organic substances from the point of view of Kekulé's theory. XII. H. Staudinger (Z. angew. Chem., 1929, 42, 37—40, 67—73, 77).—Earlier work (cf. this vol., 49, 51, 53, etc.) is summarised in reply to Meyer (Z. angew. Chem., 1928, 41, 935). R. Brightman.

Chemistry of high molecular organic substances. K. H. Meyer (Z. angew. Chem., 1929, 42, 76—77).—A reply to Staudinger (preceding abstract). In dispersions of highly polymerised substances groups or parts of the chains of indefinite size are present. The association of molecular groups as micelles in soap is not exceptional as Staudinger asserts but similar to the behaviour of tannin in water, substantive dyes, higher hydrocarbons, and fatty acids in phenol, lower fatty acids in water. Staudinger's views have been anticipated by Pólányi and by Herzog (A., 1921, ii, 531). Later views of the latter author (A., 1925, ii, 942) are endorsed.

R. Brightman.

Production of acetone. Holzverkohlungs-ind. A.-G.—See B., 1929, 235.

Synthesis of αε-dimethoxypentan-β-one. R. Paul (Bull. Soc. chim., 1929, [iv], 45, 152—154).—Magnesium γ-methoxypropyl iodide with methoxyacetonitrile in ether affords αε-*dimethoxypentan*-β-*one*, b. p. 98—99°/23 mm., d_{15}^{15} 1·001, n_D 1·42645 (*semicarbazone*, m. p. 88·5°). R. Brightman.

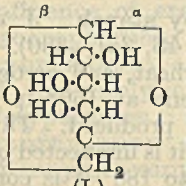
Constitution of βγ-diketones. II. Tendency and direction of enolisation. C. Weygand and H. Baumgärtel (Ber., 1929, 62, [*B*], 574—579; cf. 1927, 971).—In the series acetyl-, *n*-propionyl-, *n*-butyryl-, *n*-heptoyl-, and *n*-decoyl-acetone, the proportion of enol in the equilibrium mixture increases regularly with increasing mol. wt. until *n*-decoylacetone represents the first stable, homogeneous enol of the aliphatic series. Branching of the chain diminishes the proportion of enol, only 60% being present in pivalylacetone. Ozonisation of the diketones in ethyl chloride yields methylglyoxal (identified as the osazone) in the case of acetylacetone, probably a mixture of methyl- and *n*-propylglyoxals with *n*-propionylacetone, methylglyoxal and much butyric acid from *n*-butylacetone, much methylglyoxal and heptoic acid from heptoylacetone, impure methylglyoxal and large quantities of decoic acid from decoylacetone, which thus has the structure $CH_3{\cdot}[CH_2]_8{\cdot}C(OH){:}CHAc$. Distillation of the ketones isolated from the copper salts frequently appears to yield two distinct fractions of ketone which give rise to two distinct copper salts; the isomerism does not appear to be of the enolic structural type, and based on observations of Harries (A., 1904, i, 427), is provisionally regarded as "mesityl oxide isomerism." The following observations are recorded: *n*-propionylacetone, b. p. 43°/12 mm., and b. p. 45°/12 mm., *n*-butyrylacetone, b. p. 57—61°/11 mm. (*copper* salt, m. p. 164—165°), and b. p. 64—68°/12 mm. (*copper* salt, m. p. 161—162°); n-*heptoylacetone*, b. p. 108—112°/13 mm. (*copper* salt, m. p. 125—126°), and b. p. 114—118°/12 mm. (*copper* salt, m. p. 122—123°); *n*-decoylacetone, b. p. 150—152°/16 mm., m. p. 24—27° (copper salt, m. p. 110°) (cf. Morgan and Holmes, A., 1924, i, 496); pivalylacetone, b. p. 67—71°/18 mm. H. WREN.

Complex salts of diacetyldioxime. J. V. DUBSKÝ and F. BRYCHTA (J. Czechoslov. Chem. Comm., 1929, **1**, 137—154).—Various complex metallic derivatives of diacetyldioxime have been prepared. Interaction of equimolecular quantities of nickel chloride hexahydrate and diacetyldioxime in hydrochloric acid yields the complex *chloride*, $[DH_2NiCl_2],2H_2O$ ($D{=}{\cdot}NO{:}CMe{\cdot}CMe{\cdot}NO$, $DH_2{=}[{\cdot}CMe{:}N{\cdot}OH]_2$), which loses 2 mols. of water at 105°, yielding the same salt, DH_2NiCl_2, as is obtained by dehydration of $[DH_2NiCl_2],H_2O$ (Paneth and Thilo, A., 1925, i, 1132). In water it decomposes thus: $2[DH_2NiCl_2],2H_2O \longrightarrow Ni(DH)_2+NiCl_2+2HCl+4H_2O$. Similarly, the interaction of nickel carbonate and diacetyldioxime in hydrobromic acid furnishes the complex *bromides* $(DH_2)_2NiBr_2$ and DH_2NiBr_2, the latter decomp. 200°, m. p. 225°, the hydrates of which could not be isolated. Similarly with hydriodic acid is obtained the *periodide*, $(DH_2)_2NiI_2,I_2$, which is instantly decomposed by water, alcohol, acetone, and ether to yield $Ni(DH)_2+2HI+I_2$. It is assumed that the fixation of the oxime by the central atom depends on the anion, being weakest for the chloride ion. Analogous nitrates and sulphates could not be obtained. Similar methods yield the complex *cobalt* salts, $(DH_2)_2CoCl_2,2H_2O$ [which loses its water above 100°, yielding $(DH_2)_2CoCl_2$ (Feigl and Rubinstein, A., 1924, i, 20)] and $DH_2Co(DH)Cl$. Attempts to obtain the ethylenediamine compounds, $[Co\,en_2\,DH]Cl_2$ and $[Co\,en\,(DH)_2]Cl$, failed owing to the great solubility of these derivatives. Similar attempts to isolate the complex DH_2CuCl_2,xH_2O always yielded the anhydrous compound (Paneth and Thilo, *loc. cit.*), confirming the conclusion of the latter authors that the hydrate is probably incapable of existence. The chlorides of calcium and zinc do not form complexes with diacetyldioxime. J. W. BAKER.

Oxidative decomposition of sugars. II. Action of hydrogen peroxide on dextrose etc. in presence of calcium carbonate. K. BERNHAUER and J. NISTLER (Biochem. Z., 1929, **205**, 230—239; cf. this vol., 297).—The following products obtained by oxidation with hydrogen peroxide in presence of calcium carbonate are derived from glycerol: formaldehyde, formic, acetic, glyceric, and tartaric acids; from dextrose: formaldehyde, formic, acetic, oxalic, and *r*-tartaric acids, and pentoses; and from gluconic acid: formaldehyde, acetaldehyde, formic, acetic, oxalic, *r*-tartaric, and polyhydroxy-acids. The mechanism of the reactions is discussed.

P. W. CLUTTERBUCK.

Sugar anhydrides. I. Galactosan (α 1 : 5) (β 1 : 6). F. MICHEEL (Ber., 1929, **62**, [*B*], 687—693).—Acetobromogalactose is converted by trimethylamine in alcohol–benzene at 0° into *tetra-acetylgalactosidotrimethylammonium bromide*, m. p. 173° (decomp.), $[\alpha]_D^{20}$ +31·1° in chloroform, transformed by barium hydroxide into trimethylamine and *galactosan* (α 1 : 5) (β 1 : 6) (I), m. p. 220—221°, $[\alpha]_D^{21}$ −21·9° in water, which is not attacked by bromine, and only slowly oxidised by potassium permanganate or by boiling Fehling's solution. It is converted by acetic anhydride and pyridine into the corresponding *triacetate*, m. p. 73—74°, $[\alpha]_D^{22}$ −5·7° in chloroform, and by acetone and anhydrous copper sulphate into the 3 : 4-iso*propylidene ether*, m. p. 151—152°, $[\alpha]_D^{22}$ −61·7° in water, $[\alpha]_D^{22}$ −73·3° in chloroform, from which the galactosan is regenerated by 1% aqueous hydrochloric acid. The 1 : 6-position of the bridge is established by considerations of strain and by the formation of the *iso*propylidene ether. Galactosan is converted by 2% methyl-alcoholic hydrogen chloride into a mixture of α- and β-methylgalactosides. When heated in a vacuum at 270—360°, β-galactose yields small amounts of galactosan. *Galactosidotrimethylammonium bromide*, m. p. 162—164°, $[\alpha]_D^{20}$ +37·6° in water, is prepared by the action of hydrobromic acid on the tetra-acetyl derivative. β-Methylgalactoside is transformed by acetone and anhydrous copper sulphate into the 3 : 4-iso*propylidene ether*, m. p. 134—135°, $[\alpha]_D^{17}$ +20·96° in water, from which β-methylgalactoside is regenerated by 1% methyl-alcoholic hydrogen chloride. H. WREN.



(I.)

Attempted transformation of α- into β-penta-acetylglucose. A. GEORG (Helv. Chim. Acta, 1929, **12**, 261—263).—Since α-penta-acetylglucose is unchanged by heating with acetic anhydride and anhydrous sodium acetate, whilst this reagent converts α-glucose mainly into β-penta-acetylglucose, it is assumed that the conversion from α- into β-forms in the latter case must occur in the partly acetylated sugar before the terminal hydroxyl group is attacked.

J. W. BAKER.

Formula of digitalinum verum. A. WINDAUS and E. HAACK (Ber., 1929, **62**, [*B*], 475—476).—Analyses of the crystalline *hexa-acetyl* derivative of digitalinum verum, $C_{36}H_{50}O_{14}Ac_6$, m. p. 212—213° after slight softening at 166° when slowly heated or m. p. 175—176° followed by re-solidification and re-melting at 212—214° when placed in a bath preheated to 160°, $[\alpha]_D^{20}$ −18·1° in chloroform, confirm the formula $C_{36}H_{56}O_{14}$ assigned to digitalinum verum on the basis of the products of its hydrolysis.

H. WREN.

Rhamnoconvolvulic acid. E. VOTOČEK and F. VALENTIN (J. Czechoslov. Chem. Comm., 1929, **1**, 47—54).—Hydrolysis of commercial convolvuline with warm barium hydroxide gives *rhamnoconvolvulic acid heptahydrate*, $C_{52}H_{92}O_{32},7H_2O$ (so named in contradistinction to the ether-soluble convolvulic acid which gives rhodeose and *iso*rhodeose on hydrolysis), softening at 73—74° and effervescing at 104°. By drying at 100°, the anhydrous *acid*, m. p. 184° (decomp.) after softening at 137°, $[\alpha]_D$ −35·31°, is obtained. The last product yields, on hydrolysis by hot 10% oxalic acid, a *dihydroxypalmitic acid* (this vol., 541) and a mixture of sugars in which can be detected dextrose and *l*-rhamnose (yields 1 : 4 : 2 mols., respectively). R. J. W. Le Fèvre.

Absorption of formaldehyde by starch. J. J. Blanksma (Rec. trav. chim., 1929, **48**, 351—360).—When dry starch (potato, maize, wheat, and arrowroot) is heated with trioxymethylene at 160° in a sealed tube formaldehyde-starch is produced. This has the original starch structure, but it is unaffected by boiling with water. When heated to 180° it is converted into water-soluble dextrin, which, after a further treatment with trioxymethylene, affords an insoluble formaldehyde-dextrin. The composition of the formaldehyde-starch obtained depends on the weight of trioxymethylene used; with increasing weight of the last-named substance there is an increased formaldehyde content. Water is not eliminated during the reaction and the various products obtained are, therefore, absorption compounds. A very small formaldehyde content renders the product insoluble in water. When the capacity of the tube in which the reaction is carried out is small the formaldehyde content increases. The formaldehyde content of the reaction product is low when the heating is carried out below 160° or for less than 2—3 hrs. at 160°. In presence of water at 120—130° starch and trioxymethylene yield a gel, which when heated to 150—160° becomes a sol. The temperature at which liquefaction of formaldehyde-starch takes place rises with decrease in the amount of water added: the formaldehyde content of the product bears the same relationship. H. Burton.

Behaviour of polysaccharides in solutions. I. Solution of glycogen in resorcinol. R. O. Herzog and W. Reich (Ber., 1929, **62**, [*B*], 495—499).—Glycogen yields opalescent solutions in water which give a marked Tyndall effect. It is readily soluble in resorcinol at 120° and the solutions do not exhibit the Tyndall phenomena, thus indicating a molecular instead of a colloidal solution. Cryoscopic measurements point to the formula $(C_6H_{10}O_5)_4$, but these are considered to require confirmation. Removal of resorcinol from the solution by alcohol followed by repeated dissolution and precipitation of the residual glycogen by alcohol, purification by electrodialysis, and desiccation over phosphoric oxide at 78°/0·1 mm. gives 95% of the original glycogen, indistinguishable from the initial material in chemical or physical properties or in behaviour towards diastase. H. Wren.

Absorption of formaldehyde by cellulose. J. J. Blanksma (Rec. trav. chim., 1929, **48**, 361—362).—Treatment of dry cellulose (Swedish filter-paper, cotton-wool, wood, and viscose-silk) with trioxymethylene at 160° gives products containing amounts of formaldehyde varying according to the amount of trioxymethylene used. With large amounts of trioxymethylene at 170° the cellulose swells, forming a transparent jelly. Water does not appear to be formed during the reaction. H. Burton.

Hydrolysis of cellulose. II. R. Willstätter and L. Zechmeister (Ber., 1929, **62**, [*B*], 722—725).—Cellulose, dried at 115°, is treated with hydrochloric acid (d_4^{15} 1·21) at 19·5°; after 3 hrs., a portion of the hydrochloric acid is removed by evacuation and the residue is poured on to ice. The acid is removed by silver carbonate or by lead carbonate followed by hydrogen sulphide. The solution is treated fractionally with alcohol. The most sparingly soluble fractions are dextrin-like substances which swell in water, whereas the most freely soluble portions are cellobiose and dextrose. The intermediate fractions contain *cellotetraose*, $C_{24}H_{42}O_2$, m. p. (indef.) about 240° after softening at 205°, $[\alpha]_D$ +17·9° to +21·5° for different specimens, soluble in water without swelling, and *cellotriose*, $C_{18}H_{32}O_{16}$, m. p. about 210° (decomp.), $[\alpha]_D$ +21·9°. The course of the hydrolysis of cellulose by hydrochloric acid is not in harmony with the conception of small units. H. Wren.

Constitution of pine lignin. VIII. Investigation of pine sap. P. Klason (Ber., 1929, 62, [*B*], 635—639).—The feebly acidic sap contains about 10% of dry material, including marked amounts of peptones and amino-acids. Sugars, probably including sucrose, are present in large quantity. The pentose is mainly xylose. Isolation of lignin from the sap is effected by treatment of the dried residue successively with 66% sulphuric acid and *N*-hydrochloric acid; the product is designated "protolignin." It is probably an intermediate product between pentoses and coniferyl alcohol. Coniferin appears to be present in the sap in amount varying very greatly with the season. Treatment of coniferin with emulsin affords coniferyl alcohol, which undergoes autoxidation at the atmospheric temperature to a trimeric form of coniferaldehyde identical with the lignin of wood. The protolignin of the sap, combined with sulphurous acid and condensed with naphthylamine, passes by loss of water into polymeric forms of coniferaldehyde; it can also lose water directly and pass into coniferyl alcohol, which appears as coniferin in the sap. It is highly probable that not only the coniferyl alcohol is united with sugar to coniferin but also that lignin is present in wood as a glucoside.

The observation of Pauly and Feuerstein (this vol., 446) that the author's synthetical naphthylamine salt of coniferylhydrosulphonic acid is derived from condensed acetaldehyde is not compatible with its very considerable methoxyl content. Coniferaldehyde exists in two forms, one of which is labile and combines with sulphurous acid and is found in living matter, whereas the other (Pauly's) is stable and does not unite with sulphurous acid. H. Wren.

Catalytic reduction of dioximes. Preparation of βγ-diaminobutane by reduction of dimethylglyoxime. J. Frejka and (Mlle.) L. Zahlová (J. Czechoslov. Chem. Comm., 1929, **1**, 173—187).—A 50% yield of βγ-diaminobutane, b. p. 60—64°/56 mm., d^{20} 0·86011, n_D^{20} 1·44426, $n_F-n_C=0\cdot00843$, is obtained by catalytic reduction of diacetyldioxime with platinum-black in glacial acetic acid suspension. Under prescribed conditions the same catalyst can be used for eleven successive reductions. Distillation of the acetic acid solution of the products in a vacuum at 110°, redistillation in a vacuum of the residue saturated with potassium hydroxide, and a further vacuum distillation of the distillate after again treating with potassium hydroxide yields the diamine as a mixture of its mono- and hemi-hydrates, from which it is obtained anhydrous by distillation over sodium. No reduction occurs in alcoholic solution. The base is characterised by preparation of the following derivatives: *diacetyl*; *dibenzoyl*; *phenylurethane*, m. p. 230°; condensation *product* with ethyl acetoacetate $[\cdot CHMe\cdot NH\cdot CMe{:}CH\cdot CO_2Et]_2$, m. p. 59° (corr.); hydrochloride; *hydrobromide*; oily *hydriodide*; *sulphate*; *chromate*; *chloroaurate*; *chloroplatinate*; *oxalate*, $+H_2O$ and anhydrous; *succinate*, *picrate*, and *picrolonate*. J. W. Baker.

Cobaltic derivatives of ββ′β″-triaminotriethylamine. F. G. Mann (J.C.S., 1929, 409—411).—Mononuclear compounds of ββ′β″-triaminotriethylamine with cobalt are described in which co-ordination occurs at all four amine groups (cf. Jaeger and Koets, A., 1926, 697). Gentle boiling of an aqueous solution of roseo-cobaltic chloride and triaminotriethylamine trihydrochloride gave, after addition of potassium thiocyanate, *dithiocyanatotriaminotriethylaminecobaltic monothiocyanate monohydrate*, $[(SCN)_2Co\ tren]SCN,H_2O$, m. p. 208—210° (decomp.) [corresponding *mononitrate monohydrate*, m. p. 226° (decomp.); anhydrous *monochloride*, m. p. 225—226° (decomp.); *chloroplatinate*, m. p. 203—204° (decomp.)]. R. J. W. Le Fèvre.

Basic chlorides and additive compounds from metallic chlorides and hexamethylenetetramine. Exceptional behaviour of nickel chloride. J. C. Duff and E. J. Bills (J.C.S., 1929, 411—419).—Boiling hexamethylenetetramine solution does not react with chlorides of magnesium, calcium, strontium, or barium; zinc, ferric, chromic, aluminium, antimony, and tin chlorides all yielded the corresponding hydroxide; cadmium, lead, bismuth, manganese, ferrous, cobaltous, and cupric chlorides gave the respective basic chlorides [*basic ferrous chloride*, $3Fe(OH)_2,FeCl_2$]; nickel chloride gave a *compound*, $N(CH_2\cdot OH)_3,3Ni(OH)_2$. The following new additive *compounds* from metallic chlorides and hexamethylenetetramine, $M,2C_6H_{12}N_4,xH_2O$, are described: $M=3ZnCl_2$, $x=6$; $M=CaCl_2$, $x=10$; $M=SrCl_2$, $x=9$; $M=FeCl_2$, $x=9$; $M=CuCl\cdot OH,CuCl_2$, $x=2$; $M=2Cu_2(SO_4)_3$, $x=2$; $M=SnCl_4$, $x=0$; $M=BiCl_3$, $x=0$; $M=ZnCl_2$, $x=0$. The *compounds* $SnCl_4,4C_6H_{12}N_4$, $SbCl_3,3C_6H_{12}N_4$, and $SbCl_5,6C_6H_{12}N_4$ have also been prepared. R. J. W. Le Fèvre.

Nitrogen trichloride and unsaturated acids. G. H. Coleman and G. M. Mullins (J. Amer. Chem. Soc., 1929, 51, 937—940).—The *hydrochloride* of *α-chloro-β-aminobutyric acid*, m. p. 161—161·5° (*benzoyl* derivative, m. p. 174—174·5°), slowly separates (9·3—19·7% of theory) from a solution of crotonic acid and nitrogen trichloride in carbon tetrachloride (cf. A., 1928, 1362). Nitrogen, chlorine, αβ-dichlorobutyric acid, and small amounts of ammonium chloride are also formed. The chloroamine is reduced by sodium amalgam in methyl alcohol to β-aminobutyric acid. Cinnamic acid and nitrogen trichloride yield the *hydrochloride*, m. p. 228—230°, of *α-chloro-β-amino-β-phenylpropionic acid*, m. p. 199—200°, which is reduced by sodium amalgam to β-amino-β-phenylpropionic acid (*benzoyl* derivative, m. p. 194—195°). H. E. F. Notton.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on the decomposition of certain polypeptides. E. Abderhalden and V. Vlassopoulos. **Specificity of enzymolytic degradation of polypeptides. Polypeptides containing *dl*-norleucine.** E. Abderhalden and H. Mayer. **Specific action of enzyme complexes on fission of polypeptides.** E. Abderhalden and F. Reich.—See this vol., 604, 605.

[Composition of] Buff's and Bunsen's salts. F. Hölzl [with W. Khünl-Brady] (Monatsh., 1929, **51**, 157—168; cf. Bäyer and Villiger, A., 1902, i, 355).—When the salt, $H_4Fe(CN)_6,6EtOH,2HCl$ (I) (Buff, Annalen, 1854, **91**, 253; cf. Freund, A., 1888, 571), obtained by the action of hydrogen chloride on an alcoholic solution of hydroferrocyanic acid, is allowed to decompose in a vacuum there is almost a complete loss of all the alcohol and hydrogen chloride after 34 hrs. Hydroferrocyanic acid remains as the end product (cf. Freund, *loc. cit.*). During the early stages (up to 10 hrs.) of the decomposition the ratio of the evolved hydrogen chloride and alcohol is approximately 1 : 2, hydroferrocyanic acid dialcoholate being a primary decomposition product: for longer times the ratio is 1 : 3. The existence of mono-, di-, tri-, and probably tetra-alcoholates of hydroferrocyanic acid is shown by vapour-pressure measurements. When Bunsen's salt, $(NH_4)_4Fe(CN)_6,2NH_4Cl,3H_2O$ (II), is treated with silver nitrate, silver ferrocyanide and silver chloride (2 mols.) result. The same silver salts are obtained from silver nitrate and I, showing the similarity of the dissociation of I and II in aqueous solution. H. Burton.

Reaction between magnesium phenyl bromide and alkyl esters of acids of fifth group of elements. H. Gilman and J. Robinson (Rec. trav. chim., 1929, 48, 328—331).—Magnesium phenyl bromide reacts with *n*-butyl nitrite yielding diphenyl, diphenylamine (formed presumably through the intermediate nitrosobenzene), and butyl alcohol. With methyl phosphite and magnesium phenyl bromide 42% of diphenylmethylphosphine oxide was obtained: ethyl phosphite gives 10% of triphenylphosphine oxide. Ethyl phosphate affords diethyl phenylphosphinate (16%) together with diphenylphosphinic acid (17%), whilst ethyl arsenite gives 85·3% of triphenylarsine. Ethyl arsenate and magnesium phenyl bromide yield an unidentified substance, m. p. 270°. Ethyl nitrate and methyl phosphate gave no definite products, and methyl vanadate afforded a quantitative yield of diphenyl. No alkylbenzene was produced in any experiment, as with alkyl sulphates. H. Burton.

Derivatives of trimethylethylstannane. R. H. Bullard and R. A. Vingee (J. Amer. Chem. Soc., 1929, **51**, 892—894).—Trimethylethylstannane (cf. Pope and Peachey, Proc. C.S., 1903, **19**, 290) prepared in 80% yield from sodium trimethylstannide and ethyl bromide in liquid ammonia, is converted by bromine in carbon tetrachloride into *dimethylethylstannic bromide*, b. p. 175—180°. *Sodium dimethylethylstannide* and ammonium bromide in liquid ammonia give *dimethylethylstannane*, b. p. 90°. This, unlike trimethylstannane (Kraus and Greer, A., 1923, i, 26), is oxidised by air to *dimethylethylstannic hydroxide*, also obtained from dimethylethylstannic bromide and 30% sodium hydroxide.

H. E. F. Notton.

Silver cacodylates. K. V. Zappi and (Mlle.) A. Manini (Bull. Soc. chim., 1929, [iv], **45**, 154—155).—Normal silver cacodylate, Me_2AsO_2Ag, is obtained by dissolving moist silver oxide in cacodylic acid. Double decomposition between silver nitrate and sodium cacodylate solutions always affords the double salt, $Me_2AsO_2Ag,AgNO_3$. R. Brightman.

Non-existence of isomerism among dialkyltelluronium dihalides. H. D. K. Drew (J.C.S., 1929, 560—569).—Absence of isomerism between the supposed isomeric dimethyltelluronium bromides and iodides of Vernon (*ibid.*, 1920, **117**, 86, 897; 1921, **119**, 105, 687) is demonstrated. Halides of the α-series are normal in type, non-polar, and have a tellurium atom with a tetrahedral valency distribution. The compounds of the β-series are salt-like complex substances having the same empirical formulæ as the corresponding substances in the α-series.

Vernon's β-base (new formula: $TeMe_3{\cdot}O{\cdot}TeMeO$) was treated in aqueous solution with hydriodic acid; the product contained trimethyltelluronium iodide (decomp. 240°) and the *anhydride* of *methylhydroxytellurium oxide* (*telluracetic acid*), blackens above 230°. The last-named product was easily converted by excess of hydriodic acid into *methyltelluronium tri-iodide*, decomp. 100°, m. p. 180°. Vernon's β-iodide was synthesised by mixing trimethyltelluronium iodide and methyltelluronium tri-iodide in acetone solution.

Similarly, the action of hydrobromic acid on the β-base gave *trimethyltelluronium bromide*, decomp. 250—280° (complex *salts* with ferric chloride and stannic bromide), accompanied by *methyltelluronium tribromide*, discoloured 140—150°, m. p. 156° (decomp.), and an anhydride of methyltellurium oxide or oxybromide (which accounts for traces of α-dibromide also isolated). Methyltelluronium tribromide and trimethyltelluronium bromide united, in acetone solution, to give Vernon's β-dibromide. In addition, the following "mixed β-dihalides" have been prepared from their constituents: $TeMe_3I,TeMeBr_3$, m. p. 120° (decomp.), $TeMe_3Br,TeMeI_3$, blackening below 90°. The following complex *iodides* are also described: $TeMe_3I,\alpha TeMe_2I_2,TeMe_2I_4$, m. p. about 80°, and $TeMe_3I,2TeMe_2I_2$.

The constitution of the β-salts is probably $[Me_3Te]^+[TeMeX_4]^-$, since the β-di-iodide and potassium iodide gave, in acetone solution, trimethyltelluronium iodide and a *substance* (probably $K^+[TeMeI_4]^-$). Attention is directed to the possible analogy between tellurium "β-dihalides" and the salts which trisacetylacetone silicon, germanium, and titanium halides form with metallic chlorides.

R. J. W. Le Fèvre.

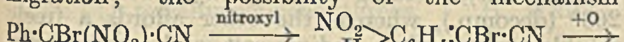
***Ortho–para* ratio in aromatic substitutions.** A. Lapworth and R. Robinson (Mem. Manchester Phil. Soc., 1927—1928, **72**, 43—52).—The relation between constitutional conditions and the rate of substitution in the *o*-*p*-positions and allied phenomena in aromatic substitutions is discussed. Applied in the case of cationoid reagents, the hypothesis advanced, which is applicable to anionoid reagents in the opposite sense, is that the agent seeks a position of high electron density. This presupposes first a molecular polarisation, secondly a definite frequency of polar molecular phase. The disturbance of an *o*–*p* ratio in favour of increasing *p*-isomeride by augmenting the activity of the cationoid reagent is explained, on the activated phase hypothesis, as greater frequency of activation. Experimental confirmation is derived from the results of Gattermann and Liebermann (A., 1912, i, 1038) on the formation of azo-compounds. The electrical fields in the molecule or surrounding medium due to the presence of constituent groups control the availability of electrons, and hence the *o*–*p* ratio. The wide applicability is shown by numerous examples.

G. E. Wentworth.

Aromatic nitro-compounds and organomagnesium halides. H. Gilman and R. McCracken (J. Amer. Chem. Soc., 1929, **51**, 821—830).—Previous work on this reaction is reviewed (cf. A., 1928, 536; Oddo, A., 1904, i, 862; Hepworth, J.C.S., 1920, **117**, 1004). Nitrobenzene reacts with 4 mols. of magnesium phenyl bromide in ether at the ordinary temperature, mainly according to the scheme $PhNO_2+4MgPhBr \longrightarrow NHPh_2+PhOH+Ph_2$. Traces of *p*-phenyldiphenyl and aniline are also obtained, but attempts to detect the intermediate formation of nitroso-, azoxy-, and hydroxylamino-derivatives and tetraphenylhydrazine were unsuccessful. Similar results are obtained with α-nitronaphthalene and *o*- and *p*-nitrotoluenes. Nitrobenzene and magnesium phenylacetylenyl bromide give, among other products, diphenyldiacetylene, m. p. 88° (previously obtained, but not identified, by Yocich, J., Russ. Phys. Chem. Soc., 1903, **35**, 555), and αβ-di-iodostyrene. Aliphatic Grignard reagents give hydrazines in addition to the above products. Thus, nitrobenzene and magnesium benzyl chloride give dibenzyl, aniline, *p*-ditolyl, and 1 : 2-diphenyl-1 : 2-dibenzylhydrazine. Diphenyldiethylhydrazine is similarly obtained with magnesium ethyl bromide. Tetraphenylhydrazine does not react with magnesium phenyl bromide, but dimethylaniline oxide gives phenol, diphenyl, and dimethylaniline, and ethyl nitrate at −80° gives phenol and diphenyl, but no nitrobenzene. H. E. F. Notton.

Alternating effect in carbon chains. XXX. Nitration of phenylbromocyanonitromethane; an alleged example of intramolecular *meta*-rearrangement. J. W. Baker and C. K. Ingold (J.C.S., 1929, 423—447).—The speeds of the side reactions which accompany the normal *meta*-nitration of phenylbromocyanonitromethane and lead to products giving by oxidation *p*-nitro- and *m*-bromobenzoic acids have been determined under formerly described conditions with nitric acid (d_4^{15} 1·490—1·517) and are found to be, unlike velocities of nuclear nitration, only comparatively slightly affected by the concentration of acid. Longer contact with more dilute acids increases lateral decomposition (as measured by brominated products) but decreases direct nitration (as measured by *meta*-nitration); *op*-nitro-derivatives arise partly by nitration and partly by side reactions.

The mechanisms advanced by Flürscheim and Holmes to explain the lateral decomposition process, namely, intramolecular *meta*-migration of bromine and extramolecular *para*-nitration of nucleus, are disputed, since (1) the former conception is foreign to a theory of aromatic substitution which postulates inductive *m*-deactivation in *m*-orientation, (2) free bromine (by elimination) is shown to be present in the reaction mixture under all conditions in which *m*-bromo-products, including *m*-bromophenylbromocyanonitromethane, are formed, (3) much evidence exists to show that the *m*-bromo-products are formed by extramolecular bromination of the nucleus by some external brominating agent which either is, or depends on, free bromine and that the *p*-nitro-derivatives are formed by an internal change involving group migration.

Tentative suggestions are made regarding (i) the form in which the bromine is originally eliminated; thus (since in absence of nitric acid benzoyl cyanide is found to be the main thermal decomposition product of phenylbromocyanonitromethane): (1) $\mathrm{C_6H_5{\cdot}CBr(NO_2){\cdot}CN} \longrightarrow \mathrm{C_6H_5{\cdot}CO{\cdot}CN+NOBr}$: $\mathrm{2NOBr \rightleftharpoons Br_2+2NO}$; or (2) $\mathrm{C_6H_5{\cdot}CBr(NO_2){\cdot}CN} \longrightarrow \mathrm{C_6H_5{\cdot}C(OH)(NO_2){\cdot}CN} \longrightarrow \mathrm{C_6H_5{\cdot}CO{\cdot}CN+HO{\cdot}NO}$ [mechanism (2) is illustrated by the conversion of α-bromo-α-nitro-α-phenylethane into acetophenone by action of silver oxide and water] and (ii) the nature of the internal change involving *para*-migration; the possibility of the mechanism  $\mathrm{Ph{\cdot}CBr(NO_2){\cdot}CN} \xrightarrow[\text{migration}]{\text{nitroxyl}} \mathrm{{}^{NO_2}_{H}{>}C_6H_4{:}CBr{\cdot}CN} \xrightarrow[-\mathrm{HBr}]{+\mathrm{O}} \mathrm{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CN}$ is enhanced by (*a*) the observation of the formation of *p*-nitrobenzoyl cyanide by the action of reagents known to be present in the original decomposition on *p*-nitrophenylacetonitrile (by the action of bromine alone p-*nitrophenylbromoacetonitrile*, m. p. 96°, is obtained), and (*b*) the isolation of dicyanostilbene by thermal decomposition of dry phenylbromocyanonitromethane.

An improved process for the preparation of phenylbromocyanonitromethane is described. m-*Bromobenzyltrimethylammonium bromide*, m. p. 216°, decomp. 220—225°, and the corresponding *picrate*, m. p. 150°, were prepared from *m*-bromotoluene by bromination and treatment of the resulting crude product with alcoholic trimethylamine. *Benzylmethylammonium bromide* has m. p. 235°. R. J. W. LE FÈVRE.

Oxidation of unsaturated substances with perbenzoic and peracetic acids. II. J. BÖESEKEN and G. ELSEN (Rec. trav. chim., 1929, 48, 363—369; cf. A., 1927, 39).—Oxidation of αγ-diphenylpropene, b. p. 164—168°/11 mm., d_4^{17} 1·0003, $n_{\mathrm{D}}^{17\cdot5}$ 1·6010 (cf. von Braun and Köhler, A., 1918, i, 162), with peracetic acid gives αγ-diphenylpropane-αβ-diol monoacetate. Similar oxidation of α-*p*-methoxyphenyl-Δ^{α}-propene and β-*iso*safrole yields essentially the corresponding diol monoacetate. The above unsaturated hydrocarbons all have a double linking adjacent to the aryl group and are oxidised rapidly. When the double linking is further away from the aryl group as in allylbenzene and safrole oxidation is slow. The former compound affords the corresponding diol diacetate, whilst the latter gives a complex mixture, presumably because of oxidation of the benzene nucleus. Eugenol, however, is rapidly oxidised and yields the diol monoacetate, and although indene is oxidised rapidly a mixture of the mono- and di-acetates results. Oxidation of *cyclo*hexene with peracetic acid gives *trans-cyclo*hexane-1 : 2-diol, separated by heating the oxidation mixture in a cathode vacuum, and a mixture of the diol mono- and di-acetates. H. BURTON.

Structure of certain phenylated olefines. K. VON AUWERS (Ber., 1929, 62, [*B*], 693—701).—On the basis of a rule that "an unsaturated carbon atom is capable of adding sodium only when it is united to aryl groups," Schlenk and Bergmann (A., 1928, 1031) have proposed alterations in the formulæ of various styrenes, for example, $\mathrm{CHPh{:}CMe_2}$, $\mathrm{CMePh{:}CMe_2}$, $\mathrm{CPh_2{:}CHMe}$, and $\mathrm{CPh_2{:}CMe_2}$ to $\mathrm{CH_2Ph{\cdot}CMe{:}CH_2}$, $\mathrm{CHMePh{\cdot}CMe{:}CH_2}$, $\mathrm{CHPh_2{\cdot}CH{:}CH_2}$, and $\mathrm{CHPh_2{\cdot}CMe{:}CH_2}$, respectively. The mode of formation of the hydrocarbons renders the new constitution highly improbable, since they are uniformly produced by the loss of water or halogen hydride from carbinols or the corresponding halides containing the substituent in the α- or β-position to the benzene nucleus. The older formulæ are in complete harmony with spectrochemical behaviour as shown by a study of styrene, α-phenyl-Δ^{α}-propene, α-phenyl-β-methyl-Δ^{α}-propene, α-methylstyrene, α-phenyl-α-methyl-Δ^{α}-propene, α-phenyl-αβ-dimethyl-Δ^{α}-propene, *as*-diphenylethylene, αα-diphenyl-Δ^{α}-propene, αα-diphenyl-β-methyl-Δ^{α}-propene, stilbene, 7-methylstilbene, triphenylethylene, and ααβ-triphenyl-Δ^{α}-propene. Schlenk's rule for the addition of alkali metal to the ethylenic linking does not appear generally applicable in its simple form.

The following data amongst others appear to be new: αα-Diphenyl-Δ^{α}-propene, m. p. 51—52°, $d_4^{78\cdot2}$ 0·9710, $n_{\mathrm{He}}^{78\cdot2}$ 1·57329; αα-diphenyl-β-methyl-Δ^{α}-propene, b. p. 152—154°/14 mm., d_4^{20} 1·000, n_{He}^{20} 1·5875, which yields acetone when oxidised with chromic acid in glacial acetic acid; triphenylethylene, b. p. 219—221°/15 mm., m. p. 67—69°, $d_4^{78\cdot4}$ 1·0373, $n_{\mathrm{He}}^{78\cdot4}$ 1·64012; αα-diphenyl-γ-methyl-Δ^{α}-butene, b. p. 166—168°/18 mm., d_4^{20} 0·978, n_{He}^{20} 1·5753. δδ-*Diphenyl*-β-*methylbutan*-β-*ol*, from ethyl ββ-diphenylpropionate and magnesium methyl iodide, has b. p. 180—182°/12 mm., d_4^{20} 1·036, n_{He}^{20} 1·5636. H. WREN.

Orientation effects in the diphenyl series. VII. Effect of substituents in one nucleus on ratio of *ortho* : *para* nitration in the other. Nitration of 2- and 4-nitro- and of 2 : 4- and

2 : 4′-dinitro-diphenyl and of diphenyl-4-carboxylic acid. H. C. Gull and E. E. Turner (J.C.S., 1929, 491—500).—Results of quantitative nitration experiments have confirmed the postulation (Le Fèvre and Turner, A., 1928, 630) of independent nuclear conjugation. 4-Nitrodiphenyl is nitrated by nitric acid (*d* 1·448) at 40—50° to the extent of 37% and 63% in the 2′- and 4′-positions, respectively, whilst 2-nitrodiphenyl (nitric acid, *d* 1·420 at 35°) gives 39% of the 2′-nitro- and 61% of the 4′-nitro-compound. Diphenyl by treatment with nitric acid (*d* 1·448 at 35—50°) undergoes nitration to the extent of 47% in the 4-position and 53% in position 2; further nitration of 4-nitrodiphenyl also occurs and 30% of the product is 4 : 4′-dinitrodiphenyl. 4 : 4′-Dinitrodiphenyl, by dissolution in boiling nitric acid (*d* 1·5), gives 2 : 4 : 4′-*trinitrodiphenyl*, m. p. 176°, which by further nitration by mixed acids at 100° gives 2 : 4 : 2′ : 4′-tetranitrodiphenyl. 2 : 4-*Dinitrodiphenyl*, m. p. 110° (prepared by heating iodobenzene, chloro-2 : 4-dinitrobenzene, and copper bronze), is nitrated by dissolution for 1 min. in nitric acid (*d* 1·5) at 100° to the extent of 45% in position 2′ and 55° in position 4′. Less than 1% of a third product is formed. Similar treatment of 2 : 4′-dinitrodiphenyl produces 47·5% of 2 : 4 : 2′- and 52·5% of 2 : 4 : 4′-trinitrodiphenyl. From 2 : 2′-dinitrodiphenyl (nitric acid, *d* 1·5 at 75—80°) 2 : 4 : 2′-*trinitrodiphenyl*, m. p. 150—151°, is formed to the extent of 80—85%. 2 : 4 : 6-*Trinitrodiphenyl*, m. p. 130°, is obtained by heating together picryl chloride, iodobenzene, and copper bronze.

Diphenyl-4-carboxylic acid (prepared by hypochlorite or permanganate oxidation of 4-acetyldiphenyl) is dinitrated by nitric acid (*d* 1·5) at −15°, giving 49% of 2 : 4′-dinitrodiphenyl-4-carboxylic acid (decarboxylation of which gives 2 : 4′-dinitrodiphenyl) and 51% of 2 : 2′-*dinitrodiphenyl*-4-*carboxylic acid*, m. p. 194—195° (decarboxylation of which gives 2 : 2′-dinitrodiphenyl) (all m. p. corr.).

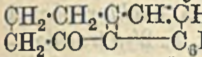
R. J. W. Le Fèvre.

Pyrogenic decomposition of aromatic compounds under pressure of hydrogen in presence of a mixed catalyst. II. V. Ipatiev and N. Orlov (Ber., 1929, 62, [*B*], 593—597; cf. A., 1927, 1060).—The experiments are performed at 440—465° under an initial pressure of about 70 atm. in the presence of a mixture of the oxides of aluminium and iron. α-Methylnaphthalene gives methane, naphthalene, benzenoid hydrocarbons, hydronaphthalene, and methylhydronaphthalene. β-Methylnaphthalene behaves similarly. The isolation of β-methylnaphthalene from 1 : 6- and 2 : 6-dimethylnaphthalenes is recorded. A technical paraffin, m. p. 25—56°, yielded exclusively paraffin hydrocarbons, b. p. 50—170°, d_0^{25} 0·7211, n_D^{25} 1·412. Carbazole is remarkably stable, whereas quinoline suffers partial decomposition into ammonia and hydrocarbons. Diphenylene oxide is completely unchanged. Indene is partly transformed into hydrindene, partly degraded to substituted benzenes, and partly polymerised to resin. 1 : 2 : 3 : 4-Tetrahydronaphthalene is dehydrogenated to naphthalene and decomposed in the hydrogenated nucleus. Dibenzyl is smoothly converted into toluene. H. Wren.

Scission of certain sulphohydroxamic acids. A. Angeli, D. Bigiavi, and Z. Jolles (Atti R. Accad. Lincei, 1928, [vi], 8, 116—120).—According to Raschig ("Schwefel- und Stickstoffstudien," 89), the hydroxamic acid formed when sodium hydroxylaminosulphonate and benzaldehyde react in presence of alkali is difficult to detect by means of the violet coloration with ferric chloride because of the necessity of using a large proportion of alkali at 70° to effect the decomposition of the sulphonate. The authors find, however, that such decomposition occurs rapidly at the ordinary temperature and that the non-appearance of the coloration with ferric chloride is due to reduction of this reagent to the ferrous state by the sulphite formed. Angeli, Angelico, and Scurti's statement that the action of aqueous potassium hydroxide on naphthalene-1-sulphohydroxamic yields naphthalene-2-sulphinic acid (A., 1904, i, 310) requires correction, the compound formed being naphthalene-1-sulphinic acid, m. p. 103° (cf. Hinsberg, A., 1917, i, 328). T. H. Pope.

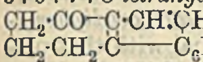
Hydrogenation of phenanthrene. II. G. Schroeter, H. Müller, and J. Y. S. Huang (Ber., 1929, 62, [*B*], 645—658; cf. A., 1925, i, 130).—Hydrogenation of phenanthrene, like that of anthracene, occurs in three distinct stages, 9 : 10-dihydro-, 1 : 2 : 3 : 4-tetrahydro-, and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-phenanthrenes being successively produced. Phenanthrene, purified from fluorene by distillation and from diphenylene sulphide by sodium, is partly hydrogenated in tetrahydronaphthalene. Tetrahydrophenanthrene is removed from the product as the picrate, leaving a mixture of *ms*-dihydrophenanthrene and octahydrophenanthrene which cannot be separated into its components by distillation. The mixture is treated with concentrated sulphuric acid, whereby octahydrophenanthrene is transformed into the sparingly soluble monosulphonic acid (corresponding chloride, m. p. 131°). The filtrate contains two isomeric meso*dihydrophenanthrenedisulphonic acids*, one of which gives a sparingly soluble *barium* salt (*sodium* salt), yielding a *disulphonyl chloride*, m. p. 263° (decomp.), whereas the other affords a freely soluble *barium* salt, a *sodium* salt, and a *disulphonyl chloride*, m. p. 184—185°. Treatment of the acids regenerated from the chlorides with fuming hydrochloric acid at 200° yields ms-*dihydrophenanthrene*, b. p. 168—169°/15 mm., m. p. 34·5—35°, d_4^{14} 1·0953, d_4^{40} 1·0757. Technical phenanthrene is converted by sodium and amyl alcohol into resinous products, *ms*-dihydro- and tetrahydro-phenanthrene; the latter compound partly forms mixed crystals with unchanged phenanthrene which can be separated from one another by fractional crystallisation. Octahydrophenanthrene is not produced. The synthesis of the *ms*-compound from 2 : 2′-dibromomethyldiphenyl and sodium is described. The compound described in the literature as *ms*-dihydrophenanthrene, m. p. 95° (picrate, m. p. 137°), is a mixture of phenanthrene and a small proportion of its tetrahydro-derivative. Tetrahydrophenanthrene has b. p. 173°/11 mm., m. p. 33—34°, d_4^{40} 1·0601 (picrate, m. p. 111°). Oxidation of 5 : 6 : 7 : 8-tetrahydrophenanthrene by chromic acid in 92% acetic acid affords 5-*keto*-

5 : 6 : 7 : 8-*tetrahydrophenanthrene*,



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}C{\cdot}CH{:}CH \\ CH_2{\cdot}CO{-}C{-\!-\!-\!-}C_6H_4 \end{array}$$

, m. p. 69° [*semicarbazone*, m. p. 225° (decomp.); *oxime*, m. p. 172—173°; *picrate*, m. p. 101—102°]. With permanganate in the presence of acetone, tetrahydrophenanthrene gives a mixture of the 5-keto-compound and 8-*keto*-5 : 6 : 7 : 8-*tetrahydrophenanthrene*,



$$\begin{array}{l} CH_2{\cdot}CO{-}C{\cdot}CH{:}CH \\ CH_2{\cdot}CH_2{\cdot}C{-\!-\!-\!-}C_6H_4 \end{array}$$

, m. p. 96—97° [*semicarbazone*, m. p. 247° (decomp.); *oxime*, m. p. 165—166°; *picrate*, m. p. 106—107°]. Oxidation of tetrahydrophenanthrene with boiling aqueous permanganate gives a mixture of *o*-phthalic acid and benzene-1 : 2 : 3 : 4-tetracarboxylic acid.

Synthesis of the two ketones is effected as follows. Naphthalene is converted by chloroacetyl chloride in presence of phosphoric oxide at 150—180° into a mixture of unchanged naphthalene, 1-naphthacyl chloride (84%), and 2-naphthacyl chloride (16%). The chlorides are separated from one another by picric acid in alcohol. 1-*Naphthacyl chloride* has b. p. 203°/12 mm., m. p. 40—41·5° (corresponding *picrate*, m. p. 94—95°), whilst 2-*naphthacyl chloride* has m. p. 67—68° (corresponding *picrate*, m. p. 90—91°). 1-Naphthacyl chloride is transformed by methyl malonate and sodium in presence of benzene into *methyl* 1-*naphthacylmalonate*, which yields the corresponding dicarboxylic *acid* and β-1-*naphthoylpropionic acid*, m. p. 131—132°, reduced by amalgamated zinc and concentrated hydrochloric acid to γ-1-*naphthyl*-n-*butyric acid*, b. p. 217°/15 mm., m. p. 106—107°. Treatment of the last-named acid with phosphorus pentachloride followed by distillation of the product affords 8-keto-5 : 6 : 7 : 8-tetrahydrophenanthrene. Similarly, 2-naphthacyl chloride is converted successively into *methyl* 2-*naphthacylmalonate*, 2-*naphthacylmalonic acid*, m. p. 162° (which is monobasic towards methyl-orange in aqueous solution but dibasic towards phenolphthalein in alcohol), β-2-*naphthoylpropionic acid*, m. p. 174°, and γ-2-*naphthyl*-n-*butyric acid*, m. p. 94—95°. Distillation of the chloride of the last-named acid affords 5-keto-5 : 6 : 7 : 8-tetrahydrophenanthrene. H. WREN.

Pyrogenic dissociation of some condensed ring systems. N. A. ORLOV (Ber., 1929, 62, [*B*], 710—719).—Tetrahydrophenanthrene is converted by treatment with hydrogen at 450—470°/70—75 atm. (initial pressure) in the presence of the oxides of iron and aluminium (1 : 1) into benzenoid hydrocarbons, tetrahydronaphthalene, naphthalene, β-methylnaphthalene and its hydrides, and hydrogenated dimethyl-(or ethyl-)naphthalenes; the residue consists of phenanthrene and unchanged tetrahydrophenanthrene. The tetramethylene ring is thus ruptured with production of alkylnaphthalenes, which then become de-alkylated and hydrogenated. Similarly, retene affords large amounts of saturated hydrocarbons formed by de-alkylation of the phenanthrene nucleus, naphthalene, (?) methylnaphthalene, and methylphenanthrene. The same products are derived under similar conditions from the resin oil of colophony which corresponds with a hydrogenated retene. With fluorene hydrogenation of the aromatic ring takes place only to a limited extent, the main action consisting in fission of the molecule into benzene and toluene. Distillation of phenanthrene or anthracene with aluminium chloride yields an oil consisting mainly of hydronaphthalenes containing hydrogenated methylnaphthalenes and initial hydrocarbons. Similarly, fluorene affords hydrofluorenes and benzenoid hydrocarbons. The products are therefore identical with those obtained by "berginisation." The action of aluminium chloride consists of primary, intensive dehydrogenation with production of coke. The liberated hydrogen is added by the unchanged material in the same manner as in customary hydrogenation. Fission of the hydrides takes place between the methylene groups. H. WREN.

Pyrogenic decomposition of chrysene under pressure of hydrogen. N. A. ORLOV and N. D. LICHATSCHEV (Ber., 1929, 62, [*B*], 719—722).—Chrysene, m. p. 250°, is converted by exhaustive hydrogenation at 440—450°/85—100 atm. (initial pressure) in the presence of ferric chloride into coke and saturated gaseous hydrocarbons. The liquid product contains aliphatic and benzenoid hydrocarbons, and naphthalene; dehydrogenation of the higher fractions by platinised charcoal leads to a mixture of naphthalene, phenanthrene, α- and β-methylnaphthalenes. H. WREN.

Action of acids on rubrene. C. MOUREU, C. DUFRAISSE, and E. ENDERLIN (Compt. rend., 1929, 188, 673—675).—Hydriodic acid reacts with rubrene in the presence of solvents to afford colourless ψ-rubrene, which first melts with loss of solvent of crystallisation and then remelts at 276—278°. A small amount of a *substance*, m. p. 230°, possibly a hydrogenated rubrene, is also produced in some cases. Hydrogen bromide, hydrogen chloride, and 98% sulphuric acid, but not fatty acids, effect the same change. G. A. C. GOUGH.

Elimination of the nitroso-group from nitrosoamines. W. G. MACMILLAN and T. H. READE (J.C.S., 1929, 585—586).—Secondary amines, *e.g.*, *m*- and *p*-nitromethylanilines, may be obtained in good yield from the nitroso-derivatives by heating with a solution of carbamide or thiocarbamide in 50% sulphuric acid. Nuclear nitroso-groups are unaffected. R. K. CALLOW.

Nitration of *m*-acetamido-*tert*.-butylbenzene. J. B. SHOESMITH and A. MACKIE (J.C.S., 1929, 476—477).—Nitration of *m*-acetamido-*tert*.-butylbenzene with nitric acid (*d* 1·46) at 25—30° gives 4-nitro-3-acetamido-*tert*.-butylbenzene, m. p. 116°, and not the 2-nitro-derivative as stated by Gelzer (A., 1889, i, 42). Hydrolysis of the nitro-compound with alcoholic potassium hydroxide yields 4-nitro-3-amino-*tert*.-butylbenzene, m. p. 91—92° (cf. *loc. cit.*), which after reduction with stannous chloride and hydrochloric acid and subsequent condensation with phenanthraquinone affords the corresponding phenazine, m. p. 148·5—149° (Gelzer gives m. p. 144° and 146·5°). The same phenazine is obtained from 3-nitro-4-amino-*tert*.-butylbenzene by the same reactions. H. BURTON.

Nitration of phenyl*cyclo*hexane and its *p*-halogeno-derivatives. H. A. Mayes and E. E. Turner (J.C.S., 1929, 500—508).—Nitration of phenyl*cyclo*hexane with nitric acid (*d* 1·5) at 0° gives *p*-nitrophenyl*cyclo*hexane (I), b. p. 198°/16 mm., m. p. 58·5°, together with 2 : 4-*dinitrophenyl*cyclo*hexane*, m. p. 57°. When nitration is effected with a mixture of nitric and acetic acids 62% of I and 38% of o-*nitrophenyl*cyclo*hexane*, b. p. 174°/16 mm., d_4^{25} 1·111, n_D^{25} 1·5472, are obtained. Nitration of *p*-aminophenyl*cyclo*hexane, m. p. 55° (*acetyl* derivative, m. p. 129°), with nitric and sulphuric acids affords 2-*nitro*-4-*aminophenyl*cyclo*hexane*, m. p. 66°, reduced by iron, water, and a small amount of hydrochloric acid to 2 : 4-*diaminophenyl*cyclo*hexane*, m. p. 108°. Nitration of p-*chlorophenyl*cyclo*hexane*, b. p. 145°/19 mm., d_4^{25} 1·065, n_D^{25} 1·5386 (obtained from *cyclo*hexyl chloride and chlorobenzene in presence of aluminium chloride), with nitric acid at −5° to 0° gives 4-*chloro*-2 : 5-*dinitrophenyl*cyclo*hexane* (II), m. p. 92° (4-*piperidino*-derivative, m. p. 108°), reduced by iron and dilute acetic acid at 100° to 4-*chloro*-2 : 5-*diaminophenyl*cyclo*hexane*, m. p. 95—96°. The constitution of this last substance, and hence of II, follows from the observation that it gives the usual *p*-diamine reactions. Nitration of the chloro-compound in acetic acid solution yields 4-*chloro*-2-*nitrophenyl*cyclo*hexane* (45%), nitrated further to II, and 4-*chloro*-3-*nitrophenyl*cyclo*hexane* (55%); the amount of the latter is determined by the amount of piperidine hydrochloride obtained when the mixture of nitro-compounds is treated with piperidine. Similar analysis of the mixture produced by nitrating p-*bromophenyl*cyclo*hexane*, b. p. 160°/23 mm., d_4^{25} 1·283, n_D^{25} 1·5584, shows the presence of 61% of the 2-nitro- and 39% of the 3-nitro-isomerides. The main product formed by the action of nitric acid on p-*iodophenyl*cyclo*hexane*, b. p. 174°/11 mm., d_4^{19} 1·448, n_D^{25} 1·5900 (prepared by the Sandmeyer reaction from the corresponding amine), is *p*-iodonitrobenzene. Condensation of phenyl*cyclo*hexane with acetyl chloride in presence of aluminium chloride and carbon disulphide yields p-*acetylphenyl*cyclo*hexane*, m. p. 68—69° (*phenylhydrazone*, m. p. 105°), oxidised by acidified potassium permanganate to terephthalic acid, and by aqueous sodium hypobromite to p-cyclo*hexylbenzoic acid*, m. p. 199° (*sodium* salt). This acid is also obtained by hydrolysis of the reaction product from diazotised *p*-aminophenyl*cyclo*hexane and sodium cuprocyanide. H. Burton.

Preparation of substituted diphenylamines. A. W. Chapman (J.C.S., 1929, 569—572).—Diphenylamines with similar or different substituents may be prepared in good yield from substituted amines, $R'\cdot NH_2$, and phenols, $R''\cdot OH$, through the anilide-iminochlorides, $R\cdot CCl{:}NR'$, and benzimino-ethers, $RC(OR''){:}NR'$ (*ibid.*, 1922, **121**, 1676). When heated these last yield benzoyldiphenylamines, $R\cdot CO\cdot NR'R''$ (A., 1925, i, 1400; 1927, 874), which can be hydrolysed with alcoholic potassium hydroxide to the free bases. This method of synthesis has been employed to determine the constitution of the tetrachlorodiphenylamine obtained by chlorination of diphenylamine (Gnehm, A., 1876, i, 265), which is shown to be the 2 : 4 : 2′ : 4′-compound. The following substances are described: N - o - *Chlorophenylbenzimino* - 2 : 4 : 6 - *trichlorophenyl ether*, m. p. 99—100°; *benzoyl*-2 : 4 : 6 : 2′-*tetrachlorodiphenylamine*, m. p. 131—132° (*base*, m. p. 87—88°); N - p - *chlorophenylbenzimino* - 2 : 4 : 6 - *trichlorophenyl ether*, m. p. 121—122°; *benzoyl*-2 : 4 : 6 : 4′-*tetrachlorodiphenylamine*, m. p. 154° (*base*, m. p. 63—64°); N - 2 : 4 - *dichlorophenylbenzimino*-2 : 4 - *dichlorophenyl ether*, an oil; *benzoyl*-2 : 4 : 2′ : 4′-*tetrachlorodiphenylamine*, m. p. 153—154° [base, identical with that prepared from diphenylamine, m. p. 141—142° (lit. 133—134°)]; 2 : 4 : 6-*trichlorodiphenylamine*, m. p. 43—44°. The final product of chlorination of diphenylamine is 2 : 4 : 6 : 2′ : 4′ : 6′-*hexachlorodiphenylamine*, m. p. 138—139°. The constitution, however, could not be confirmed, for the base could not be benzoylated, nor could the benzoyl derivative (A., 1927, 874) be hydrolysed. R. K. Callow.

Perylene and its derivatives. XX. K. Funke, F. Kirchmayr, and H. Wolt (Monatsh., 1929, **51**, 221—227).—Reduction of dinitroperylene (Zinke, Funke, and Lorber, A., 1927, 350) with phenylhydrazine, hydrazine hydrate at 170—180°, hydrazine hydrate in boiling xylene, or with sodium hydrogen sulphide in alcoholic sodium hydroxide affords *diaminoperylene*, crystalline, with dark green reflex, not melted at 400° [*diacetyl*, *di*(*chloroacetyl*), *dibenzoyl*, *di*-p-*chlorobenzoyl*, *di*-p-*bromobenzoyl*, *di*-α-*naphthoyl*, *dibenzylidene*, *disalicylidene*, *phthaloyl*, *diphthaloyl*, and *phthaloyl*-p-*chlorobenzoyl* derivatives], which reacts with ethyl chloroformate to give the corresponding *urethane* derivative. H. Burton.

Preparation of *p*-azoxyanisole and derivatives. W. Davies and R. A. R. Down (J.C.S., 1929, 586—587).—The preparation of *p*-azoxyanisole from *p*-chloronitrobenzene (cf. Jackson and Fiske, A., 1902, i, 362; Brand, A., 1903, i, 371) is best carried out under such conditions that substitution precedes reduction. This is accomplished by boiling with 0·86 mol. of 4*N*-methyl-alcoholic sodium methoxide for 12 hrs., adding a further 0·64 mol. of sodium methoxide, distilling off about half the methyl alcohol, and boiling for a further 12 hrs. *p*-Azoxyanisole was obtained in 64% yield. 1 : 2-Dichloro-4-nitrobenzene, obtained by chlorination of *p*-chloronitrobenzene at 100° in presence of antimony trichloride (cf. G.P. 167297), yields similarly 3 : 3′-*dichloro*-p-*azoxyanisole*, m. p. 182°, which does not form liquid crystals. R. K. Callow.

Relationship between absorption spectra and constitution of azo- and azoxy-compounds. L. Szegö (Ber., 1929, 62, [*B*], 736—744; cf. A., 1928, 1367, 1369).—Comparison of the absorption spectra in the ultra-violet of *p*-bromo-, *p*-nitro-, and *p*-methylazobenzene, *p*-methylazoxybenzene, azo- and azoxybenzene shows that the transformation of azo- to azoxy-compound causes no or only slight alteration in the frequency of the bands in the region examined. The bands of the azo-substances are usually more sharply defined and flatter than those of the azoxy-compounds. With the *p*-hydroxy- and *p*-amino-azo- and -azoxy-compounds, the α-form of the latter has two bands, whereas the β-isomeride has only one band and the common band is displaced by about

50 units towards the region of greater frequency. The β-*p*-amino-compound has a second band in the extreme ultra-violet. Similar observations are made with *m*-nitro-*p*-hydroxyazobenzene and the corresponding azoxy-derivatives. A close analogy exists therefore between the azo- and α-azoxy-compounds, whereas the β-azoxy-derivatives stand apart. The spectra of the 4-bromo-4′-nitroazoxybenzenes and the corresponding azo-compound, of 4-bromo-4′-methylazo- and -azoxy-benzene, and of 4 : 4′-dinitro- and 4 : 4′-dihydroxy-azo- and -azoxy-benzenes have been measured. H. WREN.

Manufacture of azo-dyes [and new arylamidosulpho-derivatives of anthranilic acid]. I. G. FARBENIND. A.-G.—See B., 1929, 239.

Decahydroquinoline derivatives. V. Synthesis of *trans*-1-dimethylamino-2-*n*-propyl*cyclo*hexane and elimination of water from 2-*n*-propyl*cyclo*hexanol. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 83—89).—Reduction of *o*-allylphenol with hydrogen in presence of platinum-black and acetic acid affords 2-*n*-propyl*cyclo*hexanol, b. p. 84°/6 mm., d_4^{25} 0·9115, n_D^{25} 1·46036, oxidised by chromic acid in acetic acid solution to 2-*n*-propyl*cyclo*hexanone, b. p. 199°, d_4^{25} 0·9056, n_D^{25} 1·45097 (cf. Vavon, A., 1928, 167). When 2-*n*-propyl*cyclo*hexanoneoxime, m. p. 67—68°, is reduced with sodium and alcohol, 2-*n*-propyl*cyclo*hexylamine results. Hydrolysis of the *benzoyl* derivative, m. p. 146—147°, of this with concentrated hydrochloric acid at 150—160° gives *trans*-2-*n*-propyl*cyclo*hexylamine, b. p. 193° (*hydrochloride*, m. p. 231°; *hydrobromide*, m. p. 229—230°; *picrate*, m. p. 168—169°), converted by heating with a mixture of formaldehyde and formic acid at 150—155° into *trans*-1-dimethylamino-2-*n*-propyl*cyclo*hexane, b. p. 205—207° (picrate, m. p. 114·5—115·5°; chloroaurate, m. p. 146—147°). This is identical with the product obtained by the degradation of *trans*-decahydroquinoline (A., 1928, 1022). Dehydration of 2-*n*-propyl*cyclo*hexanol by heating with potassium hydrogen sulphate yields Δ^1-propyl*cyclo*hexene (Wallach, A., 1908, i, 429). H. BURTON.

3 : 5 - Diphenyl - Δ^2 - *cyclo*hexenone. A. D. PETROV (Ber., 1929, **62**, [*B*], 642—645).—3 : 5-Diphenyl-Δ^2-*cyclo*hexenone, m. p. 82—83°, dissolved in hexahydrotoluene, is hydrogenated under pressure in the presence of nickel at 240° to a mixture of 1 : 3-di*cyclo*hexyl*cyclo*hexanes, m. p. 66° and b. p. 202°/14 mm., respectively. Dehydrogenation of the unsaturated ketone is effected by platinised charcoal at 300°, thus giving 3 : 5-*diphenylphenol*, m. p. 82—92° (*phenylurethane*, m. p. 180°). Reduction of the ketone with sodium and boiling alcohol affords 3 : 5-*diphenyl*cyclo*hexanol*, m. p. 127° (*phenylurethane*, m. p. 152°), oxidised to 3 : 5-diphenyl*cyclo*hexanone, m. p. 139—140° (*oxime*, m. p. 201°). H. WREN.

Oxidising action of alkalis. R. LEMBERG (Ber., 1929, **62**, [*B*], 592; cf. Lock, this vol., 67).—Fusion of sodium phenoxide with alkali containing water in a nickel apparatus in a current of nitrogen yields the same products as are derived from phenol and molten sodium hydroxide. Marked evolution of hydrogen is observed at a definite temperature. H. WREN.

Thermal behaviour of phenols. A. HAGEMANN (Z. angew. Chem., 1929, **42**, 355—361).—The effect of heat on phenol, cresol, the dihydroxybenzenes, and the naphthols, in presence of pumice, of nickel, and of active charcoal, has been examined. S. I. LEVY.

New condensation of ketones with phenols. II. "Cresol-phorones." J. B. NIEDERL and R. CASTY (Monatsh., 1929, **51**, 86—92; cf. A., 1928, 1137).—Treatment of a mixture of *o*-cresol and acetone or phorone with cold concentrated sulphuric acid gives a condensation product, termed "*di*-o-*tolylphorone*" [*di*-β-(2-*hydroxy*-m-*tolyl*)-β-*methyl*-n-*propyl ketone*], m. p. 245° (*dibenzoate*, m. p. 130°, *dimethyl ether*, m. p. 154°), which gives *sodium* and *potassium* salts when treated with alcoholic alkali hydroxide solution. Bromination of the ketone in chloroform solution yields a *dibromo*-derivative, m. p. 220°. Similar treatment of *p*-cresol and acetone furnishes "*di*-p-*tolylphorone ether*" [*anhydrodi*-β-(6-*hydroxy*-m-*tolyl*)-β-*methyl*-n-*propyl ketone*], m. p. 137°. The constitution of "di-*m*-tolylphorone ether," namely, anhydrodi-β-(6-hydroxy-*p*-tolyl)-β-methyl-*n*-propyl ketone (cf. *loc. cit.*), follows from the production of thymol, menthol, and trimethylcoumaran from it, by successive oxidation, elimination of carbon dioxide or water, and hydrogenation (cf. B.P. 279,855, 279,857, and 280,924; B., 1929, 237, 316). H. BURTON.

Scission of diaryl ethers and related compounds by means of piperidine. II. Nitration of 2 : 4 : 4′-trichlorodiphenyl ether, and of 2 : 4-dichlorophenyl *p*-toluenesulphonate and benzoate. L. G. GROVES, E. E. TURNER, and (in part) G. I. SHARP (J.C.S., 1929, 512—524).—Nitration of 2 : 4 : 4′-*trichlorodiphenyl ether* is found to take place successively in positions 2′, 5, and 5′, in accordance with Robinson's electron repulsion theory, with no subsidiary nitration in position 3′, as might be expected on Flürscheim's theory. The nitration of analogous compounds was studied, and the constitution of certain of the products proved.

4 : 4′-Dichloro-2-nitrodiphenyl ether is prepared by fusion of 2 : 5-dichloronitrobenzene with potassium *p*-chlorophenoxide. Reduction yields the 2-*amino*-compound, m. p. 67°, converted by a Sandmeyer reaction into 2 : 4 : 4′-*trichlorodiphenyl ether* (I), b. p. 183°/11 mm., m. p. 54—55°. Mononitration of I in acetic acid yields 2 : 4 : 4′-*trichloro*-2′-*nitrodiphenyl ether*, m. p. 86—87°, which yields 2 : 4-dichlorophenol and 4-chloro-2-nitrophenylpiperidine when heated with piperidine. Dinitration of I in nitric acid yields 2 : 4 : 4′-*trichloro*-5 : 2′-*dinitrodiphenyl ether* (II), m. p. 103—104°, which gives with piperidine 2 : 4-*dichloro*-5-*nitrophenol*, m. p. 105—106° (see below), 4-chloro-2-nitrophenylpiperidine, and piperidine hydrochloride. The formation of the last compound is discussed. Reduction of II yields the 5 : 2′-*diamino*-compound, m. p. 93—94°, from which the pentachloro-derivative (III) could not be obtained. 4 : 5-*Dichloro*-2-*nitrodiphenyl ether*, m. p. 69—70°, is prepared from 4 : 5-dichloro-1 : 2-dinitrobenzene and potassium phenoxide. 4 : 5 : 4′-*Trichloro*-2-*nitrodiphenyl ether*, m. p. 77°, obtained similarly, yields on nitration 4 : 5 : 4′-*trichloro*-2 : 2′-*dinitrodiphenyl ether*, m. p. 131—132°,

which yields with piperidine 4-chloro-2-nitrophenylpiperidine. 4 : 5 : 2′ : 4′-*Tetrachloro-2-nitrodiphenyl ether*, m. p. 125—126°, obtained similarly, is reduced to the 2-*amino*-compound, m. p. 97—98°, from which the pentachloro-compound (III) could not be prepared. Trinitration of I in fuming sulphuric acid yields the 5 : 2′ : 5′-*trinitro*-compound, m. p. 155—157°, which gives with piperidine 2 : 4-dichloro-5-nitrophenol and 4-*chloro*-2 : 5-*dinitrophenylpiperidine*, m. p. 70—71°. 4-*Chloro*-2 : 6-*dinitrophenylpiperidine* (from piperidine and 4-chloro-2 : 6-dinitroanisole) has m. p. 165—166°.

2 : 4-*Dichloro*-2′ : 4′-*dinitrodiphenyl ether*, m. p. 118—119° (from 1-chloro-2 : 4-dinitrobenzene and potassium 2 : 4-dichlorophenoxide), yields on nitration 2 : 4-*dichloro*-5 : 2′ : 4′-*trinitrodiphenyl ether*, m. p. 128°, giving 2 : 4-dichloro-5-nitrophenol and 2 : 4-dinitrophenylpiperidine or 2 : 4-dinitrodiphenylamine, on scission with piperidine or aniline, respectively.

2 : 4-Dichlorophenol (best prepared from *p*-chlorophenol) yields the p-*toluenesulphonate*, m. p. 125°, which yields on nitration 2 : 4-*dichloro*-5-*nitrophenyl* o-*nitro*-p-*toluenesulphonate* (IV), m. p. 103°, reduced to the *diamino*-compound, m. p. 159—161°. The latter, by a Sandmeyer reaction, yields the tetrachloro-compound (not isolated), giving with piperidine 2 : 4 : 5-trichlorophenol, m. p. 66—67° [benzoate, m. p. 91—92° (Holleman, A., 1921, i, 102)], thus proving the occurrence of nitration in position 5 and, indirectly, the constitution of 2 : 4-dichloro-5-nitrophenol. The constitution of 2 : 4 : 5-trichlorophenol was confirmed by preparing it from 2 : 5-dichlorophenol by chlorination, and from 2 : 4 : 5-trichloroaniline by the method of Noelting and Kopp (A., 1905, i, 872). Scission of IV with piperidine yields 2 : 4-dichloro-5-nitrophenol and 1-o-*nitro*-p-*toluenesulphonylpiperidine*, m. p. 112°. The latter was also prepared from piperidine and *o*-nitro-*p*-toluenesulphonyl chloride. 1-p-*Toluenesulphonylpiperidine* has m. p. 103°.

2 : 4-Dichlorophenyl benzoate yields on nitration 2 : 4-*dichloro*-5-*nitrophenyl* m-*nitrobenzoate*, m. p. 154°, with traces of isomeric nitrobenzoates. It is best obtained pure by nitration of 2 : 4-*dichlorophenyl* m-*nitrobenzoate*, m. p. 115—116°, and is also prepared by nitration of 2 : 4-*dichloro*-5-*nitrophenyl benzoate*, m. p. 111—112°, or condensation of 2 : 4-dichloro-5-nitrophenol with *m*-nitrobenzoyl chloride. 2 : 4-*Dichloro*-6-*nitrophenyl* m-*nitrobenzoate* [from 2 : 4-dichloro-6-nitrophenol (Tarugi, A., 1901, i, 146)] has m. p. 149—150°.

The constitution of 2 : 4-dichloro-5-nitrophenol could not be proved directly. It is unaffected by thionyl chloride, and phosphorus pentachloride yields a *substance*, b. p. 150—160°/15 mm., m. p. 80—89°. Nitration of N-2 : 4-*dichlorophenylphthalimide*, m. p. 155° (from 2 : 4-dichloroaniline and phthalic anhydride), yields the 5-*nitro*-compound, m. p. 217—219°, which was hydrolysed to 2 : 4-dichloro-5-nitroaniline (Körner and Contardi, A., 1909, i, 220), but this could not be transformed into the phenol. Chlorination of *m*-nitrophenol yields 2 : 4-dichloro-3-nitrophenol, m. p. 85—87°. Reduction of the p-*toluenesulphonyl* derivative, m. p. 122°, yields 2 : 4-*dichloro*-3-*aminophenyl* p-*toluenesulphonate*, m. p. 113—114°. Diazotisation of this in concentrated sulphuric acid and a Sandmeyer reaction, followed by decomposition of the product with piperidine yields 2 : 3 : 4-*trichlorophenol*, m. p. 80—81° [benzoate, m. p. 143° (Holleman, *loc. cit.*)], also obtained by chlorination of 3 : 4-dichlorophenol (prepared by the method of Noelting and Kopp, *loc. cit.*).

R. K. CALLOW.

Rearrangement of phenyl benzyl ethers. W. F. SHORT and M. L. STEWART (J.C.S., 1929, 553—559).—Further evidence has been obtained that the rearrangement of phenyl benzyl ethers when heated with zinc chloride (van Alphen, A., 1928, 57; Short, *ibid.*, 516) takes place mainly, if not exclusively, by an intermolecular and not an intramolecular process, as stated by van Alphen.

Rearrangement of phenyl benzyl ether in presence of zinc chloride or zinc chloride and hydrogen chloride gives phenol, 2-hydroxydiphenylmethane (*benzyl ether*, m. p. 38°), 4-hydroxydiphenylmethane (*benzyl ether*, m. p. 49·5°), and 2 : 4-*dibenzylphenol*, b. p. 252—254°/10 mm. (α-*naphthylurethane*, m. p. 143—144°). When hydrogen chloride alone is used as catalyst, benzyl chloride is also present in the product. 2 : 4-Dibenzylphenol was synthesised from benzyl chloride and the sodium derivative of 4-hydroxydiphenylmethane in dry toluene (cf. Claisen, A., 1925, i, 655). 2-Hydroxydiphenylmethane and 2 : 6-*dibenzylphenol*, b. p. 237·5—238°/10 mm. (*benzyl ether*, m. p. 65°; α-*naphthylurethane*, m. p. 165—166°), are obtained from benzyl chloride and sodium phenoxide in dry toluene. Condensation of equimolecular quantities of phenol and anisole with benzyl chloride (1 mol.) yields 2- and 4-hydroxydiphenylmethanes, 2 : 4-dibenzylphenol, 4-methoxydiphenylmethane (oxidised by chromic anhydride to 4-methoxybenzophenone), and dibenzylanisole, the benzyl chloride being appropriated to an approximately equal extent by the phenol and anisole. Rearrangement of phenyl benzyl ether in presence of anisole (1 mol.) yields the same products. Quinol monomethyl ether and benzyl chloride with zinc chloride at 100° yield 2-*hydroxy*-4-*methoxydiphenylmethane*, m. p. 77°.

R. K. CALLOW.

Condensation products of dextrose and *p*-anisidine. M. AMADORI (Atti R. Accad. Lincei, 1929, [vi], 9, 226—230).—Like *p*-phenetidine (this vol., 439), *p*-anisidine condenses with dextrose giving two isomeric compounds, $C_{13}H_{19}O_6N$: (1) a glucosidic *compound*, m. p. 86°, $[\alpha]_D^{20}$ —86°, and (2) a *compound*, m. p. 140°, $[\alpha]_D^{20}$ —28°, having the constitution of a Schiff's base.

T. H. POPE.

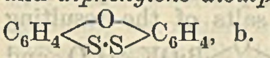
2 : 5-Dichlorophenetidine. G. BARGELLINI and (SIGNA.) L. MONTI (Atti R. Accad. Lincei, 1928, [vi], 8, 590—593; cf. this vol., 438).—The dichlorophenetidine obtained by treating phenacetin in acetic acid solution with nascent chlorine and hydrolysing the resulting dichlorophenacetin (cf. Reverdin and Düring, A., 1899, i, 266) yields 2 : 5-dichlorobenzoquinone, m. p. 161° (cf. Levy and Schulz, A., 1882, 509), when converted into the 2 : 5-*dichloro*-4-*aminophenol*, m. p. 178—179°, and then oxidised, so that it is the 2 : 5-dichloro-compound. 2 : 5-Dichlorophenetidine condenses with 2 : 4-dinitrochlorobenzene, giving 2 : 5-*dichloro*-2′ : 4′-*dinitro*-4-*ethoxydiphenylamine*, m. p. 136—138°, and gives a *piperonylidene* derivative, m. p. 148°. T. H. Pope.

Constitution of some dichlorophenetidines. G. Bargellini (Gazzetta, 1929, **59**, 16—32).—See this vol., 438, and preceding abstract.

6-Amino-*m*-cresol and derivatives. M. T. Bogert and G. H. Connitt (J. Amer. Chem. Soc., 1929, **51**, 900—915).—Acetylation of 6-amino-*m*-cresol [hydrochloride; *salicylidene*, m. p. 111—111·5° (+EtOH, m. p. 92·5°), N-*chloroacetyl*, m. p. 133°, and *phthalyl*, m. p. 204°, derivatives] in presence of water gives 6-acetamido-*m*-cresol (Staedel and Kolb, A., 1891, 186), converted by hypochlorite into 2 : 4-*dichloro*-6-*acetimidotoluquinone*, m. p. 159—159·5°, from which 2 : 4-dichloro-*p*-toluquinone and 2 : 4-dichloro-6-acetamido-*m*-cresol were prepared (cf. Raiford, A., 1914, i, 524). Nitration of 6-*acetamido*-m-*tolyl acetate*, m. p. 127·5—128°, in acetic anhydride below 5° gives (*a*) a 5-*nitro*-derivative, m. p. 190—190·5°, hydrolysed by potassium carbonate to 5-*nitro*-6-*acetamido*-m-*cresol*, m. p. 188·5°, and (*b*) a little 2 : 4-*dinitro*-6-*acetamido*-m-*cresol* (I), m. p. 231°, hydrolysed by hydrochloric acid to 2 : 4-dinitro-6-amino-*m*-cresol, m. p. 166·5—167·5° (*hydrochloride*, decomp. 200°; diacetyl derivative, m. p. 170·5°; cf. Nietzki, A., 1891, 308). The sodium salt of 6-*benzylideneamino*-m-*cresol*, m. p. 135·5°, gives with ethyl bromide or sulphate an *ethyl ether*, b. p. 215—217°/20 mm., hydrolysed by acid to 6-*amino*-m-*tolyl ethyl ether*, b. p. 253—255° (*hydrochloride*, m. p. 212°, decomp. from 200°; *salicylidene*, m. p. 48·5°, *chloroacetyl*, m. p. 140·5—141°, *salicoyl*, m. p. 153·4—154°, *oxalyl*, m. p. 205°, and *phthalyl*, m. p. 140·5°, derivatives), which gives an *acetyl* derivative, m. p. 118·5° (N-*carbethoxymethyl* derivative, b. p. 210—212·5°/22 mm.). This yields with hypochlorite a 2 : 4-*dichloro*-derivative, m. p. 162·5—163°, hydrolysed to 2 : 4-*dichloro*-6-*amino*-m-*tolyl ethyl ether*, m. p. 244°, darkening from 220°, and with nitric and acetic acids 4-*nitro*-, m. p. 192·5—193°, and a little 5-*nitro*-, m. p. 160°, derivatives, which are hydrolysed, respectively, to 4-*nitro*-, m. p. 86—87° (*hydrochloride*, decomp. 249°, darkening from 240°), and 5-*nitro*-, m. p. 101—101·5° (*hydrochloride*, decomp. 200—240°), -6-*amino*-m-*tolyl ethyl ethers*. Further nitration of the acetyl derivative affords 4 : 5-*dinitro*-6-*acetamido*-m-*tolyl ethyl ether*, m. p. 257—258°. The sodium salt of I (above) is converted by ethyl sulphate into 2 : 4-*dinitro*-6-*acetamido*-m-*tolyl ethyl ether*, m. p. 167—167·5°, hydrolysed to the 6-*amino*-compound, m. p. 96—97° (*hydrochloride*, decomp. 195—197°). 4 : 6-*Diacetamido*-m-*tolyl ethyl ether*, m. p. 200—200·5°; 3-*hydroxy*-3′-*ethoxy*-6 : 6′-*azotoluene*, m. p. 132·5°; 3 : 3′-*diethoxy*-6 : 6′-*azotoluene*, m. p. 149·5°, and 2-*acetamido*-5-β-*hydroxyethoxytoluene*, m. p. 117—117·5° (*acetyl* derivative, m. p. 117°), are described. Unsuccessful attempts have been made to convert these derivatives, many of which are of therapeutic interest, into heterocyclic compounds. H. E. F. Notton.

Reduction of naphthol-yellow by stannous chloride. J. G. F. Druce (Chem. News, 1929, **138**, 209).—When naphthol-yellow is reduced by a hot solution of stannous chloride in hydrochloric acid, the 3-*chlorostannate*, m. p. about 112°, of 3 : 4-diamino-β-naphthol-6-sulphonic acid is produced. H. Burton.

o-Thiolphenylhydrazine. P. C. Guha and T. N. Ghosh (J. Indian Inst. Sci., 1929, **12 A**, 31—35).—Attempts to convert *o*-aminothiophenol into *o*-thiolphenylhydrazine through 2 : 2′-diaminodiphenyl disulphide by reduction of its bisdiazonium chloride failed. The latter does not interact with aniline or potassium ethyl xanthate, but decomposes in presence of water, giving 2 : 2′-dihydroxydiphenyl disulphide and *diphenylene disulphide* 2 : 2′-*oxide*,



$C_6H_4<\genfrac{}{}{0pt}{}{O}{S\cdot S}>C_6H_4$, b. p. 231° (decomp. 200—210°). Failure to nitrosate 2 : 2′-*diacetamidodiphenyl disulphide*, m. p. 154°, is recorded. 2-*Phenyl*-5 : 6-*benzo*-1 : 3 : 4-*thiodiazine*, m. p. 109°, obtained by fusing together sulphur and benzoylphenylhydrazine, decomposes when fused with potassium hydroxide, hydrogen sulphide and benzoic acid being among the reaction products. R. J. W. Le Fèvre.

Condensation products from *m*- or *p*-cresol and aliphatic ketones. Alkyl*iso*propylphenols and alkylated coumarans. Chem. Fabr. auf Actien (vorm. E. Schering).—See B., 1929, 236.

Introduction of thiocyano-groups into organic compounds. I. G. Farbenind. A.-G.—See B., 1929, 236.

Production of *N*-monoalkyl derivatives of aminophenols. W. Traube and E. Hellriegel.—See B., 1929, 236.

Manufacture of halogenated organic compounds [aromatic sulphonarylamides and arylamines]. Comp. Nat. Mat. Col.—See B., 1929, 276.

Manufacture of 2 : 3-aminonaphthol and derivatives. I. G. Farbenind. A.-G.—See B., 1929, 276.

Importance of acetone and boric acid methods in the study of alicyclic 1 : 2-diols. C. J. Maan (Rec. trav. chim., 1929, 48, 332—350).—Oxidation of substituted *cyclo*hexenes with potassium permanganate in presence of alcohol and magnesium sulphate solution at −50° to −40° gives the corresponding *cis*-1 : 2-diols in 20—30% yield. When the *cyclo*hexenes (or *cyclo*pentenes) are oxidised with perbenzoic acid in chloroform solution the corresponding oxides result. These are hydrated (usually by shaking with cold 0·02*N*-hydrochloric acid) giving the corresponding *trans*-1 : 2-diols. 1-Phenyl*cyclo*hexene-1 : 2-oxide yields a mixture of the *cis*- and *trans*-glycols when hydrated with 0·05*N*-sulphuric acid. 1-Phenyl*cyclo*pentene-1 : 2-oxide could not be converted into the diol. Condensation of *cis*-1 : 2-diols with acetone in presence of concentrated sulphuric acid affords the *iso*propylidene ethers. The following are described: 1-*methyl*cyclo*pentane*-1 : 2-*diol* iso*propylidene ether*, b. p. 157·5—157·8°/760 mm., d^{18} 0·9469, n_D^{18} 1·4300; 1-*phenyl*cyclo*pentane*-1 : 2-*diol* iso*propylidene ether*, m. p. 52·5—53·5°; 1-*methyl*cyclo*hexane*-1 : 2-*diol* iso*propylidene ether*, b. p. 183·5—

184°/760 mm., d^{16} 0·9701, n_D^{16} 1·4496; 1-*phenyl*cyclo*hexane*-1 : 2-*diol* iso*propylidene ether*, b. p. 155—157°/18 mm., d^{15} 1·066, n_D^{15} 1·5304. The *trans*-diols do not furnish *iso*propylidene derivatives. The specific conductivity of boric acid is increased by the addition of *cis*-1-methyl*cyclo*pentane-1 : 2-diol, but is lowered by the *trans*-derivatives. The conductivity is also lowered by addition of either the *cis*- or *trans*-forms of 1-methyl- and 1-phenyl-*cyclo*hexane-1 : 2-diols. Treatment of *cis*-1-methyl*cyclo*pentane- and 1-methyl*cyclo*hexane-1 : 2-diols with a saturated aqueous solution of boric acid and 50% potassium hydroxide solution gives the *potassium* salts of the resulting boric acid complexes, $C_6H_{10}{<}{}^{O}_{O}{>}B{\cdot}OK,4H_2O$ and $C_7H_{12}{<}{}^{O}_{O}{>}B{\cdot}OK,4H_2O$, respectively. In aqueous solution these salts undergo hydrolysis, since continuous extraction with chloroform furnishes the free diol. The degree of hydrolytic dissociation is, however, much smaller for the *cyclo*pentane than for the *cyclo*hexane derivative: the same relationship is also found for the corresponding 1-phenyl derivatives. Addition of *trans*-1-methyl*cyclo*pentane- and -1-methyl*cyclo*hexane-1 : 2-diols to potassium borate does not result in the formation of any complex. cis-1-*Phenyl*cyclo*pentane*-1 : 2-*diolboric acid*, $C_{11}H_{12}O_2B{\cdot}OH$, m. p. 107—110°, is obtained by treating the diol with boric acid in aqueous solution. The boric acid complex from the same diol described by Coops (Diss., Delft, 1928, 91) has the composition $[(C_{11}H_{12}O_2)_2B]H$. Neither of the 1-phenyl*cyclo*hexane-1 : 2-diols gave boric acid complexes.

It is shown that the decomposition constant of the diol–borate complex is smaller in borate solution than in boric acid, and conductivity measurements should be carried out in the former. H. Burton.

Action of sulphites on aromatic amino- and hydroxy-compounds. XIII. Action of sulphites on resorcinol (synthesis of *m*-hydroxyazo-dyes), *p*-phenylenediamine and its derivatives. H. T. Bucherer and E. Hoffmann (J. pr. Chem., 1929, [ii], **121**, 113—152).—By prolonged heating of resorcinol with sodium hydrogen sulphite solution, a *sodium sulphurous* ester of resorcinolsulphonic acid (I) is formed. This reacts very slowly with aqueous ammonia, forming probably a sulphite compound of sodium *o*-hydroxysulphanilate. Interaction of resorcinol, sodium hydrogen sulphite, and phenylhydrazine in boiling aqueous solution gives, in small yield, a hydrogen sulphite compound of 3-hydroxyazobenzene-4-sulphonic acid (*sodium* salt). The yellowish-red dye is turned blue by mineral acid. It is decomposed by boiling sodium hydrogen sulphite solution into aniline and (?) *m*-aminophenol-6-sulphonic acid. It is obtained in better yield from phenylhydrazine and I. When *p*-phenylenediamine is boiled with an equivalent of resorcinol in sodium hydrogen sulphite solution or with a solution of I good yields of p-*amino*-m-*hydroxydiphenylamine*-p′-*sulphonic acid*, darkening at 180° and charring at 270° (*benzoyl* derivative, m. p. 107°), are obtained, from which, by diazotisation and coupling, various azo-*dyes* were prepared.

No reaction occurs between acetyl-*p*-phenylenediamine, *p*-aminophenol, or *p*-aminosalicylic acid and resorcinol–sodium hydrogen sulphite mixture.

m-Phenylenediamine by interaction with aqueous sodium hydrogen sulphite loses ammonia giving the same product as is obtained directly from resorcinol. *m*-Tolylenediamine also loses ammonia, but from the character of the azo-dye obtained by coupling the product with diazotised *p*-nitroaniline, does not appear to form a sulphonic acid. Phenol is unattacked by sodium hydrogen sulphite solution even in the presence of *p*-phenylenediamine.

By the action of *p*-phenylenediamine on 1 : 4-, 1 : 5-, and 1 : 6-naphthylaminesulphonic acids and 1 : 2 : 4-aminonaphtholsulphonic acid in the presence of sodium hydrogen sulphite solution the corresponding p-*aminophenylnaphthylaminesulphonic acids* and 1-p-*aminophenylamino*-2-*naphthol*-4-*sulphonic acid* (which readily undergoes oxazine ring formation by oxidation) respectively are obtained. The *benzoyl* derivative of *p*-aminophenyl-α-naphthylamine-6-sulphonic acid couples with diazotised *p*-nitroaniline to give a bluish-violet *dye*. R. J. W. Le Fèvre.

Cholesterol and phytosterol and the spectroscopy of the colour reactions of the sterols in general. J. Moir (J. S. African Chem. Inst., 1929, **12**, 16—20).—Spectroscopic examination of the closely similar colour reactions of cholesterol and sitosterol shows that there is a slight difference in the position of the bands; these sterols are therefore not exactly isomeric. The reactions of ergosterol, zymosterol, and coprosterol are also described.

F. R. Ennos.

Oxidation of cholesterol. Mechanism of oxidation with chromic acid. S. Minovici and M. Vanghelovici (Bull. Acad. Sci. Roumaine, 1929, 11, 20—25).—See this vol., 440.

Transformation of cholesterol by *X*-rays. A. H. Roffo and L. M. Correa.—See this vol., 523.

Mobile anion tautomerism. III. Activation of three-carbon anionotropic systems by alkyl and aryl groups. H. Burton (J.C.S., 1929, 455—458).—When a solution of α-*methylallyl* p-*nitrobenzoate*, m. p. 43—44°, in acetic anhydride is boiled for 24 hrs. no interconversion into the γ-substituted allyl ester occurs, as with the corresponding phenyl derivative (A., 1928, 880). The activation of the three-carbon anionotropic system by the methyl group is, therefore, small. Magnesium phenyl bromide reacts with crotonaldehyde yielding α-*phenyl*-γ-*methylallyl alcohol*, b. p. 121·5—123·5°/14 mm., which when acetylated with boiling acetic anhydride affords γ-*phenyl*-α-*methylallyl acetate* (I), b. p. 141—144°/15 mm., showing that activation by the phenyl group predominates. Hydrolysis of I with alcoholic potassium hydroxide gives γ-phenyl-α-methylallyl alcohol [phenylcarbimide derivative, m. p. 92—93° (lit. 94—95°)], also acetylated to I, whilst treatment with ozone in chloroform solution, and subsequent decomposition of the ozonide with boiling water, affords benzoic and pyruvic acids. The activation of three-carbon prototropic systems by the phenyl group (Ingold and Shoppee, this vol., 556) in addition to the anionotropic systems shows that the phenyl group is able, by tautomeric electron-displacements of either sign promoted by the requirements of the system, to absorb an electric charge of either sign produced by the ionisation of an attached atom or group. H. Burton.

Dehydration of s-disubstituted αβ-glycols and the isomerisation of the corresponding ethylene oxides. Influence of the affinity capacities of cyclic and aliphatic radicals. (Mlle.) J. Lévy and F. Gombinska (Compt. rend., 1929, **188**, 711—713).—In continuation of previous work (A., 1927, 662), the following pairs of glycols and ethylene oxides are found each to yield the same ketone in accordance with theory: γ-phenylpropane-βγ-diol and α-phenyl-Δ^{α}-propylene oxide give benzyl methyl ketone; δ-phenylbutane-γδ-diol and α-phenyl-Δ^{α}-butylene oxide give benzyl ethyl ketone; ε-phenylpentane-δε-diol and α-phenyl-Δ^{α}-*n*-amylene oxide give benzyl propyl ketone; δ-phenyl-β-methylbutane-γδ-diol and α-phenyl-γ-methyl-Δ^{α}-*n*-butylene oxide give benzyl *iso*propyl ketone; αγ-diphenylpropane-αβ-diol and αγ-diphenylpropylene oxide give dibenzyl ketone; α-*p*-methoxyphenylpropane-αβ-diol and α-*p*-methoxyphenyl-Δ^{α}-propylene oxide give *p*-methoxybenzyl methyl ketone; α-*p*-methoxyphenylbutane-αβ-diol and α-*p*-methoxyphenyl-Δ^{α}-*n*-butylene oxide give *p*-methoxybenzyl ethyl ketone; α-*p*-methoxyphenylpentane-αβ-diol and α-*p*-methoxyphenyl-Δ^{α}-*n*-amylene oxide give *p*-methoxyphenyl propyl ketone.

G. A. C. Gough.

Stovaine. I. Ribas and A. Rancaño (Anal. Fís. Quím., 1928, **26**, 430—434).—The relationship of the optically inactive "stovaine" (hydrochloride of methylethyldimethylaminomethylcarbinol benzoate) to the *d*- and *l*-forms (A., 1928, 49) has been investigated. Inactive stovaine is found to be a true racemic compound. The saturated solution of the racemate in brine readily dissolved either active form. The m. p. curve of mixtures of the *d*- and *l*-forms is of the characteristic symmetrical type corresponding with the formation of a racemate, m. p. 175°, with eutectics at 172°. *r*-Stovaine has d_4^{25} 1·1860, whereas *l*-stovaine has d_4^{25} 1·1698. Dilatometric measurements show that the racemate is stable between —10° and 170°, the range of observation.

R. K. Callow.

Di- and tetra-hydro-β-naphthoic acids obtained by catalytic hydrogenation. A. León and A. Charro (Anal. Fís. Quím., 1928, **26**, 423—429; cf. Ranedo and León, A., 1928, 173).—Catalytic hydrogenation of β-naphthoic acid was carried out in acetic acid solution in presence of platinum oxide–platinum-black. Using 1 mol. of hydrogen, two new *dihydro-β-naphthoic acids* were obtained, one, m. p. 140—141° (*chloride*, b. p. 181—182°/29 mm., *amide*, m. p. 191°), and, in small quantity, a second, m. p. 132—133° (*chloride*, b. p. 182°/25 mm., *amide*, m. p. 133—134°). Hydrogenation by 2 mols. of hydrogen yielded a single product, a new *tetrahydro-β-naphthoic acid*, m. p. 153° (*chloride*, b. p. 196—197°/50 mm.; *amide*, m. p. 139°), which was also obtained by hydrogenation in aqueous alkaline solution and by further hydrogenation of the dihydro-acid of m. p. 132—133°. Hydrogenation of Sowinski's tetrahydro-β-naphthoic acid, m. p. 97° (A., 1891, 1380), or of the new tetrahydro-acid yielded decahydro-β-naphthoic acid, m. p. 72—76°, identical with the product of complete hydrogenation of β-naphthoic acid (*loc. cit.*).

R. K. Callow.

ζ-Phenyl-$\Delta^{\alpha\gamma\epsilon}$-heptatrienoic acid. D. Vorländer and E. Daehn (Ber., 1929, **62**, [*B*], 545—549; cf. Engelberg, Diss., Berlin, 1914).—δ-Phenyl-$\Delta^{\alpha\gamma}$-pentadienal is converted by malonic acid in presence of aqueous-alcoholic ammonia or pyridine into ε-phenyl-$\Delta^{\beta\delta}$-pentadienylidenemalonic acid, $\text{Ph}\cdot[\text{CH}{:}\text{CH}]_2\cdot\text{CH}{:}\text{C}(\text{CO}_2\text{H})_2$, m. p. about 191° (corr. decomp.) according to the rate of heating, which passes in acetic anhydride at 120—130° into ζ-phenyl-$\Delta^{\alpha\gamma\epsilon}$-heptatrienoic acid, m. p. I about 199°, II 189—190° (corr.). In chloroform the acid absorbs 3 mols. of bromine without marked evolution of hydrogen bromide. The *potassium*, *sodium*, and *ammonium* salts, *methyl* ester, m. p. 114° (corr.), *ethyl* ester, m. p. 91° (corr.), *chloride*, *anilide*, m. p. 213° (corr.), p-*toluidide*, m. p. 209° (corr.), p-*anisidide*, m. p. 203—204° (corr.), and p-*phenetidide*, m. p. 210—211° (corr.), are described. Reduction with sodium amalgam appears to give a tetrahydro-product.

Luminescence phenomena do not appear definitely related to the more or less saturated state of the compounds. The tetrabromide of *p*-methoxyphenylpentadienoic acid phosphoresces almost more strongly than the doubly-unsaturated acid. Anisic acid phosphoresces at least as strongly as *p*-methoxycinnamic acid or methyl phenylheptatrienoate, whereas benzoic acid is less powerful than cinnamic acid. The luminescence phenomena vary with the position of the double linking. Complete hydrogenation has a weakening effect, but the rule is not without exception. The condensation products of amines and aldehydes appear black in the light of the quartz–mercury lamp whether they contain more or fewer C:C linkings or methoxy-groups. Ethyl *p*-azoxycinnamate appears black. Phenylhydrazones shine brightly and anilides and anisidides of acids appear more or less bright. H. Wren.

Amino-derivatives of hydroxybenzoic acids. E. Puxeddu (Gazzetta, 1929, **59**, 10—15).—The preparation of 5-aminosalicylic acid by the reduction of benzeneazosalicylic acid (*acetyl* derivative, m. p. 145°) by phenylhydrazine (cf. A., 1906, 8, 995) is repeated; o-*tolueneazosalicylic acid*, m. p. 186° (obtained from diazotised *o*-toluidine and salicylic acid) is also used, with advantage. 5-Aminosalicylic acid (*diacetyl* derivative, m. p. 184°) can be converted into the 5-hydroxy-compound (gentisic acid) by preparing diazosalicylic acid (explodes at 162°; cf. Goldberg, A., 1879, 928), and heating this in dilute sulphuric acid. Similarly, 6-benzeneazo-*m*-hydroxybenzoic acid is reduced by phenylhydrazine to 6-amino-*m*-hydroxybenzoic acid (darkens 235°, decomp. 252°; cf. Limpricht, A., 1891, 1037), which may be converted into the diazo-compound (explodes 169°); this also when heated in dilute sulphuric acid gives rise to gentisic acid. E. W. Wignall.

Syntheses in the amino-acid group. II. α-Anisylideneamino-β-lactones. G. Minunni and S. D'Urso (Gazzetta, 1929, **59**, 32—39).—The condensation of aldoximes with β-ketonic esters in the presence of phosphoric acid (cf. A., 1928, 1245) is effected with α-anisaldoxime.

[With V. Bellecci.]—With ethyl acetoacetate, this gives *α-anisylideneaminocrotono-β-lactone*, m. p. 179—180°, which is readily decomposed by phenylhydrazine or by alkali.

[With I. Ottaviano.]—With ethyl benzoylacetate, the product is *α-anisylideneaminocinnamo-β-lactone*, m. p. 166—166·5°, which is similarly decomposed.

E. W. Wignall.

Syntheses in the amino-acid group. III. Behaviour of α-arylideneaminocinnamo-β-lactones with phenylhydrazine and with hydroxylamine. New method for the replacement of hydrogen by the amino-group. G. Minunni [with I. Ottaviano and V. Spina] (Gazzetta, 1929, 59, 116—128).—In an attempt to hydrolyse off the arylidene group from α-arylideneaminocinnamo-β-lactones, it was found that the lactone ring was also affected. Thus the product from the benzylidene derivative is *α-amino-β-hydroxycinnamic acid phenylhydrazide*, m. p. 148—149° (decomp.), which has the formula $C_{15}H_{15}O_2N_3$ (cf. A., 1928, 1245); benzaldehydephenylhydrazone is also formed. The anisylidene derivative (cf. preceding abstract) gives rise to the same phenylhydrazide, with anisaldehydephenylhydrazone.

Hydroxylamine, on the other hand, does not open the lactone ring, and when it reacts with a suspension of α-benzylidene- or α-anisylidene-aminocinnamo-β-lactone in alcohol, *α-aminocinnamo-β-lactone*, m. p. 154—154·5° (after darkening), is produced, together with the oxime of the respective aldehyde. Condensation with an araldoxime and treatment with hydroxylamine thus gives a new method by which, in certain compounds, hydrogen may be replaced by the amino-group.

E. W. Wignall.

Mobility of symmetrical triad (prototropic) systems. IV. Mobility in simple three-carbon system terminated by aryl groups. C. K. Ingold and C. W. Shoppee (J.C.S., 1929, 447—455).—Condensation of sodium β-*p*-methoxyphenylpropionate with benzaldehyde in presence of acetic anhydride at 150—170° gives a mixture of α-*p*-methoxybenzylcinnamic acid (I*a*), m. p. 165·5°, and γ-phenyl-α-*p*-methoxyphenyl-Δ^{β}-propene (II*a*), having b. p. 179—180°/3 mm., n_{5461}^{26} 1·60246, when regenerated from its dibromide, m. p. 94° (cf. Ingold and Piggott, J.C.S., 1922, **121**, 2381), by treatment with zinc dust and alcohol. Similar condensation of sodium β-phenylpropionate and anisaldehyde yields *p*-methoxy-α-benzylcinnamic acid (I*b*), and α-phenyl-γ-*p*-methoxyphenyl-Δ^{β}-propene (II*b*), b. p. 185—186°/3 mm., n_{5461}^{26} 1·60598 (dibromide, m. p. 119°). Interconversion of I*a* and I*b* occurs when either substance is boiled with alcoholic sodium ethoxide and the equilibrium values are 44% of the former and 56% of the latter. Similar equilibration of II*a* and II*b* with 1·45*N*-alcoholic sodium ethoxide at 85° gives a mixture containing 29·5% of the former and 70·5% of the latter, the proportions being determined refractometrically. The coefficient of the velocity of interconversion (k_1+k_2) is 0·79 hr.$^{-1}$, and the equilibrium ratio k_1/k_2 is 0·42. *Methyl* α-p-*methoxybenzylcinnamate*, b. p. 237—238°/14—15 mm., n_{5461}^{19} 1·60221, and *methyl* p-*methoxy*-α-*benzylcinnamate*, b. p. 245°/11—12 mm., m. p. 55°, are only slowly interconverted by methyl-alcoholic sodium methoxide at 100°, but *ethyl* α-p-*methoxybenzylcinnamate* (III*a*), b. p. 235°/13—14 mm., n_{5461}^{22} 1·58972, and *ethyl* p-*methoxy-α-benzylcinnamate* (III*b*), b. p. 240—241°/10—11 mm., m. p. 45°, are equilibrated by heating with 1·45*N*-alcoholic sodium ethoxide into 43·5% of III*a* and 56·5% of III*b*. The velocity coefficient (k_1+k_2) is 0·0585 hr.$^{-1}$, and the equilibrium ratio (k_1/k_2) is 0·770. The above substances are not interconverted by boiling with alcoholic potassium hydroxide (cf. Ingold and Piggott, *loc. cit.*).

H. Burton.

Goldschmiedt's condensation products of 2-hydroxy-3-naphthoic acid with aromatic aldehydes and their relationships to the triphenylmethane group. M. Rebek and V. Kramarsic (Ber., 1929, 62, [*B*], 477—487).—In presence of dry hydrogen chloride, methyl 2-hydroxy-3-naphthoate and *p*-dimethylaminobenzaldehyde condense in ether, affording the hydrochloride of *methyl 2-hydroxy*-1-*α-chloro*-p-*dimethylaminobenzyl*-3-*naphthoate*, $CO_2Me\cdot C_{10}H_5(OH)\cdot CHCl\cdot C_6H_4\cdot NMe_2,HCl$, decomp. above 200°; attempts to isolate the corresponding dye salt were unsuccessful. The chlorine atom is unusually mobile. The compound is converted by successive treatment with aqueous acetone and sodium hydrogen carbonate into *methyl* 2-*hydroxy*-1-*α-hydroxy*-p-*dimethylaminobenzyl*-3-*naphthoate*, m. p. 152—154° after becoming discoloured at about 140° (*picrate*); separation of the *hydrochloride*, m. p. 173—175°, from acid solutions of the ester could not be achieved, but the compound is prepared by the action of a small proportion of water on the chloro-compound dissolved in acetone. Methyl alcohol followed by sodium hydrogen carbonate converts the chloro-compound into *methyl* 2-*hydroxy*-1-*α-methoxy*-p-*dimethylaminobenzyl*-3-*naphthoate*, m. p. (indef.) 190°, whereas methyl alcohol alone affords the corresponding *hydrochloride oxonium chloride*, $C_{22}H_{25}O_4NCl_2$, m. p. 155—160° (decomp.), whilst in presence of benzene the *compound*, $C_{22}H_{25}O_4NCl_2,C_6H_6$, m. p. (indef.) 82° (decomp.), is produced. Spontaneous loss of hydrogen chloride from the oxonium compound leads to *methyl* 2-*hydroxy*-1-*α-methoxy*-p-*dimethylaminobenzyl*-3-*naphthoate hydrochloride*, m. p. 155—160° (decomp.), preferably prepared by the successive action of methyl alcohol and acetone on the chloro-compound. Triphenylmethyl chloride appears to be transformed by slightly aqueous acetone into a very labile oxonium chloride and by methyl alcohol and acetone into a somewhat more stable methyloxonium chloride. *Methyl* 2-*hydroxy*-1-*α-methoxybenzyl*-3-*naphthoate hydrochloride*, m. p. 169°, is described. Pyridine and aniline with methyl 2-hydroxy-1-α-chlorobenzyl-3-naphthoate afford the *compounds* $(C_5H_5N)Cl\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me$ and $(NHPh,HCl)\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me$, m. p. 179°. The action of water on triphenylmethyl chloride in pyridine, of hydrogen chloride on triphenylcarbinol in pyridine, and of anhydrous pyridine on triphenylmethyl chloride gives a product identical with the "triphenylcarbinol hydrochloride" of Helferich and others (A., 1925, i, 790, 1269) which is shown to be triphenylmethylpyridinium chloride.

The action of copper powder on methyl 2-hydroxy-1-α-chlorobenzyl-3-naphthoate in absence of oxygen and moisture gives the dimeride, $C_{38}H_{30}O_6$, m. p. 223—224°, in about 70% yield. The *compound* $[CO_2Me\cdot C_{10}H_5(OH)\cdot CH(C_6H_4\cdot NO_2)-]_2$, m. p. 185—195°, is prepared similarly. H. Wren.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. Abderhalden and H. Brockmann. **Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds.** E. Abderhalden and E. Schwab. **Specific action of enzyme complexes in fission of polypeptides.** E. Abderhalden and F. Schweitzer. **Behaviour of *N*-sodium hydroxide, erepsin, and trypsin-kinase towards polypeptides containing a 3 : 5-halogen-substituted tyrosine residue, glycyl-*d*-tyrosine, glycyl-*dl*-nitrotyrosine, and glycyl-*dl*-*o*-tyrosine.** E. Abderhalden and A. Schmitz.—See this vol., 604, 605.

Synthesis of homogentisic acid. G. Hahn and W. Stenner (Z. physiol. Chem., 1929, 181, 88—100).—A synthesis of homogentisic acid in 26% final yield is described. Quinol monobenzoate (Witt and Johnson, A., 1893, i, 571) is converted by shaking with allyl bromide in acetone solution in the presence of anhydrous potassium carbonate into its *allyl ether*, m. p. 71—72° (quinol itself yields mainly the *diallyl ether*, m. p. 36—37°). This is converted by distillation in a vacuum (bath temperature 130—280°) into a mixture of 2-allylquinol, and its mono- and *di-benzoate* (I), m. p. 107—108°, the latter (57% of the theoretical) being separated by utilising its smaller solubility in ether. Benzoylation of the mixture of the other two products yields a further quantity of I, which is converted (yield 83%) by ozonolysis in acetic acid at 80° into *dibenzoylhomogentisic acid* (II), m. p. 180—181° (*methyl*, m. p. 125°, and *ethyl*, m. p. 130—131°, esters). Hydrolysis of II with 2*N*-sodium hydroxide in an atmosphere of nitrogen gives a 90% yield of homogentisic acid. J. W. Baker.

Anomalies of condensation and ring-formation. R. Cornubert and C. Borrel (Compt. rend., 1929, 188, 919—921).—Two isomerides of α-benzyl-δ-methyladipic acid, m. p. 103—106° and 133—135°, when treated with acetic anhydride, yield samples of 2-benzyl-5-methyl*cyclo*pentanone which afford the same *semicarbazone*, m. p. 188—189°, and the same *tetrahydropyrone* derivative, m. p. 156·5°, when heated with benzaldehyde and hydrochloric acid. It was observed by Mohr (A., 1901, i, 364) that the corresponding dimethyladipic acids appear to form an equilibrium mixture. G. A. C. Gough.

Synthesis of γ-phenylglutamic acid. A. von Beznák (Biochem. Z., 1929, 205, 414—419).—Ethyl β-chloro-α-phenylpropionate was condensed with ethyl sodiomalonate and the resulting ester, a viscous oil, b. p. 215°/15 mm., converted by ethyl nitrite in the cold into the *ethyl* ester (crystallised with difficulty) of *α-oximino-γ-phenylglutaric acid*, m. p. 143·5° (*benzoyl* derivative, m. p. 173—175°). Reduction with sodium amalgam gave *γ-phenylglutamic acid*, m. p. 185° (decomp.). J. H. Birkinshaw.

β-Amino-β-aryl-aliphatic acids from aromatic aldehydes and malonic acids. W. M. Rodionov and E. A. Postovskaja (J. Amer. Chem. Soc., 1929, 51, 841—847).—The view that the amino-acids formed in Knoevenagel's cinnamic acid synthesis (cf. A., 1927, 137, 451) are produced by the condensation of malonic acids or esters with aldehyde-ammonias, and not from ammonia and the cinnamic acids, is supported by the observation that the latter reaction (cf. Engel, A., 1887, 793) can be effected only under much more drastic conditions and that alkylmalonic esters also give amino-derivatives, although they cannot give cinnamic acids. Thus *ethyl α-amino-α-phenylpropane-ββ-dicarboxylate hydrochloride*, m. p. 158°, is obtained almost quantitatively from benzaldehyde, ethyl methylmalonate, and alcoholic ammonia at 100°. *Hydrochlorides* of the following are obtained similarly : *ethyl α-amino-α-piperonylpropane-ββ-dicarboxylate*, m. p. 125—127° ; *ethyl α-amino-α-phenyl-* and *-α-piperonyl-butane-ββ-dicarboxylates*, m. p. 166° and 157°. The β-aminopropionic acids obtained by hydrolysing these esters are also formed, together with unsaturated acids of uncertain constitution, from the alkylmalonic acids, aldehydes, and alcoholic ammonia at 100—145°. The following *hydrochlorides* of β-aminopropionic acid derivatives have been prepared by the latter method, other reaction products being given in parentheses : *γ-amino-γ-phenylpropane-β-carboxylic*, m. p. 225° [*acid*, $C_9H_{10}O_2$, m. p. 173° (decomp.)] ; *γ-amino-γ-piperonylpropane-β-carboxylic* (*acid*, $C_{10}H_9O_4$, m. p. 201—202°) ; *δ-amino-δ-phenyl*-n-*butane-γ-carboxylic*, m. p. 249° (*acid*, $C_{11}H_{12}O_2$, m. p. 107°) ; *δ-amino-δ-piperonyl*-n-*butane-γ-carboxylic*, m. p. 215° (decomp.) (*acid*, $C_{12}H_{12}O_4$, m. p. 135°) ; *γ-amino-αγ-diphenylpropane-β-carboxylic*, m. p. 222° [*acid*, $C_{16}H_{14}O_2$, m. p. 160°, also hydrocinnamic acid and (?) α-amino-αγ-diphenylpropane], which is also obtained from benzhydramide and benzylmalonic acid in alcohol at 100—125° ; and *γ-amino-α-phenyl-γ-piperonylpropane-β-carboxylic acids*, m. p. 203—205° (*acid*, $C_{17}H_{14}O_4$, m. p. 205°). H. E. F. Notton.

β-Amino-β-arylethane-αα-dicarboxylic acids ; mechanism of Knoevenagel synthesis of cinnamic acids. W. M. Rodionov [with V. B. Zenkovich and J. A. Holmogorzeva] (J. Amer. Chem. Soc., 1929, 51, 847—852).—Primary amines may be substituted for ammonia in the synthesis of β-aminopropionic acids described in the preceding abstract, but secondary amines give mainly unsaturated acids. At the ordinary or reduced temperatures benzaldehyde gives with malonic acid and amines high yields of β-amino-β-phenylethane-αα-dicarboxylic acids, which decompose when warmed into mixtures of cinnamic acid and β-amino-β-phenylpropionic acids in proportions varying widely with the conditions. Piperonal gives smaller yields of the primary products and veratraldehyde only the cinnamic acid. β-Amino-β-arylpropionic acid hydrochlorides also decompose when heated with hydrochloric acid into β-arylalanines and with sodium acetate into cinnamic acids.

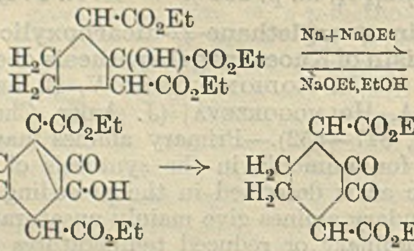
Reactions of this kind may account for the presence of these last in natural products. The following are described: β-*ethylamino*-β-*piperonylpropionic acid*, m. p. 198—200° (*nitroso*-derivative, m. p. 136—138°); β-*dimethylamino*-β-*piperonylpropionic acid hydrochloride*; β-*amino*-β-*phenyl*-, m. p. 148°; β-*piperidyl*-β-*phenyl*-, m. p. 163—164° (decomp.); β-*piperidyl*-β-*piperonyl*-, m. p. 150—152°; β-*ethylamino*-β-*phenyl*-, m. p. 163—164°, and β-*ethylamino*-β-*piperonyl*-, m. p. 155—157°, -*ethane*-αα-*dicarboxylic acids*.

H. E. F. Notton.

Phenylhydroxymaleic anhydride. J. Bougault and (Mlle.) B. Leroy (Compt. rend., 1929, 188, 921—923).—Ethyl phenylcyanopyruvate when treated with sulphuric acid at 0° affords ethyl β-carboxylamido-β-phenylpyruvate as well as phenylhydroxymaleic anhydride (A., 1914, i, 839). The latter combines with equimolecular amounts of primary or secondary amines to form unstable additive compounds which possess definite m. p. and pass, when heated, into the corresponding amides of phenylpyruvic acid. The additive compounds, together with those formed from tertiary amines, are insoluble in ether and yield the parent anhydride on treatment with dilute hydrochloric acid.

G. A. C. Gough.

Action of sodium ethoxide on ethyl *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate. L. Dedusenko (Acta Univ. Asia Med., 1928, 6, 3—16).—In the presence of an excess of alcohol ethyl *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate (I) is converted by the action of sodium ethoxide into ethyl 2-hydroxy*cyclo*pentane-1 : 2 : 3-tricarboxylate (II), the reverse change being effected by the action of sodium ethoxide and metallic sodium in absence of alcohol. Condensation of ethyl adipate with ethyl oxalate yields, in addition to ethyl *cyclo*pentanone(? ol)carboxylate, I, ethyl Δ¹-*cyclo*pentene-1 : 2 : 3-tricarboxylate (III), and ethyl oxaloadipate. The mechanism of the production of the *cyclo*pentene ester is thus left undecided, but it is considered probable that the primary product of the rearrangement of ethyl oxaloadipate is II, which then, under the influence of dry sodium ethoxide and excess of sodium, may either eliminate water to yield III, or alcohol to yield I. Conversion of II into I is explained by the scheme

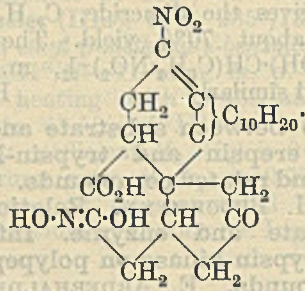


(II.) (I.)

I being in equilibrium with its various mono- and dicyclic enol forms. The reverse conversion of I into II is explained by a benzil–benzilic acid type of change, $\text{-CO·CO-} + \text{EtOH} \rightleftharpoons \text{>C(OH)·CO}_2\text{Et}$, occurring in the presence of alcoholic sodium ethoxide.

J. W. Baker.

Bile acids. XXIII. M. Schenck and H. Kirchhof (Z. physiol. Chem., 1929, 181, 185—198).—Treatment of deoxybilianic acid oxime with nitric acid (*d* 1·4) gives deoxybilianic acid together with an amorphous substance. Similar treatment of dehydrocholic acid trioxime affords a *compound* (I), $C_{24}H_{34}O_9N_2$, decomp. about 280° after previous sintering and darkening. This is soluble in sodium hydroxide solution, does not give hydroxylamine by



(I.)

heating with 20% hydrochloric acid probably because of its insolubility, when heated with diphenylamine and concentrated sulphuric acid gives a blue coloration, and with phenol and concentrated sulphuric acid a dark green coloration. Hydrolysis of I with hot 5% sodium hydroxide solution yields bilianic acid, the nitro-group being replaced by hydroxyl and subsequent ketonisation.

The nitro-compound, $C_{24}H_{36(or 34)}O_{10}N_2$ (A., 1928, 1008), is unaffected by treatment with hot sodium hydroxide solution and does not give a colour reaction either with diphenylamine or phenol and sulphuric acid.

H. Burton.

Manufacture of new carboxylic acids of the fatty-aromatic series. I. G. Farbenind. A.-G.—See B., 1929, 237.

Manufacture of alkoxynaphthamides. I. G. Farbenind. A.-G.—See. B., 1929, 276.

Dehydration of *cyclo*hexene oxide and transformation of the *cyclo*hexane to the *cyclo*pentane ring. P. Bedos and A. Ruyer (Compt. rend., 1929, 188, 962—964).—When *cyclo*hexene oxide is passed over thorium oxide at 330°, Δ¹ʼ³-*cyclo*hexadiene (I), b. p. 81°/755 mm., and *cyclo*pentanealdehyde (II), are formed. The amounts vary greatly with small variations in experimental procedure. Dehydration is also effected with boiling phthalic anhydride, and in one experiment 15% of the theoretical amount of I and 40% of II were obtained. Similar treatment of *cyclo*hexane-1 : 2-diol gives the same products. The formation of II is also effected by using potassium hydrogen sulphate or anhydrous oxalic, sulphuric, and phosphoric acids as dehydrating agents.

H. Burton.

Action of semicarbazide hydrochloride and 2 : 4-dinitrophenylhydrazine hydrochloride on aldoximes and their derivatives. O. L. Brady and F. H. Peakin (J.C.S., 1929, 478—479).—When a solution of an aldoxime is treated with a solution of semicarbazide hydrochloride at the ordinary temperature, the aldehydesemicarbazone is precipitated. Both α- and β-forms of three substituted benzaldoximes examined gave only one form of the semicarbazone in each case. No reaction occurs if semicarbazide is used, indicating that the oxime is first hydrolysed to the aldehyde. The *N*-methyl ethers react more rapidly than the *O*-methyl ethers presumably because of the greater ease of hydrolysis of the former. An analogous change occurs when oximes and their *N*- and *O*-ethers are treated with a solution of 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The sparing solubility of the resulting aldehyde-2 : 4-dinitrophenylhydrazone allows this change to be used as a convenient method for the determination of small amounts of oximes.

H. BURTON.

ε-Phenyl-$\Delta^{\beta\delta}$-pentadienal and η-phenyl-$\Delta^{\beta\delta\zeta}$-heptatrienal. II. D. VORLÄNDER and E. DAEHN (Ber., 1929, **62**, [*B*], 541—545).—The aldehydes (cf. A., 1925, i, 1068) are known to some extent in the perfume industry and have been examined by Engelberg (Diss., Berlin, 1914). Re-investigation of the products derived from the residues obtained from the fractionation of synthetic cinnamaldehyde establishes the identity of all the specimens of the phenylpentadienal, but the data for derivatives of phenylheptatrienal are not in harmony with those of Engelberg. The following data are new or amended. ε-Phenyl-$\Delta^{\beta\delta}$-pentadienal yields *compounds* with aniline, m. p. 112° (corr.); *p*-toluidine, m. p. 105° (corr.); *p*-anisidine, m. p. 147° (corr.); *p*-phenetidine, m. p. 137° (corr.); *p*-aminoazobenzene, m. p. I 168°, II 163° (corr.); β-naphthylamine, m. p. 145° (corr.), and *p*-aminoacetophenone, m. p. 154—155° (corr.). The *phenylhydrazone*, m. p. 178° (corr.), and dimorphous *hydrazone*, m. p. 210° (corr.) or 217° (corr.) are described. The condensation *products* with acetone, acetophenone, *cyclo*pentanone, and *cyclo*hexanone have m. p. 189°, 79°, 203—204°, and 202° (corr.), respectively. Isolation of η-phenyl-$\Delta^{\beta\delta\zeta}$-heptatrienal from the residues of the technical cinnamaldehyde synthesis appears difficult. The products derived from a suitable fraction with phenylhydrazine [m. p. 189° (corr.)], *p*-phenetidine [m. p. I 188° (corr.), II 164° (corr.)], and *p*-aminoazobenzene [m. p. I 250—252° (corr.), II 208—210° (corr.)] have uniformly lower m. p. than those recorded by Vorländer and Kunze (*loc. cit.*). The possibility therefore exists that the properties assigned previously to the trienal actually belong to a higher homologue. The difficulty cannot be elucidated analytically. H. WREN.

Salicylaldehyde and its methyl ether. M. COPISAROW (J.C.S., 1929, 588—589).—*o*-Tolyl carbonate is prepared in 83% yield by the action of carbonyl chloride on *o*-cresol in aqueous sodium hydroxide solution. Chlorination (Raschig, G.P. 233631) and hydrolysis of the product by methyl-alcoholic sodium hydroxide gives salicylaldehyde in 50% yield. The action of methyl sulphate on the reaction mixture obtained by hydrolysis of the chlorination product gives *o*-anisaldehyde in 38% yield. R. K. CALLOW.

Influence of substituents on Reimer–Tiemann reaction. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1929, 469—471).—A standardised Reimer–Tiemann reaction has been carried out with seven phenols, and the amounts of the corresponding *o*- and *p*-hydroxybenzaldehydes produced were determined as *p*-nitrophenylhydrazones. The *o*/*p* ratios show that with phenol, *o*- and *m*-cresols, *m*-chloro-, -bromo-, and -iodo-phenols the *para* position is more reactive than the *ortho*, and a preponderance of the *p*-hydroxy-aldehyde results: if the reaction mixture is acidified with mineral acid the yield of the *p*-hydroxy-aldehyde is considerably reduced. The *m*-halogenophenols give higher *o*/*p* ratios (0·71—0·78) than phenol (0·6), the 4-position being deactivated more than the 2-position owing to the direct and inductive effects of the halogen atom: deactivation is in the order Cl > Br > I. With *m*-cresol the *o*/*p* ratio (0·46) is smaller, activation of the 4-position being increased by the direct and inductive effects of the methyl group. *o*-Chlorophenol gives a ratio of 1·6, and it is assumed that the positive field of the chlorine atom attracts the negative field of the oxygen sufficiently to relieve the 2-position of a considerable amount of steric hindrance due to the oxygen. With *o*-cresol (ratio 0·46) the reverse influence is shown.

H. BURTON.

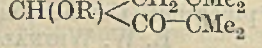
Coupling of diazonium salts in the side-chains of unsaturated compounds. II. A. QUILICO and E. FLEISCHNER (Gazzetta, 1929, **59**, 39—49).—The reaction of unsaturated phenol ethers with diazonium salts (cf. A., 1928, 997) is extended to *iso*eugenol. This, in contrast to its behaviour in aqueous solutions (cf. Oddo and Puxeddu, A., 1905, i, 492; Puxeddu, A., 1906, i, 774), in alcoholic or acetic acid solutions reacts in the side-chain, which is partly eliminated. Thus with *p*-nitrobenzenediazonium sulphate, vanillin-*p*-nitrophenylhydrazone is formed, identical with a synthesised specimen; the substance forms an *acetyl* derivative, m. p. 151°, also obtained by acetylation of *acetylvanillin*-p-*nitrophenylhydrazone*, m. p. 179°. Reduction of the substance yields a *hydrazo*-compound (?), $C_{14}H_{15}O_4N_3$, m. p. 192° (decomp.). The product from 2 : 4-dinitrobenzenediazonium sulphate is similarly identified with *vanillin*-2 : 4-*dinitrophenylhydrazone*, m. p. 250° (decomp.). The difference in behaviour between unsaturated phenol ethers containing the $\cdot CH{:}CHMe$ and the $\cdot CH_2\cdot CH{:}CH_2$ groupings, respectively, is discussed with reference to Angeli's rule (A., 1924, i, 626). For piperonal-*p*-nitrophenylhydrazone, obtained from either *iso*safrole (A., 1928, 997) or piperonal, the new m. p. 208° is given. E. W. WIGNALL.

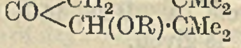
[Hadromal, lignin, and coniferaldehyde, preparation and identification.] Coniferaldehyde. A. HILLMER and E. HELLRIEGEL (Ber., 1929, **62**, [*B*], 725—727; cf. Pauly and Feuerstein, this vol., 446).—Coniferaldehyde is yellow when dissolved in water, lower alcohols, glycol, and glycerol, very pale yellow in *iso*amyl alcohol, benzyl alcohol, and pyridine, colourless in ether, acetone, methyl ethyl ketone, hexane, carbon tetrachloride, carbon disulphide, benzene, and xylene. It may be used as indicator in alkalimetry, the end-point lying at p_H 7·6. The absorption spectra of coniferaldehyde and of its methoxymethyl ether are quite distinct from that of vanillin. The maximum of absorption of coniferaldehyde lies at $\lambda=321$ and 301 μμ, of methoxymethyl-coniferaldehyde at $\lambda=312$ and 292 μμ, and of vanillin at $\lambda=303$ and 282 μμ. The characteristic absorption minima of the compounds lie at $\lambda=262$, 257, and 248 μμ. The extinction values ε of coniferaldehyde and its methoxymethyl ether in the mid ultra-violet are about three times that of vanillin. The absorption spectrum of lignin resembles those of coniferyl alcohol and certain of its derivatives but not that of coniferaldehyde. H. Wren.

The keto-group. R. Cornubert and C. Borrel (Compt. rend., 1929, **188**, 798—800).—A series of 5-substituted 2-methyl*cyclo*pentanones was prepared to investigate the influence of the substituting group on the ease of formation of the "tetrahydropyrone derivatives" (cf. A., 1926, 953). Tetrahydropyrone derivatives of the following ketones are prepared under standardised conditions by condensation with benzaldehyde (the m. p. and yield of the derivative are given in parentheses): 2 : 5-dimethyl*cyclo*pentanone (127°; 73%); 2-methyl-5-ethyl*cyclo*pentanone, b. p. 164—165° (98—99°; 59%); 2-methyl-5-*n*-propyl*cyclo*pentanone, b. p. 78—79°/18 mm. (116—116·5°; 59%); 2-methyl-5-*iso*propyl*cyclo*pentanone, b. p. 178° (125·5°; 10%); 2-methyl-5-*n*-butyl*cyclo*pentanone, b. p. 93—94°/16 mm. (101—102°; 54%); 2-methyl-5-*iso*butyl*cyclo*pentanone, b. p. 82—83°/13 mm. (118°; 35%); 2-methyl-5-benzyl*cyclo*pentanone, b. p. 150°/16 mm. (156·5°; 77%). 2 : 6-Dibenzyl*cyclo*hexanone affords a semicarbazone, m. p. 190—191°, and two *oximes*, m. p. 90° and 188°.

G. A. C. Gough.

Mobile hydrogen tautomerism analogous to the Wagner–Meerwein rearrangement. II. Tautomerism of 1(or 5)-hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentan-5(or 1)-one and its derivatives. C. W. Shoppee (J.C.S., 1928, 1662—1670; cf. A., 1928, 414).—When 5-acetoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone is hydrolysed with aqueous-alcoholic sodium hydroxide, the *hydroxy-ketone* named in the title, m. p. 142° [p-*nitrobenzoyl* derivative, m. p. 85°; p-*nitrophenylhydrazone*, m. p. 223—224° (decomp.)], is obtained. With acid reducing agents it affords a mixture of 2 : 2 : 3 : 3- and 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanones, and must be represented by both I and II (R=H). Similarly, by benzoylation

(II.)

$CH(OR){<}\begin{matrix}CH_2\cdot CMe_2\\ CO-CMe_2\end{matrix}$


$CO{<}\begin{matrix}CH_2-CMe_2\\ CH(OR)\cdot CMe_2\end{matrix}$
(I.)

in pyridine solution it yields a mixture of 1-*benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-5-*one*, m. p. 105° (I, R=Bz) [*oxime*, m. p. 115° (III)], and 5-*benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-1-*one*, m. p. 60° (II, R=Bz) [*oxime*, oily (IV)]; III (*benzoyl* derivative, m. p. 135°) by reduction with sodium amalgam in glacial acetic acid gives 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamine, whilst IV (*benzoyl* derivative, b. p. 200—215°/15 mm.), similarly reduced, yields 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. When oximated the hydroxy-ketone yields a mixture of the oximes of I and II, converted by benzoylation with excess of benzoyl chloride in pyridine solution into the benzoyl derivatives of III, m. p. 135°, and IV, b. p. 200—215°/14 mm. Methylation with methyl sulphate and 10% sodium hydroxide at 100° yields mainly 5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-1-*one*, b. p. 88—90°/10 mm., n_D^{19} 1·4574 (II, R=Me), reduced by hydriodic acid *d* 1·7 to 3 : 3: 4 : 4-tetramethyl*cyclo*pentanone, and giving an oily *oxime* which affords 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine by reduction; the isomeric 1-methoxy-ketone (I, R=Me) may be present in small quantity. C. W. Shoppee.

Methylation of *cyclo*heptanone. M. Godchot and (Mlle.) Cauquil (Compt. rend., 1929, **188**, 794—796).—Methylation of *cyclo*heptanone by the action of methyl iodide on an ethereal suspension of its sodium derivative (prepared by Haller's method), followed by separation of the resultant products by means of their semicarbazones, affords small amounts of 2 : 2-dimethyl*cyclo*heptanone, b. p. 191—192° (corr.)/770 mm. (semicarbazone, m. p. 174—175°; cf. Tarbouriech, A., 1913, i, 181), and 2-methyl*cyclo*heptanone, b. p. 185—186°(corr.)/760 mm., d^{18} 0·9395, n_D^{18} 1·461 (semicarbazone, m. p. 117—118°; oxime, b. p. 126°/16 mm.; oxime phenylcarbamate, m. p. 96—97°). The last-named ketone on oxidation with aqueous potassium permanganate yields ε-acetyl-*n*-hexoic acid (semicarbazone, m. p. 113—114°, cf. Wallach, A., 1906, i, 370).

G. A. C. Gough.

Three-carbon system. XX. *cyclo*Pentylideneacetone and *cyclo*pentylidenemethyl ethyl ketone. A. H. Dickins, W. E. Hugh, and G. A. R. Kon (J.C.S., 1929, 572—580).—The interconversion of cyclo*pentylidenemethyl ethyl ketone* (I) and Δ¹-cyclo*pentenylmethyl ethyl ketone* (II) and of cyclo*pentylideneacetone* (III) and Δ¹-cyclo*pentenylacetone* (IV) has been studied in the same way as the interconversion of the *cyclo*hexane analogues (A., 1928, 887). Equilibrium is attained much more rapidly in the *cyclo*pentane compounds, and is on the side of the αβ-forms instead of the βγ-forms.

*cyclo*Pentylidenemethyl ethyl ketone is prepared from *cyclo*pentylideneacetyl chloride (*loc. cit.*) and purified by conversion into the *semicarbazone*, m. p. 174°, which is accompanied by the *semicarbazidosemicarbazone*, m. p. 215°. The ketone regenerated from the semicarbazone has b. p. 96°/20 mm., $d_4^{22\cdot9}$ 0·93179, $n_D^{22\cdot9}$ 1·47801, $[R_L]_D$ 41·96. Δ¹-*cyclo*Pentenylacetic acid is prepared from its ester or by dry distillation of *cyclo*pentylidenemalonic acid under reduced pressure. The acid chloride and zinc diethyl or magnesium methyl iodide yield only the αβ-compound (I); the Blaise–Maire reaction under carefully controlled conditions gives a low yield of *cyclo*pentenylmethyl ethyl ketone, which, regenerated from the *semicarbazone*, m. p. 135°, has b. p. 90°/21 mm., $d_4^{22\cdot5}$ 0·92429, $n_D^{22\cdot5}$ 1·46509, $[R_L]_D$ 41·31. Condensation with ethyl sodiomalonate, followed by hydrolysis, yields cyclo*pentane*-spiro-4-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 174—175°. The equilibrium between I and II in presence of *N*-alcoholic sodium ethoxide is practically reached after 20 min., and the mixture contains about 85% of I. The compounds III and IV were previously obtained as an equilibrium mixture (Kon, J.C.S., 1921, **119**, 810; Kon and Linstead, A., 1925, i, 633). *cyclo*Pentylideneacetone is prepared from *cyclo*pentylideneacetyl chloride and purified by conversion into the semicarbazone, m. p. 189°. The regenerated ketone has b. p. 70°/12 mm., $d_4^{16\cdot9}$ 0·94205, $n_D^{16\cdot9}$ 1·47937, $[R_L]_D$ 37·16. The iodine absorption of this material corresponds with a higher percentage of βγ-compound than the equilibrium mixture, an effect which is attributed to the action of acid, and the ketone was best purified by repeated fractionation. Δ¹-*cyclo*Pentenylacetone (from Δ¹-*cyclo*pentenylacetyl chloride), best purified by regeneration from the semicarbazone and subsequent treatment with aluminium amalgam, has b. p. 69—70°/16 mm., $d_4^{20.4}$ 0·93568, $n_D^{20.4}$ 1·46211, $[R_L]_D$ 36·58. The ketone obtained by distillation of calcium *cyclo*pentanediacetate (Kon, *loc. cit.*) contains only 64% of the αβ-form. Distillation of calcium acetate and calcium *cyclo*pentenylacetate yields a similar product. The equilibrium between III and IV with *N*-alcoholic sodium ethoxide is practically established after 10 min., and the mixture contains 84% of III.

Examination of *cyclo*pentylidene*cyclo*pentanone indicates that the point of equilibrium lies near the αβ-compound. The iodometric method breaks down in the case of *cyclo*hexenyl*cyclo*hexanone.

R. K. CALLOW.

Transposition and purity of naphthyl methyl ketones. L. CHOPIN (Bull. Soc. chim., 1929, [iv], 45, 167—168).—β-Naphthyl methyl ketone is slowly transformed into the α-isomeride at the ordinary temperature, the isomerisation being, however, dependent on the initial presence of traces of the α-isomeride. The isomerisation is accelerated by heat and acids, especially by warm concentrated hydrochloric acid. Sulphuric acid and phosphoric acid are much less effective. Solvents used in the synthesis are without influence. The β-isomeride is usually contaminated with aniline or phenylcarbimide, and in contrast to the α-ketone darkens on keeping. Treatment with phosphoric acid effects partial purification. R. BRIGHTMAN.

Use of magnesium and methyl alcohol as reducing agent. L. ZECHMEISTER and P. ROM (Annalen, 1929, 468, 117—132).—Benzophenone gives a 90% yield of benzhydrol when reduced by absolute methyl alcohol and magnesium (small pieces of ribbon). A quantitative yield is obtained by the ammonium chloride method (A., 1926, 720). Using the new method of reduction, dibenzyl ketone gives dibenzylcarbinol (90% yield), whilst acetophenone gives phenylmethylcarbinol (45% yield), acetophenone pinacol (11%) and tarry by-products. *p*-Methoxyacetophenone gives 47% of carbinol and some pinacol. Phenacyl bromide is converted (68% yield) into phenylmethylcarbinol. Styryl methyl ketone gives β-phenylethylmethylcarbinol in 77% yield, whilst distyryl ketone gives di-β-phenylethylcarbinol (71%) and a small amount of a *substance*, m. p. 279°. αα′-Dichloroethylbenzene gives an 86% yield of αα′-dimethoxyethylbenzene, also obtained from the dichloro-compound and magnesium methoxide. Magnesium and moist methyl alcohol convert the dichloro-compound into benzhydrol, benzpinacol, etc.

Chlorobenzene is unaffected by magnesium and methyl alcohol. Bromobenzene is to a large extent dehalogenated, but gives no diphenyl. Iodobenzene gives an 80% yield of benzene, α-bromonaphthalene gives a 96% yield of naphthalene, and α-chloronaphthalene is largely dehalogenated.

Nitrobenzene, according to conditions, may give β-phenylhydroxylamine, azoxy-, azo-, or hydrazobenzene, or aniline, but some usually escapes reduction. The nitrotoluenes are reduced more smoothly. Some unchanged material is usually recovered, and some of the hydroxylamine and the toluidine is formed. The main product is in each case, however, the azoxy-compound (yields: *o*, 57%; *m*, 70%; *p*, 61%).

Magnesium and methyl alcohol convert *o*-, *m*-, and *p*-chloro- or -bromo-nitrobenzenes into the corresponding dihalogenoazoxybenzenes, the yields being of an order similar to that using the ammonium chloride method (*loc. cit.*). Some dehalogenation also occurs. During the reduction of all compounds with halogen *ortho* to a nitro-group, intense colorations are observed. 2 : 5-Dibromonitrobenzene gives a 30% yield of 2 : 5 : 2′ : 5′-*tetrabromoazoxybenzene*, m. p. 166°.

E. E. TURNER.

Nitration of 4-chloro-4′-bromo-benzophenone and -diphenylsulphone, and attempted nitration of 4-chloro-4′-bromodiphenyl. L. G. GROVES and E. E. TURNER (J.C.S., 1929, 509—511).—4-*Chloro-4′-bromobenzophenone*, m. p. 150° (corr.), was obtained by a Friedel–Crafts reaction from chlorobenzene and *p*-bromobenzoyl chloride. In sulphuric acid it is nitrated to the extent of 51% in position 3 and 49% in position 3′, as determined by the mixed halogen displaced from the product by piperidine. 4-*Chloro-4′-bromodiphenylsulphone*, m. p. 157° (corr.) (from bromobenzene and *p*-chlorobenzenesulphonyl chloride), is mononitrated to the extent of 34% in position 3 and 66% in position 3′. Dinitration yields the 3 : 3′-*dinitro*-compound, m. p. 219° (corr.). The results are concordant with the behaviour of benzophenone and diphenylsulphone and of bromo- and chloro-benzene on nitration. 4-*Chloro-4′-bromodiphenyl*, m. p. 147° (corr.), was obtained from 4-chloro-4′-aminodiphenyl by diazotisation and decomposition of the diazonium perbromide in hot acetic acid. Attempted nitration yielded only decomposition products. R. K. CALLOW.

Relative ease of formation of 5-, 6-, and 7-membered carbon rings. J. VON BRAUN and G. MANZ (Annalen, 1929, 468, 258—277).—The preparation of βγ-diphenylpropyl chloride described previously (A., 1928, 174) is unsuitable for obtaining large quantities, for a considerable amount of α-methylstilbene is also produced. βγ-Diphenylbutyric acid is therefore more conveniently prepared as follows: Reduction of ethyl α-phenylcinnamate with alcohol and a large excess of sodium gives some αβ-diphenylpropane, b. p. 145—148°/13 mm., m. p. 50° (cf. Klages and Heilmann, A., 1904, i, 487, who describe it as a liquid), but mainly βγ-*diphenylpropyl alcohol*, b. p. 185—188°/13 mm. (yield 60%). The latter is converted by fuming hydrobromic acid at 130° into βγ-*diphenylpropyl bromide*, b. p. 188—190°/13 mm., which with aqueous-alcoholic potassium cyanide gives some methylstilbene, but a 50% yield of βγ-*diphenylbutyronitrile*, b. p. 204—206°/13 mm. The corresponding acid, obtained by heating the nitrile with concentrated hydrochloric acid at 120°, is converted by thionyl chloride into a chloride (not isolated) which with aluminium chloride in carbon disulphide gives 1-*keto*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 65—66° (yield 75%) (*oxime*, m. p. 190°; *semicarbazone*, sinters 204°, m. p. 208°), reduced by Clemmensen's method to 2-*phenyltetrahydronaphthalene*, b. p. 180—181°/13 mm., d_4^{18} 1·0579, n_D^{18} 1·5980. The constitution of the last-named follows from its oxidation (heated litharge) to β-phenylnaphthalene.

γ-Phenylpropyl bromide and ethyl sodiobenzylmalonate give a 70% yield of *ethyl benzyl-γ-phenylpropylmalonate*, b. p. 244—247°/13 mm., hydrolysed to the *acid*, which begins to lose carbon dioxide at 96°, and, when heated in a vacuum, gives *δ-phenyl-α-benzyl*-n-*valeric acid*, b. p. 243—245°/13 mm. (yield 80%). Thionyl chloride gives the acid chloride (not isolated), which is converted by carbon disulphide and aluminium chloride into 2-*γ-phenylpropyl*-1-*hydrindone*, b. p. 227—229°/13 mm. (yield 60%) (*semicarbazone*, m. p. 172°; p-*nitrophenylhydrazone*, m. p. 161°; *oxime*, oily, reduced to 1-amino-2-γ-phenylpropylhydrindene, b. p. 217°/13 mm., which forms a *hydrochloride*, m. p. 169°, and a *picrate*, m. p. 203°). Clemmensen reduction of the ketone gives 2-*γ-phenylpropylhydrindene*, b. p. 197°/13 mm., d_4^{18} 1·0128, n_D^{18} 1·5667. Bromine converts the hydrindone in chloroform solution into a *bromo*-derivative, m. p. 82°, presumably the 2-compound. The constitution of the hydrindone follows from its formation by reducing 2-*cinnamylidene*-1-*hydrindone*, m. p. 124° (from α-hydrindone and cinnamaldehyde), with palladised charcoal.

When anhydrous ethyl sodiobenzylmalonate is heated at 100° with ethyl β-iodo- or β-chloro-propionate, an 85% yield of *ethyl α-phenylbutane-ββδ-tricarboxylate*, b. p. 219—221°/13 mm., is obtained. The ester is hydrolysed by aqueous-alcoholic alkali to *α-phenylbutane-ββδ-tricarboxylic acid*, m. p. 166° (decomp.), together with some α-phenylbutane-βδ-dicarboxylic acid. The tricarboxylic acid, when heated in a vacuum, gives α-benzylglutaric acid, b. p. 231—236°/0·5 mm., m. p. 76° (not an oil, as lit.). Thionyl chloride converts this acid into the *anhydride*, m. p. 81°, which with aluminium chloride in nitrobenzene gives (yield 30%) 2-*ethyl*-1-*hydrindone*-ω-*carboxylic acid*, m. p. 238—243°/14 mm. (*oxime*, m. p. 145°; *semicarbazone*, m. p. 244—246°), converted by heating with soda-lime into α-hydrindone (yield 50%).

Reduction of *o*-phenylbenzonitrile with hydrogen (15—20 atm.) in presence of nickel at 120—130° gives a 45% yield of o-*phenylbenzylamine*, b. p. 163°/12 mm. (*hydrochloride*, m. p. 212°; *picrate*, m. p. 188°; *acetyl* derivative, m. p. 125°; *benzoyl* derivative, m. p. 95°), which is converted by sodium nitrite and acetic acid into o-*phenylbenzyl alcohol*, b. p. 174°/13 mm. Concentrated hydrochloric or hydrobromic acid at 100° converts this into o-*phenylbenzyl chloride*, b. p. 154°/12 mm., or o-*phenylbenzyl bromide*, b. p. 166°/12 mm. The latter is converted (1) by ammonium dithiocarbamate into the *dithiourethane*, $C_6H_4Ph·CH_2·S·CS·NH_2$, m. p. 106°, hydrolysed to o-*phenylbenzylmercaptan*, b. p. 160°/12 mm., (2) by sodium in presence of ether into 2 : 2′-*bisdiphenylylethane*, b. p. 260°/12 mm., (3) by aqueous-alcoholic potassium cyanide into ω-*cyano*-2-*methyldiphenyl*, b. p. 182°/12 mm., which is readily hydrolysed to 2-*methyldiphenyl*-ω-*carboxylic acid*, m. p. 114°, and (4) by sodiomalonic ester into *ethyl 2-ethyldiphenyl-ωω-dicarboxylate*, b. p. 245—258°/12 mm. (yield 80%). The latter is readily hydrolysed to the acid, which loses carbon dioxide in hot aqueous solution to give β-2-*diphenylylpropionic acid*, m. p. 125°. The latter is converted by thionyl chloride into the chloride (not isolated), which with aluminium chloride in light petroleum gives 4-*phenyl*-1-*hydrindone*, b. p. 200—205°/11 mm. (*semicarbazone*, m. p. 192°). When heated with 30% nitric acid at 200° the latter gave a crude product containing no diphenic acid (proof of constitution). E. E. TURNER.

Ease of substitution of aromatically bound hydrogen atoms. J. VON BRAUN, G. MANZ, and E. REINSCH (Annalen, 1929, 468, 277—303).—Phenyl *m*-tolyl ketone, b. p. 183—185°/16 mm., reacts with zinc and ethyl bromoacetate to give crude *ethyl* β-m-*tolylcinnamate*, b. p. 208—210°/16 mm., which cannot be freed from unchanged ketone. Hydrolysis of the product gives β-m-*tolylcinnamic acid*, m. p. 114°, b. p. 229—232°/17 mm. Hydrogenation of the latter affords β-*phenyl*-β-m-*tolylpropionic acid*, m. p. 109°, b. p. 206—210°/13 mm., the *chloride*, b. p. 200°/16 mm., of which is converted (yield 60%) by aluminium chloride in carbon disulphide into 3-*phenyl*-5-*methyl*-1-*hydrindone*, b. p. 210—215°/16 mm. (*oxime*, formed slowly, m. p. 163°, is difficult to hydrolyse, but gives the hydrindone as a solid, m. p. 61°). Oxidation of the hydrindone with alkaline permanganate gives *benzophenone*-2 : 5-*dicarboxylic acid*, m. p. 285°, which establishes the constitution.

From ethyl *m*-methylbenzylmalonate and benzyl chloride may be obtained *ethyl benzyl*-m-*methylbenzylmalonate*, b. p. 231—233° (?), hydrolysed to *benzyl*-m-*methylbenzylmalonic acid*, melting at 168° to give *benzyl*-m-*methylbenzylacetic acid*, $C_6H_4Me·CH_2·CH(CH_2Ph)·CO_2H$, m. p. 67—68°. Aluminium chloride converts the chloride of the latter into 2-*benzyl*-5-*methyl*-1-*hydrindone*, m. p. 87—89° (*oxime*, m. p. 103°; *semicarbazone*, m. p. 196°), and a liquid which appears to be mainly the same hydrindone (oxidation gives benzoic and trimellitic acids). The constitution of the hydrindone follows from the following synthesis: the chloride of β-*m*-tolylpropionic acid is converted by aluminium chloride into the known 5-methyl-1-hydrindone, oxidised to trimellitic acid and therefore not a mixture, as thought by Young (A., 1892, i, 1221). 5-Methyl-1-hydrindone readily condenses with benzaldehyde in presence of alkali. The 2-*benzylidene*-5-*methyl*-1-*hydrindone*, m. p. 134°, so obtained is hydrogenated in methyl alcohol in presence of palladium to give the above benzylmethylhydrindone.

Phenyl *o*-tolyl ketone, zinc, and ethyl bromoacetate give *ethyl* β-o-*tolylcinnamate*, b. p. 160—180°/14 mm. (about 35% of unchanged ketone is present), hydrolysed to β-o-*tolylcinnamic acid*, m. p. 114°, b. p. 218—220°/14 mm. The latter when reduced affords β-*phenyl*-β-o-*tolylpropionic acid*, m. p. 129°, and the *chloride*, b. p. 189°/16 mm., of the latter is converted (80% yield) by aluminium chloride into 3-o-*tolyl*-1-*hydrindone*, m. p. 87°, b. p. 195—196°/14 mm. (*oxime*, m. p. 166°; *semicarbazone*, m. p. 267°), oxidised to *benzophenone*-2 : 2′-*dicarboxylic acid*, m. p. 148—150° (*anhydride*, m. p. 212°). Clemmensen reduction of the hydrindone gives 1-o-*tolylhydrindene*, m. p. 57°, b. p. 160—162°/14 mm.

From phenyl *p*-tolyl ketone, β-p-*tolylcinnamic acid*, m. p. 140° (*ethyl* ester, b. p. 205—210°/14 mm.), is obtainable in good yield. The derived β-*phenyl*-β-p-

tolylpropionic acid, m. p. 140°, b. p. 230—232°/14 mm., forms a *chloride*, b. p. 194°/14 mm., which is converted in 70% yield into 3-p-*tolyl*-1-*hydrindone*, m. p. 92°, b. p. 202—204°/14 mm. (*oxime*, m. p. 200°; *semicarbazone*, m. p. 219°). The constitution of this ketone follows from its oxidation to benzophenone-2 : 4′-dicarboxylic acid, m. p. 241° (lit. 235°). Reduction affords 1-p-*tolylhydrindene*, b. p. 168—170°/ 14 mm., d_4^{20} 1·0455, n_D^{20} 1·5878.

ω-Bromo-*p*-xylene and ethyl benzylmalonate give rise to the *ethyl* ester, b. p. 232—235°/14 mm., of *benzyl*-p-*methylbenzylmalonic acid*, melting and decomposing at 155—157° to give β-p-*tolyl*-α-*benzylpropionic acid*, m. p. 88—89°, b. p. 235—237°/13 mm. (*amide*, m. p. 131°). The chloride of the latter is converted by aluminium chloride in carbon disulphide mainly into 2-p-*methylbenzyl*-1-*hydrindone*, b. p. 221—223°/14 mm. [*oxime* (not pure), m. p. 131—142°; *phenylhydrazone* (not pure), decomp. 105—113°; *semicarbazone*, m. p. 195—197°], but also some (?) 2-benzyl-6-methyl-1-hydrindone. The composition of the product is deduced as follows: α-Hydrindone readily condenses with *p*-tolualdehyde to give 2-p-*methylbenzylidene*-1-*hydrindone*, m. p. 138°, reduced to 2-p-*methylbenzyl*-1-*hydrindone*, b. p. 223—226°/ 15 mm. (*oxime*, m. p. 132°; *phenylhydrazone*, m. p. 109°, both depressing the m. p. of the corresponding derivatives of the Friedel–Crafts product). 6-Methylhydrindone and benzaldehyde give 6-*methyl*-2-*benzylidene*-1-*hydrindone*, m. p. 165°, reduced to 2-*benzyl*-6-*methyl*-1-*hydrindone*, m. p. 38—39°, b. p. 206—210°/ 12 mm. (*oxime*, m. p. 130—143°, depressing the m. p. of the Friedel–Crafts product). Moreover, oxidation of the Friedel–Crafts ketone mixture gives terephthalic, trimellitic, and benzoic acids. A limited amount of ring-closure must therefore occur in the tolyl nucleus *meta* to the methyl group.

Catalytic reduction of the above ethyl β-*p*-tolylcinnamate in an autoclave in presence of nickel gives *ethyl* β-*phenyl*-β-p-*tolylpropionate*, m. p. 41°, b. p. 205—207°/14 mm., reduced by sodium and alcohol to γ-*phenyl*-γ-p-*tolyl*-n-*propyl alcohol*, b. p. 210—215°/ 20 mm. The latter is converted by fuming hydrobromic acid at 100° into γ-*phenyl*-γ-p-*tolyl*-n-*propyl bromide*, b. p. 202—203°/14 mm., and thence into γ-*phenyl*-γ-p-*tolyl*-n-*butyronitrile*, b. p. 211—222°/ 14 mm., and γ-*phenyl*-γ-p-*tolyl*-n-*butyric acid*, b. p. 238—239°/14 mm. The *chloride*, b. p. 205—208°/ 14 mm., of the latter is converted (yield 70%) by aluminium chloride in carbon disulphide into 4-p-*tolyl*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 75°, b. p. 198—200°/14 mm. (*semicarbazone*, m. p. 204°), oxidised to benzophenone-2 : 4′-dicarboxylic acid (proof of constitution), and containing a small quantity of 4-phenyl-7-methyl-1-ketotetrahydronaphthalene.

Zinc, ethyl bromoacetate, and phenyl β-naphthyl ketone produce the *ethyl* ester, b. p. 250—260°/13 mm., of β-2-*naphthylcinnamic acid*, m. p. 217°, reduced to β-*phenyl*-β-2-*naphthylpropionic acid*, m. p. 132°. The chloride of this acid is converted by aluminium chloride in carbon disulphide into 3-*phenyl*-6 : 7-*benzhydrindone*, m. p. 119°, b. p. 257—259°/13 mm. [*oxime*, m. p. 190—192°; *semicarbazone*, m. p. 235—238° (decomp.)], reduced to 3-*phenyl*-6 : 7-*benzhydrindene*, m. p. 79°, b. p. 226—229°/13 mm. The constitution of the product follows from its oxidation by alkaline permanganate to 2-*benzoyl*-α-*naphthoic acid* (converted by alkali fusion into α-naphthoic and benzoic acids), and from the fact that the hydrindene is different from 1-β-*naphthylhydrindene*, m. p. 47°, b. p. 229—230°/13 mm., obtained by hydrogenation (palladium) of 1-β-*naphthylindene*, m. p. 88°, b. p. 246—250°/14 mm., which is obtained by treating α-hydrindone with magnesium β-naphthyl bromide.

From ethyl benzylmalonate and ω-bromo-β-methylnaphthalene is obtainable (60% yield) the *ethyl* ester, b. p. 225—230°/0·3 mm., of α-*phenyl*-γ-2-*naphthylpropane*-ββ-*dicarboxylic acid*, melting at 111—113° to give β-2-*naphthyl*-α-*benzylpropionic acid*, m. p. 103—104°, b. p. 235—240°/vac. The chloride of the latter is converted by aluminium chloride in nitrobenzene into 2-*benzyl*-6 : 7-*benzhydrindone*, m. p. 72—74°, b. p. 205—210°/0·5 mm., identical with the product of reducing 2-*benzylidene*-6 : 7-*benzhydrindone*, m. p. 166°, with hydrogen and palladium in methyl-alcoholic solution.

α-*Phenyl*-γ-1-*naphthylpropane*-ββ-*dicarboxylic acid* (*ethyl* ester, b. p. 225—230°/0·5 mm.) decomposes when heated in a vacuum to give β-1-*naphthyl*-α-*benzylpropionic acid*, m. p. 101—103°, b. p. 245—250°/0·8 mm. The chloride of this acid undergoes Friedel–Crafts ring closure to give (not less than 50% yield) 2-*benzyl*peri*naphthindanone*, b. p. 205—210°/4 mm. (*oxime*, m. p. 163—164°). The other product is apparently not 2-α-*naphthylmethylhydrindone*, m. p. 87—88° (obtained by reducing 2-α-*naphthylidene*-1-*hydrindone*, m. p. 128°, from α-hydrindone and α-naphthaldehyde), but is apparently formed by ring-closure in the β-position in the naphthalene nucleus. The constitution of the *peri*-ketone follows from its synthesis: *peri*naphthindanone (from β-1-naphthylpropionyl chloride and aluminium chloride in light petroleum or in carbon disulphide, but not in nitrobenzene, which gives rise to peri-*naphthindone*, m. p. 130—143°, reducible to the indanone) condenses with benzaldehyde to give *benzylidene*-peri*naphthindanone*, m. p. 163°, reduced to the above ketone formed in the ring-closure.

From ω-bromo-2-methylnaphthalene and ethyl α-naphthylmethylmalonate, $C_{10}H_7\cdot CH_2\cdot CH(CO_2Et)_2$, is obtainable the *ethyl* ester, b. p. 255—260°/0·05 mm., of α-*naphthylmethyl*-β-*naphthylmethylmalonic acid*, an oil, decarboxylation of which produces α-1-*naphthyl*-γ-2-*naphthylpropane*-β-*carboxylic acid*, b. p. 280—290°/0·8 mm. Aluminium chloride converts the chloride of the latter in nitrobenzene solution into a mixture of 2-α-*naphthylmethyl*-6 : 7-*benzhydrindone*, m. p. 139°, b. p. 250—255°/0·1 mm. (also obtained by reducing α-*naphthylidenebenzindanone*, m. p. 189—190°), and another product or products formed by β- or *peri*-ring-closure (?).

The ring-closures effected with the benzene derivatives show that the *para*-hydrogen atom in toluene is more reactive than a hydrogen atom in benzene, the latter hydrogen atom being in turn more reactive than a *meta*-hydrogen atom in toluene. The ring-closures with the naphthalene derivatives show that an α-hydrogen atom in naphthalene is more reactive than a benzene hydrogen atom, and that the latter is (probably) less reactive than a β-hydrogen atom in naphthalene. E. E. TURNER.

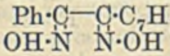
Manufacture of hydroxydiaryl ketones. I. G. FARBENIND. A.-G.—See B., 1929, 276.

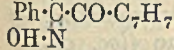
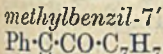
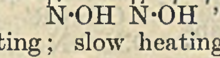
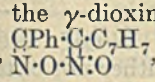
Isomeric relationships in the chalkone series. VI. Relationships between polymorphism and ethylenic isomerism. C. WEYGAND [with E. BAUER and H. HENNIG] (Ber., 1929, 62, [*B*], 562—573; cf. A., 1928, 180).—The known forms of β-hydroxychalkone and its methyl and ethyl ethers are summarised as follows: β-Methoxychalkone (*o*-methyl ether), m. p. 65°, 78°, 81°, ?; series III. β-Ethoxychalkone (*o*-ethyl ether), m. p. 63°, 74°, 78°, 81°; series II. β-Hydroxychalkone (dibenzoylmethane), m. p. ?, 73°, 78°, 81°; series I. All the forms which exist in a number of closely allied substances are termed a "family." The hylotropic–isomeric varieties of a single structurally homogeneous compound are designated a "series," whilst the members of two or more series arranged in the same vertical column are "corresponding members." It is proposed to designate the individual members for the time being by a figure based on the m. p.; thus the variety m. p. 72—73° is known as form 73. Dibenzoylmethane, m. p. 72—73°, is not identical with the variety m. p. 70—71° of Dufraisse and Gillet (A., 1927, 58). The scheme of the polymorphic family is based on the following observations. (i) The m. p. serve as criteria for the mutual relationship of individual members; the scheme is complete except for the absence of two extreme members and the absence of a place for the very unstable variety 71. (ii) A second criterion is to be sought in the stability relationships of the individual members. The expectation that the most stable members of related series must be corresponding forms is not completely realised, but the relationships support rather than condemn the internal justification of the scheme. (iii) The third criterion is purely chemical and demands the hydrolysis of the corresponding members of the alkoxy-series II and III by acids to the corresponding members of the enol series I. The ethyl ether 81 gives the corresponding dibenzoylmethane 81. The stable dibenzoylmethane 78 is derived from the methyl ether 81 and the ethyl ether 78. From the methyl ether 65 the corresponding (unknown) dibenzoylmethane is not produced, its place being taken by the metastable form 73. The stable dibenzoylmethane 78 is derived from the ethyl ether 63. Conversely, dibenzoylmethane 78 yields mainly the corresponding methyl ether 81 and the ethyl ether 78. (iv) Corresponding forms may be expected to be crystallographically similar. According to Dufraisse and Gillet (*loc. cit.*), the methyl ethers 65 and 81 are to be regarded as very labile, ethylenic stereoisomerides. The corresponding members of the ethyl series, 63 and 78, lie on the boundary between isomerism and polymorphism. The more freely soluble, metastable compound can be extracted by light petroleum from the conglomerate. They give mixed m. p. but no depression. The supercooled mixture can be caused to crystallise as either variety by suitable inoculation and the metastable 63 form passes either spontaneously or on contact with the 78 variety into the latter. With the methyl ethers 65 and 81, this is not the case. These observations are confirmed by microscopic observation of the solidification mechanism of molten preparations. In two pairs of corresponding members of a polymorphic family, the one pair appears to behave as labile stereoisomerides, whereas the other consists of monotropic, polymorphic forms. The boundaries between ethylenic isomerism and polymorphism in the classic sense are therefore ill-defined. H. WREN.

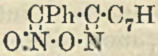
Green varieties of *p*-dihydroxydibenzylidene ketones. D. VORLÄNDER and O. KOCH (Ber., 1929, 62, [*B*], 534—540).—Contrary to the previous observation that the green varieties of di-*p*-hydroxystyryl ketone are free from halogen (A., 1925, i, 1106), it is found that the presence of a minute amount of strong acid is necessary for the production of the green colour; the Beilstein test is much less sensitive than is supposed. Decolorisation of the green forms in solution or transition from green to yellow variety when preserved is not due solely to loss of the minute amount of hydrogen chloride, but also to transition from the colloidal state of the green form into the more coarsely crystalline condition of the yellow variety. If the black hydrochloride *A* is dissolved in cold, dilute alkali hydroxide and the solution is immediately acidified with acetic acid a green precipitate results; if, however, the solution is preserved for some time and then acidified, the yellow ketone separates. Explanation is found in the markedly colloidal condition of aqueous alkaline solutions of the hydroxy-ketones which causes retention of small amounts of adsorbed hydrogen chloride for variable periods even in the presence of excess of hydroxyl ions. Precisely similar phenomena are shown by other hydroxybenzylidene ketones, the behaviour of divanillylideneacetone being described in detail. The green coloration of the yellow preparations depends on the concentration and strength of the aqueous acid. In addition to the halogen acids, nitric, perchloric, and sulphuric but not acetic acids give green products. Both forms yield the same *dibenzoate*, m. p. 191° (corr.). Solutions of the green variety are markedly colloidal, whereas those of the yellow form are almost optically empty; in excess of alkali hydroxide all preparations give identical colloidal red solutions of the alkali salts. The "time reaction" is dependent on the concentration of alkali hydroxide and the temperature. *Divanillylidene*cyclo*hexanone* has m. p. 179° (corr.). H. WREN.

Oximes of the three methylbenzils. J. MEISENHEIMER, O. BEISSWENGER, H. O. KAUFFMANN, U. VON KUMMER, and J. LINK (Annalen, 1929, 468, 202—258).—Benzaldehyde and *o*-tolylnitromethane condense in alcoholic methylamine to give a small amount of a *compound*, $C_{21}H_{17}O_2N$, m. p. 195° (decomp.), but mainly (98% yield) α-*nitro*-2-*methylstilbene*, $C_7H_7{\cdot}C(NO_2){:}CHPh$, m. p. 92°. The latter is converted by methyl-alcoholic potassium hydroxide (cf. A., 1907, i, 860) into α-2-*methylbenzil*-7-*monoxime dimethylacetal* (the α_2-acetaloxime), m. p. 179°, hydrolysed by glacial acetic acid at 100° to α-2-*methylbenzil*-7-*monoxime*,  $COPh{\cdot}C(:N{\cdot}OH){\cdot}C_7H_7$ (the α_2-monoxime),

m. p. 117—118° (*benzoyl* derivative, m. p. 110°; o-*toluoyl* derivative, m. p. 82—83°). The monoxime is far more stable than any α-benzilmonoxime previously described, is partly decomposed when heated for a short time with concentrated hydrochloric acid, giving *o*-toluonitrile and benzoic acid, and is almost unaffected when heated under pressure with alcohol at 100°. Aqueous sodium hydroxide at 100° gives *o*-toluamide and benzoic acid, whilst the aqueous-alcoholic alkali gives the latter and *o*-toluonitrile (showing an α-configuration). The effects produced by these reagents correspond with a Beckmann change of the second order (Werner and Piguet, A., 1905, i, 66), usually observed only with acyl derivatives. This removes the doubts raised by Brady and Bishop (A., 1925, i, 930) in connexion with the relation between the configuration of benzilmonoximes and of their acyl derivatives. The tendency to undergo Beckmann changes of the second order is characteristic of the α-benzilmonoximes.

Cold or hot oximation of the α-oxime gives the α-*dioxime*,  $\begin{array}{l}Ph\cdot C{-}C\cdot C_7H_7\\ OH\cdot N\quad N\cdot OH\end{array}$, m. p. 250° (taken slowly) or 260° (taken quickly) (decomp.). The dioxime undergoes no transformation when heated with alkali or with alcohol; the *diacetyl* and *dibenzoyl* derivatives melt respectively at 139° and 162—163°. The former is readily, and the latter with difficulty, hydrolysed to the parent substance.

Condensation of *o*-tolualdehyde with phenylnitromethane gives β-*nitro*-2-*methylstilbene*, m. p. 99°, together with a small quantity of a *substance*, $C_{22}H_{19}O_2N$, m. p. 195° (decomp.), apparently different from, but not depressing the decomp. point of, the above compound, $C_{21}H_{17}O_2N$. From the stilbene is obtained α-2-*methyl*-7′-*benzilmonoxime dimethylacetal* (the α_1-acetaloxime), m. p. 174°, and thence α-2-*methylbenzil*-7′-*monoxime* (the α_1-monoxime),  $\begin{array}{l}Ph\cdot C\cdot CO\cdot C_7H_7\\ OH\cdot N\end{array}$, m. p. 119° (*benzoyl* derivative, m. p. 87—88°, hydrolysing normally). Concentrated hydrochloric acid converts the α_1-acetaloxime into β-2-*methylbenzil*-7′-*monoxime* (the β_1-monoxime),  $\begin{array}{l}Ph\cdot C\cdot CO\cdot C_7H_7\\ \quad N\cdot OH\end{array}$, m. p. 121° (with or without $0{\cdot}5C_6H_6$) (*benzoyl* derivative, m. p. 129°, hydrolysing normally). Oximation of the β_1-monoxime in alcoholic alkali gives γ-2-*methylbenzildioxime*,  $\begin{array}{l}Ph\cdot C{-\!\!-\!\!-}C\cdot C_7H_7\\ \quad N\cdot OH\ N\cdot OH\end{array}$, m. p. 188·5° (decomp.) (rapid heating; slow heating produces the α-dioxime) (*dibenzoyl* derivative, m. p. 127—128°; acetylation produces much α-derivative). The γ-dioxime is converted by alkali at 100° into the α-dioxime and 3-*phenyl*-4-o-*tolylfurazan*, m. p. 49°, also formed in the hot oximation of the β_1-monoxime, or, together with benzoic acid, by the action of boiling alkali on the dibenzoate. Sodium hypochlorite converts the γ-dioxime into α-3-*phenyl*-4-o-*tolylfurazan oxide*,  $\begin{array}{l}CPh\cdot C\cdot C_7H_7\\ N\cdot O\cdot N{:}O\end{array}$, m. p. 103°, also formed, together with the β-isomeride, by oxidising α-2-methylbenzildioxime, and reducible to the γ-dioxime. Reduction of a mixture of α- and β-furazan oxides gives a mixture of the two *amphi*-dioximes, benzoylated to a mixture of γ- and δ-dioxime benzoates.

The above α-nitro-2-methylstilbene is converted by 50% aqueous sodium hydroxide at 150—160° into 4-*phenyl*-3 : 5-*di*-o-*tolyl*isooxazole, m. p. 111·5°, oxidised by ozone to the o-*toluate*, $C_7H_7\cdot CBz{:}N\cdot O\cdot CO\cdot C_7H_7$, m. p. 114°, of β-2-*methylbenzilmonoxime* (the β_2-monoxime), m. p. 124°, which is not appreciably affected by acid or alkali, whilst the β-nitrostilbene similarly affords 3 : 5-*diphenyl*-4-o-*tolyl*isooxazole, m. p. 126°, oxidised to the benzoate, m. p. 192° (above), of the β_1-monoxime. Oximation of the β_2-monoxime affords δ-2-*methylbenzildioxime* (*dibenzoyl* derivative, m. p. 112—113°), melting at 184°, then solidifying and passing into the α-dioxime. The δ-dioxime is oxidised to β-3-*phenyl*-4-o-*tolylfurazan oxide*,  $\begin{array}{l}\quad CPh\cdot C\cdot C_7H_7\\ O{:}N\cdot O\cdot N\end{array}$, m. p. 86—87°.

Benzaldehyde and *m*-tolylnitromethane undergo condensation in presence of aliphatic amines, and *phenyldi*-m-*tolyl*isooxazole, m. p. 170° (indef.), is produced in addition to the desired α-*nitro*-3-*methylstilbene*, but this substance, m. p. 82°, once nuclei have been obtained by careful procedure in absence of light, is readily prepared. Methyl-alcoholic potassium hydroxide converts it into α-3-*methylbenzil*-7-*monoxime dimethylacetal* (the α_2-acetaloxime), m. p. 176°, hydrolysed by cold concentrated hydrochloric acid (10 min.) to α-3-*methylbenzil*-7-*monoxime* (the α_2-monoxime), m. p. 83°, much β_2-oxime also being produced. The β_2-oxime (β-3-*methylbenzil*-7-*monoxime*, m. p. 122°; *benzoyl* derivative, m. p. 136°, hydrolysed partly to oxime; *acetyl* derivative, m. p. 67°, readily hydrolysed to the oxime) is formed when the α_2-oxime is boiled with alcohol, and is prepared by treating the α_2-acetaloxime with cold concentrated hydrochloric acid for 24 hrs.

Cold alkaline oximation of the α_2-monoxime produces α-3-*methylbenzildioxime*, m. p. 216° (rapid heating) [*benzoyl* derivative, m. p. 185° (decomp.), hydrolysed mainly to oxime], converted in 2 hrs. at 170—175° (more rapidly when impure) into the β-*dioxime*. Hot alkaline oximation of the β_2-monoxime gives α- and β-dioximes (method of preparing latter) and some phenyltolylfurazan. The β-dioxime has m. p. 150°, and may crystallise $+1C_6H_6$ (exchanged for $1H_2O$ by air-drying) (*dibenzoyl* derivative, m. p. 141·5°, partly hydrolysable to oxime). Cold oximation of the β_2-monoxime gives δ-3-*methylbenzildioxime* (the δ-dioxime), m. p. 135° (decomp.) or $(+xC_6H_6)$ m. p. 70—75° and 135°. The readily obtained *disodium* salt gives a δ-dioxime of m. p. 141° (hydrated). Both preparations appear to contain some of the next-mentioned furazan. The *dibenzoyl* derivative, m. p. 152°, is very slowly hydrolysed by cold alkali, but the hot reagent produces 3-*phenyl*-4-m-*tolylfurazan*, m. p. 37°, b. p. 175—185°/vac., also formed, together with the α-dioxime, by boiling the δ-dioxime with alkali. Sodium hypochlorite oxidises the δ-dioxime to β-3-*phenyl*-4-m-*tolylfurazan oxide*, m. p. 77·5°, reduced by zinc dust and methyl-alcoholic acetic acid to the δ-dioxime.

The preparation of β-*nitro*-3-*methylstilbene*, m. p. 51°, b. p. 195°/14 mm., requires great attention to detail. The crude material is converted by methyl-alcoholic alkali etc. into a little 3 : 5-*diphenyl*-4-m-*tolyl*isooxazole, m. p. 156°, much α-*nitro*-β-*methoxy*-

α-phenyl-β-m-*tolylethane*, m. p. 89° (also obtained by dissolving the pure nitrostilbene in methyl-alcoholic alkali), and a *stereoisomeride* (?), m. p. 129°, of the ethane. Reduction of these two stereoisomerides gives two bases, the *hydrochlorides* of which melt respectively at 235° (becoming brown) and 223°, and may be those of the two stereoisomeric *α-amino*-β-*methoxy-α-phenyl*-β-m-*tolylethanes*.

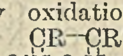
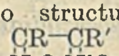
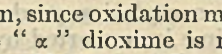
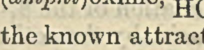
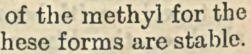
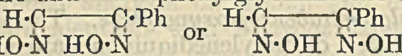
3-*Methylbenzil-7'-monoxime dimethylacetal* (the α_1-acetaloxime), decomp. 214°, is obtained from the nitrostilbene or from the ethane, and, when crystallised from methyl alcohol, is partly converted into the above *iso*oxazole, m. p. 156°. The α_1-acetaloxime is readily converted into α-3-*methylbenzil-7'-monoxime* (the α_1-monoxime), m. p. 113° (*benzoyl* derivative, m. p. 91°, hydrolysed to benzonitrile, and benzoic and *m*-toluic acids), together with some β-3-*methylbenzil-7'-monoxime* (the β_1-monoxime), m. p. 134° (*benzoyl* derivative, m. p. 120°, hydrolysable to the oxime), which is best obtained by treating the above acetaloxime with concentrated hydrochloric acid.

Cold oximation of the β_1-monoxime gives γ-3-*methylbenzildioxime* (the γ-dioxime), m. p. 126·5° or $(+1C_6H_6)$ 118° (*benzoyl* derivative, m. p. 108—116°, converted by hot alkali into the furazan, m. p. 37°). Crystallisation of the dioxime from benzene produces the β-dioxime, whilst boiling benzene slowly converts it into the α-dioxime, also formed (together with the furazan) by the action of hot alkali. Sodium hypochlorite converts the γ-dioxime into β-3-*phenyl*-4-m-*tolylfurazan oxide*, m. p. 75·5°, reducible to the γ-dioxime (trace of α-dioxime).

p-Tolylnitromethane and benzaldehyde condense readily in aqueous-alcoholic methylamine to give *α-nitro*-4-*methylstilbene*, m. p. 75—76°, convertible into 4-*methylbenzil*-7-*monoxime dimethylacetal* (the α_2-acetaloxime), m. p. 217°, which in turn gives α-4-*methylbenzil*-7-*monoxime* (the α_2-monoxime), m. p. 115° (*benzoyl* derivative, m. p. 118°, hydrolysed mainly to *p*-toluonitrile, *p*-toluic acid, and benzoic acid). Concentrated hydrochloric acid slowly converts the α_2-monoxime or the acetaloxime into β-4-*methylbenzil*-7-*monoxime* (the β_2-monoxime), m. p. 134° (*benzoyl* derivative, m. p. 156°, hydrolysed to the oxime).

Cold alkaline oximation of the α_2-monoxime affords α-4-methylbenzildioxime (the α-dioxime), m. p. 223—224° (*dibenzoyl* derivative, m. p. 184°, hydrolysed to dioxime) (cf. Ponzio and Bernardi, A., 1924, i, 293, who named it β-phenyl-*p*-tolylglyoxime). The α-dioxime is converted by alcohol at 150° under pressure into β-4-*methylbenzildioxime* (the β-dioxime), m. p. 184° $(+0{\cdot}5C_6H_6)$ (*dibenzoyl* derivative, m. p. 140°, hydrolysed to dioxime), also obtained in appreciable quantities by oximation of the α_2-monoxime. Cold alkaline oximation of the β_2-monoxime gives δ-4-*methylbenzildioxime* (δ-dioxime), m. p. $(+0{\cdot}5C_6H_6)$ 160°, which with hot alkali passes into the β-dioxime. The *dibenzoyl* derivative, m. p. 119°, is converted slowly by cold alkali into 3-*phenyl*-4-p-*tolylfurazan*, m. p. 80°, and benzoic acid. Oxidation of the δ-dioxime with sodium hypochlorite gives β-3-*phenyl*-4-p-*tolylfurazan oxide*, m. p. 117°, reducible to the δ-dioxime.

p-Tolualdehyde and phenylnitromethane condense in presence of methylamine to give β-*nitro*-4-*methylstilbene*, m. p. 79°, together with a *substance*, $C_{21}H_{19}O_2N$ (cf. the 2-methyl series), and *α-nitro*-β-*methoxy-α-phenyl*-β-p-*tolylethane*, m. p. 93°. The last, converted by alkali into the nitrostilbene, is different from the *products*, m. p. 101—102° and 95—96°, respectively, of dissolving the nitrostilbene in methyl- or ethyl-alcoholic alkali (stereoisomerides ?), and is converted by methyl- or ethyl-alcoholic alkali into the substance, m. p. 101—102°. 4-*Methylbenzil*-7'-*monoxime dimethylacetal* (the α_1-acetaloxime), decomp. 215°, obtained normally from the nitrostilbene, is converted by concentrated hydrochloric acid into β-4-*methylbenzil*-7'-*monoxime* (the β_1-monoxime), m. p. 120—121° (*benzoyl* derivative, m. p. 94°, hydrolysed to oxime). The latter is oximated to give γ-4-*methylbenzildioxime* (the γ-dioxime) (amphi), m. p. 150° or $(+xH_2O)$ 142° (sintering at 110°) or $(+CHCl_3)$ 146° (*dibenzoyl* derivative, m. p. 137°, hydrolysed to the furazan, m. p. 80°), which with sodium hypochlorite gives α-3-*phenyl*-4-p-*tolylfurazan oxide*, m. p. 121°, reduced to the γ-dioxime. E. E. TURNER.

Constitution of oximes. X. J. MEISENHEIMER and W. THEILECKER (Annalen, 1929, 469, 128—146).—A reply, in support of the Hantzsch–Werner view of the isomerism of oximes, to Ponzio (A., 1928, 888). α-4'-Methoxybenzil-7-monoxime (Meisenheimer and Lange, A., 1924, i, 433) when pure has m. p. 95—96° (*loc. cit.* 88—89°) and the dioxime obtained from this specimen has m. p. 218° and is identical with the " β "-phenyl-*p*-anisylglyoxime obtained by Ponzio and Bernardi (A., 1924, i, 293). (To avoid confusion the symbols in inverted commas apply to the nomenclature of Ponzio.) This does not vitiate the authors' conclusions that the isomerism is explained by the Hantzsch–Werner theory, since the existence of four dioximes is based on differences in chemical behaviour. Ponzio's view regarding the nature of " β "-methylphenylglyoxime (*loc. cit.*) is criticised on the grounds (1) that as a single crystalline substance it cannot be an equilibrium mixture of " α " and " γ " forms, and (2) that it gives a red nickel salt sparingly soluble in acetic acid, whilst the nickel salts of the " α " and " γ " oximes are greenish-yellow and readily soluble in acetic acid. The authors consider that the " β " oxime has the α-(*anti*)structure, giving, by oxidation, two structurally isomeric furazans,  $\overset{\mathrm{CR{-}CR'}}{\mathrm{O{:}N{\cdot}O{\cdot}N}}$ and  $\overset{\mathrm{CR{-}CR'}}{\mathrm{N{\cdot}O{\cdot}N{:}O}}$, the peroxide formulation of Ponzio, even if correct, being no evidence of configuration, since oxidation must involve a rearrangement. The " α " dioxime is regarded as the γ- or δ-(*amphi*)oxime,  $\begin{array}{ll}\mathrm{Me{\cdot}C} & \mathrm{CAr}\\ \mathrm{HO{\cdot}N} & \mathrm{HO{\cdot}N}\end{array}$. In agreement with the known attraction of the methyl for the oximino-hydroxyl group, both these forms are stable. The forms  $\begin{array}{ll}\mathrm{Me{\cdot}C} & \mathrm{CAr}\\ \mathrm{N{\cdot}OH} & \mathrm{N{\cdot}OH}\end{array}$ and  $\begin{array}{ll}\mathrm{Me{\cdot}C} & \mathrm{CAr}\\ \mathrm{N{\cdot}OH} & \mathrm{HO{\cdot}N}\end{array}$ are regarded as unstable and are either not obtained, or obtained only in an impure condition, and thus is explained the existence of Ponzio's " γ " glyoxime which has not been obtained pure, being always contaminated with the " β " form into which it passes. Similarly with the monoarylglyoximes, only two forms are stable, " β "-phenylglyoxime having the *anti*-structure and " α "-phenylglyoxime the *amphi*-structure  $\begin{array}{ll}\mathrm{H\cdot C}\text{———}&\mathrm{C\cdot Ph}\\ \mathrm{HO\cdot N}&\mathrm{HO\cdot N}\end{array}$ or $\begin{array}{ll}\mathrm{H\cdot C}\text{———}&\mathrm{CPh}\\ \mathrm{N\cdot OH}&\mathrm{N\cdot OH}\end{array}$. Contrary to Ponzio, the authors consider that the action of benzenediazonium chloride on " α "-phenylglyoxime does involve a rearrangement (*e.g.*, the " α "-glyoxime yields a nickel salt, whilst the resulting β-benzildioxime does not), the resulting β-benzildioxime being formed by a rearrangement of the unstable γ-(*amphi*)-benzildioxime, which is considered to be the primary product, since hydrolysis of its acetyl derivative yields a trace of diphenylfurazan, showing the presence of a trace of the γ-compound. In attempts to prepare a stable *amphi*-derivative condensation with *o*-, *m*-, and *p*-toluenediazonium chlorides was attempted. In the first two cases the evidence is doubtful, since mainly unchanged " α "-phenylglyoxime and resinous products are obtained, but with the *p*-compound there results a mixture containing β- (14%), α- (0·7%), and *amphi*- (0·5%) dioximes and it is believed that the α- and β- are produced from the *amphi*-form which is the primary product of the reaction. The discrepancies between the results of Russanoff (A., 1892, 321) and of Ponzio and Avogadro (A., 1923, i, 472) relating to " β "-phenylglyoxime are explained by the fact that the product designated " β " by the former author is really the unchanged " α "-compound, the true " α " and " β " compounds giving different and not identical diacetyl derivatives. The sufficiency of the Hantzsch–Werner view in explaining oxime isomerism is maintained and the untrustworthiness of physical properties for the determination of configuration is discussed. J. W. BAKER.

Perylene and its derivatives. XXI. A. PONGRATZ and E. PÖCHMÜLLER (Monatsh., 1929, 51, 228—233).—When 4 : 10-dichloro- or 4 : 10-dibromo-3 : 9-dibenzoylperylene is heated with cuprous cyanide in presence of quinoline, 4 : 10-*dicarbylamino*-3 : 9-*dibenzoylperylene*, not melted at 360°, is obtained; hydrolysis of this with concentrated sulphuric acid gives 4 : 10-*diamino*-3 : 9-*dibenzoylperylene*, not melted at 360° (*dibenzoyl* derivative, sinters at 350° without melting) (cf. A., 1927, 1190).

Perylene reacts with *p*-bromobenzoyl chloride in presence of aluminium chloride and carbon disulphide forming 3 : 9-*di*-p-*bromobenzoylperylene*, m. p. 308°, which when treated with cuprous cyanide in boiling quinoline gives the corresponding *dicarbylamino*-derivative, m. p. 293°. Hydrolysis of this with concentrated sulphuric acid yields an uncrystallisable product, insoluble in alkali. Distillation of *dipropionyl*- and *dibutyryl-perylene*, m. p. 247° and 253°, respectively (obtained by the Friedel–Crafts reaction), with zinc dust gives perylene as the chief product. H. BURTON.

Triquinoyl. F. BERGEL (Ber., 1929, 62, [*B*], 490—491).—Intensive desiccation of triquinoyl octahydrate, $C_6O_6,8H_2O$ (cf. Henle, A., 1907, i, 144), by phosphoric oxide at 78° causes almost complete removal of water. The constitution of the yellowish-brown product as a polymeric carbon monoxide appears established by its behaviour towards barium chloride; it cannot, however, be re-converted into the octahydrate. H. WREN.

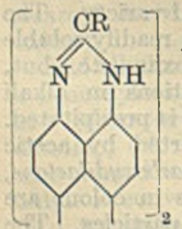
Differently coloured conditions of anthraquinolcarboxylic acids and anthraquinol-α-carboxylactones. R. SCHOLL, O. BÖTTGER, and S. HASS (Ber., 1929, 62, [*B*], 616—628).—Sodium anthraquinone-1-carboxylate is reduced by sodium hyposulphite in aqueous solution to *anthraquinol*-1-*carboxylic acid*, permanganate-like crystals which dissolve in alkaline solution in the absence of air to red solutions from which mineral acids precipitate the organic acid as a red gel which passes in 10—15 min. into a violet, readily-filterable condition. The acid is converted by short treatment with boiling acetic anhydride into *anthraquinol*-1-*carboxylactone* and by more protracted treatment into the corresponding *acetyl* derivative, $C_{17}H_{10}O_4$, m. p. 196°. Anthraquinone-1 : 5-dicarboxylic acid dissolved in sodium hydroxide is reduced by sodium hyposulphite at the atmospheric temperature to a red vat from which hydrochloric or sulphuric acid immediately gives a violet precipitate. The sparing solubility of the violet acid in organic media at the ordinary temperature and its instability at higher temperature inhibit its preparation in the crystalline condition. The quantitative reduction of sodium anthraquinone-1 : 5-dicarboxylate to a dark red solution requires 2·09 atoms of hydrogen in the presence of spongy platinum, whilst the oxidation of the vat (obtained with zinc dust and alkali) by sodium hypochlorite is effected by 2 atoms of oxygen. There can therefore be no doubt that the violet compound is pure *anthraquinol*-1 : 5-*dicarboxylic acid* and that the colour is not due to radical- or quinhydrone-like impurities. Solutions obtained from sodium anthraquinone-1 : 5-dicarboxylate or from free anthraquinone-1 : 5-dicarboxylic acid with sodium hyposulphite yield a violet precipitate when shaken with air; this is attributed to oxidation of the excess of hyposulphite to hydrogen sulphite and sulphate which thereby causes acidification of the solution. If the solution obtained by the action of anthraquinol-1 : 5-dicarboxylactone on methyl-alcoholic potassium hydroxide is acidified with not too dilute sulphuric acid previous to dilution with water a gelatinous red acid is precipitated which usually passes into the violet form but can occasionally be dried as the red variety. The latter, in contrast to the violet form, is readily soluble in nitrobenzene, acetic anhydride, dioxan, etc., but, like the violet acid, gives red solutions in alkali hydroxide from which the violet form is precipitated. The red and violet acids are converted by acetic anhydride into *anthraquinol*-1 : 5-*dicarboxydilactone*, decomp. about 380°. The differences in colour are attributed to difference in the size of particles. The violet powder gives a reddish-brown mark when rubbed with a glass rod on porous earthenware; in thin layers it appears under the microscope to be violet-red in transmitted light, otherwise black. The violet colour is therefore a surface effect.

H. WREN.

Derivatives of 3 : 4-phenanthraquinone. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 940—952).—4-Amino-3-phenanthrol hydrochloride is oxidised by chromic anhydride in glacial acetic acid, or by nitrous acid (cf. Werner, A., 1902, i, 437), to 3 : 4-phenanthraquinone (cf. Barger, J.C.S., 1918, 113, 218) (characteristic blue to green colour reaction with sulphuric acid). This is converted by concentrated aqueous sodium hydrogen sulphite into *sodium* 3 : 4-*dihydroxyphenanthrene*-1-*sulphonate* (I) (corresponding p-*toluidine* salt, decomp. 182°), oxidised by chromic and sulphuric acids to *sodium* 3 : 4-*phenanthraquinone*-1-*sulphonate* (*ammonium* salt), which gives with *p*-toluidine in hot aqueous solution red 1-p-*toluidino*-3 : 4-*phenanthraquinone*, m. p. 260° (decomp.), reduced by zinc, acetic anhydride, and sodium acetate to 1-p-*toluidino*-3 : 4-*diacetoxyphenanthrene*, m. p. 208°. Orange-yellow 3-*hydroxy*-1 : 4-*phenanthraquinone*, m. p. 230°, sintering from 200° (*sodium* and *ammonium* salts; *methyl ether*, m. p. 170°; 1 : 4-*diacetoxy*-3-*methoxyphenanthrene*, m. p. 168·5°), is best obtained by oxidising I with hydrogen peroxide and alkali. Its *silver* salt yields with allyl bromide in boiling benzene 1-*allyloxy*-3 : 4-*phenanthraquinone* (17% of the theoretical), m. p. 161°, and 3-*hydroxy*-2-*allyl*-1 : 4-*phenanthraquinone* (63%), m. p. 155°, which is converted by cold sulphuric acid into a *compound*, $C_{17}H_{12}O_3$, red needles, m. p. 198—199°. 3-Hydroxy-1 : 4-phenanthraquinone behaves like a β-diketone towards boiling 6*N*-sodium hydroxide, being hydrolysed to 2-*acetyl*-1-*naphthylglyoxylic acid*, m. p. 196° (decomp.) (*methyl* ester, m. p. 181°). This is converted by hydrogen peroxide and alkali into naphthalene-1 : 2-dicarboxylic acid, and by potassium dichromate and acid into 1 : 3-diketo-α-naphth-hydrindene, m. p. 174—175° (benzylidene derivative, m. p. 179°; cf. Noto, A., 1915, i, 973), and gives with aniline at 175° 2-*acetyl*-1-*naphthylideneanil*, m. p. 202°.

H. E. F. Notton.

Perylene and its derivatives. XIX. A. Zinke, W. Hirsch, and E. Brozek (Monatsh., 1929, **51**, 205—220).—Reduction of 3 : 4 : 9 : 10-tetranitroperylene (Zinke and Unterkreuter, A., 1920, i, 541) with alkaline sodium hyposulphite, sodium sulphide, or stannous chloride gives the corresponding *tetra-amino*-derivative (*dibenzylidene* derivative), which in view of its intense colour is probably admixed with some diaminoperylenequinonedi-imine. The tetra-amino-compound reacts with 2 mols. of oxalyl chloride forming a *dioxalyl* derivative, not melted at 360°, and with acetic anhydride, benzoyl, *p*-bromobenzoyl, and *p*-chlorobenzoyl chlorides, forming the corresponding *benziminazole* derivatives (annexed formula, R=Me, Ph, C_6H_4Br, C_6H_4Cl, respectively), all of which have m. p. above 360°.



When 3 : 9-dichloro-4 : 10-dinitroperylene is heated with concentrated sulphuric acid at 150—160°, *perylene*-3 : 4 : 9 : 10-*diquinone* (I) results. The same diquinone is obtained also from dinitroperylene and 3 : 4 : 9 : 10-tetranitroperylene by similar treatment with sulphuric acid. Reduction of this with alkaline sodium hyposulphite and subsequent treatment with the appropriate aroyl chloride gives the *tetrabenzoate* and *tetra*-p-*bromobenzoate* of 3 : 4 : 9 : 10-tetrahydroxyperylene. The tetrabenzoate is hydrolysed and oxidised at the same time by warm concentrated sulphuric acid, yielding I. Bromination of I in nitrobenzene suspension affords a *tetrabromo*-derivative, whilst chlorination furnishes a product, probably a mixture of di- and tetra-chloro-derivatives, which after reduction and benzoylation yields a *dichlorotetrabenzoyloxyperylene*. The halogenated derivatives of perylenediquinone are mordant dyes.

H. Burton.

Manufacture of benzanthraquinone derivatives and substitution products. I. G. Farbenind. A.-G.—See B., 1929, 237.

Manufacture of vat dyes [of the dibenzanthrone series] and intermediate products thereof. I. G. Farbenind. A.-G.—See B., 1929, 238.

Euphorbons from euphorbium resin. J. A. Müller (J. pr. Chem., 1929, [ii], **121**, 97—112).—By the process of extraction described a sterol-free preparation of euphorbon, sintering at 118°, melting at 121·5—122·5° to a cloudy liquid which becomes clear at 125°, $[\alpha]_D^{16}$ +16·58°, is obtained. This, like all hitherto believed uniform specimens, is a mixture, since acetylation (acetic anhydride alone or in presence of anhydrous sodium acetate or pyridine) leads to the simultaneous formation of *vitorbol acetate* (yield 60%), sintering at 85°, melting to a cloudy liquid at 90—91°, which becomes clear at 98°, $[\alpha]_D^{16}$ +11·34°, and *novorbol acetate*, m. p. 123—124° (clear liquid), $[\alpha]_D^{16}$ −12·52°. Each of these compounds may have either of two formulæ: $C_{26}H_{41}\cdot OAc$ or $C_{27}H_{43}\cdot OAc$. Similarly, treatment of euphorbon with *p*-bromobenzoyl chloride gives *vitorbol* p-*bromobenzoate*, m. p. 132—133° (cloudy liquid), 137° (clear), $[\alpha]_D^{19}$ +20·45°, accompanied by *novorbol* p-*bromobenzoate*, which exists in two crystalline forms, both with m. p. 183·5—184·5°, $[\alpha]_D^{19}$ +18·88°.

Hydrolysis of the foregoing acyl derivatives yields *vitorbol*, m. p. 120·5°, 122·5—123·5°, 125°, $[\alpha]_D^{16}$ +11·34°, and *novorbol*, m. p. 123·5—124·5°, $[\alpha]_D^{17}$ +29·61°. Vitorbol gives no digitonin precipitate.

Dibromovitorbol acetate, m. p. 163—164° (decomp.), after sintering at 156°, $[\alpha]_D^{17}$ −5·615°, is formed by addition of bromine in chloroform solution. All rotations were taken in benzene solution.

R. J. W. Le Fèvre.

Saponin of the sugar beet. K. Rehorst (Ber., 1929, **62**, [*B*], 519—534).—Dried beetroot shavings are extracted with cold 0·5% sodium hydroxide and the extract is acidified with hydrochloric acid. The crude saponin is dried, extracted with boiling ethyl alcohol, and the extract evaporated to dryness. The solution of the residue in methyl alcohol is treated with ether, the precipitate is removed, and the filtrate again evaporated. Further purification of the residue is effected by dialysis and treatment with methyl alcohol and ether. Final extractions with light petroleum and water leave a product which cannot be separated into appreciably different portions by fractional extraction with ether. The saponin, $C_{37}H_{56}O_9$, has m. p. 215—216°, $[\alpha]_D^{18}$ +31·07° in methyl alcohol. It has strongly hæmolytic properties which are not inhibited by addition of cholesterol. Hydrolysis affords 30% of *d*-glycuronic acid and 68·67% of sapogenin. The latter compound, which appears saturated, after desiccation at 105° has m. p. 301—302°, $[\alpha]_D^{20}$ +78·82° in 96% alcohol. Analyses and determinations of mol. wt. agree better with the formula $C_{31}H_{48}O_3$ than with $C_{31}H_{50}O_3$, and the amended composition appears to accord better with the recorded analyses of oleanol and caryophyllin, which are identical with beetroot sapogenin. The proportion of water of crystallisation in the air-dried substance varies somewhat with the mode of preparation, 2, 1·5, and 1 mol. being recorded. Specimens which have been preserved for a considerable period and then dried at 140° appear to have the composition $C_{31}H_{48}O_3,0{\cdot}5H_2O$, but the observations may be caused by partial autoxidation. Distillation of the sapogenin with zinc dust affords carbon dioxide, water, substances with an odour of petroleum, and a viscous, fluorescent oil which can be separated by steam into a volatile and a non-volatile portion. The most volatile fraction from the former portion appears to be a sesquiterpene, $C_{15}H_{24}$, *d* 0·9079, $n_D^{21\cdot5}$ 1·5126, $[\alpha]_D$ +3·75°, which absorbs 1 mol. of hydrogen in presence of palladium chloride. Dehydrogenation with selenium affords an oil which partly crystallises. The crystalline portion, m. p. 273—275°, is a largely dehydrogenated product, $C_{30}H_{20}O$ or $C_{30}H_{18}O$, in which the carbon skeleton of the sapogenin remains almost intact. The oil gives a yellow product with picric acid, the first portions of which have m. p. 114—116°, whereas later fractions have a lower and less distinct m. p. Regeneration of the hydrocarbon and treatment of it with trinitroresorcinol permits the isolation of a styphnate, m. p. 119—123°; the observations agree moderately well with the recorded m. p. of cadalene picrate (114—115°) and eudaline styphnate (119—120°). It is concluded with reserve that two hydrogenated naphthalene hydrocarbons are present in beetroot sapogenin.

The scheme $C_{37}H_{56}O_9+H_2O=C_{31}H_{48}O_3+C_6H_{10}O_7$ is suggested for the hydrolysis of the saponin.

H. Wren.

Plant colouring matters. XI. Lycopin. P. Karrer and W. E. Bachmann (Helv. Chim. Acta, 1929, 12, 285—291).—When lycopin is shaken with lithium, sodium, or potassium powder in a mixture of dry ether and benzene, intensely coloured solutions of *lithium, sodium,* and *potassium additive* compounds are obtained and, in the first two cases, separation of the metal additive compound ultimately occurs. Titration of the solution of the potassium compound shows that two atoms of the metal are taken up. The action of dry, oxygen-free carbon dioxide on the sodium compound gives a *lycopincarboxylic acid* which, after being freed from non-acidic impurities by dissolution in ammonia, has a composition corresponding with $C_{40}H_{56}(CO_2H)_4$, but titrates as a dibasic acid, and with diazomethane yields an *ester* which contains only 6·1% OMe (the dimethyl ester requires 8·6%). Decomposition of the lithium or sodium compound with water yields an orange-yellow, amorphous *substance* (C, 86·4; H, 10·5%) containing some oxygen, which is autoxidisable. By the action of methyl iodide on the solution of the potassium compound, lycopin is not regenerated, and hence it is improbable that the two potassium atoms are attached to adjacent carbon atoms. The action of dry oxygen on the potassium compound regenerates lycopin, accompanied by an amorphous (? oxidation) product. Ozonolysis of lycopin yields acetaldehyde, acetic acid, acetone, and a substance which gives the reactions of lævulic acid; the structure $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}[CMe{:}CH{\cdot}CH{:}CH]_5{\cdot}CMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CHMe$ is suggested for lycopin (cf. Karrer and others, this vol., 49). No metallic derivatives could be obtained from carotin, xanthophyll, γ-crocetin, or bixin methyl ester.

J. W. Baker.

Constituents of red sandal wood. Homopterocarpin and pterocarpin. H. Dieterle and H. Leonhardt (Arch. Pharm., 1929, 267, 81—116; cf. A., 1926, 618).—Fifty kg. of red sandal wood furnished 214 g. of homopterocarpin, $C_{17}H_{16}O_4$, m. p. 83—84°, $[\alpha]_D^{20}$ −216·3° in chloroform, and 44 g. of pterocarpin, $C_{14}H_{12}O_4$, m. p. 162·5—163°, $[\alpha]_D^{24}$ −220·1°, the two constituents being separated by fractional crystallisation from chloroform and alcohol. Homopterocarpin reacts abnormally with hydriodic acid and red phosphorus, but it contains two methoxyl groups. The remaining two oxygen atoms are not present as hydroxyl groups, since, although acetyl chloride in hot benzene solution affords *acetyldihydrohomopterocarpin*, $C_{19}H_{20}O_5$, m. p. 130—131°, and *acetyldemethylhomopterocarpin*, $C_{18}H_{16}O_5$, darkening at 205°, decomp. 220°, the one derivative is a reduction product and the other a demethylated compound. Homopterocarpin appears to be a lactone of a phenolic acid, since treatment with methyl sulphate and potassium hydroxide solution furnishes a *monomethyl* ester, which affords another lactone, *acetylhomopterocarpin*, m. p. 195°, when acetylated. The lactone ring is reduced by hydrogen in presence of palladised charcoal at 76°, with the formation of l-*dihydrohomopterocarpin*, m. p. 153—154°, $[\alpha]_D^{24}$ −12·8° in chloroform, which contains two methoxyl groups and a phenolic hydroxyl group, although it is insoluble in alkalis (*monoacetyl* derivative, m. p. 130·5—131°, $[\alpha]_D^{24}$ +18·8°; *benzoyl* derivative, m. p. 99—100°, $[\alpha]_D^{24}$ +34·0°; *methyl ether*, m. p. 57—58°), and an optically inactive isomeride, i-*dihydrohomopterocarpin*, yellowish-red, m. p. 76°, soluble in alkalis (*benzoyl* derivative, m. p. 67—70°). These compounds are saturated, bromination of homopterocarpin and of *l*-dihydrohomopterocarpin by means of pyridine perbromide affording *dibromohomopterocarpin*, m. p. 184—185°, $[\alpha]_D^{24}$ −273·0°, and *dibromodihydrohomopterocarpin*, m. p. 199—200° (decomp.), respectively, both of which furnish a mixture of homopterocarpin and its dihydro-derivatives when reduced with sodium and alcohol. Homopterocarpin is resistant to potassium permanganate and unidentified complex products result from oxidation with chromic acid or ozone. Dehydrogenation with molten selenium under pressure, however, produces a *substance*, $C_{34}H_{34}O_8$, m. p. 110° (decomp.) (*diacetyl* derivative, m. p. 132°), containing two phenolic hydroxyl groups, whilst concentrated nitric acid in boiling glacial acetic acid solution affords *dinitrohomopterocarpin*, m. p. 136—138°, a *compound*, m. p. 122°, a *substance*, $C_{16}H_{13}O_9N_3$, m. p. 244° (decomp.), oxalic acid, and styphnic acid. Homopterocarpin is resistant towards molten potassium hydroxide, the only insoluble products, besides a considerable amount of unchanged material, being resorcinol and phloroglucinol, whilst resorcinol dimethyl ether and a *methylanthracene*, m. p. 167°, are obtained on distillation with zinc dust.

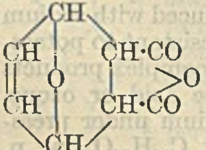
Pterocarpin, which contains only one methoxyl group, is insoluble in alkalis; it cannot be acetylated, and reduction with hydrogen and palladised charcoal affords *dihydropterocarpin*, m. p. 141—142°. Bromine gives *monobromopterocarpin*, m. p. 143—144°, and methyl sulphate and potassium hydroxide have no action. Most of the above compounds give characteristic colour reactions with 65% nitric acid, concentrated sulphuric acid, and mixtures of these.

S. COFFEY.

Optical activity and polarity of substituent groups. X. Influence of ionisable groups on rotatory power of *l*-menthyl benzoate. H. G. RULE and W. E. MACGILLIVRAY (J.C.S., 1929, 401—409).—The influence of the groups NH_2, NMe_2, OH, and CO_2H on the rotatory power of *l*-menthyl benzoate has been studied. The most definite variations were found with the *o*-substituted esters; increase in the rotatory power occurs with the *m*-orienting groups CO_2H, $NMe_2H^{\cdot}$, and $NH_3^{\cdot}$, whilst a decrease was observed with the *o-p*-orienting groups CO_2', NMe_2, and O'. *l*-Menthyl salicylate and anthranilate give an unexpected increase in rotatory power, which is attributed to their chelated condition. The following are described: l-*menthyl salicylate* (from acid chloride and menthol), b. p. 156°/0·5 mm.; l-*menthyl* m-*hydroxybenzoate* (from acid chloride and menthol in pyridine), b. p. 182°/1·2 mm.; l-*menthyl* p-*hydroxybenzoate*, b. p. 178°/0·1 mm.; l-*menthyl anthranilate*, b. p. 156°/0·33 mm., m. p. 62·5—63·5° (*hydrochloride*, m. p. 150—170°); l-*menthyl* m-*aminobenzoate* (by reduction of *l*-menthyl *m*-nitrobenzoate with titanous chloride and alcohol), b. p. 168°/1·8 mm.; l-*menthyl*-p-*aminobenzoate*, b. p. 175°/0·2 mm. (decomp.); l-*menthyl* o-*dimethylaminobenzoate*, b. p. 170°/0·2 mm., m. p. 36—37°.

A. I. VOGEL.

Syntheses in the hydroaromatic series. II. Cantharidin. O. DIELS and K. ALDER [with E. NAUJOKS] (Ber., 1929, 62, [*B*], 554—562; cf. A., 1928, 1018).—Maleic anhydride is quantitatively converted by furan in the presence of ether into the *compound* I, m. p. 125° (decomp.) with regeneration of its components. Similarly, *cyclo*pentadiene and dimethylmaleic anhydride in benzene at 100° afford the *substance* II, m. p. 155°. The compound I is converted by hydrogenation in ethyl alcohol in presence of colloidal palladium into *ethyl hydrogen* 3 : 6-*endoxyhexahydrophthalate*, m. p. 107—108°, and by similar treatment in aqueous alkaline solution into 3 : 6-endoxohexahydrophthalic anhydride (norcantharidin), III, m. p. 116—117° (cf. von Bruchhausen and Bersch, this vol., 192). 3 : 6-*Endoxohexahydrophthalic acid* (+1H_2O), m. p. 122—123° (decomp.), and its *methyl hydrogen* ester, m. p. 146° (decomp.), are described. The constitution of norcantharidin is established as follows. The substance is converted by concentrated hydrochloric acid at 100° into 3 : 6-*dichlorohexahydrophthalic acid*, m. p. 111°, and by glacial acetic and hydrobromic acids at 100° into α-3 : 6-*dibromohexahydrophthalic acid*, m. p. 218—219° (decomp.), whereas aqueous hydrobromic acid at 100° affords β-3 : 6-*dibromohexahydrophthalic acid*, m. p. 177° (decomp.). The β-dibromo-acid is transformed by 25% potassium hydroxide into $\Delta^{1:3}$-*cyclo*hexadiene, identified as its additive compound, m. p. 147°, with maleic anhydride. Reduction of the dibromo-acid with sodium amalgam in alkaline solution affords *trans*-hexahydrophthalic acid, m. p. 219—220° after softening. Maleic anhydride and 2 : 5-dimethylfuran afford 3 : 6-*endoxo*-3 : 6-*dimethyl*-Δ^4-*tetrahydrophthalic anhydride*, catalytically hydrogenated to 3 : 6-*endoxo*-3 : 6-*dimethylhexahydrophthalic anhydride* (iso*cantharidin*), m. p. 121·5°. Concentrated hydrochloric acid at 100° transforms the anhydride into 3 : 6-*dimethyl*-$\Delta^{2:6}$-*dihydrophthalic anhydride*, m. p. 159° after softening, oxidised by nitric acid (*d* 1·4) at 100° to 3 : 6-dimethylphthalic acid, m. p. 142—143°.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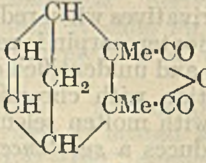
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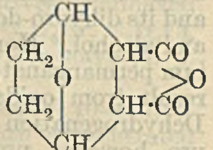
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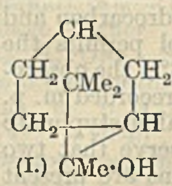
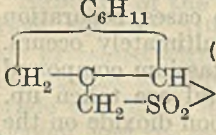
H. WREN.

Constitution of *iso*borneol. E. PUXEDDU (Gazzetta, 1929, 59, 59—69).—Ordinary methods of oxidation are too violent to distinguish between borneol and *iso*borneol. Oxidation by an ethereal solution of ferric chloride exposed to light (cf. A., 1920, ii, 406; 1922, ii, 415) furnishes, however, a delicate method, by which borneol is oxidised to camphor, with a dark brown precipitate, whilst *iso*borneol furnishes other, unidentified, products, including an oil containing chlorine, but not including camphor. It is concluded that *iso*borneol may be I.


(I.)

E. W. WIGNALL.

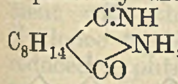
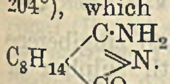
Problem of addition in the camphene series. P. LIPP and M. HOLL (Ber., 1929, 62, [*B*], 499—504; cf. Lipp and others, A., 1927, 883).—Camphene, $[\alpha]_D$ +82° in alcohol, is converted by sulphur trioxide in glacial acetic acid at 100° into a mixture of *iso*bornyl acetate and 2-*hydroxycamphane-ω-sulpholactone* (I), b.p. 147·5—148° (corr.)/0·6 mm., m. p. 133·5° (corr.), [α] ±0; the compound is obtained with greater difficulty from nearly optically inactive camphene. It is converted by alkali hydroxides into the salts of 2-hydroxycamphane-ω-sulphonic acid, of which the *sodium*, *barium*, and *ammonium*, decomp. 186°, compounds are described. The constitution of the sulpholactone is elucidated as follows. Reychler's camphorsulphonic acid is reduced by sodium and alcohol to a mixture of 2-hydroxycamphane-ω-sulphonic acids, which is treated with ammonia in ether, whereby the *ammonium* salt of the "*endo*"-acid, decomp. 232°, is precipitated; the filtrate from the salt contains 2-hydroxycamphane-ω-sulpholactone, identical with that described above; the p-*toluidine* salts of *endo*-2-hydroxycamphane-ω-sulphonic acid and of *d*-camphorsulphonic acid, m. p. 152—153° (decomp.) and 161—162° (corr.) after softening, are described. Treatment of the "*endo*"-acid with glacial acetic and fuming hydrochloric acids at 70° causes formation of 2-hydroxycamphane-ω-sulpholactone in 73% yield.

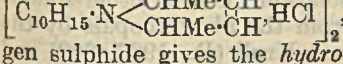

(I.)

H. WREN.

Manasse's α- and β-hydroxycamphors (*ortho-exo-* and *ortho-endo*-hydroxycamphors). II. J. Bredt [and in part H. Ahrens and P. Scholl] (J. pr. Chem., 1929, [ii], **121**, 153—172).—The crude hydroxycamphor obtained by reduction of camphorquinone by zinc dust and acetic acid or by aluminium amalgam and ether was resolved, by treatment with methyl-alcoholic hydrogen chloride, into *ortho-exo*-hydroxycamphor [acetate, m. p. 61—62° (lit. 63—64°); *benzoate*, b. p. 168°/0·33 mm.; *benzenesulphonate*, m. p. 79—80°; *sulphite* (obtained by treatment with thionyl chloride in the presence of pyridine), m. p. 130°; *semicarbazone*, m. p. 183—184°] and bis-*ortho-endo*-hydroxycamphor methyl ether. The last compound gave by boiling with methyl-alcoholic hydrogen chloride monomeric ortho-en-*hydroxycamphor methyl ether*, m. p. 37—38°, b. p. 81°/4 mm., 105—106°/12 mm., $d_{D}^{42\cdot3}$ 0·9996, $n_{D}^{42\cdot3}$ 1·4636 (*semicarbazone*, m. p. 124°). The corresponding monomeric ortho-exo-*hydroxycamphor methyl ether*, b. p. 105—107°/15 mm., d_4^{11} 1·0202, n_D^{11} 1·47426 (*semicarbazone*, m. p. 204°), was obtained by direct esterification. Magnesium methyl iodide and *ortho-endo*-hydroxycamphor interacted in ethereal solution to give allo*methylbornylene glycol*,  $C_8H_{14}<\begin{matrix}CH\cdot OH\\ CMe\cdot OH\end{matrix}$, m. p. 163—164°. The following derivatives of *ortho-endo*-hydroxycamphor are also described: semicarbazone, m. p. 215—216°, 210—211° (according to rate etc. of heating); *benzoate*, m. p. 84—85°; *benzenesulphonate*, m. p. 110°.

R. J. W. Le Fèvre.

New camphor bases. H. W. Egli (Helv. Chim. Acta, 1929, **12**, 270—277).—**I. Two isomeric ketimides of camphoric acid imide.** The base $C_{10}H_{16}ON_2$ obtained by the action of methyl-alcoholic potassium hydroxide on α-camphoronitrile acid amide (Tiemann and Kerschbaum, A., 1901, i, 19), or as a by-product in the preparation of *iso*nitrosocamphor, is probably the *α-ketimide* of camphoric acid imide,  $C_8H_{14}<\begin{matrix}C{:}NH\\ CO\end{matrix}>NH$, m. p. 278° (*hydrochloride*, $+2H_2O$, and anhydrous, m. p. 250°; *picrate*, m. p. 269°; *benzoate*, m. p. 230°; *hydrogen tartrate*, m. p. 180°; *hydrogen oxalate*, m. p. 146°; corresponding *phenylthiocarbamide*, m. p. 234°; *benzoyl* derivative, m. p. 204°), which may be tautomeric with the form  $C_8H_{14}<\begin{matrix}C\cdot NH_2\\ CO\end{matrix}>N$. It is readily converted by nitrous acid into camphoric acid imide. Similarly, β-camphoronitrile acid amide with methyl-alcoholic potassium hydroxide gives the isomeric β-*ketimide*, m. p. 238° (*hydrochloride*, m. p. 230°; *picrate*, m. p. 293°).

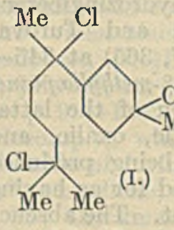
II. Condensation of α-aminocamphor with γ-diketones and γ-keto-esters. α-Aminocamphor (I) condenses with acetonylacetone in glacial acetic acid to yield α-2 : 5-*dimethylpyrrylcamphor* (II), b. p. 176°/10 mm., m. p. 90°, reduced by tin and alcoholic hydrogen chloride to the *double stannochloride*, m. p. 149°, of α-2 : 5-dimethyl-2 : 5-dihydropyrrylcamphor,  $\left[C_{10}H_{15}\cdot N<\begin{matrix}CHMe\cdot CH\\ CHMe\cdot CH\end{matrix},HCl\right]_2,SnCl_2$, which with hydrogen sulphide gives the *hydrochloride*, m. p. 232°, of the dihydro-base (*picrate*, m. p. 194°). Similar condensation of I with ethyl acetonylacetoacetate yields the corresponding 3-*carbethoxy*-derivative, m. p. 139°, of II, which is hydrolysed to the free *acid*, m. p. 232°. The latter, when heated above its m. p., gives carbon dioxide and II. With ethyl lævulate I condenses to give a poor yield of a *substance*, m. p. 150°, probably $C_{10}H_{15}O\cdot N{:}CMe\cdot[CH_2]_2\cdot CO_2Et$. Molten zinc chloride converts I into a *double zincichloride*, $(C_{10}H_{15}O\cdot NH_2)_2,ZnCl_2$, m. p. 217—234°, whilst monochloroacetone and I yield a neutral *substance*, m. p. 226°, and a basic *substance*, m. p. 186°.

J. W. Baker.

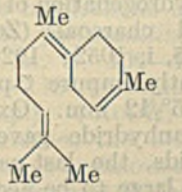
Fenchene. J. L. Kondakov (Chem. Listy, 1929, **23**, 49—54).—*D-l*-Fenchyl alcohol, m. p. 45°, $[\alpha]_D$ −12·3°, when heated at 180° with potassium hydrogen sulphate yields fenchene and α-fenchyl alcohol, m. p. 48·5—49°. The latter alcohol, submitted to similar treatment, gives a product, m. p. 47°, which after repeated heating with potassium hydrogen sulphate gives finally an alcohol, m. p. 49°. The alcohol, m. p. 48·5—49°, differs from that of Kenyon and Priston (A., 1925, i, 941) in its rotatory power, as does also its hydrogen phthalate. Two urethanes, having m. p. 84° and 82—83°, are prepared from α-fenchyl alcohol at the ordinary temperature and at 100°, respectively. α-Fenchyl chloride, b. p. 90°/13 mm., prepared from the alcohol, m. p. 48·5—49°, was converted by alcoholic potassium hydroxide into *D-l*-α-fenchene, b. p. 157·5—160°/752 mm., $[\alpha]_D$ −34·5°. Oxidation of the fenchene so obtained with cold alkaline permanganate yields *D-l*-α-fenchylcamphorone (*semicarbazone*, m. p. 210—211°) and α-oxyfenchenic acid. The above results indicate that Kenyon and Priston's alcohol was contaminated with the β-isomeride, and consequently that the hydrogen phthalate method of separation of the α- and β-forms is imperfect.

R. Truszkowski.

Higher terpene compounds. XXXV. Constitution of bisabolene. L. Ruzicka and A. G. van Veen (Annalen, 1929, 468, 133—143).—An investigation of bisabolene, obtained either from opopanax oil by redistillation or from the trihydrochloride (I). The hydrocarbon has the constitution (II) for the following reasons: ozonolysis of bisabolene in carbon tetrachloride or in glacial acetic acid produces acetone and lævulic and succinic acids. This agrees with II but could be accounted for on the two other possible formulæ. Reduction of bisabolene in *cyclo*hexane solution, using platinum-black and hydrogen, gives the tetrahydro-derivative, also obtained using platinum oxide. On the other hand, using platinum oxide in glacial acetic acid, hexahydrobisabolene is formed (cf. Semmler and Rosenberg, A., 1913, i, 377). The slow addition of the last two atoms of hydrogen is best explained by formula III for tetrahydrobisabolene, corresponding with II for bisabolene.



(I.)



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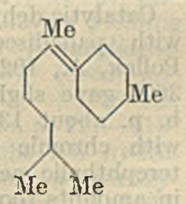


(III.)

Tetrahydrobisabolene is III, since when it is submitted to ozonolysis a mixture of β-methylheptan-ζ-one and 4-methyl*cyclo*hexanone results, recognised by oxidation to a mixture of δ-methylhexoic and β-methyladipic acids.

The absence of diacetylvaleric acid and of formaldehyde or formic acid in the products of ozonolysis of bisabolene excludes the possibility of the sesquiterpene being a mixture of II (the γ-form) with the α- and β-forms.

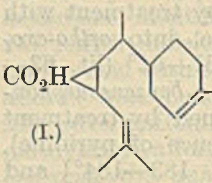
Dehydrogenation of bisabolene using 2 atoms of sulphur gives a benzene derivative (oxidised to terephthalic acid, which is not obtained when bisabolene itself is oxidised) and not a naphthalene derivative. Selenium gives results similar to those obtained using sulphur. E. E. TURNER.

Higher terpene compounds. XXXVI. Constitution of zingiberene. L. RUZICKA and A. G. VAN VEEN (Annalen, 1929, 468, 143—162).—Crude zingiberene from ginger oil is a mixture of zingiberene and γ-bisabolene (preceding abstract), for when it is treated with hydrogen chloride in anhydrous ethereal solution, bisabolene trihydrochloride separates. If moisture is not rigorously excluded, some *iso*zingiberene dihydrochloride is also formed. When crude zingiberene is treated with glacial acetic and sulphuric acids, *iso*zingiberene is produced, converted by absolute ether and hydrogen chloride into *iso*zingiberene dihydrochloride. Ozonolysis of crude zingiberene gives acetone and lævulic and succinic acids (once, a trace of formaldehyde was observed). The yield of the acids shows that the amount of bisabolene present in the mixture does not exceed 20—30%, a fact in accord with the possibility of isolating analytically pure dihydrozingiberene by a reduction process (sodium and alcohol) which does not affect bisabolene.

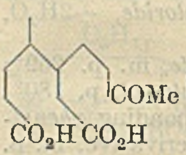
Crude zingiberene undergoes catalytic hydrogenation in presence of platinum-black to give *tetrahydrozingiberene*, b. p. 130—135°/18 mm., d_4^{15} 0·842, n_D^{20} 1·463. Ozonolysis of the crude reduction product gave methylheptanone (from the tetrahydrobisabolene) as the only recognisable product.

Catalytic dehydrogenation of hexahydrozingiberene with palladised charcoal (Zelinski and Turova-Pollak, A., 1925, i, 1052; 1926, 277, 365) at 345—360° gave slightly impure ζ-p-*tolyl*-β-*methylheptane*, b. p. about 135°/12 mm. Oxidation of the latter with chromic anhydride gave acetic, oxalic, and terephthalic acids, the last-named being produced in amounts too large to be accounted for as having originated from any bisabolene present. The absence of a tri- or tetra-carboxylic acid of benzene in the oxidation mixture shows that the skeleton of zingiberene is similar to that of bisabolene. The above heptane, b. p. 135—136°/15 mm., d_4^{15} 0·8524, n_D^{15} 1·4832, was synthesised by treating methylheptenone with magnesium *p*-tolyl bromide, heating the resulting mixture of hydrocarbon and carbinol with potassium hydrogen sulphate at 200°, and reducing the product catalytically (platinum-black). Chromic acid oxidation of the heptane gave terephthalic acid in yield similar to that obtained from the naturally-derived heptane.

Since bisabolene does not react with ethyl diazoacetate, which adds readily to conjugated double linkings, crude zingiberene was treated with this ester. Hydrolysis of the product gave an oily *acid*, $C_{17}H_{26}O_2$, b. p. 170—180°/0·3 mm. (alkaline solution is a soap), together with a little dizingiberene (?). The acid is regarded as being I. It is converted by ozone into much acetone. Catalytic reduction of the crude ester obtained from ethyl diazoacetate and crude zingiberene underwent catalytic hydrogenation in presence of platinum oxide, but the product decomposed when distilled. It was therefore heated with selenium at 270—300°; the dehydrogenation product (b. p. 140—180°/12 mm.) so obtained gave some terephthalic acid on oxidation, proving that zingiberene is a 1 : 4-substituted *cyclo*hexane derivative.


(I.)

Reduction of crude zingiberene with sodium and absolute alcohol (Semmler and Becker, A., 1913, i, 742) gave dihydrozingiberene, having b. p. 135—136°/15 mm., d_4^{15} 0·865, and n_D^{20} 1·4881. It was unaffected by ethyl diazoacetate, gave an amorphous product when treated with hydrogen chloride, and gave some cadalene when heated with sulphur at 180—250°. Ozonolysis of dihydrozingiberene gave merely acetone and succinic and lævulic acids, but oxidation of the ozonide with permanganate gave a mixture of acids, converted into a mixture of two *esters*, $C_{14}H_{24}O_5$, A, b. p. 145°/0·3 mm., and B, b. p. 150°/0·3 mm., corresponding with a dicarboxylic acid of the formula $C_{12}H_{20}O_5$ (exclusion of one possible formula for dihydrozingiberene). Oxidation of the ester mixture with sodium hypobromite gave a mixture of two *esters*, $C_{14}H_{24}O_6$, A′, b. p. 140—145°/0·3 mm., and B′, b. p. 145—150°/0·3 mm., corresponding with a tricarboxylic acid, $C_{11}H_{18}O_6$. The C_{12} acid is therefore II, the C_{11} acid is III, zingiberene is IV, and dihydroginziberene is V.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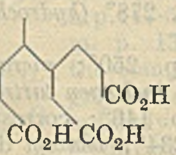
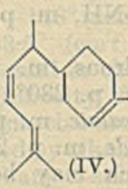
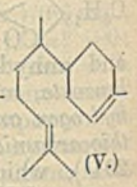

(III.)


(IV.)


(V.)

The fact that bisabolene does not and zingiberene does give cadalene when heated with sulphur or selenium is clearly due to hindrance of dehydrogenation by the hemicyclic double linking in bisabolene. Similarly, it is possible to account for the fact that zingiberene is much more readily converted, by acids, into a hydrogenated naphthalene hydrocarbon (*iso*zingiberene). E. E. TURNER.

Higher terpene compounds. XXXVII. Agathicdicarboxylic acid, the crystalline resin acid, $C_{20}H_{30}O_4$, of kauri, hard and soft Manila copals. L. RUZICKA and J. R. HOSKING (Annalen, 1929, 469, 147—192; cf. Tschirsch and Koch, A., 1902, i, 478).—The isolation of the ether-soluble crystalline resin acids from the above copals by the method of Horrmann and Kroll (B., 1927, 609) and careful fractionation of the product with ammonium carbonate, sodium carbonate, and sodium hydroxide is described. From each copal is isolated the same crystalline dibasic acid, $C_{20}H_{30}O_4$, m. p. 203—204°, $[\alpha]_D$ varying from +52° to +56° in alcohol, for which the name *agathicdicarboxylic acid* (I) is suggested. The various dibasic acids isolated from different copals and described under various names in the literature are probably more or less impure forms of this acid. By a large number of analyses and direct comparison of the acids (crystallographic data by Goedhart) and the derivatives described below, the identity of the parent acids from various sources is definitely established and the above composition assigned in preference to the alternative $C_{20}H_{28}O_4$. Molecular refractivity data of the various derivatives support this conclusion. The systematic nomenclature used throughout this abstract is that suggested by the authors to replace the various names occurring in the earlier literature. By the silver salt method I yields a *dimethyl* ester, b. p. 196—198°/0·6 mm., $[\alpha]_D$ +61·2° to +54·6° in alcohol, d_4^{14} 1·076, n_D^{14} 1·5178. Catalytic reduction (by various methods) of I yields the saturated *tetrahydroagathicdicarboxylic acid*, purified through its *dimethyl* ester, b. p. 189—190°/1 mm., 165—166°/0·1 mm., $[\alpha]_D$ +47·9° to +42·2° in alcohol, d_4^{20} 1·040, n_D^{20} 1·4910. By heating it above its m. p. I is converted (17—20% yield) by loss of carbon dioxide into *noragathic acid*, $C_{19}H_{30}O_2$, b. p. 195—197°/0·9 mm., 180—183°/0·4 mm., m. p. 146—147° [Horrmann and Kroll (*loc. cit.*) describe it as a glass, m. p. 60°], $[\alpha]_D$ +59·3° in alcohol (*methyl* ester, b. p. 151—152°/0·6 mm., $[\alpha]_D$ +57·02° in alcohol, d_4^{23} 1·002, n_D^{23} 1·5087), which is reduced catalytically to *tetrahydronoragathic acid*, m. p. 133°, $[\alpha]_D$ +50·3° in alcohol (*methyl* ester, b. p. 141—142°/0·3 mm., m. p. 52—53°, $[\alpha]_D$ +53·7° in alcohol, d_4^{72} 0·9411, n_D^{72} 1·4693). I thus contains two double linkings which, unlike those in abietic acid, exhibit no difference in reactivity and the molecular refractivity data are in good agreement with the dicyclic structure thus required. Evidence to be published later shows that I is a reduced naphthalene derivative which is isomerised by strong acids to a hydrophenanthrene derivative. Catalytic dehydrogenation of the amorphous, ether-soluble resin acids from kauri copal with selenium (Diels and others, A., 1928, 169) yields the methylethylnaphthalene obtained similarly from soft Manila copal (Ruzicka, Steiger, and Schinz, A., 1927, 60), a *hydrocarbon*, $C_{17}H_{20}$ (*picrate*, m. p. 138°), and some retene, but no pimanthrene. Similarly, dehydrogenation of the pure acid I (subsequent communication) yields the same hydrocarbon $C_{17}H_{20}$, and pimanthrene, but no retene. J. W. Baker.

[Acid from] Finnish pine resin. A. M. Nordström (J. pr. Chem., 1929, [ii], **121**, 204—222).—The acid fraction of the resin, obtained by extraction with sodium carbonate solution and subsequent acidification, gives after extraction with ether and light petroleum, followed by ten-fold crystallisation from alcohol, 14% of an *acid* (I), $C_{20}H_{30}O_2$, m. p. 142—143°, $[\alpha]_D^{18}$ −102·73° in alcohol, −71·8° in benzene, $[\alpha]_D^{19}$ −14·7° in acetic acid (*silver* salt). This furnishes a crystalline *ammonium* salt, and belongs therefore to the pimaric acid group. The acid is practically unaffected by repeated crystallisation from alcohol (cf. Dupont, A., 1921, i, 510), but prolonged heating of an alcoholic solution causes a diminution in the rotation; in acetic acid–alcohol solution the change is more rapid. When fused at 150°, I is converted into an isomeric *acid*, m. p. 144—145°, $[\alpha]_D$ +56·59° in benzene, +35·83° in alcohol; at 180—205° this change is followed by the production of a *lævo*-acid (cf. Ruzicka, A., 1923, i, 818). Both of the above acids are isomerised by treatment with a 2·6% alcoholic hydrogen chloride solution (cf. Kesler, Lowy, and Faragher, A., 1928, 60), or by heating above 150° into abietic acid, m. p. 166—167°, $[\alpha]_D^{18}$ −92·54° in alcohol (gelatinous ammonium salt).

The neutral constituents of the resin are a turpentine oil (3%), b. p. 156—158°, $[\alpha]_D^{18}$ −8·35° when distilled over sodium, and small amounts of a monoterpene *alcohol*, b. p. 90—95°/9 mm. (*phenylcarbimide* derivative, m. p. 110°), and a *hydrocarbon*, $C_{20}H_{34}$, b. p. 178°/9 mm., n_D^{15} 1·52307, $[\alpha]_D^{16}$ +77·24°, easily oxidised by air. H. Burton.

Preparation of 1 : 3-benzdioxin. F. D. Chattaway and F. Calvet (Anal. Fís. Quím., 1928, **26**, 417—422).—1 : 3-*Benzdioxin*, the parent substance of the condensation products of formaldehyde, chloral, dichloroacetaldehyde, and butylchloral with *p*-substituted phenols (A., 1926, 1242; 1927, 458, 967; 1928, 632, 750; this vol., 65), could not be obtained from the product of condensation of phenol and formaldehyde. It was, however, obtained indirectly from 6-nitro-1 : 3-benzdioxin (Borsche and Berkhout, A., 1904, i, 415), prepared by the condensation of formaldehyde and *p*-nitrophenol. When reduced with zinc in aqueous-alcoholic hydrochloric acid this yielded 6-*amino*-1 : 3-*benzdioxin*, isolated as the *hydrochloride*, m. p. 230° (decomp.). Diazotisation and heating with potassium stannite solution and steam-distillation of the reaction mixture yielded 1 : 3-*benzdioxin*, b. p. 211—212°/758 mm., a colourless liquid with a peculiar odour. R. K. Callow.

Reactions between furfuraldehyde, aniline, and malonic acid. T. Boehm (Arch. Pharm., 1929, **267**, 129—141).—Furfuraldehyde, aniline, and malonic acid condense in alcoholic solution yielding the violet-black salt, *furfuraniline furfurylidenemalonate*, [+½EtOH, m. p. 106—107° (decomp.); +½MeOH, m. p. 109—110° (decomp.); +½Pr$^{\beta}$·OH, m. p. 99—100° (decomp.); +AcOH, m. p. 117—118° (decomp.)], which furnishes the bright red hydrochloride of furfuraniline (ε-anilino-α-anilo-β-hydroxy-$\Delta^{\beta\delta}$-pentadiene) (cf. Zincke and Mülhausen, A., 1906, i, 33; Dieckmann and Beck, *ibid.*, 109; König, *ibid.*, 109), m. p. 173—174° [H_2O, m. p. 167—169° (decomp.)], when treated with hydrochloric acid. Similar *compounds* are produced when the aniline is replaced by other amines (given in parentheses): (*p*-toluidine) ½EtOH, greenish-violet, m. p. 128—129° (decomp.); (*m*-toluidine) ½EtOH, violet, m. p. 98—100°; (*p*-chloroaniline), black, m. p. 120—121°; (*p*-bromoaniline), greenish-black, m. p. 121—122°; (*p*-phenetidine), dark blue, m. p. 135—136°; (ψ-cumidine), ½EtOH, dark green, m. p. 97—99°. The following salts of furfuraniline are obtained when aniline and furfuraldehyde are allowed to react in molecular proportions with the appropriate acid : *oxalate*, violet, m. p. 138—139° (EtOH), red, m. p. 135—136° (decomp.); *acetate*, bluish-violet, giving blood-red solutions (AcOH), m. p. 63°; *fumarate* (½EtOH), m. p. 137—138°; *tartrate* (½EtOH), reddish-violet, m. p. 159—162° (decomp.); *citrate* (½EtOH), dark violet, m. p. 130—131°. The *malonate* (½EtOH), wine-red, m. p. 107—108°, is obtained by treating the furfurylidenemalonate with ammonia and dissolving the precipitated base in an alcoholic solution of malonic acid. S. COFFEY.

Manufacture of alkyl*iso*propenylphenols and alkylated coumarans. CHEM. FABR. AUF ACTIEN.—See B., 1929, 236, 237.

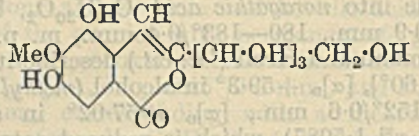
Coumarin condensations. I. Condensation of ethyl allylacetoacetate with phenols. K. G. NAIK, R. D. DESAI, and H. R. DESAI (J. Indian Chem. Soc., 1929, 6, 83—87).—Ethyl allylacetoacetate condenses with resorcinol in presence of cold concentrated sulphuric acid, yielding 7-*hydroxy*-4-*methyl*-3-*allylcoumarin*, m. p. 221—222° (*acetyl* derivative, m. p. 152—153°), since hydrolysis with boiling 50% aqueous potassium hydroxide gives resorcinol. When this condensation is carried out in presence of glacial acetic acid and dry hydrogen chloride the product formed is 7-*hydroxy*-4-*methyl*-3-*chloropropylcoumarin*, m. p. 200—201° (*acetyl* derivative, m. p. 122—123°; *benzoyl* derivative, m. p. 193°). This substance is unaffected by boiling with sodium acetate solution. Condensation of ethyl allylacetoacetate with α-naphthol, *m*-cresol, and phloroglucinol in presence of concentrated sulphuric acid gives 4-*methyl*-3-*allyl*-1 : 2-α-*naphthopyrone*, m. p. 155—156°, 4 : 7-*dimethyl*-3-*allylcoumarin*, m. p. 126—127°, and 5 : 7-*dihydroxy*-4-*methyl*-3-*allylcoumarin*, m. p. 207—208° (*acetyl* derivative, m.p. 130—131°), respectively. With phosphoryl chloride as the condensing agent pyrogallol furnishes 7 : 8-*dihydroxy*-4-*methyl*-3-*allylcoumarin*, m. p. 175—176° (*acetyl* derivative, m. p. 145—146°). A definite product was not isolated using phenol, and condensation did not proceed with pyrocatechol, guaiacol, thymol, quinol, and β-naphthol. H. BURTON.

Non-tannin substances in the extract of the root of badan (*Saxifraga crassifolia*). I. Bergenin. A. E. TSCHITSCHIBABIN, A. V. KIRSSANOV, A. J. KORELEV, and N. N. VOROSCHZOV, jun. (Annalen, 1929, **469**, 93—127; cf. Garreau and Machelart, Compt. rend., 1880, 91, 942).—Bergenin, $C_{14}H_{16}O_9$ (also $+H_2O$ which is lost at 100°), $[\alpha]_D$ −37·25° in alcohol (*mono*- and *di-sodium*, and *potassium* salts), isolated from the acetone extract of badan roots after removal of tannins, contains six hydroxyl groups (by Zerevitinov's method) and one methoxyl group, but no carbonyl or free carboxyl groups. With excess of acetic anhydride it yields a *penta-acetyl* derivative, m. p. 199—203°, which still contains one hydroxyl group. Methylation of bergenin with diazomethane yields *dimethylbergenin*, $+2H_2O$, m. p. 80°, anhydrous, m. p. 194—196°, which when oxidised with alkaline potassium permanganate yields 5 : 6 : 7-*trimethoxy*iso*coumarin* (I), m. p. 84°, 5 : 6 : 7-*trimethoxy*iso*coumarin*-3-*carboxylic acid*,

$$C_6H(OMe)_3<\begin{matrix}CH{:}C{\cdot}CO_2H\\ CO{-}O\end{matrix}$$

(II), m. p. 254° (decomp.) (*silver* salt which yields I by distillation in a vacuum; *methyl* ester, m. p. 155—156°), and 3 : 4 : 5-trimethoxyphthalic acid, b. p. 226°/17 mm., m. p. 139—140° with conversion into its anhydride, but in a bath at 170° it has m. p. 176—177° (decomp.). By the action of the theoretical quantity of boiling 0·1*N*-sodium hydroxide I is converted into a *substance*, m. p. 129°, probably $C_6H(OMe)_3(CO_2H){\cdot}CH_2{\cdot}CHO$ or $CH{:}CH{\cdot}OH$) (resinous derivative with phenylhydrazine), whilst with excess of 0·5*N*-sodium hydroxide it yields a *substance*, m. p. 185—186° (cf. Bamberger and Frew, A., 1894, i, 192). Further oxidation of I with alkaline potassium permanganate converts it into 3 : 4 : 5-*trimethoxyhomophthalic acid*, m. p. 145—146° (converted by distillation at 14 mm. into its *anhydride*, m. p. 124—125°). This acid is synthesised from 4-hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (Alimchandani and Meldrum, J.C.S., 1920, 117, 964) by reduction with hydriodic acid and red phosphorus and rapid methylation (in an atmosphere of hydrogen) of the resulting trihydroxyhomophthalic acid with methyl sulphate. By fusion with potassium hydroxide at 200° bergenin is converted into 3 : 5-dihydroxy-4-methoxybenzoic acid. On the basis of these results the structural conclusions of Sadikov and Guthner (A., 1928, 207) are criticised and the structure III is assigned to bergenin, and in

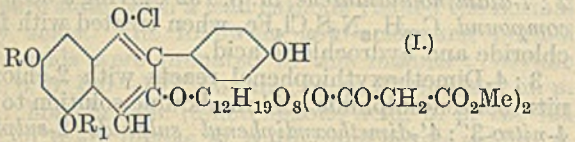
(III.)



agreement with this it titrates as a lactone. The following reactions are rather less readily explained. Bergenin couples normally in alkaline solution with one molecule of benzenediazonium chloride to yield *benzeneazobergenin*, decomp. 200°, which, however, can couple with a second molecule of the diazonium salt to yield the *substance* $C_{14}H_{14}O_9(N_2Ph)_2$. The monoazo-derivative is reduced by stannous chloride to yield (3-)*aminobergenin*, $+3H_2O$ and anhydrous, m. p. 244° (decomp.) (yielding a *diazo-oxide*, $+2H_2O$, with nitrous acid). Like the parent *iso*coumarin, I and II are converted by ammonia under suitable conditions into the corresponding *trimethoxy*iso*carbostyril*, m. p. 165—167° (reduced by hydriodic acid to tetrahydroxy*iso*quinoline), and *trimethoxy*iso*carbostyrilcarboxylic acid*, m. p. 280° (decomp.). The possible biosynthesis of bergenin from gallic acid and dextrose and its relationship to glucogallic acid (Feist, A., 1913, i, 70; Fischer and Bergmann, A., 1918, i, 224) are discussed. J. W. BAKER.

Plant colouring matters. XII. Constitution of monardæin and salvianin. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1929, 12, 292—295).—Monardæin (A., 1928, 1255) is shown to be identical with salvianin (Willstätter and Bolton, A., 1917, i, 42) on the basis of the following evidence. Like salvianin, hydrolysis of monardæin with 20% hydrochloric acid yields 24—26% of malonic acid, whilst hydrolysis of salvianin chloride with 10% sodium hydroxide yields *p*-hydroxycinnamic acid and salvinin chloride, m. p. 184° (lit. 168°), $[\alpha]_D$ −236° ±20°, identical with monardin chloride, m. p. 184° (mixed

m. p.), $[\alpha]_D$ −241° ±20°. The identity of these two compounds is confirmed by a comparison of their colours at various p_H values (Robinson). The structure


(I.)

I is provisionally assigned to salvianin (monardæin) chloride (R and R_1=either H or $HO\cdot C_6H_4\cdot CH{:}CH\cdot CO$).

J. W. Baker.

Bixin. F. Faltis and F. Vieböck (Ber., 1929, **62**, [*B*], 701—708).—In reply to Kuhn and Winterstein (A., 1928, 644), who, on the basis of microanalyses, have regarded the formula $C_{25}H_{30}O_4$ as correct for bixin (cf. Heiduschka and Panzer, A., 1917, i, 408), the analyses on which the authors base their formula $C_{26}H_{30}O_4$ are tabulated. If Kuhn's formula be correct, completely hydrogenated bixin and norbixin must have the compositions $C_{25}H_{48}O_4$ and $C_{25}H_{46}O_4$, respectively, and the latter substance must be a purely aliphatic, dicarboxylic acid. If, however, the formula $C_{26}H_{30}O_4$ be retained for bixin, perhydronorbixin has the composition $C_{25}H_{46}O_4$, which permits the presence of a ring system in the molecule, thus accounting better for the intense colour of bixin for which the structure

$$CH\left\langle\begin{array}{l}CMe{-}\underset{|}{C}{:}CH\cdot[CH{:}CMe]_2\cdot CH{:}CH\cdot CO_2Me\\ CH{=}C\cdot CMe{:}CH\cdot CH{:}\overset{|}{C}H\cdot CMe\cdot CH\cdot\overset{|}{C}O_2H\end{array}\right.$$

is suggested.

Bixin, dissolved in glacial acetic acid, is converted by hydrogen in presence of palladised barium sulphate into perhydrobixin, transformed by methyl-alcoholic hydrogen chloride into *perhydromethylbixin*, b. p. 278—285°/12 mm. The last-named compound is hydrolysed to perhydronorbixin, in which the presence of two carboxyl groups is established by conversion into the corresponding chloride and thence into the *diamide*, $C_{25}H_{48}O_2N_2$, m. p. 107—109° after softening at 100°, and (?) the *imide*, $C_{23}H_{44}\!<\!\genfrac{}{}{0pt}{}{CO}{CO}\!>\!NH$. Treatment of perhydronorbixin with red phosphorus and bromine and subsequently with methyl alcohol yields an ester which appears to contain 5 atoms of bromine.

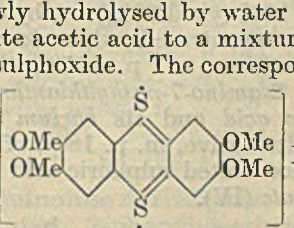
H. Wren.

Thianthrene. III. K. Fries, H. Koch, and H. Stukenbrock (Annalen, 1929, **468**, 162—201).—**I. 2 : 3 : 6 : 7-Tetramethoxythianthrene and its oxidation products.** An improved method is given for preparing 4-aminoveratrole, the *acetyl* derivative, m. p. 135°, of which is converted by phosphorus pentasulphide and potassium sulphide in boiling toluene into 4 : 5-*dimethoxythioacetanilide*, m. p. 114° (yield 55%). Oxidation of the latter with alkaline ferricyanide gives 4 : 5-*dimethoxy*-1-*methylbenzthiazole*, m. p. 75°, b. p. 184°/11 mm. (yield 40%). This substance is converted by alcoholic potassium hydroxide at 100° (pressure) into the *sodium* derivative of 2-amino-4 : 5-dimethoxythiophenol, which with nitrous acid gives 4 : 5-*dimethoxybenzthiodiazole*, m. p. 138°, converted by heat into 2 : 3 : 6 : 7-tetramethoxythianthrene, m. p. 174°, b. p. 280—300°/14 mm.

The conditions for converting veratrole into potassium 3 : 4-dimethoxybenzenesulphonate and thence into 3 : 4-dimethoxybenzenesulphonyl chloride (yield 50—60%) are given. Reduction of the chloride with zinc dust and hydrochloric acid in presence of ether gives 3 : 4-*dimethoxythiophenol*, b. p. 138°/14 mm., converted by alcoholic hydrogen peroxide into 3 : 4 : 3′ : 4′-*tetramethoxydiphenyl disulphide*, m. p. 89°. When the thiophenol is treated with sulphuric acid and then with stannous chloride, there again results tetramethoxythianthrene (m. p. 176°). Oxidation of the latter with dilute nitric acid in acetic acid gives the *monosulphoxide*, m. p. 196°, whilst concentrated nitric acid and acetic acid gives the *disulphoxide*, m. p. 259°, converted into the thianthrene by hydrobromic and acetic acids and sodium hydrogen sulphite. When chlorine is passed into an aqueous-acetic acid solution of tetramethoxythianthrene, the *sulphonesulphoxide*, m. p. 275°, is formed. This is converted by sulphuric acid into the monosulphone, m. p. 253° (below), together with a red *compound* which with sodium hydrogen sulphite and glacial acetic acid gives the *trimethyl ether*, m. p. 270°, of 2 : 3 : 6 : 7-*tetrahydroxythianthrenesulphonesulphoxide*. Tetramethoxythianthrenesulphonesulphoxide when treated first with hydrogen bromide and acetic acid and then with sodium hydrogen sulphite gives 2 : 3 : 6 : 7-*tetramethoxythianthrenemonosulphone*, m. p. 253°, converted into the former compound by nitric and acetic acids. Oxidation of tetramethoxythianthrene with hydrogen peroxide and glacial acetic acid gives 2 : 3 : 6 : 7-*tetramethoxythianthrenedisulphone*, m. p. 296°, which with boiling alcoholic potassium hydroxide affords 4 : 5-*dimethoxy*-2-*ethoxybenzenesulphinic acid*, sintering at 75°, m. p. 118—120° (decomp.). This substance is converted by hydrogen bromide and glacial acetic acid, followed by sodium hydrogen sulphite, into 3 : 4 : 3′ : 4′-*tetramethoxy*-2 : 2′-*diethoxydiphenyl disulphide*, m. p. 84°, reduction of which or of the sulphinic acid (stannous chloride, glacial acetic acid) produces the readily oxidised 3 : 4-dimethoxy-2-ethoxythiophenol (not isolated).

When a solution of tetramethoxythianthrene in concentrated sulphuric acid is allowed slowly to absorb atmospheric moisture, the deep blue *meriquinonoid dithionium* salt (I, $X{=}SO_4H$), m. p. 230—232° (decomp.), is formed. This is (1) reduced by stannous chloride or hydriodic acid to the thianthrene and (2) slowly hydrolysed by water or more rapidly by hot dilute acetic acid to a mixture of the thianthrene and its sulphoxide. The corresponding *perchlorate* (I, $X{=}ClO_4$) explodes at 245°, and the *chloride* (I, X=Cl) has m. p. 164—166° (decomp.). The *perbromide* (I, $X{=}Br_3$), m. p. 220—222° (decomp.), results when excess of bromine is added to a solution of the thianthrene in carbon disulphide. So great is the tendency for the formation of the perbromide that the latter is formed when the monosulphoxide or the disulphoxide is treated with hot hydrogen bromide and glacial acetic acid.

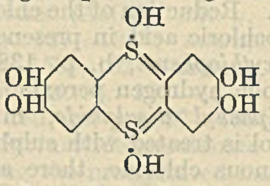
(I.)



Tetramethoxythianthrene is converted by boiling hydriodic and acetic acids into 2 : 3 : 6 : 7-*tetra*-

hydroxythianthrene, m. p. 273° (*tetra-acetyl* derivative, m. p. 224°), which, when treated in acetic acid with hydrogen peroxide gives the blue *anhydride* of 2 : 3 : 6 : 7 : 9 : 10-*hexahydroxythianthrene* (II), isomeric with the sulphoxide which might have been expected to result. Acetylation of the blue compound gives the colourless 2 : 3 : 6 : 7-*tetra-acetoxythianthrene sulphoxide*, m. p. 213°, hydrolysable to the blue substance.

(II.)



When tetramethoxythianthrenemonosulphone is heated with hydriodic and acetic acids, 2 : 3 : 6 : 7-*tetrahydroxythianthrenemonosulphone*, charring above 300°, results (*tetra-acetate*, m. p. 203°). Similar treatment of the disulphone produces 2 : 3 : 6 : 7-*tetrahydroxythianthrenedisulphone*, m. p. above 310° (*tetra-acetate*, m. p. 245°). Bromination of the latter gives the 1 : 4 : 5-*tribromo*-derivative, m. p. above 340°, or the 1 : 4 : 5 : 8-*tetrabromo*-derivative, m. p. above 350° (*tetra-acetate*, decomp. 300°).

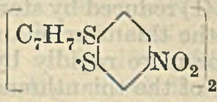
When a solution of tetrahydroxythianthrene in concentrated sulphuric acid is allowed to absorb moisture, a *meriquinonoid dithionium sulphate* is formed (I, OH instead of OMe and X=SO_4H). This is reducible to the thianthrene and is hydrolysed in excess of water. The corresponding *perchlorate*, *bromide*, and *chloride* are described.

Nitric and acetic acids convert tetramethoxythianthrene into 1 : 8(?)-*dinitro*-2 : 3 : 6 : 7-*tetramethoxydiphenylenesulphone*, m. p. 238°, also formed when tetramethoxythianthrene-monosulphone or -sulphonoxide (?) is treated with cold nitric acid.

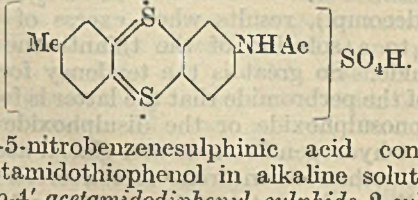
4-Bromo-5-nitroveratrole is converted by alcoholic sodium sulphide into 2 : 2′-*dinitro*-4 : 5 : 4′ : 5′-*tetramethoxydiphenyl sulphide*, m. p. 209° (60% yield), reduced by stannous chloride in hydrochloric and acetic acids to 2 : 2′-*diamino*-4 : 5 : 4′ : 5′-*tetramethoxydiphenyl sulphide*, m. p. 110°, which could not be converted into the diphenylene sulphide.

II. Amino-derivatives of thianthrene. From thio-*p*-cresol and 2-chloro-5-nitrobenzenesulphinic acid may be obtained 4-*nitro*-4′-*methyldiphenyl sulphide* 2-*sulphinic acid*, m. p. 123°, converted by hot hydrogen bromide and acetic acid into the *compound* (III), m. p. 154° (yield 60%), or, by cold concentrated sulphuric acid into 2-*nitro*-7-*methylthianthrene*, m. p. 157°, which when reduced affords 2-*amino*-7-*methylthianthrene*, m. p. 130° (1-*sulphonic acid* and its *barium* salt described). The *acetyl* derivative, m. p. 180°, of the base is converted by concentrated sulphuric acid into the half-quinonoid *sulphate* (IV).

(III.)

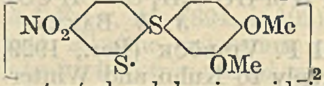


(IV.)



2-Chloro-5-nitrobenzenesulphinic acid condenses with 4-acetamidothiophenol in alkaline solution to give 4-*nitro*-4′-*acetamidodiphenyl sulphide* 2-*sulphinic acid*, converted by concentrated sulphuric acid into the *acetyl* derivative, m. p. 205°, of 2-*nitro*-7-*aminothianthrene*, m. p. 198°. This when reduced affords 2 : 7-*diaminothianthrene*, m. p. 192°, giving a deep blue *compound*, $C_{12}H_{10}N_2S_2Cl_4Fe$, when treated with ferric chloride and hydrochloric acid.

3 : 4-Dimethoxythiophenol reacts with 2-chloro-5-nitrobenzenesulphinic acid in alkaline solution to give 4-*nitro*-3′ : 4′-*dimethoxydiphenyl sulphide* 2-*sulphinic acid*, m. p. 131°, converted by hydrogen bromide and acetic acid into the *compound*, m. p. 196°, and by concentrated sulphuric acid into 2-*nitro*-6 : 7-*dimethoxythianthrene*, m. p. 194°, b. p. 192—196°/14 mm., also formed from the compound, m. p. 196°, and the same reagent. Reduction of the nitro-compound gives 2-*amino*-6 : 7-*dimethoxythianthrene*, m. p. 149° (*acetyl* derivative, m. p. 180°). When 2-bromo-5-nitroaniline is heated with alcoholic sodium disulphide and sulphur, there results 4 : 4′-*dinitro*-2 : 2′-*diaminodiphenyl sulphide*, m. p. 211° (*diacetyl* derivative, m. p. 245°), which could not be obtained when sodium sulphide was used, whilst if excess of sulphur were taken the product was 4-*nitro*-2-*aminothiophenol*, m. p. 108°, oxidised by air to 4 : 4′-*dinitro*-2 : 2′-*diaminodiphenyl disulphide*, m. p. 178°. The *diacetyl* derivative, m. p. 263°, of the latter is converted by sodium sulphide or dextrose in alkaline-alcoholic solution into 4-nitro-2-methylbenzthiazole, the corresponding *dibenzoyl* derivative, m. p. 225°, similarly giving 4-*nitro*-2-*phenylbenzthiazole*, m. p. 193°, also obtained by benzoylating 4-nitro-2-aminothiophenol in presence of alkali or from 2-*bromo*-5-*nitrobenzanilide*, m. p. 166°, and sodium disulphide. Thianthrene derivatives could not be obtained from the dinitrodiaminodiphenyl sulphide or from the related compounds.



E. E. Turner.

γ-Pyrrolidino- and γ-pyrrolino-propyl benzoates. L. H. Andrews and S. M. McElvain (J. Amer. Chem. Soc., 1929, **51**, 887—892).—Pure pyrrole, prepared by an improved method, is hydrogenated in presence of Adams' platinum catalyst to pyrrolidine (cf. Willstätter and Hatt, A., 1912, i, 545), which with γ-chloropropyl benzoate at 100° yields γ-1-*pyrrolidinopropyl benzoate hydrochloride* (I), m. p. 125—126°. Pyrroline (Knorr and Rabe, A., 1901, i, 163) yields γ-1-*pyrrolinopropyl benzoate hydrochloride* (II), m. p. 136—138°. Attempts to hydrogenate 2-carbethoxypyrrole and a mixture of 2- and 3-methylpyrroles were unsuccessful. I is a more powerful local anæsthetic than II and, unexpectedly, both are more powerful than γ-piperidinopropyl benzoate hydrochloride (A., 1928, 71). H. E. F. Notton.

Alkylated pyrrolones. Synthesis of γ-ketonic and of fatty acids. R. Lukes (J. Czechoslov. Chem. Comm., 1929, **1**, 119—136).—The following new pyrrolones have been prepared by the action of the Grignard reagent on the *N*-substituted succinimides (A., 1928, 299): 1-*methyl*-2-n-*amyl*-5-*pyrrolone*, b. p. 143—148°/10 mm., and 1-*methyl*-2-n-*hexyl*-5-*pyrrolone*, b. p. 148—150°/10 mm. Hydrolysis of the pyrrolones with dilute sulphuric acid afforded the corresponding

γ-ketonic acids, probably through the intermediate formation of a hydrate, whilst electrolytic reduction of the γ-ketonic acids, which need not be isolated in the pure state, with a lead cathode yielded the normal fatty acids. The following keto-acids and normal fatty acids were prepared in this manner: lævulic acid, b. p. 150—152°/23 mm., m. p. 33° (oxime, m. p. 96°); homolævulic (β-ketohexoic) acid, b. p. 160°/24 mm., m. p. 40° (*oxime*, m. p. 76°), and hexoic acid, b. p. 201°; γ-ketoheptoic acid, b. p. 167°/19 mm., m. p. 45—46°, and heptoic acid, b. p. 217—218°; γ-keto-octoic acid, b. p. 160—170°/25 mm. (slight decomp.), m. p. 53°, and octoic acid, b. p. 225—235°; γ-keto-nonoic acid, m. p. 69—70°, and nonoic acid, b. p. 250°; γ-ketodecoic acid, m. p. 71°, and decoic acid, b. p. 260—265°, m. p. 30°.

A. I. VOGEL.

Piperidine derivatives. VII. 1-Alkyl-4-piperidyl benzoates and *p*-aminobenzoates. N. W. BOLYARD and S. M. MCELVAIN (J. Amer. Chem. Soc., 1929, **51**, 922—928).—3-Carbethoxy-1-alkyl-4-piperidones (A., 1928, 72) have been converted by boiling 20% hydrochloric acid into the following 1-alkyl-4-piperidone hydrochlorides: *methyl*, m. p. 94—95° (corr.); *ethyl*, m. p. 105—106°; n-*propyl*, m. p. 117—118°; n-*butyl*, m. p. 178—180°; iso*amyl*, m. p. 183—185°, and *phenylethyl*, m. p. 182—184°, which are hydrogenated (platinum) and then benzoylated at 160—165° to 1-*methyl*-, m. p. 219—220°; 1-*ethyl*-, m. p. 204—205°; 1-n-*propyl*-, m. p. 210—211°; 1-n-*butyl*-, m. p. 223—224°; 1-iso*amyl*, m. p. 199—200°, and 1-*phenylethyl*-, m. p. 236—238°, 4-*piperidyl benzoate hydrochlorides*. 1-*Methyl*-, m. p. 197—199°; 1-*ethyl*-, m. p. 204—206°; 1-n-*propyl*-, m. p. 219—220°; 1-n-*butyl*-, m. p. 242—243°; 1-iso-*amyl*-, m. p. 243—245°, and 1-*phenylethyl*-, m. p. 242—244°, -4-*piperidyl* p-*nitrobenzoate hydrochlorides* are hydrogenated (platinum) to 1-*methyl*-, m. p. 231—233°; 1-*ethyl*-, m. p. 183—184°; 1-n-*propyl*-, m. p. 201—203°; 1-n-*butyl*-, m. p. 234—236°; 1-iso*amyl*-, m. p. 233—235°, and 1-*phenylethyl*-, m. p. 238—240°, -4-*piperidyl* p-*aminobenzoate hydrochlorides*. The benzoates are, in general, more powerful local anæsthetics than the *p*-aminobenzoates and the activity increases with the size of the alkyl group. The results are discussed in relation to previous work (cf A., 1926, 1044). 1-Phenylethyl-4-piperidyl benzoate hydrochloride is about seven times as powerful as cocaine hydrochloride and is much less toxic.

H. E. F. NOTTON.

Local anæsthetics from 2-β-hydroxyethyl-piperidine. C. S. MARVEL and R. S. SHELTON (J. Amer. Chem. Soc., 1929, **51**, 915—917).—1-Methyl-(*a*), b. p. 175—178°/35—40 mm., d_4^{20} 0·9840, n_D^{20} 1·4872; 1-ethyl- (*b*), b. p. 136°/27—28 mm., d_4^{20} 0·9730, n_D^{20} 1·4885, and 1-*n*-propyl- (*c*), b. p. 139—141°/27 mm., d_4^{20} 0·9657, n_D^{20} 1·4905, -2-β-hydroxyethylpiperidines (cf. Ladenburg, A., 1898, i, 687; 1910, i, 769) yield p-*nitrobenzoate hydrochlorides*, m. p. (*a*) 181—182°, (*b*) 198—199°, (*c*) 124—126°, which are readily hydrogenated (platinum) to p-*aminobenzoate hydrochlorides*, (*a*) oily, (*b*), m. p. 238—239·5°, (*c*), m. p. 175—176°. These are less active anæsthetics than the corresponding 1-alkyl-3-piperidylmethyl esters (A., 1928, 427).

H. E. F. NOTTON.

Action of aromatic acid chlorides on vinyldiacetoneamine [2 : 2 : 6-trimethyl-4-piperidone]. J. GRAYMORE (J.C.S., 1929, 587—588).—The observation that vinyldiacetoneamine cannot be benzoylated by the Schotten–Baumann method (Kipping and Greasley, A., 1924, i, 144) is confirmed with benzoyl chloride and substituted benzoyl chlorides. The effect is attributed to the existence of the base in the ammonium hydroxide form. Dilute solutions of ammonia and ethylamine are similarly non-reactive. The following derivatives of vinyldiacetoneamine were prepared by interaction of the base (2 mols.) with the appropriate acid chloride: *N*-*m*-nitrobenzoyl-, m. p. 159—160°; *N*-*p*-nitrobenzoyl-, m. p. 170°; *N*-*o*-nitro-*p*-toluoyl-, m. p. 150—151°; *N*-*p*-toluenesulphonyl-, m. p. 184°.

R. K. CALLOW.

Bromination of pyridine. S. M. E. ENGLERT and S. M. MCELVAIN (J. Amer. Chem. Soc., 1929, **51**, 863—866).—Perbromides of pyridine hydrobromide, I, m. p. 132—134° (47% perbromide-Br) and II, m. p. 101—103° (40% perbromide-Br), are conveniently prepared in acetic acid (cf. Trowbridge and Diehl, A., 1898, i, 380). At 230—250° I gives 3 : 5-dibromopyridine (40% of theory), and with pyridine hydrobromide (2 mols.) 3-bromo- (35%) and 3 : 5-dibromo- (10%) -pyridines. II gives 36—38% of the mono- and 30—36% of the di-bromo-derivative, and is the most convenient source of these compounds.

H. E. F. NOTTON.

Nitration of benzylpyridines and oxidation of benzylpiperidines. F. BRYANS and F. L. PYMAN (J.C.S., 1929, 549—553; cf. A., 1927, 255).—Nitration of the three benzylpyridines by the addition of their nitrates to concentrated sulphuric acid gave the following yields of nitration products: from 2-benzylpyridine, 10·4% *m*- and 66·7% *p*-; from 3-benzylpyridine, 63·1% *p*-; from 4-benzylpyridine, 4·8% *o*- and 70·2% *m*-. The 2- and 4-benzylpiperidines and also 2-*benzyl*-1-*methylpiperidine*, m. p. 181° (from 2-benzylpiperidine and methyl iodide at 130°), do not simulate the 1-benzyltetrahydro*iso*quinolines (cf. Pyman, *ibid.*, 1909, **95**, 1266, 1738) when oxidised with manganese dioxide and sulphuric acid. The following compounds are new: 1-*benzenesulphonyl*-2-*benzylpiperidine*, m. p. 65°; 1-*benzoyl*-2-*benzylpiperidine*, m. p. 68°; 1-*benzenesulphonyl*-4-*benzylpiperidine*, m. p. 118°; 2-*benzylpyridine nitrate*, m. p. 116°; 2-m-*nitrobenzoylpyridine*, m. p. 122°; 3-*benzylpyridine nitrate*, m. p. 140°; 3-p-*nitrobenzylpyridine*, m. p. 88° (*picrate*, m. p. 145—146°; *nitrate*, m. p. 157°); 3-p-*nitrobenzoylpyridine*, m. p. 185—187°; 4-*benzylpyridine nitrate*, m. p. 110°; 4-m-*nitrobenzoylpyridine*, m. p. 129°. 2-*p*-Nitrobenzoylpyridine hydrochloride has m. p. 187° (lit. 173°).

A. I. VOGEL.

Quinoline derivatives. XI. Synthesis of substituted 2-phenyl-4-ethylquinolines. H. JOHN [and in part M. E. SCHMIED] (J. pr. Chem., 1929, [ii], **121**, 177—192).—The following quinolines (prepared by condensation of benzylidene-ethyl methyl ketone with the requisite amine hydrochloride, in yields as indicated) are described: from aniline, 2-*phenyl*-4-*ethylquinoline* (14%), m. p. 50° (*picrate*, m. p. 189—190°); from *m*-(1 : 3 : 4)-xylidine, 2-*phenyl*-6 : 8-*dimethyl*-4-*ethylquinoline* (7·5%). m. p. 88° (*picrate*, m. p.

158°); from *o*-anisidine, 8-*methoxy-2-phenyl-4-ethylquinoline* (13·1%), m. p. 76° (*picrate*, m. p. 140°); from *m*-toluidine, 2-*phenyl-4-ethyl-5-(or -7)methylquinoline* (20%), m. p. 112° [*picrate*, m. p. 185° (decomp. 188°)]; from *m*-aminophenol, 5-(or 7)-*hydroxy-2-phenyl-4-ethylquinoline* (13·9%), m. p. 219° (*picrate*, m. p. 211°); from *m*-phenetidine, 5-(or 7)-*ethoxy-2-phenyl-4-ethylquinoline* (35·7%), m. p. 118° (*picrate*, m. p. 215—216°); from *p*-toluidine, 2-*phenyl-6-methyl-4-ethylquinoline* (10·8%), m. p. 109° (*picrate*, m. p. 188°); from *p*-aminoethylbenzene, 2-*phenyl-4 : 6-diethylquinoline*, m. p. 158°; from *p*-chloroaniline, 6-*chloro-2-phenyl-4-ethylquinoline* (23%), m. p. 65—66° (*picrate*, m. p. 170°); from *p*-aminophenol, 6-*hydroxy-2-phenyl-4-ethylquinoline* (3·6%), m. p. 149°, [*picrate*, m. p. 204° (decomp.); *potassium* salt]; from *p*-anisidine, 6-*methoxy-2-phenyl-4-ethylquinoline* (14·1%), m. p. 193° (*picrate*, m. p. 173°); from *p*-phenetidine, 6-*ethoxy-2-phenyl-4-ethylquinoline* (9·9%), m. p. 122—123° (*picrate*, m. p. 189°).

The following were prepared by interaction of alkyl halides with the appropriate quinoline (as potassium salt): 5-(or 7-)*methoxy-2-phenyl-4-ethylquinoline*, m. p. 52°; 6-iso*butoxy-2-phenyl-4-ethylquinoline*, m. p. 102°; 6-iso*amyloxy-2-phenyl-4-ethylquinoline*, m. p. 91°; 6-*allyloxy-2-phenyl-4-ethylquinoline*, m. p. 116° 6-*phenacyloxy-2-phenyl-4-ethylquinoline*, m. p. 136°.

The *hydrochlorides*, *sulphates*, *mercurichlorides*, *periodides*, and (in most cases) *nitrates*, *chromates*, and *ferrocyanides* of the above quinoline derivatives were prepared. R. J. W. Le Fèvre.

Cyclic *N*-hydroxy-compounds and *N*-oxides. G. Heller (J. pr. Chem., 1929, [ii], **121**, 269—272).—Whereas *N*-hydroxyindoles are readily obtained (cf. Reissert, A., 1909, i, 51), attempts to obtain *N*-hydroxyquinolines result in the production of *N*-oxides (cf. Meisenheimer and Stotz, A., 1926, 77; Heller, A., 1910, i, 558; 1928, 302). Thus, reduction of *o*-nitrocinnamoylformic acid with ferrous sulphate and ammonia gives quinoline-*N*-oxide-2-carboxylic acid, whilst *o*-nitrobenzylidenemalonic acid yields 2-hydroxyquinoline-*N*-oxide-2-carboxylic acid, and not "*N*-hydroxycarbostyrilcarboxylic acid" [1-hydroxy-2-keto-1 : 2-dihydroquinoline-3-carboxylic acid] (Heller and Wunderlich, A., 1915, i, 301). H. Burton.

Synthesis of dehydrogenated *iso*quinoline derivatives. E. Späth and N. Polgar (Monatsh., 1929, **51**, 190—204).—Substituted acyl-β-phenylethylamides are dehydrated with phosphoric oxide in boiling toluene into 3 : 4-dihydro*iso*quinoline derivatives, which are dehydrogenated with palladium-black at 150—180°. Thus, *formhomoveratrylamide*, m. p. 40—42°, affords 6 : 7-dimethoxy-3 : 4-dihydro-*iso*quinoline [picrate, m. p. 201—203° (lit. 206—208°)], which is dehydrogenated either with palladised asbestos at 205—210° or, better, with palladium-black at 182—185° to 6 : 7-dimethoxy*iso*quinoline, m. p. 93—94° (cf. Goldschmidt, A., 1887, 163). *Acethomoveratrylamide*, m. p. 94—95°, yields 6 : 7-dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline [picrate, m. p. 210—212° (lit. 205°)], dehydrogenated to 6 : 7-*dimethoxy-1-methyl*isoquinoline, m. p. 111—112° [*picrate*, m. p. (vac.) 247—249° (decomp.)]. Oxidation of this with potassium permanganate gives *m*-hemipinic acid, establishing the constitution. From *propion-*, m. p. 60—61°, and *butyr-homoveratrylamide*, m. p. 54—55°, there were obtained 6 : 7-*dimethoxy-1-ethyl-* [*picrate*, m. p. (vac.) 195—196°], and 6 : 7-*dimethoxy-1-propyl-3 : 4-dihydro*iso*quinoline* [*picrate*, m. p. (vac.) 180—181°], respectively, These are dehydrogenated to 6 : 7-*dimethoxy-1-ethyl-*, m. p. 75—76° (*picrate*, m. p. 213—214°), and 6 : 7-*dimethoxy-1-propyl-*iso*quinoline*, m. p. 83—84° [*picrate*, m. p. (vac.) 186—187°]. Similarly, *form-*, m. p. 62—63°, *acet-*, m. p. 105—106°, *propion-*, and *butyr-homopiperonylamides* give 6 : 7-*methylenedioxy-*, m. p. 92—94° [*picrate*, m. p. (vac.) 230—232°], 6 : 7-*methylenedioxy-1-methyl-*, m. p. 89—91° [*picrate*, m. p. (vac.), 242—244° (decomp.)], 6 : 7-*methylenedioxy-1-ethyl-*, m. p. 75—76° [*picrate*, m. p. (vac.) 205—206° (decomp.)], and 6 : 7-*methylenedioxy-1-propyl-3 : 4-dihydro*iso*quinoline*, m. p. 78—79° [*picrate*, m. p. (vac.) 183—184°], respectively. Dehydrogenation of these derivatives gives 6 : 7-*methylenedioxy-*, m. p. 127—128° [*picrate*, m. p. (vac.) 240—241°], 6 : 7-*methylenedioxy-1-methyl-*, m. p. 159—160° [*picrate*, m. p. (vac.) 263—264° (decomp.)], 6 : 7-*methylenedioxy-1-ethyl-*, m. p. 96—97° (*picrate*, m. p. 235—236°), and 6 : 7-*methylenedioxy-1-propyl-*iso*quinoline*, m. p. 88—89° (*picrate*, m. p. 210—211°), respectively. H. Burton.

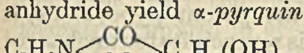
Doebner reaction. VII. Synthesis with β-aminoanthracene. R. Ciusa and L. Musajo (Gazzetta, 1929, **59**, 70—74).—The Doebner reaction (cf. A., 1928, 629) with β-aminoanthracene, benzaldehyde, and pyruvic acid gives 3-*phenyl-β-anthraquinoline-1-carboxylic acid*, m. p. 285° (*sodium* salt, $+5H_2O$; *methyl* ester, m. p. 204°), which when heated above its m. p. yields 3-*phenyl-β-anthraquinoline*, m. p. 236°. E. W. Wignall.

Doebner reaction. VIII. 3-Phenyl-β-anthraquinonequinoline-1-carboxylic acid. L. Musajo (Gazzetta, 1929, **59**, 74—78).—β-Aminoanthraquinone does not undergo the Doebner reaction as does β-aminoanthracene (preceding abstract). The product which would be expected from the reaction can, however, be obtained by oxidation of the product from 3-aminoquinoline, and is 3-*phenyl-β-anthraquinoline-7 : 12-quinone-1-carboxylic acid*, decomp. 250°; *potassium* ($+1\cdot5H_2O$), *sodium*, and *silver* salts are prepared, and a *nitrate*, $C_{24}H_{13}N,2HNO_3$. When the acid is heated, 3-*phenyl-β-anthraquinoline-7 : 12-quinone*, m. p. 284°, is formed, which on reduction furnishes blue compounds. E. W. Wignall.

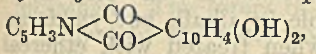
Acridine compounds. K. Matsumura (J. Amer. Chem. Soc., 1929, **51**, 816—820).—The preparation of 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane, 2 : 4 : 2′ : 4′-tetranitrobenzophenone, and 2 : 8-diaminoacridone is described. The last is hydrolysed by 40% sulphuric acid at 195° to 2 : 8-*dihydroxyacridone*, m. p. above 320°, which cannot, however, be obtained by diazotisation and warming. 2 : 8-*Dimethoxyacridone*, m. p. above 320°, is converted by phosphorus pentachloride into 5-*chloro-2 : 8-dimethoxyacridine*, m. p. 184° (*hydrochloride*), which yields with ammonia and copper acetate in absolute alcohol at 140° 5-*amino-2 : 8-dimethoxyacridine*, m. p. 268° [*hydrochloride*, m. p. 315°

(decomp.); *picrate*, m. p. 285°, decomp. from 273°]. 5-*Acetamido*-2 : 8-*dimethoxyacridine*, m. p. 277—278°, readily affords 5-*acetamido*-2 : 8-*dimethoxy*-10-*methylacridinium iodide*, m. p. 310° (decomp.), p-*toluenesulphonate*, m. p. 280°, softening from 255°, and *chloride*, m. p. above 315°. The yields are good throughout. H. E. F. NOTTON.

5 : 8-Dihydroxy-α-anthrapyridinequinone. H. RAUDNITZ [with G. LAUBE] (Ber., 1929, 62, [*B*], 509—513).—Addition of phthalic anhydride and quinol to a mixture of sodium and aluminium chlorides at 200° gives the aluminium compound of quinizarin, from which quinizarin, m. p. 198°, is obtained by successive treatment with excess of potassium hydroxide and dilute sulphuric acid. When similarly treated at 200° and finally at 230—240°, phthalic anhydride and 1 : 4-dihydroxynaphthalene afford 1 : 4-*dihydroxy*-2 : 3-*benzanthraquinone*, m. p. 349°. Analogously at 180—200°, quinol and quinolinic anhydride yield α-*pyrquinizarin*,



$C_5H_3N<\substack{CO\\CO}>C_6H_2(OH)_2$, m. p. 237° (*sodium* salt), whilst quinolinic anhydride and 1 : 4-dihydroxynaphthalene give 6 : 7-*benz*-α-*pyrquinizarin* [5 : 8-*dihydroxy*-6 : 7-*benz*-α-*anthrapyridinequinone*],



$C_5H_3N<\substack{CO\\CO}>C_{10}H_4(OH)_2$, m. p. 363° (*sodium* salt).

H. WREN.

Quinazolines. II. Synthesis of 6-ethoxy-3-*p*-ethoxyphenyl-3 : 4-dihydroquinazoline. G. MAFFEI (Gazzetta, 1929, 59, 3—9).—When 2-*nitro*-5-*ethoxybenzaldehyde*, m. p. 62°, obtained by the action of ethyl iodide and potassium hydroxide on the hydroxy-compound, is heated with *p*-phenetidine, it gives N-(2-*nitro*-5-*ethoxybenzylidene*)-p-*phenetidine*, m. p. 92°; this when reduced by sodium sulphide in alcohol gives the 2-*amino*-compound, m. p. 156°, and, on further reduction by sodium in alcohol, N-(2-*amino*-5-*ethoxybenzyl*)-p-*phenetidine*, m. p. 81°. This is converted by heating with formic acid into 6-ethoxy-3-*p*-ethoxyphenyl-3 : 4-dihydro-1 : 3-quinazoline (cf. A., 1928, 775), which can be reduced by sodium and amyl alcohol to the 1 : 2 : 3 : 4-*tetrahydro*-compound, m. p. 144°. 2-Nitro-5-ethoxybenzaldehyde forms an *oxime*, m. p. 125°, which is reduced by ammonium sulphide to 2-*amino*-5-*ethoxybenzaldoxime*, m. p. 132°, and this by sodium amalgam in alcohol to 2-*amino*-5-*ethoxybenzylamine*, forming a *dihydrochloride*, decomp. from 200°, completely at 235—237°; when this hydrochloride is heated with sodium formate and formic acid, 6-*ethoxy*-3 : 4-*dihydro*-1 : 3-*quinazoline*, m. p. 125—127°, is produced.

The physiological properties of ethoxy-*p*-ethoxyphenyldihydroquinazoline are lost when the C:N double linking is reduced, when either of the ethoxyl groups is absent, or is replaced by a methyl group, and when the ethoxyphenyl group is absent. Alkylation of the imine group modifies the anæsthetic property. E. W. WIGNALL.

Pyrimidines. CIV. *iso*Uracil and derivatives; methods of synthesis. T. B. JOHNSON and W. T. CALDWELL (J. Amer. Chem. Soc., 1929, 51, 873—880).—Further attempts have been made (cf. A., 1907, i, 559) to establish the constitution of orotic acid by synthesis. Ethyl αγ-diethoxyacetoacetate and thiocarbamide in alcohol in presence of sodium ethoxide give 6-*hydroxy*-2-*thiol*-5-*ethoxy*-4-*ethoxymethylpyrimidine*, m. p. 178°, which is desulphurised by chloroacetic acid to 2 : 6-*dihydroxy*-5-*ethoxy*-4-*ethoxymethylpyrimidine*, m. p. 168°, hydrolysed by hydrochloric acid at 120—140° to 2 : 4 : 5 : 6-*tetrahydroxypyrimidine*, m. p. above 320°. The crude product from ethyl ethoxyacetate and sodium yields with ethyl-ψ-thiocarbamide hydrobromide 6-*hydroxy*-5-*ethoxy*-2-*ethylthiol*-4-*ethoxymethylpyrimidine*, m. p. 123°, converted by phosphorus pentachloride into 6-*chloro*-5-*ethoxy*-2-*ethylthiol*-4-*ethoxymethylpyrimidine*, b.p. 165—166°/9—10 mm. This is reduced by zinc dust in aqueous alcohol to 5-*ethoxy*-2-*ethylthiol*-4-*ethoxymethylpyrimidine*, m. p. 167°, hydrolysed by hydrochloric acid to ethyl mercaptan and (?) 2-*hydroxy*-5-*ethoxy*-4-*ethoxymethylpyrimidine*, decomp. 281—284°. The sodio-derivative of ethyl ethoxyoxaloacetate yields with ethyl-ψ-thiocarbamide hydrobromide a little *ethyl* 6-*hydroxy*-5-*ethoxy*-2-*ethylthiolpyrimidine*-4-*carboxylate*, m. p. 82—83°, from which are prepared oily *ethyl* 6-*chloro*-5-*ethoxy*-2-*ethylthiolpyrimidine*-4-*carboxylate* and *ethyl* 5-*ethoxy*-2-*ethylthiolpyrimidine*-4-*carboxylate*, m. p. 55—56°. This is hydrolysed at 120° by hydrochloric acid to (?) 2 : 5-*dihydroxypyrimidine*-4-*carboxylic acid* (*iso*uracilcarboxylic acid), m. p. 259° (decomp.), which may be identical with orotic acid. Ethyl ethoxyoxaloacetate, ethyl-ψ-thiocarbamide, and aqueous sodium hydroxide give *ethyl* 2 : 6-*dihydroxy*-5-*ethoxypyrimidine*-4-*carboxylate*, m. p. 230°, and the corresponding free *acid*, m. p. 260°, hydrolysed by hydrochloric acid at 160—165° to 2 : 5 : 6-trihydroxypyrimidine (*iso*barbituric acid). H. E. F. NOTTON.

Indole derivatives of mixed function. Q. MINGOIA (Gazzetta, 1929, 59, 105—115).—When 3-chloroacetyl-2-methylindole (Salway, J.C.S., 1913, **103**, 354) is hydrolysed by alcoholic potassium hydroxide, the keto-alcohol 3-*hydroxyacetyl*-2-*methylindole*, m. p. 196° (N-*silver* derivative; *diacetyl* derivative, m. p. 101°), is produced. This is oxidised by alkaline potassium permanganate to 2-methylindolyl-3-glyoxylic acid (cf. Oddo and Albanese, A., 1928, 185). Similarly, when the chloro-compound is treated with alcoholic potassium cyanide, 3-*cyanoacetyl*-2-*methylindole*, m. p. 249°, is produced, which hydrolyses to 3-*acetyl*-2-*methylindole*-ω-*carboxylic acid*, m. p. 199—200°, of which *mercuric* and other *salts* are prepared.

The chloro-compound reacts with concentrated aqueous ammonia in a sealed tube at 90—95° to form 3-*aminoacetyl*-2-*methylindole*, m. p. 240° (decomp.) (*picrate*, m. p. 207—210°; *hydrochloride*), which gives precipitates with various alkaloid reagents. No reaction is observed between the chloro-compound and glycine or alanine in absolute alcoholic solution.

E. W. WIGNALL.

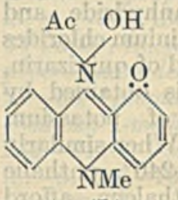
Identification and separation of organic bases with the aid of glyoxalinedicarboxylic acid. H. PAULY and E. LUDWIG (Arch. Pharm., 1929, 267, 143—144).—Polemical. A reply to criticisms by Tamamushi (J. Pharm. Soc. Japan, 1928, 48, 107) of the authors' process (A., 1922, i, 953). S. COFFEY.

Dyes derived from acenaphthenequinone. Acenaphthiminazoles and acenaphthoxazoles.

A. C. Sircar and N. C. Guha-Ray (J. Indian Chem. Soc., 1929, 6, 93—98).—Acenaphthenequinone reacts with aldehydes and ammonia, sometimes yielding the corresponding iminazoles and sometimes the oxazoles (cf. J.C.S., 1923, **123**, 1559; A., 1925, i, 980). Thus when acenaphthenequinone and *m*-nitrobenzaldehyde dissolved in boiling amyl alcohol are treated with dry ammonia 2-m-*nitrophenylacenaphthiminazole*, darkens at 220° without melting, is formed. The following substituted *acenaphthiminazoles* were prepared similarly: 2-*phenyl*-, not melted at 290°; 2-o-*hydroxyphenyl*-, m. p. 268° (decomp.); 2-p-*anisyl*-, m. p. 268°; 2-4′-*hydroxy*-3′-*methoxyphenyl*-, m. p. 263°; 2-p-*chlorophenyl*-, m. p. 264° after shrinking at 242°; 6 : 7-*dinitro*-2-5′-*bromo*-2′-*hydroxyphenyl*-, not melted at 290°; 6 : 7-*dinitro*-2-p-*anisyl*-; 6-*nitro*-2-o-*hydroxyphenyl*-, and 6-*nitro*-2-4′-*hydroxy*-3′-*methoxyphenyl*-. The following substituted *acenaphthoxazoles* were obtained from the requisite aldehyde by the above method: 2-o-*nitrophenyl*-, not melted at 290° after shrinking at 263°; 2-p-*dimethylaminophenyl*-; 6 : 7-*dinitro*-2-m-*nitrophenyl*-; 6 : 7-*dinitro*-2-3′ : 5′-*dihydroxyphenyl*-; 2-3′ : 5′-*dihydroxyphenyl*-, and 6-*nitro*-2-3′ : 5′-*dihydroxyphenyl*-. The above compounds are coloured, and dye wool with shades varying from orange-yellow to chocolate-brown, from an acid bath. The freshly-precipitated substance (by the addition of water to a solution in concentrated sulphuric acid) is best used for dyeing. H. Burton.

Quinoxaline synthesis ; derivatives of 2 : 3-dimethylquinoxaline. S. T. Henderson (J.C.S., 1929, 466—468).—The reaction between *o*-phenylenediamine and diacetylmonoxime yields the *dimethylquinoxaline* derivative of *dimethylglyoxime* (I) (m. p. 182°, completely liquid at 215°) as an intermediate (cf. Gabriel and Sonn, A., 1908, i, 60), decomposed by acid or alkali to 2 : 3-dimethylquinoxaline. I is also formed from dimethylglyoxime and dimethylquinoxaline. Bromination of I or of dimethylquinoxaline in alcoholic solution gives 5 : 6 : 7 : 8-*tetrabromo*-2 : 3-*dimethylquinoxaline*, m. p. 234° (decomp.); the latter, together with a *substance*, $C_6H_8N_2Br_2$, m. p. 150°, is formed by bromination in chloroform. 1 : 2-Naphthylenediamine and diacetylmonoxime give an intermediate *substance*, $C_{32}H_{33}O_2N_6$ (m. p. 123°, liquid at 200°), which yielded the base, m. p. 101—102°, with alkali. A. I. Vogel.

Pyocyanine, the blue colouring matter of *Bacillus pyocyaneus*. IV. Constitution and synthesis of pyocyanine. F. Wrede and E. Strack (Z. physiol. Chem., 1929 **181**, 58—76; cf. A., 1928, 1285).—Analysis of pyocyanine and its crystalline *perchlorate* and *chloroplatinate* definitely proves it to have the composition $C_{26}H_{24}O_2N_4$ and to contain two methylimino-groups. Although stable to acids, pyocyanine readily undergoes fission with 2% sodium hydroxide in the presence of oxygen (3 atoms), giving an 80% yield of 1-hydroxyphenazine (acetyl, m. p. 123°, and *benzoyl*, m. p. 176°, derivatives). With alkali and hydrogen peroxide, formic acid is also produced. Acylation of pyocyanine with acyl chlorides and pyridine yields only 1-hydroxyphenazine derivatives, but acetic anhydride and sulphuric acid yield an *acetyl* derivative (I) (*picrate*; *chloroaurate*; *chloroplatinate*), which is immediately decomposed by alkali, yielding pyocyanine. By catalytic reduction with platinum-black and hydrogen, pyocyanine takes up four atoms of hydrogen, yielding the oily 5-*methyl*-1-*hydroxydihydrophenazine* (II; R=H), which is immediately reoxidised by atmospheric oxygen to pyocyanine, and, like the acetyl derivative (I), has only half the mol. wt. of pyocyanine. The reduction product, unlike the parent pyocyanine, is readily soluble in alkali and is reprecipitated unchanged by acidification of the alkaline solution, and yields a *benzoyl* derivative, m. p. 150°, and a *picrate*. Similar reduction of the acetyl derivative, I, yields 1-*hydroxy*-9-*acetyl*-4-*methyldihydrophenazine* (II; R=Ac), m. p. 125—127°, which is soluble in alkali, but yields an alkali-insoluble product when treated with ethereal diazomethane and is converted by the action of concentrated hydrochloric acid and subsequent basification into pyocyanine. These reactions are explained assuming pyocyanine to be III (cf. the structure of methylprasindone; Kehrmann and Cherpillod, A., 1925, i, 302), the synthesis of which is effected by the action of sodium hydroxide on the *methosulphate* of 1-hydroxyphenazine, the latter being obtained by the action of methyl sulphate in a sealed tube at 100°. Benzoylation of dihydrophenazine, obtained by the catalytic reduction of phenazine with platinum and hydrogen in pyridine, yields *dibenzoyldihydrophenazine*, m. p. 206°. Similarly, 1-methoxydihydrophenazine, obtained by reduction of 1-methoxyphenazine, yields an *acetyl* derivative, m. p. 175°. The dihydrophenazine derivatives are unstable in the presence of atmospheric oxygen. J. W. Baker.



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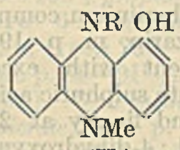

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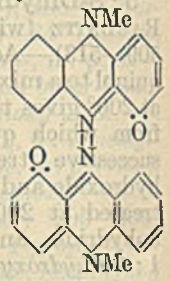


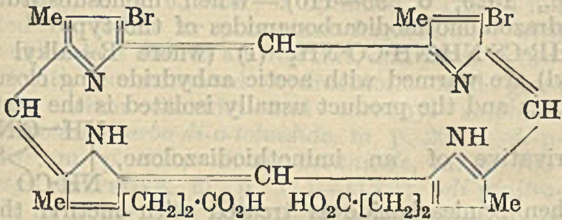
(III.)

Uric acid. T. Shimoda (J. Biochem. Japan, 1928, 9, 117—185).—Uric acid (20 mg.) dissolved in 0·01*N*-sodium hydroxide (100 c.c.) is completely destroyed in 14 days at 18—20°; on oxidation, it yielded carbamide and ammonia, but not allantoin. The change is accelerated by oxygen but delayed by nitrogen; it does not take place, even at 37°, in neutral or acid solutions. It is accelerated by rise of temperature, and the velocity is inversely proportional to the uric acid concentration. Uric acid appeared to be protected from destruction by adsorption. The destruction is markedly promoted by liver extracts (optimal p_H 7·3), and slightly stimulated by duodenal contents. Uric acid administered orally is excreted by rabbits chiefly in the urine as urea and ammonia; the destruction of intravenously injected (rabbit) uric acid proceeds in the liver alone.

Chemical Abstracts.

Natural porphyrins. XXIII. Bromoporphyrin I and its conversion into deuteropor-

phyrin. H. Fischer and G. Hummel (Z. physiol. Chem., 1929, **181**, 107—129).—The identity of bromoporphyrin I (Fischer and Kotter, A., 1927, 1094) and dibromodeuteroporphyrin (Fischer and Linder, *ibid.*, 262) is rendered highly probable on the basis of the following evidence. By oxidation of bromoporphyrin I it is impossible to isolate with certainty more than 1 mol. of bromocitraconimide (but cf. Fischer and Zeile, this vol., 333). Reduction of bromoporphyrin I by Busch's method (A., 1925, ii, 823) yields deuteroporphyrin (with "chlorin" as a by-product) the identity being established spectroscopically and by direct comparison of the methyl esters. Similarly, debromination of bromoporphyrin I, by fusion with succinic acid, yields deuteroporphyrin and no by-products. Crystallographic data (by Steinmetz) show that the esters of the bromination product of tetramethylhæmatoporphyrin (A) and dibromodeuteroporphyrin (B) (from deuterohæmin) are identical, but the ester from the product (C) of bromination of hæmatoporphyrin in acetic acid is different from the ester (D) obtained by the removal of iron from the bromination product of the iron salt of tetramethylhæmatoporphyrin. When (D) is seeded with (A), however, crystals identical with those of (B) are obtained. The esters of the tetrabromo-compounds obtained by the action of phosphorus pentabromide on bromoporphyrin I, dibromodeuteroporphyrin, deuteroporphyrin, and deuterohæmin are identical. The phyllin obtained by the action of magnesium methyl bromide on bromoporphyrin I is a ditertiary alcohol, the composition of which agrees better with the dibromodeuteroporphyrin structure (I) (*i.e.*, Br in place of a $\cdot CH(OH)\cdot CH_2Br$ side-chain). Protoporphyrin is converted by methyl-alcoholic potassium hydroxide and pyridine at 200° into mesoporphyrin. By the action of 1% methyl-alcoholic sulphuric acid hæmin is converted into the iron salt of tetramethylhæmatoporphyrin. Fusion of the latter with three parts of resorcinol at 190—200° yields deuterohæmin identical with Schumm's pyroporphyrin (A., 1928, 1263).



(I.)

J. W. Baker.

Formation of hæmin derivatives by pyrogenic reactions. III. Decarboxylation of porphyrins and iron porphyratins; preparation of ætiopyroporphyrin and ætiomesoporphyrin. Preparation of ætioporphyrins from hæmin by the paraffin–phenol–oxalic acid method. Conversion of hæmin into pyroporphyrin. Degradation of Nencki's hæmatoporphyrin, hæmateric acid, uroporphyrin, dimethoxyhæmin dimethyl ester, and hæmatohæmin by resorcinol, and of hæmin by hydroxyquinol. Bacteriochemical production of copratoporphyrin. O. Schumm (Z. physiol. Chem., 1929, **181**, 141—175).—Decarboxylation of porphyrins is effected by mixing the finely-powdered porphyrin with liquid paraffin and heating at 340—360° for several hours. The resulting mixture is diluted with ether, extracted with 5—12% hydrochloric acid or 20% sulphuric acid, the acid extract made alkaline with potassium hydroxide, and the precipitated ætioporphyrin purified by crystallisation from a mixture of chloroform and methyl alcohol. With hæmin and other iron porphyratins the product obtained as above is freed from iron either by treatment with hydrazine hydrate in acetic acid or by heating with a mixture of phenol and oxalic acid. Thus, pyroporphyrin (A., 1928, 1263) affords 5—10% of ætiopyroporphyrin, also obtained from pyratin (pyroporphyrin iron salt) by either of the above methods. When a dilute solution of ætiopyroporphyrin in hydrochloric acid is made alkaline with potassium hydroxide a colloidal solution of the porphyrin is first obtained.

Mesoporphyrin yields about 10% of ætiomesoporphyrin, also formed from mesohæmin after subsequent removal of iron. Hæmateric acid (protoporphyrin) gives a mixture of products one of which is probably ætiopyroporphyrin (spectrum). Uro- and copro-porphyrins afford the corresponding ætioporphyrins, both of which are very similar (spectrum) to ætiomesoporphyrin. When hæmin is heated with liquid paraffin at 350—360° and then freed from iron by the phenol–oxalic acid method 4% of ætiomesoporphyrin results, but when the decarboxylation is carried out in boiling paraffin (385°) ætiopyroporphyrin appears to be obtained, showing that the decomposition at the higher temperature follows a different course. Decarboxylation of hæmin by heating with anthracene and subsequent removal of iron by the phenol–oxalic acid method gives a product which appears to be identical (spectrum) with ætiomesoporphyrin. Decomposition of Nencki's hæmatoporphyrin at 340° yields an ætioporphyrin with the same spectrum as ætiomesoporphyrin, but in boiling paraffin a mixture is again obtained. One of the products is probably ætiopyroporphyrin.

When hæmin is dissolved in hot phenol and treated with potassium hydrogen sulphate, and the resulting product precipitated from an alkaline solution with acetic acid and finally purified by Willstätter and Mieg's method (cf. A., 1913, i, 1214), pyroporphyrin results. Subsequent esterification with methyl alcohol affords 20% of the dimethyl ester, m. p. 223°. Degradation of Nencki's hæmatoporphyrin or its iron salt (hæmatohæmin) and hæmateric acid with boiling resorcinol and subsequent esterification of the reaction product with methyl alcohol also yields pyroporphyrin dimethyl ester. When dimethoxyhæmin dimethyl ester is heated with resorcinol at 190—195°, the resulting product freed from iron with hydrazine hydrate and acetic acid, and then esterified with methyl alcohol, pyroporphyrin dimethyl ester is also produced. In boiling resorcinol crude pyroporphyrin results. Mesoporphyrin is unaffected by treatment with resorcinol, whilst uroporphyrin affords coproporphyrin dimethyl ester, m. p. 249°. In this last case prolonged heating causes profound decomposition. Hæmin is decomposed by heating with hydroxyquinol to pyratin, which after removal of iron by oxalic acid and subsequent esterification affords pyroporphyrin dimethyl ester.

Copratoporphyrin iron salt results from the spontaneous putrefaction of blood at 37°. No appreciable amount of any other iron porphyratin is produced at the same time. The copratin, crude or purified, is freed from iron by the hydrazine hydrate–acetic acid method, and purified from the admixed saproporphyrin-*D* by extracting the latter with chloroform in presence of hydrochloric acid. Copratoporphyrin and pyroporphyrin appear to be identical.

H. Burton.

Derivatives of 4 : 5-naphth-1 : 2-thiazole. R. Stollé and W. Badstübner (J. pr. Chem., 1929, [ii], **121**, 266—268).—Treatment of 2 : 3-diketo-5 : 6-benzo-2 : 3-dihydrothionaphthen, m. p. 171° (lit. 168°) [obtained by fission of the corresponding *p*-dimethylamino-2-anil, m. p. 195° (Pummerer, A., 1910, i, 510), with 15% hydrochloric acid], with hydrogen peroxide and aqueous ammonia gives ββ-*naphth*iso*thiazole*-2-*carboxylamide*, m. p. 208°. This is hydrolysed by 2*N*-sodium hydroxide to the corresponding *acid*, m. p. 197° (decomp.). Similar treatment of 2 : 3-diketo-4 : 5-benzo-2 : 3-dihydrothionaphthen affords as the main product a *substance*, decomp. 295°, together with small amounts of a compound, decomp. 221°, and β-*naphth*iso*thiazole*-1-*carboxylamide*, m. p. 225° with darkening.

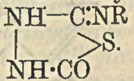
H. Burton.

Aminobenzthiazoles. XI. Synthesis of 5 : 4′-disubstituted 1-anilinobenzthiazoles from nuclear-substituted thiocarbanilides. G. M. Dyson, R. F. Hunter, and C. Soyka (J.C.S., 1929, 458—466).—*s*-Di-*p*-bromophenylthiocarbamide was converted by bromine in chloroform into the *hydropentabromide*, m. p. 170° (decomp.), which yielded 5 : 4′-*dibromo*-1-*anilinobenzthiazole* (I), m. p. 221° [*acetyl* derivative, m. p. 205—206°; *hydrobromide*, m. p. 250° (decomp.)], with sulphur dioxide; I was also obtained by condensing 1-chloro-5-bromobenzthiazole, m. p. 89° (from *p*-bromophenylthiocarbimide and phosphorus pentachloride at 170—180°), with *p*-bromoaniline and also by decomposing the bromo-additive products from 4′-*bromo*-1-*anilinobenzthiazole*, m. p. 214—215° [from phenyl-*p*-bromophenylthiocarbamide through the *hydrotribromide*, m. p. 148° (decomp.)], and from 1-anilinobenzthiazole (*hexabromide*, m. p. 140°) with hydroxylic solvents. Hugershoff's dibromoanilinobenzthiazole (A., 1903, i, 865) consists mainly of 5 : 4′-dibromo-1-anilinobenzthiazole. Bromination of I in chloroform gave a *hexabromide*, m. p. 254°; the latter yielded an impure *tetrabromo*-substitution derivative when treated with hot alcohol. *s*-Di-*p*-chlorophenylthiocarbamide and bromine yielded a *hydrotribromide*, m. p. 165—167° (decomp.), converted by reduction into 5 : 4′-*dichloro*-1-*anilinobenzthiazole*, m. p. 224° [*acetyl* derivative, m. p. 186—187°; *hydrobromide*, m. p. 217°; *hexabromide*, m. p. 253° (decomp.)].

s-Phenyl-*p*-chlorophenylthiocarbamide and bromine furnished an additive *compound*, m. p. 130° (decomp.), converted into 4-*chloro*-1-*anilinobenzthiazole*, m. p. 196° (also prepared by condensing 1-chlorobenzthiazole and *p*-chloroaniline). *s*-Di-*p*-iodophenylthiocarbamide similarly yielded additive *compounds* with bromine, m. p. 185° and 211°, respectively, both reduced to 5 : 4′-*di-iodo*-1-*anilinobenzthiazole* (also obtained from 1-anilinobenzthiazole and iodine monochloride in acetic acid), m. p. 193° (decomp.). Similarly, *s*-di-*p*-fluorophenylthiocarbamide afforded a *hydrotribromide*, m. p. 150—152° (decomp.), and 5 : 4′-*difluoro*-1-*anilinobenzthiazole*, m. p. 227—228°. 5 : 4′-*Dinitro*-1-*anilinobenzthiazole*, m. p. 280°, obtained from *s*-di-*p*-nitrophenylthiocarbamide, was identical with the compound obtained by the nitration of 1-anilinobenzthiazole. 5 : 4′-*Dicyano*-1-*anilinobenzthiazole*, m. p. 222° [prepared from dicyanodiphenylthiocarbamide through the bromo-additive *compound*, m. p. 159—160° (decomp.)], when hydrolysed with 25% hydrochloric acid gave 1-*anilinobenzthiazole*-5 : 4′-*dicarboxylic acid* (unmelted at 290°). *s*-Di-*p*-carbethoxyphenylthiocarbamide and bromine yielded a *hydropentabromide*, m. p. 110° (decomp.), converted into *ethyl* 1-*anilinobenzthiazole*-5 : 4′-*dicarboxylate*, m. p. 190—192°. A *dibromo*-5 : 4′-*dimethoxy*-1-*anilinobenzthiazole*, m. p. 240°, was obtained from *s*-di-*p*-anisylthiocarbamide through a *bromide*, m. p. 137° (decomp.). Acetyldiphenylthiocarbamide and bromine furnished a *hydrobromide*, m. p. 167° (decomp.), identical with that prepared from bromine, hydrogen bromide, and 1-acetanilidobenzthiazole; the last-named yielded a hexabromo-additive *compound*, m. p. 163° (decomp.), with bromine.

A. I. Vogel.

Ring closure of hydrazomonothiodicarbonamides with acetic anhydride. Formation of iminothiodiazolones and iminothioltriazoles. P. C. Guha and T. K. Chakraborty (J. Indian Chem. Soc., 1929, 6, 99—110).—When monosubstituted hydrazomonothiodicarbonamides of the type $NHR\cdot CS\cdot NH\cdot NH\cdot CO\cdot NH_2$ (I) (where R=alkyl or aryl) are warmed with acetic anhydride ring closure occurs and the product usually isolated is the acetyl derivative of an iminothiodiazolone,



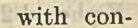
$$\begin{matrix} NH-C{:}NR \\ | \qquad\quad >S. \\ NH\cdot CO \end{matrix}$$

When semicarbazide is treated with methyl thiocarbimide, *hydrazomonothiodicarbonmethylamide* (I, R=Me), m. p. 212°, results. This is converted by warm acetic anhydride into the 4-*acetyl* derivative, m. p. 197°, of 2-*methylimino*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 232°. *Hydrazomonothiodicarbonallylamide*, m. p. 202°, yields the 3-*acetyl* derivative, m. p. 171°, of 2-*allylimino*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 210°, together with a small amount of a *substance*, m. p. 269°. Hydrazomonothiodicarbonphenylamide gives the 3-*acetyl*, m. p. 173°, and 3 : 4-*diacetyl* derivative, m. p. 213°, of 2-*anilo*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 206°. If the reaction is carried out in presence of sodium acetate at water-bath temperature, only the monoacetyl derivative results. *Hydrazomonothiodicarbon*-o-*tolylamide*, m. p. 201° (decomp), furnishes the 3-*acetyl* derivative, m. p. 183°, of 2-o-*tolylimino*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 210°, whilst *hydrazomonothiodicarbon*-p-*tolylamide*, m. p. 192°, affords a small amount of 2-p-*tolylimino*-5-*thiol*-3-*acetyl*-2 : 3-*dihydro*-1 : 3 : 4-*triazole*, m. p. 154°, together with 2-p-*tolylimino*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 247°. *Hydrazo-*

monothiodicarbonxylylamide, m. p. 200° (decomp.), yields the 3-*acetyl* derivative, m. p. 218°, of 2-*xylylimino-5-keto-2* : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 232°. *Hydrazomonothiodicarbon* - β - *naphthylamide*, m. p. 210° (decomp.), is decomposed by warm acetic anhydride into β-naphthylthiocarbimide. When the hydrazomonothiocarbonphenylamide, $NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NHPh$, is warmed with acetic anhydride the 3-*acetyl*, m. p. 275°, and 3 : 4-*diacetyl* derivatives, m. p. 160°, of 2-imino-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole are obtained in poor yields. When boiling acetic anhydride is used, the products formed are diphenylcarbamide, acetanilide, a small amount of acetimidothiodiazolone (Guha, A., 1923, i, 607), and two *substances*, m. p. 92—93° and 115°, respectively. The corresponding *hydrazomonothiodicarbon-α-naphthylamide*, m. p. ~~213°, gives~~ di-α-naphthylcarbamide. *s* - Diphenylhydrazomonothiodicarbonamide affords 2-*phenylimino-5-thiol*-1-*phenyl*-2 : 3-*dihydro*-1 : 3 : 4-*triazole*, m. p. 208°, by elimination of water; with boiling acetic anhydride the main product is diphenylcarbamide. Hydrazodicarbonamide is unaffected by boiling with acetic anhydride, but at 200° decomposition into carbon dioxide and *s*-diacetylhydrazine occurs.

H. Burton.

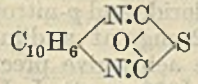
Formation of heterocyclic compounds from diethyl xanthoformate. P. C. Guha and D. N. Dutta (J. Indian Chem. Soc., 1929, 6, 65—82).—Diethyl xanthoformate (Holmberg, A., 1905, i, 323) reacts with primary aromatic amines, forming thiomonothiodicarbodiarylamides, $NHR{\cdot}CS{\cdot}S{\cdot}CO{\cdot}NHR$ (I). Thus, with aniline *thiomonothiodicarbodianilide* (I, R=Ph), m. p. 63—64°, is obtained. This is not affected by iodine or potassium ferricyanide, with ferric chloride it affords an *iron* salt, and when hydrolysed with concentrated hydrochloric acid gives aniline, carbon dioxide, and carbonyl sulphide. *Thiomonothiodicarbo-di-*o*-toluidide*, m. p. 205°; *-di-*p*-toluidide*, m. p. 85°; *-di-*m*-nitroanilide*, m. p. 105° (*diacetyl* derivative, m. p. 114—115°); *-di-*p*-nitroanilide*, m. p. 95—96°, and *-di-*β*-naphthylamide*, m. p. 90°, are prepared similarly. Phenylhydrazine and diethyl xanthoformate give the *compound*, $NHPh{\cdot}NH{\cdot}CS{\cdot}OEt$ (II), m. p. 73—74°, with evolution of carbon dioxide and hydrogen sulphide, presumably thus: $OEt{\cdot}CS{\cdot}S{\cdot}CO_2Et+NHPh{\cdot}NH_2 \longrightarrow SH{\cdot}CO_2Et+II$, the intermediate ethyl thiocarbonate being decomposed. When II is heated with concentrated hydrochloric acid the *compound*

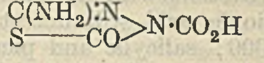


$\begin{matrix}\text{CO}-\text{S}\\ \text{NH}\cdot\text{S}\end{matrix}\!>\!\text{CO}$

(III), m. p. 135°, results, whilst with 20% potassium hydroxide solution phenylhydrazine and potassium thiocarbonate are produced. With *p*-nitrophenylhydrazine and *as*-phenylethylhydrazine the *substances* $NH{\cdot}C_6H_4(NO_2){\cdot}NH{\cdot}CS{\cdot}OEt$ and $NPhEt{\cdot}NH{\cdot}CS{\cdot}OEt$, m. p. 108—109° and 242°, respectively, are obtained. These are converted by boiling concentrated hydrochloric acid into III. When *o*-phenylenediamine is treated with diethyl xanthoformate in alcoholic solution, *o-phenylenecarbamide* (IV), m. p. 306°, its N-*monothiocarbethoxyl* derivative (V), m. p. 122—123°, and N-*carbethoxy-*o*-phenylenethiocarbamide* (VI), m. p. 93—94°, are produced. Both V and VI are formed by internal condensation of the intermediate monothiodiurethane, whilst IV results from V by loss of carbonyl sulphide. Hydrolysis of VI with 20% potassium hydroxide solution gives *o*-phenylenethiocarbamide, m. p. 301—302° (lit. 298° and 292—293°), whilst similar hydrolysis of V yields IV. With 1 : 2-naphthylenediamine hydrogen sulphide is evolved and the *compound* VII, m. p. 250°, results. When the initial reaction mixture is heated, a *substance* (VII, with $N{\cdot}C_{10}H_6{\cdot}NH{\cdot}CO_2Et$ for S), m. p. 304°, is formed,

(VII.)





$\begin{matrix}\text{C(NH}_2\text{):N}\\ \text{S}\text{———}\text{CO}\end{matrix}\!>\!\text{N}\cdot\text{CO}_2\text{H}$

(IX.)

presumably by the action of carbethoxynaphthylenediamine on VII. With ethylenediamine in alcoholic solution ethylenethiocarbamide (VIII), m. p. 193—194° (*hydrochloride*, m. p. 304—305°), and *ethylenemonothiodiurethane*, m. p. 110—111°, are produced. This last compound is converted by boiling concentrated hydrochloric acid or warm 20% potassium hydroxide solution into VIII.

Diethyl xanthoformate reacts with semicarbazide, yielding *ethyl semicarbazidomonothiocarboxylate*, m. p. 161°, but with thiosemicarbazide *ethyl thiosemicarbazidocarboxylate*, m. p. 155—156°, results. This last substance is converted by hot concentrated hydrochloric acid into the *compound* IX, m. p. 189° after shrinking at 179° (*benzylidene* derivative, m. p. 158—159°). With 4-phenyl-, 4-*p*-tolyl-, and 4-β-naphthyl-thiosemicarbazides, *ethyl 4-phenyl-*, m. p. 149—150°, *ethyl* 4-p-*tolyl-*, m. p. 183—184,° and *ethyl* 4-β-*naphthyl-thiosemicarbazidocarboxylate*, m. p. 287—288°, are obtained. Benzidine and tolidine furnish the corresponding monothiodiurethanes, m. p. 211—212° and 125—126°, respectively.

H. Burton.

Polarised light and cocaine decomposition. H. T. Dailey and H. C. Benedict (J. Amer. Chem. Soc., 1929, 51, 808—816).—Repetition of the work of Macht and Anderson (A., 1927, 991) indicates that polarised light, produced by reflexion, or by means of an "Ahrens" prism, is no more effective than ordinary light in causing the decomposition of aqueous cocaine hydrochloride. Reproducible results for the strength of this anæsthetic cannot be obtained by the goldfish method (Adams and others, A., 1926, 834) if each fish is used more than once, or if traces of tin are present in the water.

H. E. F. Notton.

Copper sulphate–sodium hydroxide test for ephedrine and related compounds. K. K. Chen (J. Amer. Pharm. Assoc., 1929, 18, 110—116).—The copper sulphate–sodium hydroxide test has been made with six optical isomerides of ephedrine and twenty-one related aromatic amines. Under the conditions described, the three ephedrines can be distinguished from the three ψ-ephedrines and the optical isomerides of ephedrine and ψ-ephedrine from the corresponding racemates. Twenty-two of the amines showed positive results and these all contained a hydroxyl group attached to the carbon atom in the β-position to the nitrogen. No amines with an α-hydroxyl group were examined, but its absence from the side-chain negated the result. Thirteen amines yielded copper complexes soluble in ether and those formed by sixteen amines were insoluble in alkaline solution.

E. H. Sharples.

Microchemical reactions of cinchonine. M. Wagenaar (Pharm. Weekblad, 1929, **66**, 250—253).—The most sensitive reagent is gentisic acid (2 : 5-dihydroxybenzoic acid), which will detect 1 mg. at a dilution of 1 : 200. The ferrocyanide and ferricyanide tests will detect 5 mg. at a dilution of 1 : 1000.
S. I. Levy.

Microchemical reactions of cinchonidine. M. Wagenaar (Pharm. Weekblad, 1929, **66**, 261—264).—The reactions with platinic chloride and *p*-nitrophenylpropionic acid will detect 2 mg. at a dilution of 1 : 2000; salicylic and picric acids give precipitates with 2 mg. at dilutions of 1 : 1000. S. I. Levy.

Microchemical reactions of quinine. M. Wagenaar (Pharm. Weekblad, 1929, **66**, 177—182).—The reactions suitable for microchemical examination are described, and directions given for securing the best results. The more sensitive tests will detect 2—5 mg. in a concentration of 1 : 1000.
S. I. Levy.

Microchemical reactions of quinidine. M. Wagenaar (Pharm. Weekblad, 1929, **66**, 197—200).—The reactions suitable for micro-detection of the alkaloid are described. Those with trihydroxybenzoic acid and gold chloride will detect 2 mg. at a concentration of 1 in 2000. S. I. Levy.

Reactions of morphine. L. Ekkert (Pharm. Zentr., 1929, **70**, 165—167).—About 0·01 g. of the hydrochloride of morphine, ethylmorphine, codeine, heroin, peronin, "paracodeine," *apo*morphine, narcotine, or "narcophin" is scattered into a porcelain dish and a few drops of an absolute-alcoholic solution of anisaldehyde are added. On the addition of a few drops of concentrated sulphuric acid the liquid immediately develops a colour which changes on careful warming; thirty-nine reactions of the above alkaloids with varying concentrations of reagents are given and also the behaviour with other alkaloids. The reaction enables morphine to be distinguished from ethylmorphine and codeine and all three from other opium alkaloids. E. H. Sharples.

Action of ammonia on halogenated arsines. V. Ipatiev, G. Razubaiev, and W. Stromski (Ber., 1929, **62**, [*B*], 598—604).—Halogenated arsines react smoothly with dry ammonia in anhydrous benzene with quantitative precipitation of ammonium chloride and formation of the corresponding amino- or imino-arsine. In these compounds the nitrogen is only feebly attached to the arsenic atom, hydrolysis being readily effected by moisture. The following compounds are described : *aminodiphenylarsine*, m. p. 53°, converted by moist air into diphenylarsenic oxide and oxidised by hydrogen peroxide to diphenylarsinic acid; *iminomethylarsine*, $\mathrm{(AsMe{:}NH)_6}$, m. p. 205°; *iminophenylarsine*, $\mathrm{(AsPh{:}NH)_4}$, m. p. about 265°.
H. Wren.

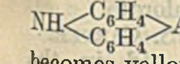
Tryparsamide type. I. Resolution of N-phenylalanine-4-arsinic acid and of its amide. C. S. Gibson, J. D. A. Johnson, and B. Levin (J.C.S., 1929, 479—488; cf. Fourneau and Nicolitch, this vol., 202).—α-Bromopropionic acid and sodium *p*-aminophenylarsinate give dl-N-*phenylalanine-4-arsinic acid* (I), m. p. 207—210° (decomp.) [*ethyl* ester, m. p. 175—177° (decomp.); *methyl* ester (II), m. p. 181° (decomp.)]. *dl-N*-Phenylalanineamide-4-arsinic acid when prepared from the methyl ester II and aqueous ammonia (*d* 0·88) has m. p. 233—240° (decomp.) and m. p. 244° (decomp.) from α-bromopropionamide and sodium *p*-aminophenylarsinate. I was resolved, as the sodium salt, with brucine in aqueous solution into the *d*-acid, the *brucine* salt of which crystallises first, m. p. 220—221° (decomp.), [α] of the sodium salt +56·40°, and into the *l*-acid, m. p. 220—221° (decomp.), [α] of the disodium salt −55·94°. Ethyl *d*-acid has m. p. 275—276° (decomp.), [α] +127·9° in ethyl alcohol, ([α] of the sodium salt +103·0°), and the *ethyl* *N*-phenylalanine-4-arsinic *l*-acid, m. p. 275—276° (decomp.) ([α] −125·8°, in ethyl alcohol; sodium salt [α] −102·8°). The corresponding methyl esters have : *d*-, m. p. 277—278° (decomp.), [sodium salt, [α] +117·6°], *l*-, m. p. 277—278° (decomp.) [sodium salt, [α] −116·3°]; these were separately converted into the optically active amide-acids with aqueous ammonia (*d* 0·88), the amide acid from the *d*-ester (III) had m. p. 242—243° (decomp.) [sodium salt [α] −13·3°] : amide acid from the *l*-methyl ester (IV) had m. p. 242—243° (decomp.) [sodium salt [α] +13·9°]. The rotatory powers of the sodium salts of the acids derived from III and IV were +26·6° and −29·5°, respectively. *dl*-Phenylalanineamide-4-arsinic acid was resolved, as the sodium salt, with quinine into the *l*-amide acid, m. p. 247° (decomp.) [sodium salt, [α] −17·88°], the *quinine* salt of which [α] −123·8°, separated first, and into the *d*-amide acid, m. p. 247° (decomp.) [sodium salt, [α] +16·5°]. I could not be reduced with sodium hyposulphite. All the above rotations are $[\alpha]_{5461}^{20}$ in water except where alcohol is stated. A. I. Vogel.

Diphenylaminearsinic acids. I. Derivatives of diphenylamine-4-arsinic acid. H. J. Barber (J.C.S., 1929, 471—476),—Sodium 4-chloro-3-nitrophenylarsinate condenses in aqueous solution with aromatic amines at 95° to form 2-nitrodiphenylamine-4-arsinic acids. Thus aniline gives 2-*nitrodiphenylamine-4-arsinic acid* [2-*aminodiphenylamine-4-arsinic acid* (I), with ferrous hydroxide at 80—90°, m. p. 170—175° (*monohydrochloride*); 2-*acetamidodiphenylamine-4-arsinic acid* yielding N-*phenyl-2-methylbenziminazole*-5(6)-*arsinic acid* with hydrochloric acid; acetone and I give a *substance* which is either 2-*iso*propylideneaminodiphenylamine-4-arsinic acid or *N*-phenyl-2 : 2-dimethyl-2 : 3-dihydrobenziminazole, whilst nitrous acid and I yield N-*phenylbenztriazole-5-arsinic acid*] : *p*-aminophenol gives 2-*nitro-4′-hydroxydiphenylamine-4-arsinic acid* (2-*amino-4′-hydroxydiphenylamine-4-arsinic acid*; 4′-*hydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole-5-arsinic acid*) : *p*-aminoacetanilide gives 2-*nitro-4′-acetamidodiphenylamine-4-arsinic acid* [2-*amino-4′-acetamidodiphenylamine-4-arsinic acid*; 2 : 4′-*diacetamidodiphenylamine-4-arsinic acid*; 2 : 4′-*diaminodiphenylamine-4-arsinic acid*] : 4-amino-2-acetamidophenol gives 2-*nitro-3′-acetamido-4′-hydroxydiphenylamine-4-arsinic acid* (2-*amino*-compound), and anthranilic acid gives 2′-*carboxy-2-nitrodiphenylamine-4-arsinic acid.* Nitration of 2-acetamidodiphenylamine-4-arsinic acid gives a 2′ : 4′(?)-*dinitro-2-acetamidodiphenylamine-4-arsinic acid.* 3 : 3′-*Diamino-4 : 4′-dianilinoarseno-*

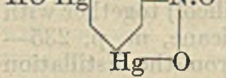
benzene and 3 : 3′-*diamino*-4 : 4′-*di*-p-*acetamidoanilinoarsenobenzene* were obtained by the reduction of the corresponding arsinic acid with sodium hyposulphite. *o*- and *p*-Nitroanilines do not condense with 4-chloro-3-nitrophenylarsinic acid. A: I. VOGEL.

Behaviour of salvarsan and neosalvarsan towards aldehydes. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 297—298).—Both compounds give colour reactions with aldehydes; the most suitable aldehyde reactions for distinguishing them are those with *o*- and *p*-nitrobenzaldehyde and with furfuraldehyde. S. I. LEVY.

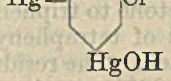
Organic compounds of arsenic. VI. Electrolytic reduction of some arylarsinic acids. K. MATSUYIMA and H. NAKATA (Mem. Coll. Sci. Kyōtō, 1929, A, 12, 63—68).—Electrolytic reduction by the method previously described (A., 1927, 785), but using platinum, nickel, or copper cathodes, did not affect the arsinic acid group. 3-Nitro-4-hydroxyphenylarsinic acid yielded 3 : 3′-*azoxy*-4 : 4′-*dihydroxyphenyl*-1 : 1′-*diarsinic acid*, darkening at 210°, decomp. without melting, and 3-amino-4-hydroxyphenylarsinic acid, with only traces of the arsine. 3-Nitro-4-aminophenylarsinic acid, with a copper cathode, yielded 3 : 4-diaminophenylarsinic acid, darkening at 140°, m. p. 158° (decomp.). Further investigation of the effect of varying concentrations of hydrochloric acid was made (cf. *loc. cit.*). With a mercury cathode, *p*-aminophenylarsinic acid yielded *p*-aminophenylarsine hydrochloride (cf. Fichter and Elkind, A., 1916, i, 444) or 4 : 4′-diaminoarsenobenzene dihydrochloride according as the concentration of acid was below or above 8*N*. *p*-Hydroxyphenylarsinic acid yielded *p*-hydroxyphenylarsine or 4 : 4′-dihydroxyarsenobenzene at concentrations below or above 4*N*, respectively. R. K. CALLOW.

Meriquinonoid derivatives of 9 : 10-dihydrophenarsazine. I. G. RAZUBAIEV (Ber., 1929, 62, [*B*], 605—616).—10-Chloro(bromo)-9 : 10-dihydrophenarsazine, its oxide, methoxy-derivative, sulphate, and acetate and tridihydrophenarsazineamine give pale yellow solutions in cold formic acid which become intensely red when warmed; the colour disappears rapidly when the solutions are cooled or shaken, but recurs when they are warmed. The *formate*,  $NH{<}{}^{C_6H_4}_{C_6H_4}{>}As{\cdot}O{\cdot}CHO$, which darkens at 100° and becomes yellow, without melting, at about 150°, does not give a red coloration when heated in acetone or alcohol; if formic acid is added to such solutions the red colour is developed and is accompanied by evolution of carbon dioxide, the liberated hydrogen being used to reduce the arsazine to a coloured derivative. Similar production of the coloured compound is effected by use of spongy platinum, particularly in the presence of hydrogen, stannous chloride, or zinc and acetic acid. With the latter reagents, a colourless solution is ultimately obtained which becomes intensely coloured when exposed to air or treated with a solution of unreduced 10-chloro-9 : 10-dihydrophenarsazine. The observations are compatible with a quinhydrone structure for the coloured compound, but this constitution does not explain the unsaturated nature (addition of oxygen, chlorine, bromine, iodine, nitric oxide, nitrogen dioxide) or the considerable electrical conductivity of the solutions which indicate the presence of a radical. The meriquinonoid structure of a half-free radical,  $[C_6H_4{<}{}^{AsH}_{NH-}{>}C_6H_4]X$, is preferred to a simpler radical constitution, since the absorption spectrum of the substance exhibits a broad band commencing in the green instead of the lines expected from a radical and the compound behaves as a salt. Coloured solutions are obtained in formic and acetic acids, alcohol, acetone, and phenol from which the colour is not extracted by benzene or other hydrocarbons. Further, the electrical conductivity of 10-chloro-9 : 10-dihydrophenarsazine in formic acid is found to have undergone marked increase after the solution has been warmed. Decolorisation of solutions of the semi-radical by halogen is effected by exactly 1 atom per molecule. The product of the direct addition could not be isolated, theoretical yields of 10-halogeno-9 : 10-dihydrophenarsazine being obtained regardless of the particular acid residue originally united with the nucleus (Cl, Br, O·CHO, HSO_3). In dihydrophenarsazine the hydrogen atom is very loosely united to arsenic, so that it is readily removed by oxygen or sulphur, 0·5 atom of which is required for each molecule of original compound. The regenerated arsazine can again be reduced by warm formic acid and the operation repeated. The action of the oxygen is, however, so vigorous that a part of the formic acid is converted into water and carbon dioxide and a portion of the compound is destroyed, so that ultimately the colour does not recur when the solution is warmed. H. WREN.

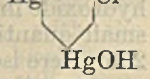
Introduction of mercury into benzene derivatives. B. KALINOWSKI (Rocz. Chem., 1929, 9, 132—148).—The following compounds have been prepared: *Bromobenzene*-2 : 4-*dimercuriacetate*, m. p. 223°, *bromobenzene*-2 : 4-*dimercurichloride*, m. p. 232°, 1 : 4 *dibromobenzenedimercuriacetate*, o-*nitrophenol*-4 : 6-*dimercuriacetate*, decomp. 250°, which on hydrolysis yields the *anhydride* of o-*nitrophenol*-4 : 6-*dimercurihydroxide* (I), p-*nitrophenol*-2 : 6-*dimercuriacetate*, decomp. 260°, an *anhydride*, decomp. 220°, analogous to the preceding, m-*nitrophenol*-2-*mercuriacetate*, m. p. 210°, the corresponding *anhydride*, decomp. 200°, 2 : 4-*dinitrophenol*-6-*mercuriacetate*, decomp. 250°, the corresponding *anhydride*, 2 : 6-*dinitrophenol*-4-*mercuriacetate*, decomp. 260°, o-*chlorophenol*-4 : 6-*dimercuriacetate*, decomp. 250°, the corresponding *anhydride* (II or III), decomp. 200°, m-*chlorophenoldimercuriacetate*, decomp. 270°, the corresponding *anhydride*, decomp. 230°, p-*chlorophenol*-2 : 6-*dimercuriacetate*, decomp. 270°, the corresponding *anhydride*, the structure of which is analogous to that of the *o*-chlorophenyl derivative (II and III). The introduction of mercury into the benzene ring



(I.)



(II.)



(III.)

follows the same rules as that of other substituents. Mercury is most readily introduced into phenols, and least so into chlorobenzenes. Substituted mercury is readily displaced by halogens, yielding the corresponding halogen derivative. R. TRUSZKOWSKI.

Mercurated halogen compounds of sulphonfluorescein. F. DUNNING and L. H. FARINHOLT (J. Amer. Chem. Soc., 1929, **51**, 804—808).—Sulphonfluorescein yields with chloramine-*T* and acid *dichlorosulphonfluorescein.* Dibromo- and di-iodo-sulphonfluoresceins were prepared by Orndorff's method (A., 1924, i, 1190). Tetrahalogeno-*o*-sulphobenzoic anhydrides and resorcinol at 110—120° give dark brown *tetrachloro-*, *tetrabromo-*, and *tetra-iodo-sulphonfluoresceins*, the first two being obtained in poor yield. *Mono-* and *di-hydroxymercuri*-derivatives have been prepared from the above seven sulphonfluoresceins by refluxing their *disodium* salts with mercuric acetate, or their *monosodium* salts with mercuric oxide, in aqueous solution. A method is given for the determination of mercury in presence of iodine. H. E. F. NOTTON.

Mercuration of anthraquinonedicarboxylic acids. F. C. WHITMORE and F. L. CARNAHAN (J. Amer. Chem. Soc., 1929, **51**, 856—862).—*Mercuric anthraquinone-*1 : 2-*dicarboxylate* is converted at 235° into *anhydro-*1-*hydroxymercurianthraquinone-*2-*carboxylic acid*, which gives with boiling hydrochloric acid anthraquinone-2-carboxylic acid and with the appropriate halogen 1-iodo- and 1-*bromo-*, m. p. 267—268°, -anthraquinone-2-carboxylic acids. Its sodium salt gives with hydrochloric acid 1-*chloromercurianthraquinone-*2-*carboxylic acid. Mercuric anthraquinone-*2 : 3-*dicarboxylate* passes at 210—215° into *anhydro-*2-*hydroxymercurianthraquinone-*3-*carboxylic acid*, from which anthraquinone-2-carboxylic acid, 3-*bromo-*, 3-*iodo-*, m. p. 289—290°, and 3-*chloromercuri-anthraquinone-*2-*carboxylic acids* were obtained. H. E. F. NOTTON.

Organic derivatives of silicon. XXXVIII. Formation of tri- and tetra-phenylsilicane and complex synthetical products from octaphenyl*cyclo*silicotetrane. F. S. KIPPING and A. G. MURRAY (J.C.S., 1929, 360—367).—Dry distillation of octaphenyl*cyclo*silicotetrane in an atmosphere of nitrogen gave a liquid distillate from which triphenylsilicane (decomposed by a 5% solution of potassium hydroxide in acetone to triphenylsilicol) together with small quantities of tetraphenylsilicane, m. p. 235—236°, were isolated. The residue from the distillation contains about 20% Si; its exact nature was not discovered. Ladenburg's triphenylsilicane (A., 1907, i, 668), m. p. 200—203°, is probably impure tetraphenylsilicane. Triphenylsilicane reacts with bromine in chloroform to give hydrogen bromide and triphenylsilicyl bromide, m. p. 114—118° (decomposed by aqueous acetone to triphenylsilicol). Distillation of octaphenylsilicotetrane under conditions similar to the above gave tetraphenylsilicane and an unidentified oil. Attempts to reduce triphenylsilicyl bromide were unsuccessful. A. I. VOGEL.

Soluble proteins of rabbit muscle. W. S. RITCHIE and A. G. HOGAN (J. Amer. Chem. Soc., 1929, **51**, 880—886).—The proteins extracted from fresh rabbit muscle by 10% sodium chloride (p_H 6) at about 0° have been separated into albumin, globulin, and non-protein fractions. At p_H 6, the globulin precipitated (*a*) by saturation with sodium chloride, (*b*) by dialysis, using finally a dialysate of known p_H (4—7), and applying a correction for the globulin precipitable from the filtrate by sodium chloride, (*c*) by exposure for 6—8 hrs. to ultraviolet light, or (*d*) by heat-coagulation at 49°, amounts in each case to 50—60% of the total protein. Similar amounts of more gelatinous material are precipitated by methods (*a*) and (*c*) at p_H 7—8, but in more acid solutions part of the albumin is also precipitated. Albumin and non-protein nitrogen (about 20% of each) are determined in the filtrates. The globulin/albumin ratio is much higher than that previously reported for muscle tissue (cf. Saxl, A., 1906, ii, 872). The p_H of the extract is increased by the precipitation of the globulin in (*b*) and (*c*), but only slightly altered in (*a*). H. E. F. NOTTON.

Hydrolysis of proteins by ammonia under pressure. W. S. SADIKOV (Biochem. Z., 1929, **205**, 360—368).—Hydrolysis of proteins by ammonium carbonate under pressure at 150—180° gives after 1—6 hrs. principally peptones, and only after 24 hrs. are crystalline products obtainable. Caseinogen gave a peptone suitable for bacteriological purposes and on further hydrolysis a number of products which were crystallisable or separable by precipitation. Leucine was obtained and nine other preparations for which empirical formulæ are suggested.

J. H. BIRKINSHAW.

Determination of small amounts of free or organically combined carbon in inorganic substances. D. STROHAL (Arhiv Hemiju, 1929, **3**, 63—72).—The method is essentially that for the determination of carbon in organic elementary analysis, but proportionately larger quantities of material are used and the material is intimately mixed with the copper oxide. The last traces of carbon dioxide are driven from the combustion tube by heating the inlet end, which contains a mixture of manganese dioxide and potassium chlorate.

J. S. CARTER.

Visual conductivity-titration as aid in the determination of phenols. Alkalimetric titration of protocatechualdehyde and its mono-alkyl ethers. O. PFUNDT and C. JUNGE (Ber., 1929, **62**, [*B*], 515—518).—The usual conductivity apparatus is modified by the substitution of a rectifier and galvanometer for the telephone and the graph is obtained by plotting galvanometer reading against volume of added alkali hydroxide; the end-point is indicated by a sharp inflexion in the graph. Protocatechualdehyde can thus be accurately titrated as a monohydric phenol by sodium hydroxide or, preferably, lithium hydroxide. Accurate results are also recorded for vanillin, *iso*vanillin, bourbonal, and *iso*bourbonal. H. WREN.

Biochemistry.

Respiration of non-medullated nerves. O. Meyerhof and W. Schulz (Biochem. Z., 1929, **206**, 158—170).—The respiration and anaërobic lactic acid formation of resting non-medullated nerves of *Maja squinado* is ten times that of the medullated nerves of the frog. Electrical stimulation causes increased oxygen consumption. With 15 min. periods of stimulation and 5—10 min. intervals the increased respiration lasts 1—2 hrs. The oxygen consumption at a stimulation frequency of 10 per sec. is twenty times as great as for frog's ischiadic nerve.

J. H. Birkinshaw.

Regulation of respiration. XXV. Lactic acid metabolism of brain. D. A. McGinty (Amer. J. Physiol., 1929, **88**, 312—325).—With normal oxidations in brain-tissue, lactic acid is absorbed from the arterial blood and utilised by the brain-cells. With impaired oxidations there occurs an excessive production of lactic acid in the brain cells with an outward diffusion into the blood-stream.

B. A. Eagles.

Regulation of respiration. XXVI. Carbon dioxide content of brain. E. E. Kleinschmidt (Amer. J. Physiol., 1929, **88**, 251—258).—A method of preparing brain-tissue for the determination of total carbon dioxide is described. Hæmorrhage or injection of sodium cyanide produced a decrease in the carbon dioxide content of the brain. The buffering capacity of the normal brain is less than that of the normal blood. B. A. Eagles.

Alkaline reserve and oxygen capacity of arterial and of venous blood. L. M. Hurxthal, A. V. Bock, J. H. Talbott, and D. B. Dill (J. Biol. Chem., 1929, **81**, 681—685).—In normal individuals at rest and in most pathological cases the carbon dioxide capacity tends to be higher in arterial than in venous blood, the reverse being true during exercise. The differences are, however, small, and are still less marked in the case of the oxygen capacity.

C. R. Harington.

Benzidine reaction [for blood]. F. Schwarz (Deut. Z. ges. gerichtl. Med., 1928, **12**, 216—218; Chem. Zentr., 1928, ii, 1701).—Glacial acetic acid (1 c.c.) is added to 50 c.c. of 2% alcoholic benzidine solution, and to 1 c.c. of this solution is then added 1 drop of quinoline or *iso*quinoline. With this reagent blood can be detected at a dilution of 1 in 4×10^6.

A. A. Eldridge.

Determination of diffusion constants and calculation of the radius and weight of the hæmoglobin molecule. J. H. Northrop and M. L. Anson (J. Gen. Physiol., 1929, **12**, 543—554).—An apparatus is described for determining the rate of diffusion of a dissolved substance through a thin membrane and the coefficient of diffusion, D, is then known if the constant of the apparatus has been found by standardising it with a simple substance of known diffusion coefficient. The mol. wt. of the substance is then found from Einstein's equation $D=RT/6\pi Nr\eta$ (N=Avogadro's constant, η=viscosity of liquid, r=radius of molecule). Suitable membranes may be prepared from discs of porous Jena glass and of alundum. The mol. wt. of carbon monoxide-hæmoglobin as determined by this method is 68,000±1000. W. O. Kermack.

Hæmoglobin concentration of blood of marine fishes. F. G. Hall and I. E. Gray (J. Biol. Chem., 1929, **81**, 589—594).—Figures are given for the hæmoglobin concentration of the blood of fifteen species of teleostean fishes and of two elasmobranchs. The concentration runs parallel with the activity of habit of the various species. C. R. Harington.

Pyridine-hæmochromogen. A. E. Mirsky and M. L. Anson (J. Gen. Physiol., 1929, **12**, 581—586).—It is considered that the conclusion of Hill (A., 1927, 65) that pyridine-hæmochromogen contains two pyridine groups to one reduced hæm group is not justified, as the equilibrium between pyridine and reduced hæm is complicated to an unknown extent by the precipitation of reduced hæm and by the aggregation of pyridine-hæmochromogen.

W. O. Kermack.

Phosphoaminolipins and sterols of blood-serum and -plasma. A. Mâchebœuf (Bull. Soc. Chim. biol., 1929, **11**, 268—293).—A more detailed account of work already published (this vol., 206).

Specificity and changes of the proteins of blood-plasma. H. Bierry (Compt. rend., 1929, **188**, 740—742).—Intravenous injection of mannose in dogs results in a rise in the protein-sugar of the plasma. Intraperitoneal injection of Witte's peptone in rabbits causes first a fall and then a rise in the free sugar and the protein-sugar of the plasma. It is suggested that in these cases, and indeed generally, the constitution of the proteins is changed under the influence of changes in the metabolism.

G. A. C. Gough.

Gravimetric and nephelometric determination of protein fractions of blood. S. Rusznyák and J. Erdös (Biochem. Z., 1929, **206**, 482—484).—The results obtained by nephelometric determination of the protein fraction (cf. A., 1923, ii, 891) agree closely with those by the gravimetric method. C. C. N. Vass.

Blood-constituents. R. Kimura (Z. Immunitäts., 1928, **56**, 330—346; Chem. Zentr., 1928, ii, 1787).—Phosphatides were prepared from red blood-corpuscles by extraction with ether, distillation, precipitation with acetone, and fractional extraction with alcohol. Immunisation of rabbits with the residues of the extracts produced no hæmolysin, whilst the extracted blood-corpuscles were still active. By fractional salting-out with ammonium sulphate were obtained albumin and globulin fractions in which the sulphur, carbon, hydrogen, total nitrogen, amide-, humin-, monoamino-, lysine-, histidine-, and arginine-nitrogen were determined. The chemical differences are reflected serologically, and even among different globulin fractions differences can be observed. The sulphur content of the albumin is generally higher; globulin fractions with more sulphur are more easily salted out. A. E. Eldridge.

Dialysis of small volumes of serum under sterile conditions. C. I. B. Voge (Biochem. J.

1929, 23, 185—187).—The serum is withdrawn by means of a sterile 1 c.c. pipette with a rubber teat. The pipette is then inserted into the dialysing sac and bound to it. The dialysing sac is placed in a vessel through which sterile water flows by gravity.
S. S. Zilva.

Ammonia content of and ammonia formation in blood. X. Origin of blood-ammonia. W. Mozołovski (Biochem. Z., 1929, 206, 150—157).—The ammonia formed in blood on keeping is not entirely accounted for by deamination of adenylic acid. The purine base content of the blood of various animals is related to the ammonia production. Adenine is present in blood chiefly as adenylic acid, which on deamination gives inosinic acid; the latter is hydrolysed, phosphoric acid being eliminated. (Cf. A., 1927, 369.) J. H. Birkinshaw.

Detection of potassium and sodium in the cytoplasm of red blood-corpuscles by micro-incineration. A. Policard and D. Pillet (Compt. rend. Soc. Biol., 1928, 99, 85—86; Chem. Zentr., 1928, ii, 1787).—The potassium and sodium are first converted into sulphates. A. A. Eldridge.

Mineral constituents of blood-platelets and white blood-corpuscles. G. Endres and L. Herget (Z. Biol., 1929, 88, 451—464).—Total solids, total inorganic content, and the concentration of the different cations and anions in the inorganic fraction of the red and white corpuscles, the platelets, and the plasma of horse blood have been studied. The platelets and the white cells appear to be closely related and with respect to their content of cations are generally intermediate between plasma and red cells. With the anions this is true only of the chlorine ion. Like the red cells, they possess a smaller concentration of sodium and calcium but a greater potassium content than the plasma; both the plasma and the red cells possess a hydrogen carbonate concentration greatly in excess of that of the white cells and the platelets and a much smaller inorganic phosphorus content. There is a marked, unbalanced excess of electropositive constituents in the constituents of the ash, 15%, 34%, 35%, and 40% in that from the plasma, white cells, platelets, and red cells, respectively. This is discussed.
F. C. Happold.

Micro-determination of blood-phosphate. A. E. Braunstein (Zhur. exp. Biol. Med., 1928, 9, 277—284).—In the molybdate method a reducing solution containing sodium sulphite and hydrogen sulphite and "eikonogen" (developer) is employed.
Chemical Abstracts.

Blood-sugar regulation in mammals. III. Effect of higher temperatures on blood-sugar. P. Weyl (Biochem. Z., 1929, 206, 485—502).—Rabbits kept at temperatures between 32° and 37° for 5—6 hrs. show a marked increase in blood-sugar usually after 5 min. which begins to decrease after 2—3 hrs. and then attains the initial value. At a subsequent external temperature of 9—12°, the animals show a transient hyperglycæmia. When the rabbits are kept for 1 hr. at 35—38° the same phenomena are observed, but the increase in the blood-sugar on the withdrawal of the animal to the lower temperatures is greater and lasts longer. With dogs only a slight change (±) in the blood-sugar was observed at 35—37° over long or short periods.
C. C. N. Vass.

Variations of capillary blood-sugar in normal young men during the 24 hrs.; effect of sleep and of mild exercise. H. C. Trimble and S. J. Maddock (J. Biol. Chem., 1929, 81, 595—611).—The capillary blood-sugar of normal young men varied from about 90—95 mg.-% during sleep at night to 140—150 mg.-% immediately following the midday meal; other normal subjects awake through the night had about 100 mg.-%, so that sleep *per se* has little effect. Mild exercise was also without significant effect on the blood-sugar. C. R. Harington.

Fermentation residue [of the blood]. Determination of blood-sugar. G. Fontès and L. Thivolle (Compt. rend. Soc. Biol., 1928, 98, 1218—1220; Chem. Zentr., 1928, ii, 1700).—Blood (10 c.c.) or oxalate-plasma is treated with 1 g. of yeast, the mixture being shaken for 30—60 min. at 20—40°. It is then deproteinised with tungstic acid and diluted to 50 c.c. The residual reducing substances (which average 0·3% of the carbohydrates originally present) are then determined on 4—5 c.c. of the filtrate by the molybdo-manganimetric method.
A. A. Eldridge.

Reducing power [blood-sugar] of filtrates from the blood of the rabbit. E. L. Scott [with L. B. Dotti] (Arch. Int. Med., 1929, 43, 393—412).—A statistical examination of 1625 observations on 215 rabbits gave a mean reducing power of 123 mg. per 100 c.c. of blood, with a mean deviation of 13 mg. The age, weight, or sex of the animals did not significantly effect their blood-sugar level. Observations made early in the laboratory experience of animals give a lower mean than the normal and a somewhat higher one after the animals have been subjected to many determinations. There is no evidence of seasonal or diurnal variation. A comparison of three series of observations taken from three separate rabbits and a similar number taken from many different animals does not reveal a marked difference in value. Injection of 1 c.c. of saline and subsequent test bleeding at short periods is accompanied by a slight but steady rise in the blood-sugar level. A short period of inanition causes a slight decrease in the reducing power of the rabbit's blood, and the variability in the results is decreased.
F. C. Happold.

Validity of determinations of "immediately reducing blood-sugars." I. Determination of blood-sugars. II. Total amount of fermentable sugar of the blood. III. Absence of influence of disulphides and thiol compounds on sugar determinations by the phosphomolybdic acid and potassium permanganate method. G. Fontès and L. Thivolle (Bull. Soc. Chim. biol., 1929, 11, 146—151, 152—158, 159—167).—I. A discussion of previously published work (A., 1928, 539, 786). The addition of yeast to plasma or to blood, stabilised with oxalic acid, results in complete elimination of the reducing sugars.

II. Deproteinisation of laked blood or of blood-plasma with tungstic acid affords a filtrate which contains only fermentable sugars; if mercuric nitrate or zinc hydroxide is used, a varying proportion of the sugar is found to be unfermentable. It is suggested that the two last-named reagents displace reducing, unfermentable substances from the proteins.

III. Although in some circumstances large amounts of sulphur compounds interfere in the determinations of sugars by the phosphomolybdic acid and potassium permanganate method (A., 1927, 690), the amounts present in blood exert no detectable influence.

G. A. C. Gough.

Fate of acetylcholine in the blood. IV. Dependence of acetylcholine decomposition on hydrogen-ion concentration. F. Plattner, O. Galehr, and Y. Kodera. **V. Influence of gum arabic and starch on the fission process.** Y. Kodera (Pflüger's Archiv, 1928, **219**, 678—693; Chem. Zentr., 1928, ii, 1680).—The fission of acetylcholine decreases with increasing hydrogen-ion concentration or by addition of starch or gum arabic. The catalytic effect of serum and blood-corpuscles is discussed. A. A. Eldridge.

Specific hæmolysis. I. Specific adsorption of hæmolysin and complement. II. Enzymes of guinea-pig serum. III. Lysinogen of erythrocytes. K. Horino (J. Biochem. Japan, 1928, **9**, 407—421, 423—433, 435—444).—I. Hæmolysin is not adsorbed by kaolin or infusorial earth in a phosphate mixture; at the acidity of a citrate buffer adsorption by kaolin is indicated, whilst it is complete by infusorial earth in a citrate–hydrochloric acid mixture. The adsorption is reversible. The complement is adsorbed by kaolin at slightly alkaline, and by infusorial earth at slightly acid, reaction; adsorption by kaolin is not reversible, and leaching of the infusorial earth adsorbate is incomplete. The complement is considered to consist of three portions, of which one is irreversibly adsorbed.

II. The enzymes of guinea-pig serum (protease, peptase, butyrase, lipase, lecithinase, amylase, and nuclease) are present only in the albumin fraction, but thrombin and the complement middle-piece are mutually replaceable, and both are inactivated when heated at 56° for 30 min.

III. Experiments with the red cells of goat's blood indicate that the erythrocyte fibrinogen-like substance which is precipitated when an aqueous extract of the cells is half-saturated with sodium chloride or treated with carbon dioxide is a lysinogen.

Chemical Abstracts.

Hæmolysis and glycolysis. K. Noshi (J. Biochem. Japan, 1928, **9**, 243—249).—An erythrocyte extract possesses hæmolytic power in a phosphate mixture, but no appreciable glycolytic activity in a citrate medium. Chemical Abstracts.

Inhibiting action of sucrose on taurocholate, saponin, and oleate hæmolysis. A. C. Roy and K. C. Sen (J. Indian Chem. Soc., 1929, **6**, 89—92).—A comparison of the times necessary for hæmolysis of sheep's red blood-corpuscles by sodium taurocholate, saponin, and potassium oleate, in presence of isotonic sodium chloride and sucrose solutions, shows that a considerable inhibition occurs in presence of the sugar (cf. Ponder and Yeager, A., 1928, 913). The time–dilution curves are normal in both cases. The order of hæmolytic power in both solutions is oleate>saponin>taurocholate. H. Burton.

Hæmolytic behaviour of mixtures of hæmolytes. K. C. Sen and N. N. Mitra (J. Indian Chem. Soc., 1929, **6**, 111—120).—Hæmolysis of sheep's erythrocytes by mixtures of saponin and sodium taurocholate, potassium oleate and sodium taurocholate, and saponin and potassium oleate has been studied. It is found that there is always an accelerating effect of one hæmolyte in presence of another, the total effect probably being additive. In all cases the time–dilution curves are normal. Hydrochloric acid exerts an accelerating effect on the hæmolysis by saponin and sodium taurocholate, but inhibits the action of potassium oleate. This inhibition is due to the liberation of oleic acid, which is a poor hæmolytic agent. The acceleration of potassium oleate hæmolysis by sodium hydroxide (this vol., 340) is probably due to the inhibition of hydrolysis of potassium oleate in low concentration. H. Burton.

Detection and determination of oxygen in the pulmonary and intestinal gases of cadavers. F. Dyrenfurth (Deut. Z. ges. gerichtl. Med., 1928, **12**, 23—29; Chem. Zentr., 1928, ii, 1701).—The tissue is boiled, the gas evolved is collected over concentrated potassium hydroxide solution, and its oxygen content is detected or determined by means of 10—20% pyrogallol solution. A. A. Eldridge.

Fœtus. I. Enzymes in the digestive tract. Trypsinogen in the pancreas. II. A peptone-splitting enzyme in the intestinal canal. III. Lipase in the stomach. T. Tachibana (J. Kinki gynæcol. Soc., 1927, **10**, Nos. 2, 6; 1928, **11**, No. 1; Chem. Zentr., 1928, ii, 1889—1890).—Trypsinogen was observed in the fœtal pancreas in the fourth month, a peptone-splitting enzyme (optimum p_H 7·8) in the intestinal mucous membrane in the third month, and a tributyrin-splitting enzyme in the mucous membrane of the stomach in the fourth month. A. A. Eldridge.

Coagulation of hen's egg-white by biological agents. E. Lagrangq (Compt. rend. Soc. Biol., 1928, **98**, 1527—1529; Chem. Zentr., 1928, ii, 1574—1575).—When kept for several days, sterile hen's egg-white yields grey masses of coagulated albumin. The egg-white, when diluted with 4 vols. of water and heated at 110—120° does not coagulate, a change in the structure of the molecule taking place. It is then not precipitated by addition of 1% sodium chloride, and only slightly by alcohol. Such egg-white has lost all anaphylactic properties towards similar or unheated egg-white. The heated egg-white is no longer resistant to microbic reactions or to trypsin, pepsin, etc. A. A. Eldridge.

Occurrence of methylguanidine in animal organism. II. Separation of methylguanidine from carnosine and creatinine. I. A. Smorodincev and A. N. Adova (Z. physiol. Chem., 1929, **181**, 77—82; cf. this vol., 342).—In an attempt to remove from meat extract substances hindering the crystallisation of methylguanidine picrate, the extract was treated with mercuric chloride and sodium acetate. An alcoholic extract was made from the precipitate and the carnosine and creatinine were removed by mercuric sulphate in sulphuric acid, and by alcoholic zinc chloride, respectively. Methylguanidine was then precipitated as the picrate.

J. H. Birkinshaw.

Guaninedeoxypentoside from thymus-nucleic acid. P. A. Levene and E. S. London (J. Biol. Chem., 1929, **81**, 711—712).—Thymus-nucleic acid was digested with intestinal juice; the solution was treated with 4 vols. of 95% alcohol and the filtrate concentrated. The precipitate which formed on keeping, after purification by the lead process, yielded a *substance*, $C_{10}H_{13}N_5O_4$, shrinking at 200° but not melting below 290°, $[\alpha]_D^{20}$ $-37 \cdot 5°$, which was rapidly hydrolysed by sulphuric acid to give guanine sulphate and a *deoxypentose*, m. p. 153° after softening at 83°.

C. R. Harington.

Glutathione and keratin. A. Giroud and H. Bulliard (Compt. rend. Soc. Biol., 1928, **98**, 500; Chem. Zentr., 1928, ii, 1783).—Glutathione is the parent of certain sulphur groups of keratin, and is present in significant quantity in the epidermis. It disappears as keratinisation proceeds.

A. A. Eldridge.

Histochemical demonstration of glutathione and its distribution in certain organs. P. Di Mattei and F. Dulzetto (Atti R. Accad. Lincei, 1928, [vi], 8, 317—320).—To detect glutathione, the organs, immediately after removal from the animal, are reduced to small fragments, immersed for at least 30 min. in 20% trichloroacetic acid solution, and cut into sections 4—5 μ thick by the freezing method. These are treated, on microscope slides, with fresh 5% sodium nitroprusside solution for 3—4 min., freed from excess of this solution by means of filter-paper, and exposed to ammonia vapour. An amaranth-red coloration, appearing immediately, reveals the location of the glutathione. The sections are rapidly cooled in ice or in a jet of carbon dioxide and examined microscopically at 5°. The distribution of glutathione in various organs is described.

T. H. Pope.

Amino-acids of flesh. III. Diamino-acid content of fish. J. L. Rosedale (Biochem. J., 1929, 23, 161—165).—The diamino-acid content of several tropical fish tissues has been determined by Van Slyke's method and in a few cases by a modification of Kossel's method. This value is higher in the muscles of fish than in similar mammalian tissues. This increase is mainly due to a higher histidine content. Incomplete hydrolysis leads to error in the Van Slyke analysis. Different tissues appear to require different lengths of time to ensure complete hydrolysis with 25% hydrochloric acid. In the separation of histidine and arginine as silver salts unless the mixture is kept slightly acid there is a danger of precipitating some of the arginine together with the histidine.

S. S. Zilva.

Distribution of arginase in fishes. A. Hunter (J. Biol. Chem., 1929, 81, 505—511).—The high content of arginase previously observed for the liver of the dogfish (A., 1925, i, 104) is found also in the livers of other elasmobranchs; on the other hand, in the *Holocephali* the liver is relatively poor in arginase, the highest concentration of the enzyme being found in the kidney, and a little in the pancreas. The presence of arginase in the cardiac tissue is not a universal characteristic of fishes; in the *Holocephali* the arginase content of the heart is low, and from the hearts of some *Teleostomi* the enzyme is absent.

C. R. Harington.

Creatine content of tissues of fishes. A. Hunter (J. Biol. Chem., 1929, **81**, 513—523).—Figures are given for the creatine content of the muscles of fishes of fifteen different species. Considerable differences were found between the various species, and smaller differences between individuals of the same species. In general, fish muscle contains more creatine than mammalian muscle; with fishes as with mammals, white muscle contains more creatine than red, and adult muscle more than fœtal.

C. R. Harington.

Lipins. VI. Lipins of the herring. B. Rewald (Biochem. Z., 1929, **206**, 275—281).—The lipin content (calculated on the basis that the phosphorus content of the pure lipin is 3·9%) of herring flesh, roe, milt, and liver has been found to be 3·561%, 13·883%, 10·295%, and approx. 12·6%, respectively, of the dry weights.

C. C. N. Vass.

Crystalline form of calcium carbonate in otoliths of *Gadus morrhua*. G. Lunde (Biochem. Z., 1929, **206**, 436—439).—Otoliths of *G. morrhua* contain 76·39% $CaCO_3$, 11·44% CaO, 11·49% H_2O, and organic matter. *X*-Ray analysis shows that the calcium carbonate is present as aragonite.

C. C. N. Vass.

Digestive enzymes of the oriental fruit moth. H. S. Swingle (Ann. Entomol. Soc. Amer., 1928, **21**, 469—475).—The p_H of various parts of the intestine of *Laspeyresia molesta* was determined colorimetrically. Invertase, lipase, trypsin, and erepsin, but not pepsin, cellulase, lactase, maltase, or amylase, were found. The adult moth contains only one digestive enzyme, invertase.

Chemical Abstracts.

Isoelectric point of muscle-protein and buffering power of muscle-juice. L. De Caro (Atti R. Accad. Lincei, 1929, [vi], 9, 87—92).—Bottazzi's myoprotein (myogen) (Arch. Sci. Biol., 1926, 8, 495) has an isoelectric point between p_H 6·0 and 6·9. The values found for the buffering power of the muscle-juice of *Emys*, *Scyllium*, and the electric organ of the torpedo, together with those previously found (Arch. Sci. Biol., 1928, **12**. 578) for the frog, toad, and dog, show that this power, measured by the ratio Δbase : Δp_H, exhibits two minima at about p_H 7·7 and 5·7, respectively. This power increases rapidly, from the former value towards the alkaline side, and from the latter value towards the acid side; in the intermediate zone it shows intermediate and varying values.

T. H. Pope.

Phosphocreatine. C. H. Fiske and Y. Subbarow (J. Biol. Chem., 1929, 81, 629—679).—Phosphocreatine (phosphagen of Eggleton and Eggleton, A., 1927, 271, 274, 990; cf. Fiske and Subbarow, A., 1927, 990) can be separated from a protein-free muscle extract by treatment of the latter with copper acetate at p_H 7·8 followed by extraction of the precipitate with 0·03N-sodium hydroxide; the copper is removed with sodium sulphide and the concentrated filtrate treated with barium hydroxide and alcohol; the precipitate is dissolved in water, excess of barium allowed to separate as carbonate, and the filtrate treated with alcohol, when the *barium hydrogen* salt of phosphocreatine crystallises. The yield by this method is not more than 5% of the labile phosphorus of the original extract. Better results are obtained as follows. Muscle is rapidly dissected, frozen in liquid air, pulverised, and extracted with 10 parts of ice-cooled 5% trichloroacetic acid; the filtered extract is neutralised and treated with calcium chloride solution saturated with calcium hydroxide, and to the filtrate are added 3 vols. of alcohol, all operations being conducted at 0°; the partly crystalline precipitate is purified by dissolving in a limited amount of water and reprecipitating with alcohol, the process being repeated four times, yielding the *calcium hydrogen* salt, $C_4H_8O_5N_3PCa,4H_2O$; the yield by this method is 70% of the labile phosphorus, and this is taken as evidence that the whole of the latter is indeed phosphocreatine, the remaining 30% being accounted for by unavoidable losses. Hydrolysis of this salt with boiling water yields the theoretical amount of creatine. On the basis of the analysis of the salt, the structure proposed for phosphocreatine is $H_2PO_3\cdot NH\cdot C(:NH)\cdot NMe\cdot CH_2\cdot CO_2H$. The titration curve of the calcium hydrogen salt indicates a second acid dissociation constant, pk'_2 4·58. Hydrolysis of phosphocreatine at p_H 5·8, which, according to Rous (J. Exp. Med., 1925, **41**, 379 etc.), approximates the intracellular reaction, liberates 0·88 equivalent of base; the possible rôle of this neutralising power in chemical processes in the muscle is discussed. The determination of the phosphocreatine content of muscle (*a*) by direct application of the colorimetric method of the authors (A., 1926, 443) to a trichloroacetic acid extract of the tissue and (*b*), more accurately, after removal of inorganic phosphorus with calcium, is described in detail, and figures are given for normal resting muscle. The phosphocreatine of muscle is hydrolysed when the muscle is stimulated, when the blood supply is cut off, or when lactic acid or potassium chloride is injected intravenously; injection of creatine is without effect.

C. R. Harington.

Adenylic acids of muscle and yeast. G. Embden and G. Schmidt (Z. physiol. Chem., 1929, **181**, 130—139; cf. Schmidt, this vol., 346).—Muscle-adenylic acid has m. p. 196—200° (rapid heating), α_D^{20} −47·5° (2% sodium hydroxide), −26·0° (10% hydrochloric acid). Yeast-adenylic acid has m. p. below 195° (mixed m. p. not sharp and lower), α_D^{20} −56·0° (2% sodium hydroxide), −36·5° (10% hydrochloric acid). Inosinic acid is easily isolated from the deaminated muscle product, but not from the yeast product. Acid hydrolysis of muscle-adenylic acid is much slower than that of yeast-adenylic acid.

J. H. Birkinshaw.

Influence of the fixation of organs by formaldehyde on the extraction of lipins. M. Mladenović and H. Lieb (Z. physiol. Chem., 1929, **181**, 221—226).—Both the ether- and the alcohol-soluble materials of normal liver are always greater than those from liver after fixation by formaldehyde. The nitrogen, phosphorus, cholesterol, and neutral fat contents of the ethereal extract of fresh liver are considerably greater than those of liver treated with formaldehyde, and since the residue on evaporating the ethereal extract was completely soluble in acetone with the fixed liver, whereas with normal liver 10% of the extract was insoluble, it would appear that the phosphatides are decomposed, some of the products being no longer extracted. P. W. Clutterbuck.

Keratolysis. P. Pulewka (Arch. exp. Path. Pharm., 1929, **140**, 181—193).—The action of alkali sulphides in swelling and dissolving keratin is not to be ascribed to the polysulphide anions, nor is it simply the effect of alkali. Experiments in presence of varying amounts of alkali indicate that the action is dependent on the bivalent sulphide ion and not on the sulphydryl ion or undissociated hydrogen sulphide. The action of the bivalent sulphide ion is not to be ascribed to its lyotropic activity in the sense of the Hofmeister series, but is rather a specific chemical action on the horn protein. The sulphide ions probably act on the cystine group in the protein molecule, and in confirmation of this view it is found that other compounds, *e.g.*, alkali cyanides, which alter the cystine molecule are also active in causing keratolysis. W. O. Kermack.

Heavy metals in human liver and their spectrographic detection. H. Turnwald and F. Haurowitz (Z. physiol. Chem., 1929, **181**, 176—181).—The liver is incinerated and the residue, dissolved in hydrochloric acid, examined spectrographically. In addition to iron, positive lines for copper, tin, zinc, and manganese were obtained. Phosphorus, calcium, and magnesium are also present. Separation of the liver into enzyme-rich and -poor fractions by extraction with acetone and ether, subsequent extraction of the residue with ammonia, and precipitation of the ammoniacal solution with acetic acid gave four fractions, all of which when incinerated and then examined as above showed the presence of the above heavy metals. There is no relationship between metal and enzyme (esterase, catalase) content.

H. Burton.

Impregnation [of tissues] with gold. R. Altschul (Atti R. Accad. Lincei, 1929, [vi], 9, 74—77).—For the impregnation of nervous, connective, muscular, corneal, etc. tissue with gold, the use of mercuric bromide in conjunction with gold chloride yields results differing totally from those furnished by the ordinary methods. T. H. Pope.

Caseinogen precipitation at the isolectric point. F. Lebermann (Biochem. Z., 1929, **206**, 56—59).—The best precipitation of caseinogen from skim milk is attained with 0·1N-acetic acid–acetate buffer in the ratio 8 : 1 at p_H 3·74. The final p_H of the solution, 4·89, differs from the isoelectric point of pure caseinogen, 4·65. J. H. Birkinshaw.

Determination of organic acids in gastric juice by Hehner's method. P. Fleury and P. Ambert (Compt. rend. Soc. Biol., 1928, **98**, 503—504; Chem. Zentr. 1928, ii, 1918).—Hehner's method is applicable only in presence of much organic acid and small amounts of other organic substances. A. A. Eldridge.

Chemical composition of " histamine " gastric juice of man. I and II. L. Grimbert and P. Fleury (J. Pharm. Chim., 1929, [viii], 9, 241—249, 321—331).—" Histamine " gastric juice contains approximately the same amount of protein as the gastric juices of the dog and of man, but is distinctly lower in acidity, total chlorine content, and ratio of total acidity to total chlorine. It has a higher ash content, due mainly to the presence of considerable quantities of phosphorus and calcium. B. A. Eagles.

Origin of the alkaline reaction in the intestinal juice. K. Oyama (J. Biochem. Japan, 1928, 9, 1—16).—Aqueous solutions of neutral salts or sucrose, when introduced into the intestinal canal, cause an increase in alkalinity. The excised intestine adsorbs anions to a greater extent than cations. Injection of aqueous isotonic solutions of neutral salts or dextrose into the intestine causes sodium chloride to pass from the blood into the canal. Chemical Abstracts.

Colorimetric determination of bile salts. M. Chiray and L. Cuny (J. Pharm. Chim., 1929, [viii], 9, 202—215, 250—258).—A method for the determination of bile salts in bile and duodenal juice is described. It is based on the colour reaction of bile salts with furfuraldehyde in the presence of acid. B. A. Eagles.

Relation of bile secretion to the velocity of ultrafiltration of blood. F Faludi (Magyar Orvosi Arch., 1928, 29, 439—443).—Experiments with the author's apparatus (*ibid.*, 435) indicate that the inhibitive effect of gelatin on the bile secretion is due to its property of decreasing the velocity of ultrafiltration of the serum. Chemical Abstracts.

Presence of urea in saliva. R. Vladesco (Compt. rend. Soc. Biol., 1928, 99, 434—436; Chem. Zentr., 1928, ii, 1895).—In man the nitrogen titratable with hypobromite is greater in the saliva than in the blood; the reverse is the case for animals. Moreover, the ammonia-nitrogen of the saliva is much higher in man than in animals. A. A. Eldridge.

Intraocular fluids. II. Magnesium, sodium, and chlorine in the aqueous and vitreous humours and the blood-serum of the ox. III. Inorganic sulphur and phosphorus. E. Tron (Arch. Ophthalmol., 1927, 117, 713—722; 1928, 119, 659—679; Chem. Zentr., 1928, ii, 1894).—The vitreous and aqueous humours of the ox contain Cl 0·44, Na 0·335, Mg 0·001%; these values are compared with those for serum. The serum, aqueous and vitreous humours contain, respectively (mg. per c.c.): inorganic phosphorus 0·047, 0·028, 0·01; sulphur 0·027, 0·012, 0·014. The ocular fluid is regarded as an ultra-filtrate of the serum. A. A. Eldridge.

Chemical nature of the secretion of the corpus luteum. M. Testa (Arch. exp. Path. Pharm., 1929, 140, 174—180).—Liquor folliculi consists of water 92·49%, solid 7·51%, globulin 2·285%, albumin 3·459%, mucoid 0·907%, dextrose 0·099%, and only traces of lipins. From histochemical observations it appears that the ovarian deutoplasm, the liquor folliculi, and the secretory vesicles of the granulose and lutein cells are similar in their chemical nature. The secretion of the corpus luteum and liquor folliculi contain a glycolipoprotein complex, consisting of globulin, albumin, mucoid, and traces of lipoid material. W. O. Kermack.

Colorimetric determination of sulphates in body fluids. E. G. Wakefield (J. Biol. Chem., 1929, 81, 713—721).—The method of Hubbard (*ibid.*, 1927, 74, V) has been developed and is applicable to protein-free blood filtrates, diluted urine, and other body-fluids; the results are usually slightly low. C. R. Harington.

Distribution of sterols in the fæces of man on a mixed diet. M. Bürger and W. Wintersteel (Z. physiol. Chem., 1929, 181, 255—263).—With a man on a mixed diet, the fæces contain besides coprosterol about 50% of other sterols, chiefly cholesterol, and on a diet containing milk and eggs, cholesterol forms the greater part of the total sterols. Administration of large amounts of cholesterol (5 g. in 100 g. of oil) causes only a slight decrease in the percentage amount of coprosterol to total sterol, only a small portion being excreted in the fæces in the first six days. P. W. Clutterbuck.

Adsorption of hydrogen and hydroxyl ions on animal charcoal. II. Measurement of the hydrogen-ion concentration of urine. H. Bohn (Arch. exp. Path. Pharm., 1929, 140, 118—128).—Erroneous results are obtained in the determination of the hydrogen-ion concentration of urine according to the method of Silberstein (A., 1922, ii, 452), since the use of animal charcoal to remove the colouring matter brings about an alteration in the hydrogen-ion concentration. Especially in the case of alkaline urines loss of carbon dioxide must be avoided. In normal individuals the variation of p_H of the urine is found to be comparatively small during the course of a day. W. O. Kermack.

Urinary elimination of ammonia and nitrogen. II, III, and IV. Some urinary constants. E. Rafflin (Bull. Soc. Chim. biol., 1929, 11, 178—188, 189—197, 198—210).—II. Chiefly polemical against Polonovski and Boulanger (Compt. rend. Soc. Biol., 1928, 98, 961). An account of the variation of the constants with a number of pathological conditions is given.

III. The effect of sodium hydrogen carbonate, sodium chloride, calcium chloride, and sulphuric acid on the urinary constants (A., 1928, 1047) is studied. The substances cause a fall, little effect, an increase, and little effect, respectively, in the ratio ammoniacal nitrogen/total nitrogen.

IV. A discussion of the effects of a number of pathological conditions on the urinary constants. G. A. C. Gough.

Mathematical relationships of urinary characteristics. L. Lematte and E. Kahane (Bull. Soc. Chim. biol., 1929, 11, 233—241).—A discussion of the constants of Rafflin and Hasselbalch (cf. preceding abstract). G. A. C. Gough.

Urinary elimination of ammonia in relation to different nitrogenous diets. M. Polonovski and P. Boulanger (Bull. Soc. Chim. biol., 1929, **11**, 211—232).—The ratio of ammoniacal nitrogen to total nitrogen of the urine appears to possess no relation to the nitrogen content of the diet. The constant of Hasselbalch (A., 1916, i, 519) possesses an approximately inverse relation to the p_H of the urine. G. A. C. Gough.

Determination of nitrogenous constituents of urine by fractional precipitation with mercuric chloride. B. Lustig and B. Speiser (Biochem. Z., 1929, **206**, 340—359).—Urine (50 c.c.) is treated at p_H 5·2 with a saturated aqueous mercuric chloride solution; the resulting precipitate contains the total purines, mucins, the greater proportion of the pigments in pathological urines, and the total proteins except peptones. The filtrate contains creatinine, ammonia, urea, and amino-acids. Treatment of the precipitate with warm 0·3% acetic acid separates the purines; subsequent treatment with 0·5% hydrochloric acid solution removes the uric acid and with highly coloured pathological urines part of the pigment. The colouring matter is then extracted with chloroform and added to the pigment obtained by finally treating the residue with a 1% alcoholic hydrochloric acid solution. The xanthine bases are precipitated quantitatively from the acetic acid solution by sodium hydroxide.

The filtrate is treated with one fourth to one third of its volume of 50% sodium acetate solution, whereby quantitative precipitation of ammonia, creatinine, the remainder of the pigments, allantoin, peptone, and a strongly reducing nitrogenous substance occurs. A deficiency of sodium acetate causes incomplete precipitation; an excess, interference with the determinations of the contents of the filtrate. Separation of the constituents of the precipitate is effected by a 35% sodium acetate solution containing 1% of acetic acid which removes the whole of the ammonia, peptone, and allantoin together with a small amount of creatine which separates out on keeping. An aliquot part of the solution is treated with potassium hydroxide and potassium sulphide and, without filtering, the liberated ammonia is collected in 0·1N-hydrochloric acid. Another portion is precipitated with sodium hydroxide and the total nitrogen in the precipitate determined. The residue is treated with warm 1% hydrochloric acid solution, when the whole of the creatinine dissolves together with any remaining pigment which can now be removed by extraction with chloroform. The residue is a strongly reducing nitrogenous substance.

Treatment of the filtrate from the sodium acetate–acetic acid precipitation with 20% sodium hydroxide solution precipitates the whole of the urea, amino-acids, hippuric acid, creatine, and hydroxyproteic acids; each of these was determined in the original solution by standard methods. The filtrate from the sodium hydroxide precipitation contains only traces of a nitrogenous substance.

The method has been adapted to investigate 5 c.c. of urine with an accuracy of ±1—5%.

C. C. N. Vass.

Iodometric determination of homogentisic acid in urine. H. Lieb and F. Lanyar (Z. physiol. Chem., 1929, **181**, 199—207).—Oxidation of homogentisic acid with iodine (cf. Metz, A., 1928, 195) is quantitative only in presence of an excess of carbonate-free sodium hydrogen carbonate. The end-point of the reaction (starch) can then be determined accurately and the blue colour persists for some time. Provided no other substance which reacts with iodine is present the direct titration with iodine can be used to determine the amount of acid present. When the homogentisic acid–iodine reaction mixture is made slightly acid the liberated iodine is only about half of the theoretical amount (cf. Metz, *loc. cit.*). A large amount of dilute sulphuric acid must be used, and if small quantities of homogentisic acid are present addition of potassium iodide is advisable. The determination is best carried out with 0·05N-solutions, when 1 c.c. of thiosulphate=0·0042016 g. of homogentisic acid. The amount of thiosulphate used in determining the amount of acid in 10 c.c. of urine is about 0·2 c.c. too small, and this factor must be applied to give correct values. The maximal error is then 0·5 mg. of acid in 10 c.c. of urine. H. Burton.

Preparation of sodium hypobromite reagent [for determination of carbamide]. O. Charro (Anal. Fís. Quím., 1928, **26**, 446—449).—Sodium hypobromite solution for the determination of carbamide may be prepared conveniently from a stock solution of sodium bromate (6 g.) and sodium bromide (20·5 g.) in water (100 c.c.). If 1 c.c. of concentrated hydrochloric acid is added to 5 c.c. of this solution and then 3·5 c.c. of 30% sodium hydroxide solution, sufficient reagent is obtained for the analysis of 2·5 c.c. of urine. R. K. Callow.

Detection of nitrite in urine. L. Popper and S. Weiss (Wien. klin. Woch., 1928, **41**, 1081—1082; Chem. Zentr., 1928, ii, 1802).—The intensity of the colour obtained with the usual benzidine–acetic acid reagent is proportional to the amount of nitrite, but with a constant quantity of nitrite it increases with increasing benzidine concentration. The benzidine reaction is equally as good with urine as the sulphanilic acid–naphthylamine test.

A. A. Eldridge.

Determination of iodine in urine by the palladous chloride method. H. Bernhardt (Z. anal. Chem., 1929, **76**, 351—354).—The residue obtained by evaporation of the urine is fused with sodium carbonate and peroxide at as low a temperature as possible. The aqueous extract is boiled, acidified, and treated with sodium sulphite to reduce iodate. The palladous chloride solution should contain 1% of alcohol, and sodium chloride must be added to the test solution, if none is already present, to assist in flocculating the precipitated palladous iodide; this is dried at 132° for weighing.

A. R. Powell.

Renal threshold for chloride in man. R. S. Aitken (J. Physiol., 1929, **67**, 199—210).—The relation between the rate of excretion of chloride by the kidney and the concentration of chloride in the plasma has been observed in two human subjects, over a wide range of plasma-chloride concentration, under uniform physiological conditions. The nearest approximation to a renal threshold for chloride is in the neighbourhood of 0·555—0·585% of plasma-sodium chloride. It is suggested that the idea of a renal threshold for chloride be abandoned.

B. A. Eagles.

Rapid determination of acetone and aceto-acetic acid in urine. J. A. Behre (J. Lab. Clin. Med., 1928, 13, 1155—1159).—The method is based on the colour reaction between acetone and salicylaldehyde, permanent standards being employed.

Chemical Abstracts.

Excretion of ammonia and carbamide by the gills of fish. H. W. Smith (J. Biol. Chem., 1929, 81, 727—742).—Fresh-water fish were kept in a tank divided by a rubber diaphragm so that the water circulating through the gills could be examined separately from that receiving the urine. The total nitrogen excreted by the gills was 6—10 times as great as that excreted by the kidneys; the branchial excretion consisted almost entirely of ammonia and carbamide, whilst the renal secretion contained the bulk of the creatinine and uric acid.

C. R. Harington.

Differentiating chemico-biological characteristics in the nasal mucus in healthy subjects and those with nasal abscess. C. A. Torrigiani (Rass. int. Clin. Terap., 1927, 8, No. 10, 7 pp.; Chem. Zentr., 1928, ii, 1791).—Nasal mucus normally nearly always contains thiocyanates, which are absent in disease. The amylolytic power of normal mucus is halved in nasal abscess, whilst a proteolytic power is then present, although normally absent (see also Lo Sperimentale, Arch. Biol. norm. pat., 1921, 81, 41—54).

A. A. Eldridge.

Experimental bone-marrow reactions. VI. Adequacy of kidney, pancreas, spleen, and brain for blood regeneration in pigeons with nutritional anæmia. G. L. Muller and E. Scorpio (Amer. J. Physiol., 1929, 88, 259—266).—Kidney as an exclusive food is not as effective as pancreas or spleen for blood regeneration in a nutritional anæmia in pigeons caused by starvation. Brain proved to be inadequate as a food.

B. A. Eagles.

Catalase content of erythrocytes in experimental anæmia. V. S. Sumbayev (Zhur. exp. Biol. Med., 1928, 10, 9—17).—When oxalated rabbit's blood is centrifuged, two layers of erythrocytes having different catalase indices separate. Increase in the catalase index of anæmia blood is ascribed to the fact that the blood is younger.

Chemical Abstracts.

Blood-cholesterol in cancer. II. Diagnostic relations. W. L. Mattick and K. Buchwald (J. Cancer Res., 1928, 12, 236—245).—In cancer the cholesterol content of plasma is generally greater than that of whole blood.

Chemical Abstracts.

Blood-cholesterol in cancer. III. Relation to non-malignant conditions. W. L. Mattick and K. Buchwald (J. Amer. Med. Assoc., 1928, 91, 1087—1090).—The cholesterol ratio for plasma/whole blood is normally (80% of cases) less than unity, and in cancer (86% of cases) greater than unity. In non-cancerous disease the ratio was normal in 67% and reversed in 33% of the cases.

Chemical Abstracts.

Pharmacological analysis of carcinoma metabolism. G. Hecht and F. Eichholtz (Biochem. Z., 1929, 206, 282—289).—A number of substances have been shown to exert a specific inhibition of the fermentation processes of tumour cells. Their common characteristic is the power to form complex compounds with the heavy metals, in particular copper, which are said to be the catalysts for the fermentation processes. Lethal doses of copper, in the case of the mouse, are deprived of their toxicity by the injection of these substances.

C. C. N. Vass.

Examination of the gastric contents as an aid to diagnosis of carcinoma of the stomach. D. M. Dunlop (Edinburgh Med. J., 1928, 35, 497—532).—Carcinoma of the stomach or œsophagus is associated with the absence of free [hydrochloric] acid and the presence of lactic acid in the gastric contents. Gunzberg's test with freshly prepared reagent, but not the Congo-red and " dimethyl " tests, is trustworthy for free hydrochloric acid; MacLean's test, but not Uffelmann's test, is specific for lactic acid.

Chemical Abstracts.

Ammonia content of normal and of pathological human blood. M. Labbé, F. Nepveux, and Hejda (Compt. rend., 1929, 188, 738—740).—The mean value of the ammonia content of normal human blood, determined by the method of Parnas and Heller (A., 1925, i, 323, 454), is 0·47 mg. per litre. In cases of cirrhosis of the liver, diabetes with moderate acidosis, and pulmonary tuberculosis the values are often higher.

G. A. C. Gough.

Blood as a physico-chemical system. VIII. Diabetic coma. D. B. Dill, A. V. Bock, J. S. Lawrence, J. H. Talbott, and L. J. Henderson (J. Biol. Chem., 1929, 81, 551—574).—Nomographic representations are given of the condition of the blood of two patients in diabetic coma.

C. R. Harington.

Probable significance of the intestinal fermentations in certain morbid conditions. G. Gherardini (Folia Clin. Chim. Micros., 1928, 3, 289—344).—Investigation of the volatile fatty acids contained in the fæces of dogs from which the pancreas had been excised showed the presence of these acids in abnormally large amounts, but it was not found possible to determine the intensity of the fermentation producing such excess of acid. An attempt is made to trace a relationship of fermentative processes, considered as the cause of acidification of the intestinal medium, to the absorption and to the chemical composition of the fats eliminated. The fundamental question of the principal seat of the fermentations in question remains unsolved.

T. H. Pope.

Chemical changes occurring in the body as the result of certain diseases. III. Composition of the plasma in severe diabetic acidosis and the changes taking place during recovery. A. F. Hartmann and D. C. Darrow (J. Clin. Invest., 1928, 6, 257—276).—Concentration of the plasma with slight diminution of total base are observed; hydrogen carbonate and chloride are diminished relatively more than ketonic acid and protein. On administration of water and insulin, with or without carbohydrate, the base released by oxidation of the salts of ketonic acids is at first largely claimed by acids other than carbonic. Later, secretion of chloride, bound to ammonia in the urine, aids in the restoration of plasma-hydrogen carbonate. CHEMICAL ABSTRACTS.

Determination of hexosephosphoric acid in blood. Its occurrence in the normal and diabetic organism. H. LAWACZECK (Deut. Arch. klin. Med., 1928, **159**, 223—234; Chem. Zentr., 1928, ii, 1801).—By precipitation of the lactacidogen with baryta the hexosephosphoric acid is separated from the blood-sugar and other reducing substances, and determined as hexose. For blood, values between 0·63 and 2·14 mg.-% (as dextrose) were obtained. Hence 1% of the dextrose of the blood is united with 1—3% of the organic soluble phosphoric acid of the blood as hexosephosphoric acid. Characteristic differences are not observed in diabetes. There is no connexion between the quantity of blood-sugar and that of hexosephosphoric acid. A. A. ELDRIDGE.

Cholesterol content of blood-plasma in diabetes mellitus. I. M. RABINOVITCH (Arch. Int. Med., 1929, **43**, 363—371).—The plasma-cholesterol content affords a trustworthy index to the true progress of the patient. F. C. HAPPOLD.

Cholesterol content of blood-plasma in juvenile diabetes. I. M. RABINOVITCH (Arch. Int. Med., 1929, **43**, 372—375).—The plasma-cholesterol content of juvenile diabetics affords the same index of progress in the child as in the adult. F. C. HAPPOLD.

Insulin reaction. J. M. MACGILLIVRAY and R. WAGNER (Biochem. Z., 1929, **206**, 136—149).—The effect of insulin injection on diabetic children was studied after a diet rich in carbohydrate and after a low-carbohydrate diet, the calorific value being made up with fat in the latter case. Insulin causes a much steeper fall in the blood-sugar curve after the carbohydrate-rich diet than after the low-carbohydrate diet. J. H. BIRKINSHAW.

Anomalous fat metabolism in diabetes. I. M. RABINOVITCH and E. S. MILLS (J. Metabol. Res., 1925—1926, **7**—**8**, 87—90).—Administration of insulin caused the blood-fat to fall from the abnormally high value of 18·6 to 2·1. Insulin may cause increased permeability of the tissues to fat. CHEMICAL ABSTRACTS.

Abnormality in the composition of human fat. S. V. TELFER (Glasgow Med. J., 1928, **110**, 137—141). —*Post-mortem* diabetic fat had an iodine value of 59·4 (normal, 71·0); the insoluble fatty acids had m. p. 36—37° (normal, 32—33°), f. p. 35° (30°), iodine value 62·8 (78·6), and contained 38·6% (25·8%) of saturated fatty acids. CHEMICAL ABSTRACTS.

Effect of synthalin on the respiratory quotient of the diabetic patient. W. G. KARR, C. SCHUMANN, and O. H. PETTY (Arch. Int. Med. 1929, **43**, 384—392). —Administration of synthalin to the diabetic patient before a meal tends to increase the carbohydrate utilisation by 10—15 g. This is indicated by an increase in the respiratory quotient. Some of the patients show an increased tolerance for dextrose as measured by the sugar in the blood and urine. F. C. HAPPOLD.

Arterial carbon dioxide pressure in cardiac dyspnœa. R. R. FRASER, C. F. HARRIS, R. HILTON, and G. C. LINDER (Quart. J. Med., 1928, **22**, 1—20).

Cause of death of animals with pancreatic fistula. S. I. PRIKLADOVITZI (Russ. J. Physiol., 1929, **12**, 3—28).—The alkali reserve of healthy, adult dogs of different races varies between 40 and 60 c.c. of carbon dioxide under laboratory conditions; the variation was less marked in dogs of the same race. The blood-sugar varies between 50 and 110 mg. per 100 c.c. of blood. There is a marked drop in the alkali reserve of dogs with pancreatic fistula, resulting in the death of the dog with a marked acidosis. There is no change from the normal in the blood-sugar level. F. C. HAPPOLD.

Cerebroside storing in Gaucher's disease. III. H. LIEB and M. MLADENOVIĆ (Z. physiol. Chem., 1929, **181**, 208—220; cf. A., 1925, i, 189; 1928, 86).—A case of splenohepatomegaly, considered to be a doubtful Gaucher type, is shown to belong to this class owing to the extraction of crude kerasin from the spleen and liver. The organs examined had been preserved in formaldehyde; these were first washed free from aldehyde and dried. The phosphorus content of the unpurified extracts of the organs does not represent the true phosphatide content.

The following optical constants for pure kerasin are given: $[\alpha]_D^{37}$ −9·18° in chloroform +10% of pyridine, $[\alpha]_D^{18}$ −9·03° in pyridine, $[\alpha]_D^{36}$ −11·59° in chloroform, and $[\alpha]_D^{69}$ −3·89° in alcohol (cf. *loc. cit.*; Walz, A., 1927, 691). H. BURTON.

Biochemistry and geochemistry of iodine. Etiology and prophylaxis of endemic goitre. G. LUNDE (Northwest. Med., 1928, **27**, 412, 479; J. Amer. Med. Assoc., 1928, **91**, 1407, 1662).—A discussion of the iodine cycle. CHEMICAL ABSTRACTS.

Iodine metabolism. II. Iodine content of normal and pathological thyroid glands. G. LUNDE, K. CLOSS, and K. WÜLFERT. **III. Blood-iodide content in primary thyrotoxicosis.** G. LUNDE, K. CLOSS, and O. C. PEDERSEN (Biochem. Z., 1929, **206**, 248—260, 261—274).—II. The average weight of a normal Norwegian thyroid gland, in the eight specimens examined, was 24·66 g., with an iodine content of 9·86 mg. Pathological glands showed large fluctuations in iodine content. Treatment with inorganic iodides increased the colloidal iodine in the glands of patients suffering from primary toxic goitre.

III. A review of the previous values obtained for the blood-iodide content is given. The normal blood-iodide content in Oslo was found to vary between 11 and 16 γ-%. A new method is described in which the blood-iodides are separated into alcohol-soluble and -insoluble fractions. In thyrotoxicosis the blood-iodide content increases, especially in the alcohol-insoluble organic fraction. Administration of iodides caused an increase in the alcohol-soluble fraction with a reduction in the insoluble fraction until normal metabolism was reached and the pathological conditions disappeared. C. C. N. VASS.

Pentosuria in rabbits in experimental stasis icterus and following subcutaneous injection of bile acids. T. Kobayashi (J. Biochem. Japan, 1928, 9, 251—260).—Bile acids provoke pentosuria, the pentose apparently arising from the body-nucleins.

Chemical Abstracts.

[Excretion of protein in] liver disease. E. Andrews, W. A. Thomas, and K. Schlegel (Surg., Gynæcol., and Obstet., 1928, 47, 178—182).—In certain diseases of the liver protein is excreted in the urine; there is also disturbance of mineral salt (calcium, sodium) balance. Chemical Abstracts.

Porphyrin modalities. A. A. Hijmans van den Bergh (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 15—19).—A pigment excreted by a subject suffering from congenital porphyrinuria has been found to be identical with coproporphyrin synthesised by H. Fischer from ætioporphyrin III.

F. G. Tryhorn.

Hydrogen-ion concentration and the calcium and phosphorus content of the fæces of rachitic children. T. Redman (Biochem. J., 1929, 23, 256—260).—The results suggest a certain degree of correlation between $p_{\rm H}$ and the percentage of calcium in the fæces of rachitic children. The phosphorus of the fæces has also been determined.

S. S. Zilva.

Sodium and potassium balances, when used as citrates in acidotic and rachitic conditions in rats. J. H. Speer, V. V. Cole, and F. W. Heyl (J. Amer. Pharm. Assoc., 1929, 18, 225—228).—The sodium and potassium balances in the previous experiments (cf. this vol., 345) have been determined. The most favourable results require all the bases, but assuming that the potassium, calcium, phosphorus, and magnesium requirements are met, the alkalisation requires a considerable preponderance of sodium, the authors' best results being obtained when Na : K= 5·9 : 1. E. H. Sharples.

Lactic acid in blood during gestation. H. Kienlin (Zentr. Gynäkol., 1926, 2358—2362; 1927, 2271—2273; Chem. Zentr., 1928, ii, 1788).—In pregnancy the lactic acid content of venous blood is approx. 7·5—10 mg.-%, during parturition 20—25 mg.-%; in two cases of eclampsia the values reached 30 mg.-%, although a causal relation is not postulated. High values are, however, associated with convulsions.

A. A. Eldridge.

Composition of the blood and the menstrual cycle. Cholesterol. C. O. Guillaumin and H. Vignes (Compt. rend. Soc. Biol., 1928, 99, 618—620; Chem. Zentr., 1928, ii, 1679).—During menstruation and between the 17th and 21st day an increase in blood-cholesterol was observed. Values during the period are recorded. A. A. Eldridge.

Cholesterol metabolism in the incubated egg. K. Kusui (Z. physiol. Chem., 1929, 181, 101—106).—The amount of free and esterified cholesterol in the various parts of the egg at different stages of incubation was determined. Incubated hens' eggs show a decrease in total cholesterol up to the fourteenth day and then an increase up to the time of hatching. Turtles' eggs show a similar fall and rise.

J. H. Birkinshaw.

Fate of diphenylene oxide in intermediary metabolism of the rabbit. A. A. Christomanos (Z. physiol. Chem., 1929, 181, 182—184).—Subcutaneous injection of diphenylene oxide results in a considerably increased excretion of hippuric acid in the urine during 12 days, showing that degradation to benzoic acid occurs. No salicylic acid derivative was isolated.

H. Burton.

Influence of diet on body-fat of white rats. H. C. Eckstein (J. Biol. Chem., 1929, 81, 613—628).—White rats on a fat-free diet deposited body-fat of similar composition regardless of variations in the relative amounts of protein and carbohydrate administered. Addition of myristic acid or of triolein to such a diet caused increased deposition of body-fat, but sodium butyrate was without effect. Marked increase in the proportion of highly unsaturated acids in the body-fat was observed only after administration of triolein. The cholesterol content of the animals was independent of the nature of the diet.

C. R. Harington.

Behaviour of the combined sugar during alimentary hyperglycæmia. C. Toscano (Folia Clin. Chim. Micros., 1928, 3, 344—358).—In dogs alimentary hyperglycæmia is almost always accompanied by diminution of the combined sugar, which may disappear entirely from the blood. Such diminution sometimes corresponds with the greatest intensity of the hyperglycæmia, but often the minimum values of the combined sugar occur when the free sugar has been lowered to about its normal value. The diminution or disappearance of the combined sugar in the blood persists even after injection of insulin. If, during insulin hypoglycæmia, dextrose is rapidly introduced into the circulation, diminution and disappearance of the combined sugar are observed even when the increase in free sugar does not exceed the normal values. Thus, the diminution of combined sugar is not a consequence of the hyperglycæmia, so that it cannot be assumed that diminution of the combined sugar resulting from rapid introduction of dextrose represents a defensive mechanism of the organism against hyperglycæmia. T. H. Pope.

Mechanism of alimentary hyperglycæmia. I. Influence of ergotamine and atropine on the course of alimentary hyperglycæmia. II. Liberation of insulin by administration of dextrose and its influence on the glycæmic reaction. L. Pollak (Arch. exp. Path. Pharm., 1929, 140, 1—27, 28—55).—The rise in blood-sugar following administration of dextrose to rabbits is partly inhibited by the administration of ergotamine and of atropine which poison the sympathetic and parasympathetic nervous systems, respectively. When atropine and ergotamine are administered simultaneously inhibition of the rise in blood-sugar is complete. When the dextrose is given intravenously these drugs do not inhibit the blood-sugar rise. The possible causes for these results have been investigated.

II. The rate of secretion of insulin by the pancreas is deduced from the change in the concentration of blood-sugar resulting from the administration of dextrose. When dextrose is given orally or intravenously the consequent secretion of insulin is inhibited partly by ergotamine or atropine separately but completely when both are given together. W. O. Kermack.

Causes of alimentary hyperglycæmia in carbohydrate feeding and deprivation. F. Schellong and H. Kramer (Klin. Woch., 1928, 7, 1726—1729; Chem. Zentr., 1928, ii, 1893).

Carbohydrate metabolism in fasting. H. M. Hines, J. D. Boyd, and C. E. Leese (Amer. J. Physiol., 1929, **88**, 240—244).—Dextrose was injected intravenously at the rate of 4 g. per kg. body-weight per hr. for a period of 2 hrs. into non-fasting and fasting dogs. Animals in the fasting condition exhibited a greater degree of glycosuria and hyperglycæmia than the non-fasting controls. The difference in response is a quantitative one and not a qualitative one. The effect of fasting on carbohydrate metabolism should be regarded as an impaired function of the organism as a whole. B. A. Eagles.

Low-carbohydrate feeding. P. György and H. Keller (Biochem. Z., 1929, **206**, 120—135).—Newly-weaned rats (15—25 days old) fed on a synthetic diet lacking carbohydrate show no inhibition of growth as compared with controls receiving the same diet + carbohydrate, and no hypoglycæmia. It is concluded that the conversion of fat and protein into sugar covers the needs of the growing organism. A diet rich in protein produces a relative kidney hypertrophy. J. H. Birkinshaw.

Fate of glycogen injected into the blood circulation of normal and depancreatised dogs. U. Lombroso (Boll. Soc. ital. Biol. sper., 1927, 2, 330—332; Chem. Zentr., 1928, ii, 1788).—Intravenous injection of glycogen (1 g. per kg.) into dogs produces considerable glycæmia, and a small increase of the reducing power of the urine; 3 g. per kg. produce intense glycosuria and elimination of polysaccharides in the urine. In depancreatised dogs, 1 g. per kg. causes increased glycosuria and excretion of polysaccharides. Hence in diabetes glycogen placed in the blood stream cannot be utilised. A. A. Eldridge.

Injection of starch into the blood circulation. G. Sunzeri (Ann. Clin. Med. sper., 1928, **17**, No. 1, 13 pp.; Chem. Zentr., 1928, ii, 1788—1789).—Soluble starch, injected intravenously into dogs, is chiefly oxidised in the body, only small quantities being eliminated in the urine. Storage of the starch in the organism is never observed. The decomposition of starch in the blood circulation takes place very rapidly. If urinary elimination of starch is prevented, hyperglycæmia is observed. A. A. Eldridge.

Metabolism of lactose. IV. Fate of lactose in the rabbit. R. C. Corley (J. Biol. Chem., 1929, **81**, 541—544).—After intravenous injection of 1 g. of lactose into rabbits 75% of the sugar was excreted in the urine within 3 hrs., by which time the non-fermentable sugar content of the blood had returned to its normal level. The elimination of lactose was not affected by insulin, but was inhibited by tartrate nephritis accompanied by anuria. Oral administration of lactose had little effect on the non-fermentable reducing substances of the blood. C. R. Harington.

Significance of respiratory quotients after administration of certain carbohydrates. W. R. Campbell and E. J. Maltby (J. Clin. Invest., 1928, **6**, 303—317).—Dihydroxyacetone, lævulose, and sucrose cause a diminution of the carbon dioxide combining power and an increase in the blood-lactic acid, whilst dextrose, maltose, lactose, galactose, and glycerol do not. Chemical Abstracts.

Gaseous exchange following the administration of dihydroxyacetone. W. R. Campbell and S. Soskin (J. Clin. Invest., 1928, **6**, 291—302).—Differences in respiratory quotient, oxygen intake, and carbon dioxide elimination for normal and depancreatised animals fed respectively with dihydroxyacetone and dextrose were observed. Chemical Abstracts.

Spleen and carbohydrate metabolism. A. Francaviglia (Folia Clin. Chim. Micros., 1928, **3**, 359—369).—In rabbits modifications of the blood-sugar are observed from the day succeeding splenectomy, with a tendency to return gradually to normal values. Such modifications consisted in a lowering of the free sugar during fasting with seven out of the ten animals and in increase in the combined sugar with four animals. When dextrose is subsequently introduced by intravenous injection, the free sugar never reaches the high values obtained similarly prior to splenectomy, but the combined sugar at first increases markedly and then decreases to fall into line with the free sugar. The oscillations in blood-sugar normal to healthy animals become wider and more disordered after splenectomy. The modifications in the blood-sugar following splenectomy thus resemble those consequent on administration of insulin, and it appears that the increased external secretion of the pancreas caused by removal of the spleen is accompanied by increase in the internal secretion. T. H. Pope.

Significance of bile acids in carbohydrate metabolism. IV. Antagonistic effect of bile acids against adrenaline. K. Murakami (J. Biochem. Japan, 1928, **9**, 261—270).—Administration of bile acids to normal or adrenalectomised rabbits lowers fasting blood-sugar, or reduces dextrose hyperglycæmia. It is considered that the diminished adrenaline content of the blood following adrenal extirpation is responsible for the increased bile acid excretion, and that the resulting hyperglycæmia is caused by the increase in bile acid concentration of the blood. Chemical Abstracts.

Significance of bile acids in carbohydrate metabolism. V. Effect of diminished bile acid and of excess of bile acid on the sugar content of the blood. T. Okamura (J. Biochem. Japan, 1928, **9**, 271—283).—Removal of bile causes hyperglycæmia, which can be abolished by administration of bile acids. Chemical Abstracts.

Significance of bile acids in carbohydrate metabolism. VI. Effect of the loss of bile acids and of excessive bile acid administration on the adrenaline content of the suprarenals. T. Okamura (J. Biochem. Japan, 1928, **9**, 445—452).—The adrenaline content of the suprarenal gland of the rabbit is increased by removal of bile and decreased by oral administration of bile acids or in stasis icterus. Chemical Abstracts.

Lactic acid excretion in urine and sweat during football. I. Snapper and A. Grünbaum (Biochem. Z., 1929, **206**, 319—333).—Prior to the game only traces of lactic acid were found in the urine of 55 players, after the game only traces of albumin were found in the urine of 74 players. After playing in warm weather (55 players) only six times was urinary lactic acid excretion of more than 60 mg. observed, whereas in cold weather (32 players) this was noticed sixteen times. Clean, salt-free shirts, extracted with water immediately after the game, contained an average of 460 mg. of lactic acid and 846 mg. of chloride; when the amount of sweat excreted was small the lactic acid concentration was higher. The physiological importance of this problem in regard to exercise and the action of the skin is discussed.

C. C. N. Vass.

Lactic acid metabolism of the central nervous system. II. H. Jungmann (Biochem. Z., 1929, **206**, 457—467).—In sodium chloride solution, containing 0·1% of dextrose, the total lactic acid content in the surviving spinal cord of the frog increased from 0·113% (average) to 0·133% in the presence of oxygen and from 0·20% to 0·30% in nitrogen. In oxygen the increase occurred solely in the external fluid. Stimulation in oxygen in the presence of dextrose caused a slight increase of lactic acid (cf. this vol., 93). Addition of insulin resulted in a decrease in lactic acid in oxygen and nitrogen. When the medium contained both sugar and insulin a smaller decrease occurred than with insulin alone. A glycolytic enzyme has been detected in the medium surrounding the cord. C. C. N. Vass.

Specific dynamic action. S. Ederer and J. Wallerstein (Biochem. Z., 1929, **206**, 334—339).—With dextrose, either *per os* or intravenously, the specific dynamic action is always obtained at the taking of food, but its duration depends on the amount taken. Subcutaneous injection of ergotamine suspends the action of the sympathetic system; subsequent feeding with sugar reduces the metabolism. The suspension of the specific dynamic action by ergotamine has been found to vary with the individual when meat and bread are absorbed. C. C. N. Vass.

Protein metabolism and organic evolution. J. Needham (Sci. Progress, 1929, **92**, 633—648).—It is suggested that the main nitrogenous excretory product of an animal depends on the conditions under which its embryos live. Ammonia and urea are associated with aquatic pre-natal life and uric acid with terrestrial pre-natal life. Without a uricotelic metabolism it would have been impossible for terrestrial oviparous animals to survive.

F. C. Happold.

Increase of hepatic proteins with a diet rich in proteins. C. Gautier (Bull. Soc. Chim. biol., 1929, **11**, 168—177).—The experiments on frogs (A., 1928, 792) are repeated with the additional determination of the liver-proteins by precipitation with 20% trichloroacetic acid. Whilst the percentage protein content falls, the total amount of protein increases 2—4 times in the animals receiving cheese.

G. A. C. Gough.

Amino-acid catabolism. II. Fate of β-alanine and of ε-aminohexoic acid in the phloridzinised dog. R. C. Corley (J. Biol. Chem., 1929, **81**, 545—549).—Administration of β-alanine and of ε-aminohexoic acid to phloridzinised dogs caused no significant increase in the excretion of dextrose.

C. R. Harington.

[Fate of] γ-butyrobetaine, crotonobetaine, and carnitine in animal metabolism. W. Linneweh (Z. physiol. Chem., 1929, **181**, 42—53).—γ-Butyrobetaine, crotonobetaine, and carnitine administered subcutaneously to dogs are excreted largely unchanged in the urine. A small amount of the γ-butyrobetaine and less of the crotonobetaine are oxidised to carnitine. γ-Butyrobetaine and crotonobetaine have a weak curare-like action and are lethal in large doses.

J. H. Birkinshaw.

Metabolism of tissues growing *in vitro*. III. Cyanic acid as a possible precursor of the ammonia and urea formed by embryo kidney tissue. B. E. Holmes and E. Watchorn (Biochem. J., 1929, **23**, 199—205; cf. A., 1927, 479).—Cyanic acid exerts no toxic effect on the tissue of embryo kidney when present in amounts up to 9·0 mg. per 100 c.c. of medium. It is broken down in its presence to ammonia and urea. *l*-Hydantoinacetic acid is also broken down by the embryonic tissue, giving rise to urea and ammonia. In the presence of cyanate, urea disappears from the cultures. This is particularly the case when the tissue is actively growing. S. S. Zilva.

Ammonia formation in muscle and its relationship to function and change of condition. VI. Relation of ammonia formation to conversion of adenine nucleotide into inosic acid. J. K. Parnas (Biochem. Z., 1929, **206**, 16—38; cf. A., 1928, 668).—In fresh muscle the purine bases are present chiefly as free nucleotides. The fresh muscle of winter frogs contains 82% of the purine-nitrogen in the adenine nucleus and 18% in the hypoxanthine nucleus, in summer frogs 89% and 11%, respectively. Mechanical injury transforms the greater part of the adenine nucleotide into inosic acid. Grinding for a few mins. gives 23% and 77% purine-nitrogen for adenine and hypoxanthine nuclei, respectively. In winter, the deamination of the adenine nucleotide corresponds quantitatively with the traumatic ammonia formation. Anaërobic stimulation of muscle produces a conversion of adenine into hypoxanthine equivalent to the ammonia production; under aërobic conditions the ammonia produced is greatly in excess. This may be due to deamination of other substances leading to a resynthesis of adenine nucleotide from inosic acid. J. H. Birkinshaw.

Oxygen absorption curve of fatigued muscle as a function of hydrogen-ion concentration. M. Comel (Atti R. Accad. Lincei, 1928, [vi], **8**, 255—257).—The curve of oxygen absorption by fatigued frog's muscle in solutions of varying p_{H} value shows two points of inflexion and a maximum. Writing $y=f(p_{\mathrm{H}})$, where y is the rate of absorption of oxygen, it is found that $y=0$ when $p_H=5·3$. The complete curve may be represented by $y=ax+bx^2+cx^3+dx^4$, where $x=(p_H-5·3)$. The coefficients a and c are positive, and b and d are negative. On analysis, the curve may be regarded as consisting of three portions divided by the points of inflexion which occur at p_H 7·0 and 6·6, respectively. The first portion, for p_H values near neutrality, corresponds with a high rate of oxygen absorption. Between p_H 6·6 and 6·0 recovery of the muscle is moderately rapid and may be taken to represent physiological conditions. At p_H values below 6·0 the absorption rate falls rapidly, becoming zero at p_H 5·3. F. G. TRYHORN.

Calcium metabolism in animals. W. DREYFUSS (Beitr. path. Anat., 1926, **76**, 254—269; Chem. Zentr., 1928, ii, 1584).—The deposition of calcium in acid and alkaline feeding was studied for mice.
A. A. ELDRIDGE.

Factors influencing calcium balance. II. Influence of potential alkalinity on the utilisation of supplementary calcium lactate in young rachitic rats. V. V. COLE, J. H. SPEER, and F. W. HEYL (J. Amer. Pharm. Assoc., 1929, **18**, 107—110; cf. this vol., 345).—Previous work has been confirmed and extended, using rachitic rats and studying the effects of various additions to their diet during recuperation. Base-forming or neutral diets are more favourable to calcium retention than an acidotic diet, and base-forming diets favour magnesium, and probably phosphorus, retention. Addition of potential alkalinity more than offsets a less favourable Ca : P ratio, showing better calcium retention than the acidotic controls. At a constant level of phosphorus intake, potassium acts somewhat in antagonism to calcium. E. H. SHARPLES.

Phosphorus metabolism. A. V. KHARIT and A. I. LIVSCHITZ (Arkh. Biol. Nauk, 1927, **27**, 89—99).—In the blood of dogs, inorganic and total phosphorus are highest in the portal, and lowest in the renal vein. The liver retains part of the inorganic and total phosphorus of the serum as well as of the whole blood; similar loss occurs in the kidneys. The constancy of the blood-phosphorus level is maintained not only by food, but also by digestive secretions and the products of tissue catabolism. The following values for inorganic phosphorus and total phosphorus as P_2O_5 (mg.-%) of serum are recorded: portal vein 3·8—7·2, 29·0—35·0; hepatic vein 3·4—6·9, 31·1; renal vein 4·6—6·5, 26·0; femoral artery 3·1—6·8, 27·0—6·8. CHEMICAL ABSTRACTS.

Phosphorus exchange. II. Rôle of the spleen. III. Effect of adrenaline. A. CHARIT (Arch. Sci. biol. [Moscow], 1928, **28**, 145—147, 149—154; Chem. Zentr., 1928, ii, 1897).—The blood leaving the spleen contains more inorganic phosphorus than that entering it. It is supposed that complex organic phosphorus compounds are dissociated in the spleen. Subcutaneous administration of adrenaline reduces the inorganic phosphorus in the blood by 28—30%; no further reduction occurs on administration of dextrose and insulin. It is considered that of the inorganic phosphorus of the blood, only one part can react with carbohydrates. A. A. ELDRIDGE.

Action of sodium chloride on normal, pregnant, and partly nephrectomised animals. I. Chlorine and water metabolism. H. LUNDIN and R. SCHARF. **II. Influence of sodium chloride on the inorganic constituents of the blood.** R. SCHARF and H. LUNDIN (J. Metabol. Res., 1925—1926, **7—8**, 259—320, 327—355).—Daily administration of large amounts of sodium chloride resulted in a considerable increase in the cation, and a slight increase in the anion, concentration of the blood; the former is apparently compensated by negative radicals of organic acids. The largest increase is shown by potassium; chloride increased by only 9%. After partial nephrectomy different results were obtained. Sodium and chlorine are excreted independently.
CHEMICAL ABSTRACTS.

Physiology of insects; metabolism. P. S. WELCH (Ann. Entomol. Soc. Amer., 1928, **21**, 476—488).—A general discussion.
CHEMICAL ABSTRACTS.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*, Fab.). III. Soluble ash and sulphates. W. RUDOLFS (J. N.Y. Ent. Soc., 1927, **35**, 219—229).—Nitrogen is shown to play an important part in the formation of the embryo, the preparation for pupation, and the transformation to the adult. Fats are used and stored for energy; they are not important at any critical stage for tissue-building. The moisture content is directly related to the rate of activity.
CHEMICAL ABSTRACTS.

Permeability of surviving animal membranes. M. JOWETT (Biochem. Z., 1929, **206**, 503—504). The large differences between the diffusion coefficients of dextrose in water and in animal membranes (Ammon, A., 1928, 913) are due to the method of calculation. C. C. N. VASS.

Effect of valency of ions on cellular permeability to water. B. LUCKÉ and M. MCCUTCHEON (J. Gen. Physiol., 1929, **12**, 571—580).—Unfertilised eggs of the sea urchin (*Arbacia punctulata*) washed with isotonic dextrose solution to remove ions were suspended in hypotonic dextrose solution containing a complex cobaltammine salt and the rate of swelling of the egg was followed quantitatively by microscopic examination. Of the series of cobaltammine salts of which the cation varied in valency from 1 to 6, the salt with univalent cation was less active than that with the bivalent cation in decreasing the permeability of the cell membrane, but under the above conditions salts with a valency of two and upwards are approximately equal in their activity, the permeability of the membrane being reduced to its permeability in sea-water, which appears to be a minimum for the membrane. If, however, the permeability is increased by adding to the dextrose solution suitable quantities of potassium citrate or potassium sulphate the cobaltammine salts show activities increasing markedly with increase in the valency of the cation. The salts potassium chloride, potassium sulphate, potassium ferricyanide, and potassium ferrocyanide increase the permeability of the cell membrane, the order given being that of increasing activity. Similar results were also obtained with another series of salts containing organic anions, the valencies of which ranged from 1 to 3. W. O. Kermack.

Biological rôle of calcium salts. L. Ambard and F. Schmid (Compt. rend. Soc. Biol., 1928, **98**, 1220—1222; Chem. Zentr., 1928, ii, 1788).—The differences between alkali and calcium chlorides in the behaviour of solutions with protein, and in affecting the solubility of glycine etc. are discussed. A. A. Eldridge.

Effect of salicylate administration on the acetone substance content of the blood. H. B. Myers and C. Ferguson (J. Pharm. Exp. Ther., 1929, **35**, 313—319).—Toxic doses of sodium salicylate administered orally or subcutaneously do not produce any marked effect on the acetone, acetoacetic acid, or β-hydroxybutyric acid content of the blood of rabbits. E. Boyland.

Basic titanium salicylate. M. Pichon (J. Pharm. Chim., 1929, [viii], **9**, 338—340).—Basic titanium salicylate, $C_6H_4(OH)\cdot CO\cdot OTiO\cdot OH$, was prepared by the action of sodium salicylate on the product obtained from the reaction between titanium chloride and sodium sulphite. The compound is used in skin diseases. B. A. Eagles.

Mechanism of synthalin action. G. Ahlgren (Biochem. Z., 1929, **206**, 99—108).—Insulin alone delays methylene-blue reduction in presence of minced muscle, insulin+dextrose accelerates it; synthalin has the reverse action in each case. Synthalin+insulin and synthalin+dextrose have a negative or a retarding action, but a mixture of all three strongly accelerates the reduction. J. H. Birkinshaw.

Amount of reducing substance in organs of rabbit with varying blood-sugar content. G. Peyer (Biochem. Z., 1929, **206**, 3—15).—The reducing power of the hydrolysed tissue of various organs of the rabbit was determined. The lungs and brain show relatively high values under normal conditions; in hyper- and hypo-glycæmic states increased reducing power of the adrenals is observed. In hyperglycæmia due to stimulation and in synthalin convulsions the brain's content of reducing substances decreases. Lethal doses of synthalin and insulin cause a complete disappearance of the reducing power of muscle but not of the liver. Various groups of muscles show different reducing powers, but symmetrical muscles on each side of the body are substantially the same. J. H. Birkinshaw.

Influence of chemical and other agents on the toxicity and antigenic power of ricin. II. Detoxification of ricin. III. Production of immunity by means of ricin and detoxified ricin. E. B. Carmichael (J. Pharm. Exp. Ther., 1929, **35**, 193—221, 223—239).—II. Ricin as prepared by the method of Osborne, Mendel, and Harris (A., 1905, ii, 753) killed animals after subcutaneous injection in doses of 0·02 mg. per kg. body-weight. This toxicity was reduced or completely removed by oxidation with potassium permanganate and to a smaller extent with hydrogen peroxide, ozone, and the halogens, by treatment with Congo-red, but not with basic stains, by boiling, or by exposure to ultra-violet light between wave-lengths 225 and 254 μμ.

III. Boiled solutions of ricin still retained part of their antigenic property, but ricin solutions oxidised with large amounts of potassium permanganate lost both antigenic and toxic properties. By careful oxidation with less permanganate it was possible to destroy the toxicity without affecting the antigenic function. E. Boyland.

Effect of hormones, parasympathetic drugs, alkaloids, and various salts on the hypoglycæmic action of bile acids. A. Taku (J. Biochem. Japan, 1928, **9**, 299—319).—The hypoglycæmic action of cholic acid is inhibited by adrenaline, atropine, pilocarpine, morphine, cocaine, caffeine, calcium chloride, or magnesium chloride, and promoted by insulin or potassium chloride; pituitrin is inactive. Chemical Abstracts.

Effect of cholagogues on the swelling of colloids. F. Faludi (Magyar Orvosi Arch., 1928, **29**, 444—446).—Sodium dehydrocholate and phenylquinolinecarboxylate diminish the swelling of gelatin and agar-agar, but a connexion between this effect and the cholagogue activity is not postulated. Chemical Abstracts.

Influence of substances of the pilocarpine group on the gaseous exchanges of animals. A. M. Preobraschenski (Russ. J. Physiol., 1929, **12**, 45—58).—The excretion of carbon dioxide and water and the absorption of oxygen in the rabbit is increased as a result of the injection of pilocarpine in doses from 1 mg. per kg. body-weight. In large doses (10 mg. per kg.), this general increase is maintained, but the oxygen absorption does not increase proportionately to the increased excretion of water and carbon dioxide. Arecoline in doses of 0·1—1 mg. gives results similar to those obtained with pilocarpine, but the general increase of all components with increasing dosage is more proportionately interrelated. With both drugs the excretion of water is the most marked. Physostigmine in doses of 0·1—1 mg. causes an increased excretion of carbon dioxide, but the excretion of water and the absorption of oxygen decrease. F. C. Happold.

Rôle of the tertiary amine group in the dipiperidine nucleus. A. Hazard and M. Polonovski (Compt. rend., 1929, **188**, 822—824).—Intravenous injection of granatoline in dogs causes a peripheral vaso-constriction which is not due to an enhanced excretion of adrenaline, since the same phenomena occur in animals from which the suprarenal glands have been removed. *N*-Methylgranatoline shows a similar action and its effect on the intracardiac endings of the vagus is greater. These properties, however, are not possessed by *N*-methylgranatoline oxide. G. A. C. Gough.

Effect of ergotamine on experimental hyperglycæmia. G. Eda (J. Biochem. Japan, 1928, **9**, 285—297).—Experimental hyperglycæmia was reduced, frequently to hypoglycæmia, by subcutaneous injection of ergotamine. Chemical Abstracts.

Effect of ergotamine on blood-sugar level. L. B. Shpiner (Amer. J. Physiol., 1929, **88**, 245—250).—Intramuscular administration of ergotamine prevents the development of an adrenaline hyper-

glycæmia and glycosuria. It lowers the blood-sugar and eliminates the glycosuria in dogs which have been partly depancreatised and given thyroid extract.
B. A. Eagles.

Poisoning by bittersweet (*Solanum dulcamara*). H. Lowe (Analyst, 1929, **54**, 153—154).—Examination of the stomach contents of a dead foal showed the presence of 0·085 g. of a mixture of solanine and solanidine in 250 g. of stomach content, 0·069 g. of mixed solanine and solanidine being found in 100 g. of stomach content of cows poisoned by eating bittersweet. No solanine was found in the dung of the affected cows,. D. G. Hewer.

Locus of action of antipyretics (quinine and similar compounds). O. Girndt (Arch. exp. Path. Pharm., 1929, **140**, 91—117).—When applied directly to the mid-brain in equal doses, quinine is as active as antipyrine in lowering the temperature of an animal in fever as the result of mid-brain puncture or of *B. coli* infection. Eucupin has no antipyretic action. Plasmoquin exerts no antipyretic action when administered intracerebrally and is active when applied subcutaneously in an almost toxic dose.
W. O. Kermack.

Influence of diuretics on the oxygen consumption of the Starling kidney preparation. H. Gremels (Arch. exp. Path. Pharm., 1929, **140**, 205—219).—The isolated kidney perfused according to Starling's technique consumes oxygen at the rate of 40—100 c.c. per kg. per min. This rate is increased when a diuresis is caused by purine bases, salyrgan, novasurol, strophanthin, and digitoxin, but no significant change takes place during sodium chloride diuresis nor after the administration of thyroxine. The rate of oxygen consumption is decreased by the action of the posterior lobe of the pituitary, and it runs parallel with the excretion of nitrogen.
W. O. Kermack.

Scilla glucosides. W. Graf (Arch. exp. Path. Pharm., 1929, **140**, 355—379).—A study of the pharmacological action of scillaren-*A* and -*B* and of scillaridin-*A* and -*B*. B. A. Eagles.

Ch'an Su, the dried venom of the Chinese toad. K. K. Chen and H. Jensen (J. Amer. Pharm. Assoc., 1929, **18**, 224—251).—The history and general characteristics of the dried venom of the Chinese toad are given and the following substances have been isolated: cholesterol containing 0·2% of ergosterol; bufagin, m. p. 217°; a nitrogenous *compound*, m. p. 200°, which is more toxic than bufagin, and adrenaline, m. p. 212°. The powdered material contains 5·04% of water, 1·09% of volatile matter, and 3·10% of ash and the alcoholic extract is very toxic to animals, causing a marked rise of blood-pressure soon followed by death. E. H. Sharples.

Determination of small amounts of alcohol in the human subject. J. Evans and A. O. Jones (Analyst, 1929, **54**, 134—141).—Southgate's apparatus for determining alcohol in urine is described; the process allows of the use of only 2 c.c. of urine, which are slowly evaporated at 80° in a current of air previously washed in sulphuric acid. The air–alcohol mixture is passed through 15 c.c. of 0·2*N*-potassium dichromate solution, wherein the alcohol is oxidised to acetic acid. The unreduced dichromate is determined by causing it to liberate iodine from potassium iodide. The alcohol concentration in the urine is at its maximum 1½ hrs. after consumption and falls at the rate of about 12 mg. per hour per 100 g. of blood. If the sample of urine has been excreted at the maximum alcohol point, 96 c.c. of absolute alcohol (235 c.c. of whisky; 1920 c.c. of beer) correspond with 200 mg. of alcohol per 100 c.c. of urine; *i.e.*, mg. of alcohol per 100 c.c. × 0·04137 for whisky gives fluid oz. consumed, or × 0·0190 for beer gives pints. Analytical verification for the method was obtained by checking against a solution of pure alcohol and in urine after different times following the consumption of known quantities of alcohol. D. G. Hewer.

Effect of anæsthesia and of decerebration on the lactic acid and glycogen of mammalian muscle. J. C. Hinsey and H. A. Davenport (Amer. J. Physiol., 1929, **88**, 286—293).—The blood-lactic acid level of decerebrate cats is higher than that of normal cats. In 10 out of 14 experiments the lactic acid content of the tonic gastrocnemius was higher than that of the atonic one. The glycogen contents were essentially the same. B. A. Eagles.

Combination of some narcotics with tissues rich and poor in lipins. S. Loewe and P. Molyavko-Vyssotski (Biochem. Z., 1929, **206**, 194—211).—The amount of chloral or bromal hydrate adsorbed by minced tissue (brain and muscle) from the surrounding solution at equilibrium was determined. A correction was applied for swelling. Brain takes up more of the narcotic than muscle, but it is undecided whether the process is one of partition or adsorption.
J. H. Birkinshaw.

Muscle poisons causing contraction. I. Novocaine antagonism. K. Zipf (Arch. exp. Path. Pharm., 1929, **140**, 56—90).—The pharmacological actions of caffeine, quinine hydrochloride, Nile-blue sulphate, methylene-blue hydrochloride, and *o*-nitroaniline in the isolated sartorius muscle of the frog have been investigated both singly and in presence of other organic and inorganic cations. Certain local anæsthetics and atropine exert an antagonistic action, decreasing or abolishing the effects of the above compounds. Base exchange appears to play an important rôle in producing the observed phenomena.
W. O. Kermack.

Arsine poisoning. E. Meyer and W. Heubner (Biochem. Z., 1929, **206**, 212—222).—In a fatal case of arsine poisoning, no methæmoglobin was detected in the blood, but hæmoglobin was present in connective tissue. The arsenic content of liver and kidneys was 0·1 g., equally divided between the two organs. The respective percentages on organ weight were 3 mg. and 10 mg.

In a non-fatal case the blood-plasma contained 13 mg.-% of arsenic and the blood-cells none. Hæmoglobin and methæmoglobin were present in the urine. The blood was free from methæmoglobin, but after a few minutes in the air methæmoglobin was detected in the hæmolytic plasma but not in the corpuscles. In non-fatal cases a portion of the arsenic present in the body is slowly excreted in the urine. The symptoms of arsine poisoning are given. J. H. Birkinshaw.

Action of chlorine on men poisoned by toxic smokes. D. C. Walton and W. A. Eldridge (J. Pharm. Exp. Ther., 1929, **35**, 241—256).—The toxic and irritant smokes, diphenylchloroarsine, diphenylcyanoarsine, and diphenylaminechloroarsine lose their irritant property on chlorination. Patients suffering from the irritant effects of these compounds are relieved by inhaling chlorine. E. Boyland.

Buffer antiseptics. I. General. II. Phenol-activity, -capacity, and -buffer effect. J. K. Gjaldbaek (Dansk Tidsskr. Farm., 1929, **3**, 10—28, 29—75).—I. Buffer antiseptics are substances which contain a supply of an active antiseptic in a more or less inactive form, and can transfer the active substance to water, tissue juices, etc., with which they are brought in contact. The terms A-activity, A-capacity, and A-buffer power are introduced. The A-activity is the concentration of the antiseptic in an aqueous solution which is in equilibrium with the buffer antiseptic, A-capacity is the total amount of removable antiseptic, in g. per 100 g. of buffer antiseptic, and the A-buffer power the ability of the antiseptic to maintain a certain activity. In a buffer antiseptic, the total concentration of the antiseptic (active and inactive form) must be greater than the A-activity, and, when the antiseptic is partly removed, the A-activity must decrease to a smaller extent than does the A-concentration. Sodium silver thiosulphate is an example of a chemically-bound buffer antiseptic. The silver ion is the active antiseptic, and when the silver ions are removed from the solution further liberation of silver ions takes place.

II. Solutions of phenols etc. in glycerol, ethyl alcohol, and certain oils furnish examples of buffer antiseptics in which the buffering is due to the greater solubility of the phenol in the solvent than in water. The author has studied the buffer effect of phenol in oils, ointments, and camphor by measuring the coefficients of distribution of the phenol between the antiseptic solvent and water. The solvents can be divided into two groups; in the first the buffer effect remains constant during the process of phenol discharge, in the second there is an increase in buffer action, since the partition coefficient increases with a decreasing concentration of the phenol in the non-aqueous phase. F. C. Happold.

Reaction kinetics in the macroheterogeneous medium. S. J. Przyłecki (Biochem. Z., 1929, **206**, 60—98).—A theoretical discussion of the factors governing the activation of reactions, with special reference to the effect of structure. J. H. Birkinshaw.

Enzyme processes. Action of amylase. Y. Schaeffer (Compt. rend. Soc. Biol., 1928, **98**, 1491—1494; Chem. Zentr., 1928, ii, 1673).—The maximum yield of sugar was 70%; the speed of its production exhibits several maxima and minima.

A. A. Eldridge.

Changes in the activity of the intestinal juice enzymes depending on the kind of food. I. Amylolytic enzyme. S. V. Andreyev and S. I. Georgievski (Zhur. exp. Biol. Med., 1928, **10**, 169—179).—The amylolytic action of intestinal juice varies according to the starch content of the food.

Chemical Abstracts.

Alleged salt-hydrolysis of starch. N. Malyschev (Biochem. Z., 1929, **206**, 401—409).—Takane's results (A., 1926, 1059) were confirmed. Even in non-sterilised solutions hydrolysis occurred only in a few examples. Treatment of the starch solution with air or with pure oxygen did not accelerate hydrolysis, as stated by Biedermann (A., 1923, i, 655).

C. C. N. Vass.

Glycolysis in muscle and other tissues. E. M. Case (Biochem. J., 1929, **23**, 210—218).—Brain, kidney, muscle, and blood-corpuscles activate the production of lactic acid from dextrose by muscle extract (cf. Meyerhof, A., 1927, 590). Grinding, filtering, or any process which destroys or removes intact cells has a corresponding effect in diminishing the activating power of the tissue. In the presence of 0·002M-potassium cyanide the activation of glycolysis by brain is not inhibited; kidney glycolysis is, on the other hand, prevented by this concentration of cyanide. The activation of the system muscle+dextrose by yeast, brain, or kidney is unaffected by cyanide. The hydrolysis of phosphoric ester is prevented when muscle-extract is acting on dextrose in the presence of brain or kidney on addition of fluoride. When yeast is employed as activator, fluoride prevents even the synthesis of hexosephosphate from dextrose. Phloridzin, phloroglucinol, amygdalin, and salicin have no effect on the activating action of yeast on glycolysis (cf. Dann and Quastel, A., 1928, 329). Cell-free extracts of Rous chicken sarcoma do not contain this activator. Suspensions of the comparatively uninjured sarcoma tissue possess this power. S. S. Zilva.

Significance of iron in biological oxidation. I. Rôle of ferrous salts as aldehydase. II. Rôle of ferrous salts as oxido-reductases for various organic substances. K. Ando (J. Biochem. Japan, 1928, **9**, 187—199, 201—214).—Similarities in action between Schardinger's enzyme and ferrous salts suggest that the former is an organic iron compound. It is supposed that the enzyme, like ferrous sulphate, attacks a molecule of water, transferring activated hydrogen to the acceptor and oxygen to the donator. Experiments using methylene-blue show that inorganic ferrous salts act as aldehydases. Organic substances which are easily oxidised *in vivo* are good donators for ferrous salts or for the methylene-blue system. Lecithin and the higher fatty acids are powerful accelerators.

Chemical Abstracts.

Occurrence of a citric-dehydrogenase in cucumber seeds and its application to a sensitive biological colour reaction for citric acid. T. Thunberg (Biochem. Z., 1929, **206**, 109—119).—A phosphate extract of cucumber seeds contains an extremely sensitive citric-dehydrogenase which produces the maximum decolorising velocity by the Thunberg methylene-blue technique in presence of less than 0·01 mg. of citric acid. From this a method of testing for small amounts of citric acid, *e.g.*, in milk, is developed. J. H. Birkinshaw.

Dehydrogenation of lactic acid. A. Hahn, E. Fischbach, and W. Haarmann (Z. Biol., 1929, **88**, 516—522).—The study of the dehydrogenation of lactic acid (lithium salt) to pyruvic acid by minced muscle preparations is continued (A., 1928, 1281). The reaction can take place with washed muscle preparations without the addition of methylene-blue, but it is greatly enhanced by such addition. Unwashed muscle pulp gives a much greater yield of pyruvic acid, and maximum dehydrogenation takes place when methylene-blue is added to such a system in excess. Dehydrogenation is also observed under anaërobic conditions without the addition of a hydrogen acceptor. F. C. Happold.

Influence of structure on the kinetics of desmolases. II. Uricase. Systems uricase–uric acid–liver and kidney pulp. S. J. Przylecki (Z. physiol. Chem., 1929, **181**, 234—254; cf. A., 1928, 1055).—The change in velocity of decomposition of uric acid by the uricase of tissue pulp on disintegration is investigated with and without addition of 1% of propyl alcohol, three sets of experiments being carried out using the whole pulp and the fine and coarse particles thereof, in each case the pulp being used after mincing, and also after grinding with sand, freezing at −12°, and after both these treatments. Both the mechanical disintegration and the presence of alcohol caused considerable acceleration of the reaction. Disintegration caused an increased adsorption of uric acid by the tissue, and addition of alcohol in all cases a considerable elution of uric acid. Most of the uricase is present in the adsorbed condition. Addition of alcohol to the pulp causes elution of about 12·6% of the enzyme. Addition of uric acid also causes a slight elution and addition of both alcohol and uric acid liberates about 30% of the enzyme. Both adsorbed and eluted uricase are active. Alcohol besides eluting uric acid and enzyme also accelerates the penetration of uric acid into the range of action of uricase by increasing cell permeability. P. W. Clutterbuck.

Mechanism of the action of oxidising catalysts. L. Stern (Compt. rend. Soc. Biol., 1928, 98, 1288—1290; Chem. Zentr., 1928, ii, 1673—1674).—Oxydones are differentiated from oxidases by the fact that they function only in presence of active oxygen, which cannot be replaced by another hydrogen acceptor. A. A. Eldridge.

Bioluminescence. VII. Solubility of *Cypridina* luciferin in organic solvents. S. Kanda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 91—98).—*Cypridina* luciferin after it has been purified by dissolution in methyl alcohol and in ethyl alcohol becomes soluble in benzene, ether, light petroleum, and chloroform, although in the crude state it does not dissolve in these solvents. The insolubility of crude luciferin in benzene is possibly due to association with protein, from which it is separated by the treatment with alcohol. The benzene solution contains active luciferin for about 1 month, whereas the ether solution loses its power to produce light when added to a luciferase solution in a few hours. W. O. Kermack.

Specific inhibitions of lipase, especially by fluoride. P. Rothschild (Biochem. Z., 1929, **206**, 186—193).—Fluoride produces a marked inhibition of liver-lipase action on various esters which becomes stronger with increasing acidity. The action is reversible. Arsenite produces strong inhibition which is, however, slightly less at lower p_H values. Certain heavy metals have the same effect independent of p_H, but in all these cases the action is irreversible. J. H. Birkinshaw.

Influence of various substances on lipase action. R. F. Corran (Biochem. J., 1929, **23**, 188—194).—In low concentration lecithin and cholesterol act slightly and to the same extent as augmenters of lipolysis. The values of the augmentations fall with increasing concentration. The influence of sodium and potassium chlorides is only slightly augmentative. Calcium chloride acts as an inhibitor. Ionic lead acts as an augmenter towards lipase in the presence and in the absence of serum. Copper and mercury under the same conditions act as inhibitors. The albumin–pseudoglobulin fraction of blood-serum possesses more than 80% of the co-enzymic activity exhibited by serum. S. S. Zilva.

Preparation and use of the bone phosphatase. M. Martland and R. Robison (Biochem. J., 1929, **23**, 237—242).—The enzyme is best prepared from the bones of young growing rachitic rabbits by extraction with chloroform water during 7—10 days, the bones being first split longitudinally and the marrow removed. Evaporation of the filtered extracts in evacuated desiccators over sulphuric acid yields 5—8 mg. of dry solid per c.c., no loss of activity occurring during this process. Purification can be carried out (*a*) by precipitation with a mixture of alcohol and ether yielding a stable preparation which possesses the original activity; (*b*) by removal of a protein by precipitation at its isoelectric point (p_H 5·8); (*c*) by dialysis through a collodion membrane previously immersed for 24 hrs. in 95% alcohol or by ultrafiltration in a Bechhold filter through a collodion disc of similar porosity which yields an inactive filtrate containing the whole of the phosphate. No evidence of the presence of a co-enzyme was obtained. No purification of the enzyme by means of specific adsorption using kaolin, calcium phosphate, or aluminium hydroxide prepared by the method of Willstätter and Kraut was obtained. The application of this method to the hydrolysis of hexosediphosphoric acid and the properties of the hexose so obtained are discussed. S. S. Zilva.

Digestion of lecithin by pancreatic enzymes. S. A. Portis (J. Amer. Med. Assoc., 1928, 91, 1248—1250).—Normal duodenal contents digest lecithin, whilst gastric contents do not. The action is depressed in cardiac decompensation and untreated gastric ulcer, but not in pregnancy. Chemical Abstracts.

Enzymic hydrolysis of keratin with the juice of the crop of *Astur palumbarius* (hawk) and *Vultur monachus* (vulture). R. Stanković, V. Arnovljevic, and P. Matavulj (Z. physiol. Chem., 1929, **181**, 291—299).—The crop juice of these birds hydrolyses pure keratin, the action being enzymic. The enzyme system is destroyed by heating for 0·5 hr. at 95°. The juice also liberates amino-acids from horny tissue. Keratinolysis proceeds more quickly in the crop of the bird than *in vitro*. P. W. Clutterbuck.

Specific action of enzyme complexes in fission of polypeptides. E. Abderhalden and F. Reich (Fermentforsch., 1929, **10**, 319—329; cf. this vol., 177).—By usual methods are obtained *glycyl*-dl-*leucyl*-β-*alanine* (I), m. p. 160° (from *chloroacetyl*-dl-*leucyl*-β-*alanine*, m. p. 124—126°), β-*alanyl*-dl-*leucine* (II), m. p. 245—246° (decomp.), β-*alanylglycyl*-dl-*leucine* (III), decomp. 125°, and β-*alanyl*-dl-*leucylglycyl*-dl-*leucine* (IV), decomp. 125°. With the exception of II, all are hydrolysed by *N*-sodium hydroxide at 37—40°, I more rapidly than the isomeric III. None is hydrolysed by erepsin, but IV is attacked by trypsin-kinase (p_H 8·2) at 37°. β-*Iodopropionylglycyl*-dl-*leucine*, m. p. 170° (containing a little of the β-chloro-compound), is unattacked by trypsin-kinase.

J. W. Baker.

Specific action of enzyme complexes in fission of polypeptides. E. Abderhalden and F. Schweitzer (Fermentforsch., 1929, **10**, 341—364).—In continuation of the investigation of Abderhalden and Schwab (this vol., 176) the hydrolysis of the following polypeptides and their derivatives (prepared by usual methods) with *N*-sodium hydroxide, erepsin (p_H 7·8), and trypsin-kinase (p_H 8·4) at 37° has been studied. No polypeptides containing a free glycine carboxyl group are attacked by trypsin-kinase, although some of their acyl derivatives suffer fission. The following are hydrolysed by trypsin-kinase, but not by erepsin: the *benzoyl*, m. p. 175° (decomp.), *phenylurethane*, m. p. 185° (corr.), and *naphthalene-2-sulphonyl*, m. p. 175° (decomp.), derivatives of *dl*-leucylglycylglycine (I), whilst the reverse is the case with (I), glycyl-*dl*-phenylalanine (II) (naphthalene-2-sulphonyl derivative hydrolysed by trypsin-kinase), diglycyl-*dl*-phenylalanine (III), *dl*-phenylalanylglycine (IV), *dl*-phenylalanylglycylglycine (V), dl-*phenylalanyldiglycylglycine* (VI), m. p. 207° (decomp.) [*phenylurethane*, m. p. 296° (decomp.), which is not attacked by trypsin-kinase] [from β-*phenyl*-α-*bromopropionyldiglycylglycine*, m. p. 278—279° (decomp.)], and *dl*-leucylglycyl-*dl*-phenylalanine (VII), m. p. 235° (corr., decomp.; lit. gives 225—228°). The following are hydrolysed by erepsin and somewhat less readily by trypsin-kinase: *diglycylglycyl*-dl-*phenylalanine* (VIII), m. p. 223° (decomp.) [from *chloroacetyldiglycyl*-dl-*phenylalanine*, m. p. 184—185° (decomp.), which is not attacked by trypsin-kinase], dl-*phenylalanyltriglycyl*-dl-*phenylalanine* [from β-*phenyl*-α-*bromopropionyltriglycyl*-dl-*phenylalanine*, m. p. 187° (decomp.)], dl-*phenylalanylglycyl*-dl-*leucine* (IX), m. p. 210° (decomp.) (from dl-β-*phenyl*-α-*bromopropionylglycyl*-dl-*leucine*, m. p. 161°, which is hydrolysed by trypsin-kinase), dl-*phenylalanylglycyl*-dl-*phenylalanine* (X), m. p. 236° (decomp.) (from dl-β-*phenyl*-α-*bromopropionylglycyl*-dl-*phenylalanine*, m. p. 174—175°, not hydrolysed by trypsin-kinase). *dl*-β-Phenyl-α-bromopropionyl-*dl*-phenylalanine is hydrolysed by trypsin-kinase. Of these various derivatives I (and its three derivatives) to X are all hydrolysed by *N*-sodium hydroxide.

J. W. Baker.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. Abderhalden and H. Brockmann (Fermentforsch., 1929, **10**, 330—340).—The conclusions previously reached (this vol., 180) are confirmed by the action of trypsin-kinase and erepsin on the following polypeptides and their derivatives, which are prepared by usual methods. dl-*Leucyltriglycylaniline*, m. p. 202—203° (oily *picrate*) [from dl-α-*bromo*iso*hexoyltriglycylaniline*, m. p. 229—230° (decomp.)], and glycyl-*dl*-α-aminobutyryl-*dl*-α-aminobutyric acid are attacked by erepsin (p_H 7·8), but not by trypsin-kinase (p_H 8·4) at 38°. *dl*-α-Bromopropionyl-*dl*-α-aminobutyryl-*dl*-α-aminobutyric acid, *dl*-α-bromopropionyl-*l*-leucylglycyl-*d*-alanine, chloroacetyl-*d*-alanyl-*l*-leucylglycyl-*d*-alanine, and d-α-*bromo*iso*hexoylglycyl*-d-*alanyl*-l-*leucylglycyl*-d-*alanine*, m. p. 206—207°, are all attacked by trypsin-kinase, but not by erepsin, whilst *dl*-alanyl-*dl*-α-aminobutyryl-*dl*-α-aminobutyric acid is attacked by both enzymes. The following are not hydrolysed either by erepsin or trypsin-kinase: chloroacetyl-*dl*-α-aminobutyryl-*dl*-α-aminobutyric acid, *dl*-α-bromo*iso*hexoyldi- and -hexaglycylglycine, *butyryldiglycylglycine*, m. p. 231—232°, and N-*methyl*-dl-*leucyldiglycylglycine*, m. p. 238° (decomp.). Trypsin-kinase has no action on chloroacetamidobenzoic acid. Both *dl*-alanyldecarboxy-*dl*-leucine and *dl*-alanylcolamine are hydrolysed by yeast extract (p_H 8·0). *Butyryltriglycylaniline*, m. p. 231—232°, is prepared. All m. p. are corrected.

J. W. Baker.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. Abderhalden and E. Schwab (Fermentforsch., 1929, **10**, 305—318).—Further information on the reasons for the specific action of enzymes is sought by a study of the action of trypsin-kinase and erepsin on a large number of polypeptides, their acyl and halogenoacyl derivatives. The action of these enzymes has no relation to the length of the chain, since dl-*phenylalanyl*-l-*tyrosine*, sintering 254°, decomp. 269—270°, and *l*-tyrosyl-*l*-tyrosine are attacked by trypsin-kinase and not by erepsin, the reverse being the case with the longest known polypeptide (19 amino-acids). The following halogenoacyl derivatives (none of which is attacked by erepsin) are hydrolysed by trypsin-kinase: chloroacetyl-*l*-leucylglycine, -glycyl-*dl*-leucine, -diglycyl-*dl*-leucine, -*d*-α-aminobutyric acid, -*l*-α-aminobutyric acid (slightly), -*dl*-valine, -*l*-leucine, -*d*-phenylalanine (slightly), -3 : 5-dibromo-*dl*-tyrosine, *dl*-α-bromo*iso*hexoyl-triglycyl-*dl*-leucine, -glycyl-*dl*-leucine, *l*-bromo*iso*hexoylglycyl-*l*-leucine, di-*dl*-α-bromopropionyl-*l*-cystine, β-*chlorobutyrylglycyl*-dl-*leucine*, m. p. 139°, -dl-*phenylalanine*, m. p. 130° (slightly), -*glycyl*-dl-*phenylalanine*, m. p. 174° (slightly), *dl*-α-bromopropionyl-*dl*-phenylalanine, -glycyl-*dl*-phenylalanine, (cf. also Waldschmidt-Leitz and others, A., 1928, 1401; Abderhalden and Schwab, this vol., 176), whilst the following are unattacked: chloroacetyl-glycylglycine, -*d*-leucine, *dl*-α-bromo*iso*valeryl-glycine, -glycylglycine, *dl*-α-bromo*iso*hexoylglycine, -glycylglycine, -*dl*-α-aminohexoic acid, -*dl*-phenylalanine, -*l*-tyrosine. The action of trypsin-kinase on the halogenoacyl derivatives of polypeptides containing leucine and glycine diminishes with an increasing number of glycine residues. The following acyl derivatives of amino-acids are attacked by trypsin-kinase; formyl-*l*-leucine, -*l*-phenylalanine,

-*dl*-tyrosine, carbomethoxyformyl-*l*-tyrosine, palmityl-*l*-phenylalanine, and stearyl-*d*-glutamic acid, whilst the following are not attacked: formyl-*dl*-valine, -*d*-leucine, -*dl*-norleucine, -*d*-*iso*leucine, -*dl*-α-aminoheptoic acid, -*d*-phenylalanine, and carbomethoxy-*l*-tyrosine. It is concluded that the hydroxyl group of tyrosine has no importance in the formation of a complex with trypsin. *dl*-Leucine ethyl ester is attacked by both trypsin-kinase and erepsin, whilst *dl*-tyrosine ethyl ester is hydrolysed only by the former enzyme. On the basis of these results it is concluded that no one specific property is concerned in the action of trypsin and erepsin and it is not improbable that trypsin has a composite character. The authors disagree with the deductions of Waldschmidt-Leitz (*loc. cit.*). It is suggested that the hydrolytic action of the enzyme is indirect. Its specific action is involved only in the formation of the ferment-substrate complex, and in so doing so modifies the whole molecule that a previously inactive hydrogen-ion concentration may then be able to effect fission, the actual hydrolysis thus not being a specific action. J. W. Baker.

Specific action of enzymes. Polypeptides containing histidine. E. Abderhalden, R. Fleischmann, and W. Irion (Fermentforsch., 1929, **10**, 446—454).—Further evidence (cf. preceding abstract) that, contrary to Waldschmidt-Leitz and others (A., 1928, 1401), the electronegative character of the substrate is not important for hydrolysis by trypsin-kinase is found in the fact that erepsin, which readily hydrolyses *l*- and *dl*-leucyl-*l*-histidine (Fischer and Cone, A., 1908, i, 1004), has no action on *d*- and *dl*-α-bromo*iso*hexoyl-*l*-histidine, whilst trypsin hydrolyses the bromo-compounds more slowly than the parent polypeptides, the latter, in turn, however, being less readily hydrolysed by this enzyme than by erepsin. α-Bromo*iso*hexoyl-*l*-histidine is readily hydrolysed by *N*- and even by 0·1*N*-sodium hydroxide, and hence the more dilute alkali must be used to hydrolyse its methyl ester in its preparation. *l*-Leucyl-*l*-histidine is unattacked by *N*-sodium hydroxide at 37° in 72 hrs. Vickery and Leavenworth's method (A., 1928, 1121) for the preparation of histidine is found to be much more costly and uncertain than the older mercuric method. J. W. Baker.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on the decomposition of certain polypeptides. E. Abderhalden and V. Vlassopoulos (Fermentforsch., 1929, **10**, 365—395).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on various polypeptides derived from α-aminobutyric and α-amino-*n*- and -*iso*-valeric acids and their derivatives has been studied. Erepsin, but not trypsin, effects the hydrolysis of *dl*-α-aminobutyrylglycine (*phenylurethane*, m. p. 188°; *naphthalene-2-sulphonyl* derivative, m. p. 165·5°) and glycyl-*dl*-α-aminobutyric acid (I) (*naphthalene-2-sulphonyl* derivative, m. p. 112—114), whilst neither enzyme attacks dl-α-*aminobutyrylglycylglycine* (II) (*naphthalene-2-sulphonyl* derivative, m. p. 140°) (from dl-α-*bromobutyrylglycylglycine*, m. p. 147°), dl-α-*aminobutyryldiglycylglycine* (*phenylurethane*, m. p. 193°) (from the α-*bromo*-compound, m. p. 175°), and *diglycyl*-dl-α-*aminobutyric acid* (III) (from *chloroacetylglycyl*-dl-α-*aminobutyric acid*, m. p. 120—121°). The *phenylurethane*, m. p. 195°, of I suffers fission by trypsin-kinase, but not the *phenylurethanes*, m. p. 172° and 208°, respectively, of II and III. In the valine series erepsin hydrolyses *dl*-valyl-*dl*-valine (IV) (*phenylurethane*, m. p. 188—189°; *naphthalene-2-sulphonyl* derivative, m. p. 208°), d-*valyl*-d-*valine* (V), m. p. above 300°, $[\alpha]_D^{20}$ −54° (water) (*phenylurethane*, m. p. 184°; *naphthalene-2-sulphonyl* derivative, m. p. 213—215°) [obtained in small yield from d-α-*bromo*-iso*valeryl*-d-*valine*, m. p. 137°, $[\alpha]_D^{20}$ +13·1° (alcohol), together with *dimethylacrylvaline*, m. p. 137°, the latter not being attacked by extract of pancreas powder or *N*-sodium hydroxide], *glycyl*-d-*valyl*-d-*valine* (VI), m. p. 220°, $[\alpha]_D^{20}$ −32° (water) (*naphthalene-2-sulphonyl* derivative), dl-*norvalyl*-dl-*norvaline* (VII), m. p. 270° (decomp.) (*phenylurethane*, m. p. 206°; *naphthalene-2-sulphonyl* derivative, m. p. 177°) (from α-*bromo*-n-*valeryl*-dl-*norvaline*, m. p. 124—125°), and *glycyl*-dl-*norvalyl*-dl-*norvaline* (VIII), m. p. 238—240° (*phenylurethane*, m. p. 156°; *naphthalene-2-sulphonyl* derivative, m. p. 195°) (from *chloroacetyl*-dl-*norvalyl*-dl-*norvaline*, m. p. 147·5°). None of these polypeptides or their derivatives is attacked by trypsin-kinase. All the polypeptides containing *dl*-α-aminobutyric acid in their structure, together with their phenylurethanes and naphthalene-2-sulphonyl derivatives, are hydrolysed by *N*-sodium hydroxide at 37°, in some cases hydrolysis of the derivatives being more rapid and in others slower than that of the parent polypeptides. In the valine series IV and V are unattacked by *N*-sodium hydroxide, whilst their derivatives, and VI suffer hydrolysis. On the other hand, VII and its derivatives and VIII are slowly hydrolysed. J. W. Baker.

Specificity of enzymolytic degradation of polypeptides. Polypeptides containing *dl*-norleucine. E. Abderhalden and H. Mayer (Fermentforsch., 1929, **10**, 464—473).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on various polypeptides containing norleucine is investigated. Trypsin-kinase effects the hydrolysis of chloroacetyl-*dl*-norleucine, dl-α-*bromohexoyl*-dl-*norleucine* (I), m. p. 104°, dl-α-*bromo*iso*hexoyl*-dl-*norleucine* (II), m. p. 136°, dl-α-*bromohexoyl*-dl-*leucine* (III), m. p. 158°, *dl*-α-bromo*iso*hexoylglycyl-*dl*-norleucine, *dl*-leucylglycyl-*dl*-norleucine (IV), dl-α-*bromohexoylglycyl*-dl-*norleucine*, m. p. 118°, dl-*norleucylglycyl*-dl-*norleucine* (V), m. p. 240°, dl-α-*bromohexoylglycyl*-dl-*leucine*, m. p. 127°, dl-*norleucylglycyl*-dl-*leucine* (VI), m. p. 245°, and the *phenylurethanes*, m. p. 186° and 202°, respectively, of dl-*leucyl*-dl-*norleucine* (VII), m. p. 256°, and dl-*norleucyl*-dl-*leucine* (VIII), m. p. 253°. Erepsin hydrolyses IV, V, VI, VIII, and *glycyl*-dl-*norleucine*. dl-*Norleucyl*-dl-*norleucine*, m. p. 259° (*phenylurethane*, m. p. 198°), and IV are too insoluble for investigation. All these polypeptides are hydrolysed by *N*-sodium hydroxide with the exception of I, II, III, VII, and VIII, and the three phenylurethanes. J. W. Baker.

Behaviour of *N*-sodium hydroxide, erepsin, and trypsin-kinase towards polypeptides containing a 3 : 5-halogen-substituted tyrosine residue,

glycyl-*d*-tyrosine, glycyl-*dl*-nitrotyrosine, and glycyl-*dl*-*o*-tyrosine. E. Abderhalden and A. Schmitz (Fermentforsch., 1929, **10**, 428—439).—Investigations of the effect of modifying the carboxyl group of an amino-acid have been made by a study of the action of the above hydrolysing agents on various synthetic polypeptides derived from glycine and substituted tyrosines, all of which are prepared by usual methods. All the undermentioned derivatives are hydrolysed by *N*-sodium hydroxide at 37°, the tripeptides most rapidly and glycyl-*l*-tyrosine most slowly. Erepsin (p_H 7·8) at 37° attacks glycyl-*l*-tyrosine, *glycyl*-dl-3 : 5-*dichloro*-, m. p. 237°, -3 : 5-*dibromo*-, m. p. 222—223° (decomp.), and -3 : 5-*di-iodo-tyrosine* (the first two being obtained, respectively, from *chloroacetyl*-3 : 5-*dichloro*-, m. p. 195°, and -3 : 5-*dibromo-tyrosine*, m. p. 207°), none of which is hydrolysed by trypsin-kinase. Conversely, trypsin-kinase (p_H 8·3), but not erepsin, at 37° effects hydrolysis of *chloroacetyl*-dl-o-*tyrosine* (cf. Ueda, this vol., 75), dl-*leucylglycyl*-dl-3 : 5-*dichloro*-, m. p. 210° (decomp.), -3 : 5-*dibromo*-, m. p. 220° (decomp.), and -3 : 5-*di-iodo*-, m. p. 205° (decomp.) -*tyrosine* (obtained, respectively, from dl-*α-bromo*iso*hexoylglycyl*-dl-3 : 5-*dichloro*-, -*dibromo*-, and -*di-iodo-tyrosine*). Neither enzyme attacks *glycyl*-dl-5-*nitrotyrosine*, m. p. 240° (decomp.) (from *chloroacetyl*-dl-5-*nitrotyrosine*, m. p. 166°), *glycyl*-dl-o-*tyrosine*, m. p. 150°, or *glycyl*-d-*tyrosine*, m. p. 160°. Addition of 0·1 or 0·02 mol. of either dichloro- or di-iodo-tyrosine to glycyl-*l*-tyrosine reduces the enzymolytic action of erepsin on this polypeptide. J. W. Baker.

Homogeneity of trypsin complexes ? I, II, and III. E. Abderhalden (Fermentforsch., 1929, **10**, 474—477, 478—480, 481—490).—**I. Behaviour of various substrates with various trypsin-kinase preparations at various p_H values.** [With O. Hermann.]—From a study of several examples it is found that the activity of trypsin-kinase preparations varies greatly according to the specimen and p_H value used. Thus although some specimens were unable to effect the hydrolysis of *dl*-leucylglycyl-*dl*-leucine at p_H 7·8, hydrolysis occurred at p_H 8·4. In general, halogenoacyl derivatives are more readily attacked at p_H 7·8 than at p_H 8·4, whilst the polypeptides themselves are more readily hydrolysed at the latter value. The significance of these results is discussed.

II. Separation of enzymes with varying activity in the preparation of "trypsin" from pancreas powder. [With E. Schwab.]—The enzyme obtained in the usual manner from pig's pancreas is subjected to three adsorptions on alumina at p_H 4·7 to remove erepsin, and the mother-liquor is subsequently adsorbed at p_H 5·6. The eluted enzyme from the latter adsorption does not hydrolyse *dl*-leucylglycine or *dl*-leucylglycyl-*dl*-leucine, but still attacks chloroacetyl-*l*-tyrosine, -*l*-phenylalanine, -*l*-leucine, and glycyl-*dl*-leucine phenylurethane. The final mother-liquor also attacked these halogenoacyl derivatives, but more slowly. By repeated adsorption at p_H 5·6 a mother-liquor is obtained from which is prepared a trypsin preparation which is very unreactive towards these derivatives. Hence the suggestion that the trypsin complex is not a single individual (Abderhalden and Schwab, this vol., 604) is confirmed.

III. Period of hydrolysis of halogenoacyl-amino-acids and polypeptides by various specimens of trypsin at various p_H values. [With W. Zeisset.]—The enzymolytic action of the same specimen of trypsin-kinase prepared by the usual methods on a series of halogenoacyl derivatives of polypeptides confirms the previous conclusion (I, above) that hydrolysis is much more rapid at p_H 7·8 than at p_H 8·4. Further, the trypsin preparation obtained by adsorption at p_H 5·6 (II, above) hydrolyses those derivatives which are only slightly attacked by the normal trypsin preparation even more slowly. J. W. Baker.

Relationship between erepsin and trypsin-kinase and their substrate polypeptides and their derivatives. Attempted isolation of erepsin from intestinal juice and trypsin from pancreas juice. E. Abderhalden and E. Schwab (Fermentforsch., 1929, **10**, 440—445).—Erepsin, which by itself does not hydrolyse the halogenoacyl derivatives of α-amino-acids and polypeptides, readily and rapidly hydrolyses a large number of these derivatives when a trace of trypsin is added. This obviously serves as a practical test for the absence of trypsin from erepsin preparations. Hydrolysis of this type of derivatives with trypsin-kinase with addition of a little erepsin proceeds more rapidly for the first hour than with trypsin-kinase alone, but as the hydrolysis proceeds the action of the former mixed enzyme decreases so that the final degree of hydrolysis is the same in each case. Possible explanations of this mutual action are discussed. J. W. Baker.

Natural activation of proteases of plant latexes. O. Ambros and A. Harteneck (Z. physiol. Chem., 1929, **181**, 24—41).—Papaw (*Carica papaya*) contains a natural activator which stimulates the hydrolytic activity of the latex towards proteins, protamines, and peptones in the same way as hydrocyanic acid for the commercial papain. This thermolabile activator is termed phytokinase. In half-ripe fruits the latex contains the activator, but in the almost ripe fruits the latex alone is comparatively inactive, the activator is found in the fruit flesh and seeds. Pineapple (*Bromelia sativa*) contains a similar activator. J. H. Birkinshaw.

Thermostability and regeneration of inactivated enzymes. V. Kulikov and M. Bobkon (Zhur. exp. Biol. Med., 1928, **10**, 147—152).—If inactivation of enzymes by heat is associated with coagulation of other substances present in the mixture, the enzyme must become adsorbed on the coagulated particles and its regeneration is probably a slow elution process. For proteolytic enzymes the regeneration takes place only when the inactivation is carried out at p_H 7·9. Chemical Abstracts.

Problems of fermentation. H. von Euler and K. Myrbäck (Z. physiol. Chem., 1929, **181**, 1—14).—The rôle of the hexosephosphoric acids, the question as to whether the Robison ester is the precursor of diphosphate, and the phenomenon of mutation are discussed. J. H. Birkinshaw.

Phosphoric esters in alcoholic fermentation. I. Sequence of the formation of phosphoric esters and carbon dioxide in fermentation by dried yeast. E. Boyland (Biochem. J., 1929, **23**, 219—229).—Up to a limiting concentration of phosphoric esters the basic rate of fermentation varies with the concentration of phosphorus present as phosphoric esters. Up to this same concentration the ratio of diphosphoric ester to monophosphoric ester remains constant, but above the limiting concentration the relative amount of diphosphoric ester increases. The addition of inorganic phosphate to dried yeast fermenting dextrose is followed by esterification and liberation of carbon dioxide, but there is a considerable lag between esterification and the evolution of carbon dioxide. The carbon dioxide liberated by phosphate is somewhat more than equivalent to the added phosphate, but is approximately equivalent to the phosphorus esterified plus the amount of phosphorus as monophosphate formed. In fermentation by dried yeast in presence of phosphate the monophosphoric esters are formed late in the reaction. Under the conditions described in this paper these esters consist mainly of trehalosemonophosphate. S. S. Zilva.

Equation of alcoholic fermentation. II. A. Harden and F. R. Henley (Biochem. J., 1929, **23**, 230—236).—In fermentations of dextrose or lævulose in presence of phosphate carried out with dried yeast the ratio of extra carbon dioxide evolved to phosphorus esterified tends to be slightly higher than unity. With maceration extract and yeast-juice this ratio tends to be somewhat lower than unity as previously found with zymin. The ratio of hexosediphosphate to hexosemonophosphate formed during the fermentation is usually high for dried yeast, but is very variable for maceration extract and yeast-juice, the product in extreme cases consisting almost entirely of either the diphosphate or monophosphate. The most constant ratio which was observed is that of extra carbon dioxide to total phosphorus esterified, which varies only about ±10%, although the proportions of diphosphate and monophosphate may vary from 96% of diphosphate to 86% of monophosphate. The equation of Harden and Young cannot be applied to those cases in which a large proportion of hexosemonophosphate is produced, whilst the ratio carbon dioxide/total phosphorus esterified remains at about 0·9. S. S. Zilva.

Alcoholic fermentation. XVIII. Behaviour of yeast to glyceraldehyde and glyceric acid. S. Kostytschev and K. Jegorova (Z. physiol. Chem., 1929, **181**, 264—280).—Glyceric acid and glyceraldehyde are not fermented by yeast to any significant extent and cannot therefore be intermediate products of alcoholic fermentation. P. W. Clutterbuck.

Mechanism of fluoride inhibition and the dissociation curve of fluor-methæmoglobin. F. Lipmann (Biochem. Z., 1929, **206**, 171—185).—The inhibition of fermentation by fluoride is completely reversible and in accordance with the mass action law. It increases with acidity; this is consistent with complex formation between enzyme and fluoride. The dissociation constant of fluor-methæmoglobin was determined. The dissociation is a unimolecular reaction. The oxidation of oxalic acid by permanganate and hydrogen peroxide decomposition by tervalent iron are inhibited by fluoride.

J. H. Birkinshaw.

Top yeast. H. von Euler and H. Nilsson (Z. physiol. Chem., 1929, **181**, 281—290).—The fermenting power and oxygen utilisation of fresh yeast and of washed and unwashed dried yeast with and without addition of boiled juice are greatly decreased by treating the yeast with hydrogen sulphide. With fresh yeast both the fermenting power and the oxygen utilisation are decreased to one quarter, whilst with unwashed dried yeast the fermenting power is decreased to one eighth and the oxygen utilisation to one fourteenth of the control values. The co-zymase of dried yeast obtained by treating fresh yeast for 24 hrs. with hydrogen sulphide and drying may be washed out with water. P. W. Clutterbuck.

Ergosterol content of yeast. A. Heiduschka and H. Lindner (Z. physiol. Chem., 1929, **181**, 15—23).—Ergosterol was prepared from yeast by heating with alcoholic potassium hydroxide. On evaporation of the alcohol crystals separated, the ether extract of which yielded ergosterol. Colorimetric determinations showed that the ergosterol content of yeast and moulds is subject to wide variations according to the method of cultivation. J. H. Birkinshaw.

Formation of fumaric acid in sugar cultures of *Rhizopus nigricans* and its behaviour with pyruvic acid. W. S. Butkewitsch and M. W. Federoff (Biochem. Z., 1929, **206**, 440—456).—The results confirm the findings of Ehrlich and Bender (A., 1928, 95). In the presence of calcium carbonate the pyruvic acid underwent a change which bore no relationship to the activity of the mould. The empirical formula of the isolated monobasic acid is $C_7H_6O_4$. C. C. N. Vass.

Metabolism of amino-acids by *Paramœcium caudatum*. F. E. Emery (J. Morph. Physiol., 1928, **45**, 555—577).—The rate of metabolism of the amino-acids was: phenylalanine 7·7, tryptophan 9·6, glycine 9·6, leucine 12·0, glutamic acid 13·2, alanine 15·5, arginine 15·9, tyrosine 17·7, aspartic acid 25·1, cysteine hydrochloride 26·3, glutamic acid hydrochloride 45·6, mixture of all except arginine 48·3%. Cystine was not utilised or converted into cysteine. The values for histidine and lysine were 10—15% and about 5%.

Chemical Abstracts.

Steric relationships in the dismutation of phenylglyoxal hydrate by various bacteria. S. Hayashi (Biochem. Z., 1929, **206**, 223—227).—*B. proteus*, *B. fluorescens*, *B. pyocyaneus*, and *B. prodigiosus* all convert phenylglyoxal hydrate into $d(-)$-mandelic acid. The optimum p_H is 7. *B. coli* produces the same change best at p_H 8·1; the acid consists of 65—75% $d(-)$-form; in the analogous dismutation of methylglyoxal hydrate this organism produces inactive lactic acid. J. H. Birkinshaw.

Decomposition of fats by bacteria. F. E. Haag (Arch. Hyg., 1928, **100**, 271—308; Chem. Zentr., 1928, ii, 1891—1892).—The ease of decomposition of fatty acids by bacteria depends on the chemical, and not on the physical, properties of the fats. A bactericidal action by the higher fatty acids was not observed; a solvent action on the bacteria by the alkali soaps is concerned. A. A. Eldridge.

Reduction of sulphates by micro-organisms in presence of fats. G. Seliber (Compt. rend. Soc. Biol., 1928, **99**, 544—546; Chem. Zentr., 1928, ii, 1781—1782).—Reducing micro-organisms decompose sulphates with production of hydrogen sulphide if fat or its products of decomposition are present, the fat being anaërobically decomposed. Both processes can proceed at the sea-bottom. A. A. Eldridge.

Proteolytic bacteria of milk. IV. Action of proteolytic milk bacteria on amino-acids and other simple nitrogenous compounds. W. C. Frazier and P. Rupp (J. Bact., 1928, **16**, 231—245).—Some of the organisms which can use carbamide as sole source of nitrogen liberate ammonia, whilst others produce an acid reaction. Organisms which can use ammonia as sole source of nitrogen appear to use any of the simpler amino-acids if a fermentable sugar is present. Differentiation of organisms may probably be based on differences in utilisation of amino-acids as sources of both nitrogen and carbon.
Chemical Abstracts.

Rennin action. I. Rennin production by *Bacillus prodigiosus*. II. Effect of rennin on sodium caseinogenate. J. G. Wahlin (J. Bact., 1928, **16**; 355—373, 375—386).—The production of rennin by *B. prodigiosus* in a medium containing complex proteins, amino-acids, and ammonia is more active at 37° than at 20°; raw cultures are more active than filtrates. The rennin is more thermostable, and less susceptible to oxalates and to the caseinogen concentration than is calf rennin. It coagulates heated milk more readily than calf rennin. Rennin renders the protein of sodium caseinogenate or milk more readily precipitable by salts. Certain types of proteolytic bacteria similarly affect sodium caseinogenate. Chemical Abstracts.

Nitrogen exchange in *Bacillus mycoides*. I. Influence of medium on growth and nitrogen exchange. II. Proteolytic enzymes. H. Glinka-Tschernorutzky (Biochem. Z., 1929, **206**, 301—307, 308—313).—I. Cultures of *B. mycoides* in 1% peptone decomposed the protein with ammonia production. Addition of dextrose (1%) reduced the decomposition. In caseinogen–peptone medium an increased ammonia content with a decreased amino-acid content was observed. Medium containing only monoamino-acids yielded light and delayed growths.

II. A trypsin-like enzyme has been extracted from *B. mycoides*. Results obtained from a dextrose medium support the views of Waksman, that dextrose forms a high energy source for the bacteria and so diminishes the decomposition of the proteins.
C. C. N. Vass.

Carnitine, crotonobetaine, and γ-butyrobetaine in putrefaction. W. Linneweh (Z. physiol. Chem., 1929, **181**, 54—57)—Both carnitine and crotonobetaine are reduced to β-butyrobetaine by putrefactive organisms. J. H. Birkinshaw.

Genesis and character of bacterial poisons. M. Eisler (Z. Immunitäts., 1928, **56**, 209—233; Chem. Zentr., 1928, ii, 1781).—Bacterial poisons are regarded as extractive materials of dead bacteria rather than as secretory products of living bacteria.
A. A. Eldridge.

Absorption of tuberculin. A. Boquet, L. Nègre, and J. Valtis (Compt. rend. Soc. Biol., 1928, **99**, 9—12; Chem. Zentr., 1928, ii, 1892).—If tuberculin is treated with a sufficient quantity of finely-divided carbon, it is freed from all active (antigenic and toxic) substances. The adsorption complex so formed is irreversible and indissociable *in vivo*.
A. A. Eldridge.

Carbohydrate content of the alcohol-soluble antigen of tubercle bacilli. K. Knowlton and M. Pinner (Amer. Rev. Tuberculosis, 1928, **18**, 502—504).—The antigen is almost certainly of lipoid nature.
Chemical Abstracts.

Bacteria. XXIII. Comparative yields of water-soluble protein carbohydrate from tubercle bacilli from various sources. T. B. Johnson and A. G. Renfrew (Amer. Rev. Tuberculosis, 1928, **18**, 505—512).—A technique is described. The yield of carbohydrate is reduced, and that of the active protein is very low, when autoclaved cells are used. Chemical Abstracts.

Physico-chemical conditions of the thermostability of diphtheria antitoxin. V. Kulikov, P. Smirnov, and M. Bobkova (Compt. rend. Soc. Biol., 1928, **98**, 1503—1504; Chem. Zentr., 1928, ii, 1579).—On addition of alkali to the antitoxin gradual precipitation takes place in the p_H range 4·8—7·0; at maximal precipitation (p_H 6·1—6·5) all the antitoxin is present in the precipitate. Heating and treatment with acid also lead to concentration of the antitoxin or removal of attendant substances.
A. A. Eldridge.

Nature of the bactericidal agents (bactericidins) in duodenal juice. W. Löwenberg (Z. ges. exp. Med., 1928, **62**, 184—216; Chem. Zentr., 1928, ii, 1585).—The substances are resistant to heat, and in their behaviour on dialysis and ultrafiltration are between proteins and crystalloids; they are not readily absorbed. They are not identical with the bactericidal substances of serum, with pancreas enzymes, or with bacteriophages. A. A. Eldridge.

Chemical constitution and germicidal activity of amines, ketones, and aldehydes. F. W. Tilley and J. M. Schaffer (J. Bact., 1928, **16**, 279—285).—For primary alkylamines and *Bacillus typhosus* the average ratio between successive molecular phenol coefficients was 2·0, and with *Staphylococcus aureus* 3·3. For alkyl ketones and *B. typhosus* the average ratio was 3·25; unsatisfactory experiments with aldehydes indicated values of 2·5 or more.
Chemical Abstracts.

Commercial bacteriological peptones. J. G. McAlpine and G. D. Brigham (J. Bact., 1928, **16**, 251—256).—A study of the nitrogen distribution in Difco-Bacto, Difco-Proteose, Fairchild, and Witte peptones. Chemical Abstracts.

Factors affecting the growth of surface colonies of bacteria. P. K. Bates (Abst. Thesis Mass. Inst.

Tech., No. 3, Jan., 1929, 39—40).—The area of a bacterial colony on an agar surface increases at a rate characteristic of each species. Growth is greater in a humid than in a dry atmosphere, and in a neutral than in an acid medium, and is inhibited by lack of oxygen. The character of the colonies varies with the concentration of the agar gel, and with the temperature; at 25°, growth is slower than at 37°, but much larger colonies are formed. E. W. Wignall.

Behaviour of calcium in administration of adrenaline. H. Lawaczeck (Deut. Arch. klin. Med., 1928, **160**, 309—322; Chem. Zentr., 1928, ii, 1893).—Administration of adrenaline does not change the total blood-calcium, but a greater proportion of the calcium is ultrafilterable. A. A. Eldridge.

Effect of insulin and adrenaline on the distribution of dextrose in the blood. S. I. Vinokurov (Zhur. exp. Biol. Med., 1928, **9**, 394—407).—Large doses of insulin remove the difference between the red cells and plasma of pigeon's blood as regards uneven distribution of dextrose and residual reduction. The effect of adrenaline is to accentuate the difference in the concentration of dextrose between cells and plasma, the cells suffering loss of dextrose. Chemical Abstracts.

Carbohydrate balance of fasting rats after insulin and adrenaline injections. C. F. Cori and G. T. Cori (Biochem. Z., 1929, **206**, 39—55).—Between the 24th and 48th hr. the total glycogen of fasting rats decreases by about 15%. The respiratory quotient is not changed by adrenaline injection, but the oxygen consumption increases. After moderate doses of insulin the respiratory quotient rises slightly, but the oxygen uptake is constant. Three hrs. after adrenaline injection muscle-glycogen is 57 mg. lower and liver-glycogen 36 mg. higher per 100 g. of animal. Muscle-glycogen is transformed into liver-glycogen by way of lactic acid. After insulin, muscle-glycogen is 34 mg. lower and furnishes part of the carbohydrate burnt. The already low liver-glycogen scarcely changes. Insulin increases the combustion of blood-sugar in the peripheral tissue. The mechanism of insulin and adrenaline action is discussed. J. H. Birkinshaw.

Insulin and gluconeogenesis. M. W. Goldblatt (Biochem. J., 1929, **23**, 243—255).—Experiments on rats, rabbits, and man show that insulin can stimulate the new formation of glycogen from endogenous sources. The theory that insulin inhibits gluconeogenesis is untenable. S. S. Zilva.

Biological characteristic of bound sugar. Fasting dogs. C. Toscano (Policlinico, 1927, 11 pp.; Chem. Zentr., 1928, ii, 1583).—By the action of insulin a general diminution of free and bound sugar first takes place. Long fasting does not increase the normal bound blood-sugar value. A state of high bound sugar regularly follows a diminution, the free sugar being lowered. Considerable increase of bound sugar does not cause a decrease of free sugar. Administration of adrenaline causes rapid increase of the free sugar with simultaneous decrease of the bound sugar. It is supposed that adrenaline causes the degradation of the former to the latter. A. A. Eldridge.

Mechanism of the reduction of blood-sugar values by the action of insulin. B. Matsuoka (Compt. rend. Soc. Biol., 1928, **98**, 1178—1179; Chem. Zentr., 1928, ii, 1786).—The hypoglycæmic action of insulin depends on the formation of lactacidogen in the liver and probably in the muscles, and on the conversion of lactacidogen into glycogen. A. A. Eldridge.

Insulin and excretion of urine. R. Agnoli (Arch. biol., 1926, 10 pp.; Chem. Zentr., 1928, ii, 1786).—Insulin decreases urinary excretion; the effect is not conditioned by hypoglycæmia, and is abolished by oral administration of urea. A. A. Eldridge.

Beta-hormone. B. P. Wiesner and J. S. Patel (Nature, 1929, **123**, 449).—The corpus luteum (cattle) contains an extractable substance which causes some of the effects ascribed to the hypothetical beta-hormone, *e.g.*, it prevents the atrophy of the uterus in ovariotomised mature mice. It is concluded that the substance is a factor responsible for pseudopregnancy in diphasic animals and for the premenstruum in monophasic animals. A. A. Eldridge.

Ovarian hormone. Influence of the corpus luteum on the sexual cycle. G. Cotte and G. Pallot (Compt. rend. Soc. Biol., 1928, **99**, 69—72; Chem. Zentr., 1928, ii, 1892).—There exist in the ovary two hormones of opposing action; one, belonging to the corpus luteum, hinders ovulation. A. A. Eldridge.

Physiology of glands. CXIV. L. Asher. **Activation of adrenal glands by thyroxine.** F. Zimmermann (Biochem. Z., 1929, **206**, 369—400).—The modification of Hagedorn and Jensen's method introduced by Issekutz and Both (cf. A., 1927, 600) was used to determine the glycogen content of the bilateral muscles, taken separately, of the hind-leg of a rat. Normal muscles showed an average glycogen content of 0·79% with a maximum absolute variation between the values obtained from the separate portions of the muscle of 2·94%. After injection of adrenaline (1 : 10,000) the glycogen content decreased by 21·8%, with 1 : 1000 by 25·28%, and in the case of adrenaline (1 : 10,000)+2% of novocaine by 28·85%. The glycogen content of the liver after injection of adrenaline (1 : 10,000) was 1·79%, after 1 : 1000 0·90%. When adrenaline (1 : 1000) was injected approximately 6 hrs. after an injection of thyroxine (1 : 1000) the glycogen content in muscle fell by 37·06% and the glycogen content of the liver was 0·257%. Thyroxine increased the action of adrenaline on the carbohydrate metabolism. C. C. N. Vass.

Chemical nature of vitamin-*A*. J. C. Drummond and L. C. Baker (Biochem. J., 1929, **23**, 274—291; cf. Drummond, Channon, and Coward, A., 1926, 206).—The unsaponifiable fraction of cod-liver oil after removal of the greater part of the cholesterol tends to decompose on fractionation (0·01—2 mm. pressure) with serious loss of the vitamin. The constituents of this unsaponifiable fraction are not readily reduced by hydrogen in the presence of platinum or palladium catalysts. The unsaponifiable fraction from sheep-liver fat also decomposes considerably on distillation in a high vacuum. This is due to the presence of the highly-unsaturated hydrocarbons resembling squalene (cf. Channon and Marrian, A., 1926, 638). The sheep-liver fractions are also resistant to hydrogenation. The distillation of the unsaponifiable fractions from Greenland shark-liver oil and Japanese shark-liver oil which consists mainly of selachyl, batyl, chimyl, and oleyl alcohols is accompanied by comparatively little destruction of the vitamin. "Biosterin" of Takahashi and his colleagues consists to a very large extent of substances other than vitamin-*A*. The structure for chimyl alcohol suggested by Heilbron and Owens (A., 1928, 616) is confirmed. S. S. Zilva.

Limitations of the antimony trichloride test for determination of vitamin-*A*. W. S. Jones, A. E. Briod, S. Arzoomanian, and W. G. Christiansen (J. Amer. Pharm. Assoc., 1929, **18**, 253—256).—Of 13 samples of cod-liver oil only 5 yielded colorimetric assays within 15% of the biological assays, and of the remaining 8, all except 2 gave colorimetric values which exceeded the biological by 20—600%. E. H. Sharples.

Biochemistry of carotin-like substances. B. von Euler, H. von Euler, and P. Karrer (Helv. Chem. Acta, 1929, **12**, 278—285).—Contrary to the results of Drummond, Channon, and Coward (A., 1920, i, 908; 1926, 206), it is found that the addition of daily doses of 0·10—0·03 mg. of purified carotin to the basic diet of rats causes an increase in growth similar to that obtained with vitamin-*A*. Moreover, the colorimetric determination of carotin in the liver by the antimony chloride reaction gives results in rats which had been given carotin (19 and 29 Lovibond units) comparable to those obtained with rats fed on a normal diet (25—35 Lovibond units). The growth increase is not a general effect of all carotin-like substances, since negative results are obtained with the isomeric lycopin (and its carboxylic acid, cf. this vol., 569), xanthophyll, α-crocetin, bixin, and capsanthin (all of which, however, give a positive antimony trichloride reaction), but positive results are obtained with dihydro-α-crocetin if vitamin-*D* (in the form of irradiated arachis oil) is included in the diet. No growth increase occurs if the latter vitamin is absent, and this absence probably explains the contrary results of the earlier investigators. J. W. Baker.

Relation of vitamin-*A* to greenness of plant tissue. II. Vitamin-*A* content of asparagus. J. W. Crist and M. Dye (J. Biol. Chem., 1929, **81**, 525—532).—Green asparagus is much more active in promoting the growth of rats on a diet deficient in vitamin-*A* than is bleached asparagus; this confirms the previously suggested relationship of vitamin-*A* to greenness in plant tissue (A., 1927, 904). C. R. Harington.

Vitamin content of tomatoes ripened artificially and naturally. M. C. House, P. M. Nelson, and E. S. Haber (J. Biol. Chem., 1929, **81**, 495—504).—The amount of vitamin-*A* and -*B* in tomatoes increases during ripening to an equal degree whether the process takes place naturally on the plants or whether the fruit is picked green and ripened by exposure to the air or to ethylene. The maximum development of vitamin-*C* is obtained only in fruit allowed to ripen naturally on the plant. C. R. Harington.

Vitamin-*A* content of the subcutaneous fat of the dolphin (*Delphinus delphis*). S. N. Natzko (Zhur. exp. Biol. Med., 1928, **10**, 163—166).—In experiments with rats, dolphin fat and cod-liver oil gave equally good results. Chemical Abstracts.

Metabolism and vitamin-*A*. C. M. McCay and V. E. Nelson (J. Metabol. Res., 1925—1926, **7—8**, 199—204).—Albumin is a normal constituent of rat's urine. In vitamin-*A* deficiency the volume, density, acidity, and nitrogen partition of the urine are unaffected. Chemical Abstracts.

Vitamin-*D* from sterols of mummified Egyptian brain. H. King, O. Rosenheim, and T. A. Webster (Biochem. J., 1929, **23**, 166—167).—Cholesteryl esters were prepared from a mummified brain of Coptic origin dating from about 500 A.D. by warming the tissue in 2% potassium hydroxide and extraction with ether. On recrystallisation from ethyl acetate and from acetone a white product, m. p. 78—80°, $[\alpha]^{16}_{5461}$ −29°, was obtained. The crude esters after the removal of "oxycholesterol" gave colour reactions for ergosterol and showed the absorption spectrum of ergosterol in the region 280—290 μμ. The irradiated esters in daily doses of 2 and 4 mg. showed the same antirachitic action as 0·05 γ of irradiated ergosterol. The ergosterol content of cholesterol isolated from the mummified brain is of the same order as that from fresh brain. S. S. Zilva.

Activity of irradiated ergosterol. R. Fabre and H. Simonnet (J. Pharm. Chim., 1929, [viii], **9**, 331—338).—A discussion of the current methods used in testing antirachitic activity. B. A. Eagles.

Photochemical action of sterols of diverse origin. L. Hugounenq and E. Couture (Compt. rend., 1929, **188**, 742—743).—Sterols derived from silk-worm moths and brewer's yeast show the action on the photographic plate already described (this vol., 359), whilst sterols obtained from ox-blood or snails show no action after 15 days' exposure. G. A. C. Gough.

Effect of excessive doses of irradiated ergosterol on the calcium and phosphorus content of the blood. L. J. Harris and C. P. Stewart (Biochem. J., 1929, **23**, 206—209).—The administration of a complete synthetic diet containing 0·1% of irradiated ergosterol produces in the rat a 50% increase of blood inorganic phosphate and a 25% increase of serum-calcium. In adult rabbits receiving a normal mixed diet the administration of 10 mg. *per diem* of irradiated ergosterol per animal is followed, after upwards of a fortnight at the normal level, by a 50% increase in the blood inorganic phosphate. On the other hand, after 6 weeks there is no significant rise in serum-calcium, although abnormal deposits of calcium are already to be observed in the body. S. S. Zilva.

Hypervitaminosis and vitamin balance. II. Specificity of vitamin-*D* in irradiated ergosterol poisoning. III. Pathology of hypervitaminosis-*D*. L. J. Harris and T. Moore

(Biochem J., 1929, **23**, 261—273; cf. Harris and Moore, this vol., 105).—A diet containing 0·1% of ergosterol in which vitamin-*D* has been destroyed by prolonged over-irradiation does not produce the condition of hypervitaminosis. Ergosterol irradiated in oil or in alcohol when fed at the same vitamin-*D* levels (0·025%) produced hypervitaminosis of the same degree of severity. Ergosterol irradiated in absence of any solvent also produces specific ill effects. This evidence supports the theory that excessive doses of vitamin-*D* are toxic *per se*. Besides the features already described in the literature, rats and rabbits suffering from hypervitaminosis show a remarkably high blood-phosphate, a tendency towards diminished p_H of fæces, diminished heart rate, and at death atrophy of the thymus. S. S. ZILVA.

Changes in rat's organs due to large over-doses of "vigantol." F. HOLTZ and T. VON BRAND (Z. physiol. Chem., 1929, **181**, 227—233).—Tables give the weight changes of normal rats and of rats to which were administered excessive amounts of "vigantol" (vitamin-*D* preparation) in olive oil (100,000 times the therapeutic dose) and the kidney, lung, heart, aorta, liver, spleen, and blood vessels were examined for metabolic changes, particularly in respect to calcium, similar to those observed by Kreitmair and Moll (A., 1928, 1406). These effects were often obtained, but it seemed possible that they were due not to hypervitaminosis but to some impurity in the "vigantol." P. W. CLUTTERBUCK.

Coloration of living vegetable cells by neutral-red. GUILLIERMOND (Compt. rend., 1929, **188**, 813—815).—Concentrated solutions of neutral-red cause a flocculation of the colloids of the vacuoles of yeast cells and coloration of the vacuole without death of the cell. G. A. C. GOUGH.

Fixation of chondriosomes of the vegetable cell. M. MASCRÉ (Compt. rend., 1929, **188**, 811—813).—Whilst the chondriosomes of *Elodea canadensis* are dissolved by treatment with acetic acid, a sufficient preliminary treatment with formaldehyde inhibits the destruction. G. A. C. GOUGH.

Fluorescence of vegetable juices in filtered ultra-violet rays. G. T. DRAGONE (Atti R. Accad. Lincei, 1928, [vi], 8, 602—605).—Under the influence of rays of wave-length 3650 Å., the resins of a number of *Coniferæ* and the essential oils of the pericarp of various *Citrus* species exhibit fluorescence, which is generally blue but sometimes green or brown. These substances evidently protect the parts of the plants producing them from harmful radiations by converting these into innocuous rays of greater wave-length. T. H. POPE.

Periodic determinations of soil respiration and the bacterial activity of forest soils. D. FEHÉR (Biochem. Z., 1929, **206**, 418—435).—Determinations of the carbon dioxide content of forest air, soil respiration, the numbers of bacteria, protozoa, and fungi, air temperature, ground temperature, humus content, and the intensity of the light in the open and in the wood have been made throughout a year. When the results are presented graphically, a remarkable correlation is observed between the bacterial content of the ground and the carbon dioxide production, which is evidenced in the parallelism of the number of aërobic bacteria and the soil respiration. Agreement is also shown in the seasonal variation of the carbon dioxide content of the forest air, the soil respiration, and the assimilation of carbon dioxide by the trees. The activities of the various groups of soil bacteria have been examined throughout the year. C. C. N. VASS.

Kinetics of photosynthesis in plants. Theoretical interpretation of Harder's results on the assimilation of carbon dioxide by *Fontinalis*. J. C. GHOSH (Jahrb. wiss. Bot., 1928, **69**, 572—586).—On the basis of the theory of Willstätter and Stoll, the following formula is deduced for the rate of assimilation of carbon dioxide by the plant under the action of light: $1/V=1/nK_1C+1/nK_3I+K_2/nK_3K_1IC+1/nK_4$, where V is the velocity of assimilation, I is the intensity of light, C is concentration of carbon dioxide. K_1, K_2, K_3 and K_4 are constants, and n is the original number of chlorophyll molecules per unit chloroplastid surface. The formula fits well the figures obtained by Harder (Jahrb. wiss. Bot., 1921, **60**, 568) for the velocity of assimilation under constant light intensity and varying carbon dioxide concentrations and with constant carbon dioxide concentrations with varying light intensity. Figures obtained by Warburg from experiments on *Chlorella* are also in harmony with the theory. W. O. KERMACK.

Photo-synthesis in absence of oxygen. E. N. HARVEY (Plant Physiol., 1928, **3**, 85—89).—Certain marine algæ can produce oxygen (detected by luminous bacteria) from carbon dioxide when illuminated in absence of oxygen. CHEMICAL ABSTRACTS.

Retardation of the ripening of pears by exclusion of oxygen. F. KIDD and C. WEST (Nature, 1929, **123**, 315—316).—When pears are preserved in an atmosphere of nitrogen the macroscopic changes of "ripening" are almost completely inhibited. With shorter time of exposure, however, ripening subsequently takes place in air, the rate of ripening being a function of the concentration of oxygen and of that of carbon dioxide over a considerable range. A. A. ELDRIDGE.

Variation in the composition of the cell-wall in oats during growth. F. ROGOZINSKI and M. STARZEWSKA (Bull. Acad. Polonaise, 1928, *B*, 127—132).—The ash content of the cell-walls in oats diminishes gradually during the growth of the plant. Cellulose, pentosan, and lignin contents increase rapidly during the development of the plant, reaching maxima 12—14 weeks after germination. E. A. LUNT.

Influence of hydrogen-ion concentration on the development of *Coffea arabica*. T. DE CAMARGO, R. BOLLIGER, and P. C. DE MELLO (Compt. rend., 1929, **188**, 878—880).—Specimens of this plant have been grown in sand moistened with a solution of the requisite salts adjusted to different p_H values (4·2—7·2) with sulphuric acid. The ash, the dry weight, and the weight of the roots of the plant increase with decreasing p_H, whilst the potassium content and the weight of the stems show an opposite effect. The nitrogen, magnesium, sodium, and calcium contents remain almost unchanged. G. A. C. Gough.

Effect of hydrogen-ion concentration on the growth of *Agaricus campestris*. D. Frear, J. F. Styer, and D. E. Haley (Plant Physiol., 1928, **3**, 91—94).—The optimal p_H of the synthetic culture media was 6·0; the value decreased by 2·0 during growth. Chemical Abstracts.

Influence of the absolute reaction of the soil on the formation and composition of tarragon essence. H. Deel and (Mme.) H. Deel (Bull. Soc. chim., 1929, [iv], **45**, 175—177).—The effect of five artificial manures on the growth and yield of essence of *Artemisia dracunculus* has been determined. The optimum p_H value of the soil at the time of harvest is about 6·2. With greater p_H values the yield of plant and of essence diminishes, but when the yield of essence is expressed as the percentage weight of the plant the influence of the p_H value of the soil is negligible. Analyses of the essences from various crops shows that the optimum p_H value also corresponds with the maximum (66·28%) phenol content. F. G. Tryhorn.

Relation of nitrogen metabolism to plant succulence. W. H. Pearsall and J. Ewing (Ann. Bot., 1929, **43**, 27—34).—In the case of the radish and turnip an abundant supply of nitrates produces amino-acid accumulation with consequent reduction of the p_H of the cell-sap in the plant. It is suggested that these conditions are the cause of the increased water content and reduced transpiration of such plants. E. A. Lunt.

Nitrogen metabolism in the soya bean. J. E. Webster (Plant Physiol., 1928, **3**, 31—43).—Analyses of high-nitrogen and low-nitrogen series of soya-bean cultures showed that, in general, the variations of the various types of nitrogen compounds in the roots, leaves, and stems of any particular series are similar. Leaves, stems, or seeds do not appear to draw on the nitrogen reserve of the roots. Amino-acids having amide-groupings are no more important than other amino-acids in protein metabolism, although amide-nitrogen may be one of the most soluble storage forms. Ammonia is the first and last product of plant metabolism. The various forms of nitrogen fluctuate daily. Chemical Abstracts.

Nitrogen metabolism in *Polyanthus narcissus*. G. T. Nightingale and W. R. Robbins (N. J. Agric. Exp. Sta. Bull., 1928, No. 472, 1—32).—Within the roots, nitrates are reduced to nitrites and ammonia, reducing sugars are oxidised, and (also in the storage tissues) the percentage and amount of higher carbohydrates are reduced. In bulbs in darkness, as a result of assimilation of nitrate, the amounts of organic protein, proteose, basic-, amide-, and amino-nitrogen increased. The active centres and tops are relatively high in the simpler carbohydrates and the less complex forms of organic nitrogen, whilst the storage tissue contains a relatively large amount of nitrogen as protein, and carbohydrates as starch and dextrin. Chemical Abstracts.

Loss of nitrogen on drying plants. N. N. Ivanov and M. J. Lischkevitsch (Biochem. Z., 1929, **205**, 329—348).—Plant materials dried at 75° to constant weight show a further loss at 105°. This consists in part of nitrogen which is lost as ammonia. The ammonia varies from almost zero in wheat and lupin flour, where the nitrogen is chiefly in the form of proteins, to nearly 20% in certain fungi, where it is present as carbamide. The ether-soluble material is increased threefold and the nitrogen extracted by alcohol and water diminishes to about half. J. H. Birkinshaw.

Root-forming substance. F. W. Went (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 35—39).—A hormone which is able to promote root formation and is non-specific and resistant to heating at 100° may be extracted from leaves of *Acalypha* and from germinating barley. That the action is non-specific was shown by the fact that the root-forming substance produced from leaves of *Carica papaya* promoted root formation in *Acalypha*. This substance seems to be transported by the phloem and is formed in leaves and sprouting buds and in considerable quantities in the branches. F. G. Tryhorn.

Nectar in relation to honey production. O. W. Park (J. Econ. Entomol., 1928, **21**, 789—790).—Most of the samples of nectar examined contained 40—55% of sugar, the proportion varying considerably for a given source. The sugar concentration was inversely proportional to the relative humidity of the air; light was less important. Chemical Abstracts.

Composition of sugar obtained by complete saccharification of pine wood. I. E. Hägglund (Biochem. Z., 1929, **206**, 245—247).—Sugar from pine wood contains 0·41% OMe. The methoxyl compound is soluble in water, undergoes fermentation with yeast, and, unlike lignin, is hydrolysed by 4% hydrochloric acid at 120° in 1 hr. or by 42% hydrochloric acid in the cold in 24 hrs. C. C. N. Vass.

Plant colloids. XXII. Potato amylopectin prepared by different methods. M. Samec (Biochem. Z., 1929, **205**, 104—110).—A variety of methods is shown to yield identical products. P. W. Clutterbuck.

Iodine liberator from *Laminaria*. H. D. Kay (Nature, 1929, **123**, 317).—The liberation of iodine from potassium iodide by an acidified extract of *Laminaria* fronds (Dillon, this vol., 360) might be due to the presence of iodate. A. A. Eldridge.

Behaviour of plants after treatment of the seed with mercury. W. Heubner (Z. physikal. Chem., 1928, **139**, 198—210).—Growth of wheat seeds which have been treated with solutions of various mercury salts has been compared with that from untreated seeds. The number of treated seeds germinating is much the greater, but the total weight of a single shoot is not increased. The length of the stalk appears to be smaller at first but eventually becomes greater than that obtained from the untreated seed. No definite support is obtained for the view that such mercury compounds have a stimulating action on the growth of the plant; the beneficial action is confined to destruction of harmful fungi on the seed.

Samples of wheat grown from treated seed have been examined for mercury and in certain cases evidence of the presence of small quantities even in the ears has been obtained. R. N. Kerr.

Physiological function of magnesium in plants. E. Canals (Bull. Soc. Chim. biol., 1929, **11**, 14—45).—Crude preparations of invertase from brewers' yeast show a rough proportionality between their activity and their magnesium content. Invertase precipitated from aqueous solution with alcohol shows a low activity which is increased to a value below that of the original material by the addition of magnesium sulphate. Activity is lower in the same sample at higher p_H values. Electrolysis of aqueous solutions of invertase, whether containing sucrose or not, results in a partial migration of the magnesium to the cathode; dialysed invertase shows little variation in magnesium content when subjected to electrolysis. From these results it is concluded that the invertase molecule contains magnesium in a non-ionic form.

When pea seeds are allowed to germinate and grow in solutions of appropriate salts, much less growth is observed if magnesium is absent. If calcium ions are absent or if solutions of magnesium sulphate alone are used, magnesium salts exert a toxic action. In these experiments and also in the growth of maize and lupins, magnesium solutions show an appreciable effect at 0·001%, an optimum effect at 0·05%, and a toxic effect at 0·1%. Magnesium salts also possess a marked influence on the growth of *Saccharomyces Kephir* and *Bacillus caucasicus*. G. A. C. Gough.

Presence of monotropitin in *Gaultheria procumbens*, L., after drying. M. Bridel and (Mlle.) S. Grillon (J. Pharm. Chim., 1929, [viii], 9, 193—202; cf. A., 1928, 1224).—Monotropitin was determined, with the aid of rhamnodiastase, in various parts of the plant, *G. procumbens*, before and after drying. The dried plant contains the glucoside, but a large proportion is destroyed on drying.
E. H. Sharples.

Glucosides of *Digitalis purpurea*. Raymond-Hamet (Compt. rend., 1929, **188**, 461—463).—Digitalin prepared according to the method of Nativelle possesses the same toxicity for dogs as digitoxin prepared by Cloetta (A., 1921, i. 39).
G. A. C. Gough.

Constituents of *Ginkgo biloba* leaves. I. S. Furukawa (Bull. Inst. Phys. Chem. Res., Tokyo, 1929, **8**, 5—7).—The alcoholic extract from the dried leaves was evaporated and from the resinous residue, by use of various solvents, were separated the following: a *substance*, $C_{11}H_{12}O_4,2H_2O$, m. p. 325°, which contains a lactone ring (*diacetyl* derivative, m. p. 290—292°); a *homologue* of flavone (?), $C_{16}H_{12}O_6,0{\cdot}5H_2O$, m. p. 240° (*triacetyl* derivative, m. p. 170—171°; *dimethyl* derivative, m. p. 224—226°); a secondary alcohol, $C_{27}H_{56}O$, m. p. 80—80·5°, probably identical with ginnol (Kawamura, A., 1928, 1291); a *phytosterol* (?), m. p. 240—241°; and a *substance*, $C_{23}H_{40}O_4$, m. p. 296° (decomp.) (*diacetyl* derivative, m. p. 169—170°). B. W. Anderson.

Constituents of corn-silk. T. Noguchi (Bull. Inst. Phys. Chem. Res., Tokyo, 1929, **8**, 143—151).—Corn-silk, the style and stigma of the pistil of maize, is used as a diuretic. The ether extract yielded an *alcohol*, $C_{33}H_{66}O$, m. p. 74—75°, which gave a *monoacetyl* derivative. Phytosterol was separated from the oil after hydrolysis. Colour reactions indicated the presence of flavones, and of ketose, aldose, and pentose sugars. A phenylhydrazone, m. p. 180—181°, was isolated. Vitamins-*A*, -*B*, and possibly -*E* were present. R. K. Callow.

Ergosterol isolated from the Japanese edible fungus *Cortinellus Shiitake*. M. Sumi (Biochem. Z., 1929, **204**, 397—411).—The ergosterol has physiological properties very similar to those of that derived from other sources. In its absorption spectrum a band at 250 μμ has been discovered.
W. McCartney.

[Determination of] nitrate content of tobacco. T. Andreadis (Biochem. Z., 1929, **204**, 484—492).—Wagner's modification of Schlösing's method for the determination of the nitrate content of tobacco (cf. Kissling, "Handbuch der Tabakkunde," 1925) gives accurate results only provided the gas to be measured is treated with potassium hydroxide after collection over water; otherwise the presence of carbon dioxide causes error. The modified method may be used for the determination of nitrate in other plants and plant preparations. W. McCartney.

Isolation of protocatechuic acid from pigmented onion scales; significance in relation to resistance to disease. K. P. Link, H. R. Angell, and J. C. Walker (J. Biol. Chem., 1929, 81, 369—375).—Onion scales were extracted with water, the extract was treated with basic lead acetate, and the precipitate decomposed with hydrogen sulphide; the lead-free filtrate was evaporated under diminished pressure and the residue extracted with alcohol. The alcoholic solution, after clearing with charcoal, concentrating, and treating with light petroleum, yielded protocatechuic acid in a yield of 0·1% of the starting material. The presence of this compound is responsible, at least in part, for the resistance of onions to fungoid diseases. C. H. Harington.

Infection of the wheat plant by *Ophiobolus graminis*. H. Fellows (J. Agric. Res., 1928, **37**, 647—661).—Microchemical analyses made on the roots of wheat plants attacked by *O. graminis* indicate a reduction in the amount of cellulose present and an increase in the amounts of lignin and suberin. Other cell constituents appeared unmodified.
E. A. Lunt.

Hexylresorcinol and phenylethylresorcinol as remedies against pathogenic plant fungi. J. Houben and H. W. Wollenweber (Biochem. Z., 1929, **204**, 448—455).—Very small amounts of these substances prevent the growth of organisms, such as *Graphium ulmi*, *Penicillium glaucum*, *Nectria galligena*, *Fusarium*, *Calonectria graminicola*. The quantities required, which differ according to the organism, vary from less than 0·0025 to 0·04% (hexyl derivative) and from 0·0164% to more than 0·0328% (phenylethyl derivative). Cultures on gelatin treated with small amounts of the substances and exposed for months in the open show neither turbidity nor growth of mould. W. McCartney.

Apparatus for filtration and precipitation with subsequent filtration in an atmosphere of

nitrogen. V. Grabe and K. Freund (Biochem. Z., 1929, 205, 259—263).—An apparatus used in the preparation of phosphatides is described which enables the filtration, precipitation of dialysate, and filtration of the precipitate to be accomplished in an atmosphere of nitrogen, thus avoiding oxidative changes.
P. W. Clutterbuck.

Micro-determination of carbon dioxide in air. A. Krogh and P. B. Rehberg (Biochem. Z., 1929, **205**, 265—272; cf. A., 1925, i, 852).—About 100 c.c. of air are aspirated through standard barium hydroxide solution, which is then titrated with hydrochloric acid from a micro-burette. Leaden tubes are to be avoided, since they absorb carbon dioxide.
J. H. Birkinshaw.

Determination of the respiration of bacteria, tissue cultures, and surviving cells. F. Silberstein and F. Rappaport (Biochem. Z., 1929, **204**, 439—447).—The respiratory exchanges of these cells can be measured with Van Slyke's apparatus for analysis of blood-gases provided that the materials are brought into a medium consisting of suitably purified hæmoglobin solution. Within certain limits the amounts of oxygen consumed and carbon dioxide produced are independent of the amount of hæmoglobin present, of the number of cells used, and of the duration of the experiment. W. McCartney.

Micro-determination of oxalic acid. A. Leulier, L. Velluz, and H. Griffon (Bull. Soc. Chim. biol., 1929, **11**, 46—57).—Details are given for an approximate micro-determination of oxalic acid in solutions containing simple organic constituents. Lime water is used as a source of calcium; phosphates do not affect the reducing power of the precipitate towards potassium permanganate. It is an advantage to add an excess of potassium permanganate in the oxidation of the calcium oxalate and to determine the excess by iodometry. G. A. C. Gough.

Sources of error in the determination of tyrosine, phenol, and uric acid by phosphotungstic acid. E. Scheiner (Biochem. Z., 1929, 205, 245—255).—The reagents of Folin and Denis used for the colorimetric determination of uric acid, tyrosine, and phenols consist essentially of a labile complex polyphosphotungstic acid which readily parts with oxygen to reducing substrates with the formation of the blue oxide. This property is unspecific and leads to misleading results. All inorganic reducing agents (except nitrous acid) and hydrogen peroxide give the blue colour. Bivalent iron reduces the reagent in very small concentration (0·01 mg. of iron gives a blue colour). Unsaturated aldehydes, fatty acids, and aromatic amines give the blue colour, the intensity of reduction in the latter case being proportional to the number of amino-groups. The leuco-base of triphenylmethane dyes, hæmoglobin, chlorophyll, and urinary pigments all reduce, giving a blue solution. P. W. Clutterbuck.

Purine substances and uric acid. L. Damas (Bull. Sci. pharmacol., 1928, **35**, 111—123; Chem. Zentr., 1928, ii, 1468—1469).—A discussion of analytical methods. A. A. Eldridge.

Detection of cantharidin [in urine etc.]. R. Fischer (Arch. Pharm., 1929, **267**, 31—35).—The specimen is distilled in steam in presence of phosphoric acid, the distillate extracted with chloroform, and the dried solution evaporated in a current of air. The residue is dissolved in ether and the solution evaporated at 60° in a special micro-sublimation apparatus. The cantharidin is subsequently sublimed at 120—130° on to a cover glass. The latter is washed in light petroleum and viewed under the microscope, when characteristic crystals of cantharidin are observed, which are identified by conversion into barium cantharidinate (cf. van Zijp, Pharm. Weekblad, 1917, **54**, 295). The reactions described by Klein (B., 1910, 1225) and David (B., 1927, 124) are not characteristic. Better results may be obtained by sublimation in a vacuum. The cantharidin in 20—30 c.c. of urine at a dilution of 1 : 150,000 can be detected and with larger volumes the dilution may be as high as 1 : 500,000. The cantharidin may be dissolved in lanolin and tested for vesicant action, the minimum dose being 0·02—0·015 mg. S. Coffey.

Determination of copper in biological material. C. A. Elvehjem and C. W. Lindow (J. Biol. Chem., 1929, **81**, 435—443).—The material is incinerated and the ash dissolved in dilute hydrochloric acid; the solution is made alkaline with sodium hydroxide, re-acidified with acetic acid, and treated with potassium thiocyanate and pyridine; it is then shaken with chloroform, which extracts the green colour (cf. Biazzo, B., 1926, 382), and the latter is compared with that given by a known amount of copper. In presence of large amounts of iron or of calcium phosphate the copper must be precipitated as the sulphide (in the former case after preliminary reduction of the iron to the ferrous condition); 0·02 mg. of copper can be determined. C. R. Harington.

Determination of small amounts of iodine by the Dupré–Winkler method. J. A. Höjer (Biochem. Z., 1929, **205**, 273—296).—The sources of error in the Fellenberg method (*ibid.*, 1923, 139, 391; A., 1925, i, 329) for the volumetric determination of iodine are critically examined. It is proposed to replace the chlorine water used for oxidising the iodide by bromine water when bromine is not determined.
J. H. Birkinshaw.

Micro-determination of mercury. J. Bodnár and E. Szép (Biochem. Z., 1929, **205**, 219—229).—A method is described for the determination of very small amounts of mercury (0·04—10 γ). The mercury in presence of a trace of copper is separated on a pure iron wire, distilled off, and collected as a droplet, the diameter of which is measured, and the weight is thus calculable. P. W. Clutterbuck.

Micro-determination of sodium in biological liquids and tissues. P. Grabar (Bull. Soc. Chim. biol., 1929, **11**, 58—64).—After oxidation of the organic matter by treatment with hot nitric acid in a silica flask, phosphates are removed from the residue as ferric phosphate and the sodium is determined by a modification of the uranium method of Blanchetière (A., 1923, ii, 579). The average error is within 1%.
G. A. C. Gough.